## DAY TWENTY ONE

# Electrochemistry

### Learning & Revision for the Day

- Conductors
- Kohlrausch's Law
- Cell
- Laws of Electrolysis
- EMF of Cell
- Electrochemical Series
- Nernst Equation
- Batteries
- Fuel Cells
- Corrosion

The study of the chemical reactions which take place in a solution at the interface of an electron conductor and an ionic conductor is considered under the branch of chemistry namely as **electrochemistry.** The reactions which involve both oxidation and reduction are called **redox reactions**, these reactions are very important and play significant role in electrochemistry.

## Conductors

Substances which allow electric current to flow through them are known as **conductors**, e.g. metals like Fe, Ag, Cu. Whereas, the substance which do not allow the passage of electricity through them are called insulators, e.g. plastics. Two types of conductors are discussed below :

### 1. Metallic Conductors or Electronic Conductors

These are metallic substances that conduct electric current due to the mobility of free electrons, without undergoing any chemical change, e.g. metals like Cu, Ag, Fe, non-metals like graphite, some minerals etc.

### 2. Electrolytic Conductors (or Electrolytes)

These are the substances which allow the electricity to pass through them in molten or fused state and their solutions. They also undergo chemical decomposition during the process. The conduction of current through electrolyte is due to the movement of ions present in them.

On the basis of dissociation in aqueous solution, electrolytic conductors are further classified into two types

(i) **Strong Electrolytes** The electrolytes which dissociate completely into ions are called strong electrolytes, e.g. NaOH, NaCl, HCl, KCl, $HNO_3$, $H_2SO_4$ etc.

(ii) **Weak Electrolytes** The electrolytes which do not ionise completely in aqueous as well as in molten state are called weak electrolytes, e.g. $H_2CO_3$, $CH_3COOH$, $ZnCl_2$, $HgCl_2$ etc.

## Conductance in Electrolytic Solutions

The power of an electrolyte to conduct electric current is called **conductance** or **conductivity**. Just like metallic conductors, electrolytic solutions also obey **Ohm's law**.

Some basic terms related to this chapter are as follows:

- The quantity that measures the obstruction to the flow of current is called **resistance**, $R$.

The resistance of any conductor varies directly with its length ($l$) and inversely with its cross sectional area ($a$), i.e. $R \propto \frac{l}{a}$ or $R = \rho \frac{l}{a}$.

where, $\rho$ is called the **resistivity or specific resistance.**

If $l = 1$ cm and $a = 1\ \text{cm}^2$, then $R = \rho$.

- Reciprocal of resistance is called **conductance**, ($C$).

  $C = \frac{1}{\text{Resistance}} = \frac{1}{R}$

  Its unit is mho ($\Omega^{-1}$) or Siemens (S).

- The inverse of reactivity is called **conductivity**, ($\kappa$).

  i.e. $\kappa = \frac{1}{\rho} = \frac{l}{a} \times \text{conductance } (C)$

  where, $\frac{l}{a}$ = cell constant, it is determined with the help of conductivity bridge, where a standard solution of KCl is used.

- The unit of conductivity or specific conductance ($\kappa$) is $\text{ohm}^{-1}\ \text{cm}^{-1}$ or $\text{S cm}^{-1}$.

  (i) The conducting power of all the ions produced by one gram mole of an electrolyte in a given solution is called **molar conductivity** ($\Lambda_m$).

  Thus, $\Lambda_m = \frac{\kappa \times 1000}{\text{molarity}}$

  The units for molar conductivity

  $= \text{ohm}^{-1}\text{cm}^2\ \text{mol}^{-1}$ or $\text{S cm}^2\ \text{mol}^{-1}$

  (ii) The conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution is called **equivalent conductivity** ($\Lambda_{\text{eq}}$).

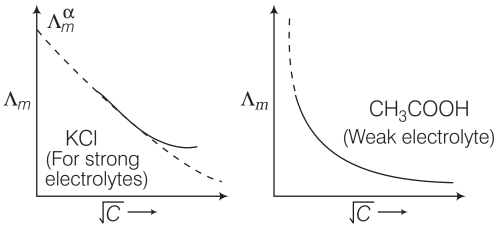
  Thus, $\Lambda_{\text{eq}} = \frac{\kappa \times 1000}{\text{normality}}$. The units for equivalent conductivity $= \text{ohm}^{-1}\ \text{cm}^2\ (\text{g eq})^{-1}$ **or** $\text{S cm}^2\ (\text{g eq})^{-1}$

## Variation of Conductivities with Concentration

Depending upon the values of molar conductivity, the electrolytes can be divided into two groups namely strong and weak electrolytes.

Equivalent as well as molar conductivity $\propto$ dilution and specific conductivity $\propto \frac{1}{\text{dilution}}$

- Strong electrolytes, like KCl have high value of conductance, even at low concentration and there is no rapid increase in their equivalent or molar conductance on dilution.
- Weak electrolytes, like acetic acid, have a low value of conductance at high concentration and there is a rapid increase in the value of equivalent conductance (molar conductance) with dilution.



The molar conductivity of electrolyte, when concentration of electrolyte approaches zero
(i.e. at infinite dilution) is known as limiting molar conductivity or infinite conductivity ($\overset{\circ}{\Lambda}_m$ or $\Lambda_m^\alpha$)

## Kohlrausch's Law

It states that molar conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions, i.e. anions and cations.

$$\boxed{\overset{\circ}{\Lambda}_m = \overset{\circ}{\Lambda}_a + \overset{\circ}{\Lambda}_c}$$

e.g. $\overset{\circ}{\Lambda}_m CH_3COOH = \overset{\circ}{\lambda}_m CH_3COO^- + \overset{\circ}{\lambda}_m H^+$

$\overset{\circ}{\Lambda}_m Al_2(SO_4)_3 = 2 \times \overset{\circ}{\lambda}_m Al^{3+} + 3 \times \overset{\circ}{\lambda}_m SO_4^{2-}$

The applications of this law are given below:

(i) For the determination of equivalent/molar conductivity at infinite dilution as discussed above.

(ii) For the determination of degree of dissociation.

Degree of dissociation ($\alpha$)

$$= \frac{\text{molar conductance at a given concentration}}{\text{molar conductance at infinite dilution}} = \frac{\Lambda^c_{\text{m}}}{\Lambda_{\text{m}}}$$

(iii) For the calculation of dissociation constant of a weak electrolyte.

$$K_a = \frac{C\alpha^2}{1-\alpha} = C\alpha^2 \quad [\because \text{For weak electrolyte, } \alpha <<< 1]$$

Here, $K_a$ = equilibrium dissociation constant

$C$ = molar concentration of weak electrolyte

(iv) For the determination of solubility of sparingly soluble salt.

$$\text{Solubility} = \frac{\kappa \times 1000}{\overset{\circ}{\Lambda}_m}$$

## Cell

- Cells are the devices in which interconversion of electrical energy and chemical energy takes place, A cell is made up of various components, i.e. electrolytic solution, salt bridge and electrodes.
- **Salt-bridge** It is a U-shaped tube contains a gel permeated with a solution of an inert electrolyte such as $Na_2SO_4$.

  The ions of the inert electrolyte do not react with the other ions in the solutions and they are not oxidised or reduced at the electrodes. The salt-bridge is necessary to complete the electrical circuit and to maintain electrical neutrality in both compartments (by flow of ions).

## Electrode and Half-Cells

- Electrode at which oxidation takes place is called as **anode**, whereas the electrode at which reduction takes place is called **cathode**.
- The combination of the metal electrode and solution is called a **half-cell**.
- Three kinds of interactions are possible between metal atom on the electrode and metal ion in solution.

$$\Lambda_m^\circ = \Lambda_a^\circ + \Lambda_c^\circ$$

  (i) A metal ion, $M^{n+}$ may collide with the electrode and undergoes no change.

  (ii) A metal ion, $M^{n+}$ may collide with the electrode, gains $n$ electrons and converted to a metal atom, $M$. The ion is reduced.

  (iii) A metal atom $M$ on the electrode may lose $n$ electrons and enter the solution as ion $M^{n+}$. The metal atom is oxidised.

$$M\,(s) \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} M^{\,n+}\,(aq) + ne^-$$

## Electrode Potential

- If we connect two different electrodes, electrons will flow from the electrode of higher negative electric charge density to the electrode with a lower negative electric charge density. A property closely related to the density of negative electric charge is called the electrode potential. Potential difference between the metal and the metal ion in which electrode is dipped, is called electrode potential denoted as $E$.
- In the standard state, when pressure is 1 atm (latest IUPAC correction use 1 bar) and concentration is 1 M, electrode potential is called **standard electrode potential** denoted as $E^\circ$. Temperature is generally taken as 298 K (i.e. 25°C).
- According to international convention, standard reduction potentials are now called standard electrode potentials. If the standard electrode potential of a half-cell is 0.34 V, it means it is the standard reduction potential $E^\circ_{M^{n+}/M}$, of the half-cell $M^{n+}/M$ with half-cell reaction

$$M^{n+} + ne^- \longrightarrow M$$

- If $E^\circ_{\text{ox}} = x$ V, then $E^\circ_{\text{red}} = -x$ V, i.e.,

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V, then } E^\circ_{\text{Cu}^{2+}/\text{Cu}} = -\,0.34 \text{ V}$$

- $E^\circ_{\text{cell}}$ or $E_{\text{cell}}$ is the potential difference between the two half-cells. Since, the potential difference is the driving force for electrons, it is also called the electromotive force (emf) of the cell or the cell potential or the cell voltage.
- This driving force pushes the negatively charged electrons away from the anode (–ve electrode) and pulls them towards the cathode (+ve electrode). The SI unit of cell potential is volt (V) and the potential of a galvanic cell is defined as the positive quantity.

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}\,,\; E_{\text{cell}} = E_{\text{ox}} + E_{\text{red}}$$

  For such cases, take values according to the reaction. Electrons should be equal in both half-cell reactions.
- Standard Hydrogen Electrode, SHE is used as a reference electrode. Its reduction potential is taken as zero. It is represented as
  Pt, $H_2(1\text{ atm})|\ H^+(1\text{M})$ or $H^+\ (1\text{ M})|H_2\ (1\text{ atm})$, Pt depending upon whether it acts as anode or cathode respectively.
- The difference between the potential required for the evolution of gas and the standard electrode potential of that gas is called overvoltage/overpotential.

## Types of Cell

Cells are of two basic types as discussed below:

### 1. Electrochemical Cell (Daniell cell)

An electrochemical cell or simply a 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.

### Representation of Electrochemical Cell

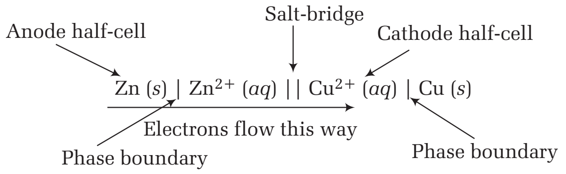
- The following convertions are used in representing an Galvanic or electrochemical cell.
- The anode is written on the left hand side and cathode on the right hand side.
- A vertical line (|) or semicolon (;) indicates a contact between two phases.
- The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution.
- The cathode of the cell is represented by writing the cation of the electrolyte first and then metal.
- The salt bridge which separates the two half-cells is indicated by two parallel vertical lines.
- Sometimes, molar concentration or signs are also indicated on the electrodes.
- Consider the Daniell cell with following cell reaction:

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

In writing a cell diagram, following points are considered. We divide the cell into two half-cells.

| | The anode | The cathode |
|---|---|---|
| Reaction | Oxidation takes place | Reduction takes place |
| | $\text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2e^-$ | $\text{Cu}^{2+}(aq) + 2e^- \longrightarrow \text{Cu}(s)$ |
| Terminal | Negative | Positive |
| Side | LHS | RHS |
| Diagram | $\text{Zn}\,(s)\,|\,\text{Zn}^{2+}(aq)$ | $\text{Cu}^{2+}(aq)\,|\,\text{Cu}(s)$ |

Complete cell diagram may be represent as follows:



## 2. Electrolytic Cells and Electrolysis

- It is a process in which electrical energy is used to bring some chemical changes. It is carried out in an **electrolytic cell** which involves conversion of electrical energy to chemical energy. In electrolysis, cations move towards cathode, while anions move towards anode.
- During electrolysis, all the ions are not discharged at the electrodes simultaneously, certain ions are liberated at the electrodes in preference to other. The preference will depend upon their discharge potential, which is defined as the potential at which discharge of cation occur at cathode and that of anion occurs at anode.
- The **cation** which is stronger oxidising agent is discharged first at the cathode. The increasing order of decomposition of few cation is

$$\underset{\text{Increasing order of discharge}}{\underrightarrow{\text{K}^+, \text{Ca}^{2+}, \text{Na}^+, \text{Mg}^{2+}, \text{Al}^{3+}, \text{Zn}^{2+}, \text{Fe}^{2+}, \text{H}^+, \text{Cu}^{2+}, \text{Ag}^+, \text{Au}^{3+}}}$$

- The **anion** which is stronger reducing agent is liberated first at anode. The increasing order of discharge of few anion is,

$$\underset{\text{Increasing order of discharge}}{\underrightarrow{\text{SO}_4^{2-}, \text{NO}_3^{2-}, \text{OH}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-}}$$

# Laws of Electrolysis

The quantitative relationships based on the electrochemical researches published by Faraday. The two laws given by the Faraday are below:

### 1. First Law

It states that the deposited mass of the substance is directly proportional to the quantity of charge passed in a voltameter.

$$\boxed{w \propto Q, \Rightarrow w = ZQ, \ \Rightarrow w = Zit}$$

where, $w$ = mass, $Q$ = charge (in coulomb)

$i$ = current (in amperes), $t$ = time (in second)

$$Z = \text{electrochemical equivalent} = \frac{\text{equivalent weight}}{96500\ \text{C}}$$

$$\left[\text{Equivalent weight} = \frac{\text{atomic weight}}{\text{valency}}\right]$$

1 Faraday = charge of one mole of electrons

$1\text{F} = 6.022 \times 10^{23} \times 1.6 \times 10^{-19} = 96500$ C (approx.)

Number of gram equivalents = Number of Faraday's of electricity,

i.e. 1 g eq of any substance = 1F of electricity

- Other forms of Faraday first law expression are

$$w = ZQ = \frac{E}{F} \times Q = \frac{Q}{F} \times \frac{M}{Z} = \frac{it}{F} \times \frac{M}{Z}$$

- One Faraday or 96500 C or 1 mole of electrons cause the reduction of 1 mole of monovalent cation or 1/2 mole of divalent cation or 1/3 mole of trivalent cation.

### 2. Second Law

It states that the number of equivalents of any substance produced by a given quantity of electricity during electrolysis are same.

$$\frac{w_A}{w_B} = \frac{E_A}{E_B}$$

where, $w_A$ = deposited mass of substance $A$,

$E_A$ = equivalent weight of $A$

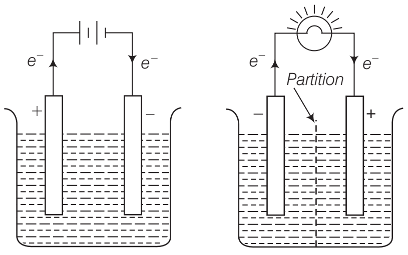
$w_B$ = deposited mass of substance $B$,

$E_B$ = equivalent weight of $B$

| | Electrolytic cell | | Voltaic or Galvanic cell | |
|---|---|---|---|---|
| | **Anode** | **Cathode** | **Anode** | **Cathode** |
| Sign | + | − | − | + |
| Electron flow | out | in | out | in |
| Half-reaction | oxidation | reduction | oxidation | reduction |

## Difference between Electrolytic and Electrochemical Cells

- In electrolytic cell, anode is positive electrode, while cathode is negative electrode. On the other hand, in galvanic cell, anode is negative electrode and cathode is positive electrode. In both the cells, anode is always the site of oxidation and cathode is of reduction.
- In electrolytic cell, ions are discharged at both the electrodes, while in galvanic cell, ions are discharged only at cathode.
- In electrolytic cell, both the electrodes are fitted in same compartment, while in galvanic cell, both the electrodes are fitted in different compartments.



(a) Electrolytic cell (emf is applied to cell)

(b) Voltaic or galvanic cell (emf is generated by cell)

- Besides, salt-bridge in both the cells, both the electrodes are connected externally with the help of a wire connected through a voltmeter. Flow of current and electrons occur through this wire.

## EMF of a Cell

In electrochemical cell, the electrodes in different half-cells have different reduction potential.

As a result of this, different flow of electrons is seen from the electrode with higher tendency to lose electrons to other electrode.

This difference in electrode potential of electrodes is called electromotive force or cell potential of a cell.

This is the driving force for all cell reactions.

## Electrochemical Series

It is the arrangement of metals in decreasing order of tendency to lose electrons or it is the series in which the elements are arranged on the basis of the values of their standard reduction potential at 25°C.

| **Element** | | **Electrode reaction** (reduction) | | **Standard electrode reduction potential, $E°$** (volt) |
|---|---|---|---|---|
| Li | ↑ Increasing tendency for reduction<br>Increasing strength of oxidising agent | $Li^+ + e^- \longrightarrow Li$ | Increasing strength of reducing agent<br>Increasing tendency for oxidation ↓ | – 3.05 |
| K | | $K^+ + e^- \longrightarrow K$ | | – 2.925 |
| Ca | | $Ca^{2+} + 2e^- \longrightarrow Ca$ | | – 2.87 |
| Na | | $Na^+ + e^- \longrightarrow Na$ | | – 2.714 |
| Mg | | $Mg^{2+} + 2e^- \longrightarrow Mg$ | | – 2.37 |
| Al | | $Al^{3+} + 3e^- \longrightarrow Al$ | | – 1.66 |
| Zn | | $Zn^{2+} + 2e^- \longrightarrow Zn$ | | – 0.7628 |
| Cr | | $Cr^{3+} + 3e^- \longrightarrow Cr$ | | – 0.74 |
| Fe | | $Fe^{2+} + 2e^- \longrightarrow Fe$ | | – 0.44 |
| Cd | | $Cd^{2+} + 2e^- \longrightarrow Cd$ | | – 0.403 |
| Ni | | $Ni^{2+} + 2e^- \longrightarrow Ni$ | | – 0.25 |
| Sn | | $Sn^{2+} + 2e^- \longrightarrow Sn$ | | – 0.14 |
| $H_2$ | | $2H^+ + 2e^- \longrightarrow H_2$ | | 0.00 |
| Cu | | $Cu^{2+} + 2e^- \longrightarrow Cu$ | | + 0.337 |
| $I_2$ | | $I_2 + 2e^- \longrightarrow 2I^-$ | | + 0.535 |
| Ag | | $Ag^+ + e^- \longrightarrow Ag$ | | + 0.799 |
| Hg | | $Hg^{2+} + 2e^- \longrightarrow Hg$ | | + 0.885 |
| $Br_2$ | | $Br_2 + 2e^- \longrightarrow 2Br^-$ | | + 1.08 |
| $Cl_2$ | | $Cl_2 + 2e^- \longrightarrow 2Cl^-$ | | + 1.36 |
| Au | | $Au^{3+} + 3e^- \longrightarrow Au$ | | + 1.50 |
| $F_2$ | | $F_2 + 2e^- \longrightarrow 2F^-$ | | + 2.87 |

The important applications of electrochemical series are:

- Greater is the reduction potential, more easily is the substance reduced and thus act as stronger oxidising agent, while the substance having lower reduction potential is difficult to reduce, thus is a weak oxidising agent.
- A metal with greater oxidation potential can displace metals with lower oxidation potential from their salt solution.

## Nernst Equation

This equation represents the relationship between electrode potential and concentration of solution.

$$E_{cell} \text{ or } \text{EMF} = E^\circ_{cell} - \frac{2.303RT}{nF} \log Q$$

where, $n$ = total number of electrons lost or gained

1F = 96500 C, $T$ = 298 K, R = 8.314 J/K

$$Q = \text{reaction coefficient of overall reaction} = \frac{[OS]}{[RS]}$$

where, [OS] = concentration of oxidised state

[RS] = concentration of reduced state

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log Q$$

There are two important applications of Nernst equation as given below:

- **To find equilibrium constant**

  At equilibrium, $E_{cell}$ = zero

  $$\therefore \quad E^\circ_{cell} = \frac{0.0591}{n} \log K$$

  where, $K$ = equilibrium constant
- **To find Gibbs free energy change**

  $$\Delta G^\circ = -n\, E^\circ_{cell} F$$

  $\Delta G^\circ$ = standard Gibbs free energy change

## Some Important Relationships in Electrochemistry

**Relationship between EMF of a Cell Gibbs Energy Change** ($\Delta G$) In an electrochemical cell, maximum work done is given by,

$$\boxed{\Delta G = nF \times E_{cell}}$$

where, $F$ = Faraday's constant

$n$ = number of moles of electrons transferred

A galvanic cell does electrical work by transferring electrical charge through an external circuit. When small amount of current is drawn from the cell then

$$\boxed{-\Delta G = W_{elec}}$$

(i) If $\Delta G$ of the system is positive, then the process would be possible only if the surroundings do electrical work on the system (as in electrolysis).

(ii) If $\Delta G$ of the system is negative, then the system does electrical work on the surroundings (as in galvanic cells). For a voltaic cell, the work is done on the surroundings, thus gives a negative sign. Hence,

$$\Delta G = W_{max} = -nF\, E_{cell}$$

and the standard free energy is given by,

$$\Delta G^\circ = -nFE^\circ_{cell}$$

- **Relation between Cell Potential ($E^\circ_{\text{cell}}$), Free Energy ($\Delta G^\circ$) and Equilibrium Constant ($K$)**

  These are related to each other by the following relation:

  $$\Delta G^\circ = -\,2.303\,RT\ \log K_C$$

  as $\Delta G^\circ = -\,nFE^\circ_{\text{cell}}$ and $E^\circ_{\text{cell}} = \frac{2.303\,RT}{nF}\log K_C$

- **Relation between Standard Potentials of Half-cells Containing a Metal in Different Oxidation States**

  If two half-reactions having potentials $E_1^\circ$ and $E_2^\circ$ are combined to give a third half-reaction having a potential $E_3^\circ$, then $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$ or $-\,n_3FE_3^\circ = -\,n_1FE_1^\circ - n_2FE_2^\circ$

  or $\quad n_3E_3^\circ = n_1E_1^\circ + n_2E_2^\circ$

  or $\quad E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3}$

# Batteries

A cell or a battery (arrangement of one or more cells connected in series) is basically a galvanic cell and used where the chemical energy of redox reaction is converted into electrical energy.

There are two types of batteries:

## 1. Primary Batteries

In these batteries the cell reaction occurs only once and the battery becomes dead after use over a period of time and cannot be reused again. Hence, these not rechargeable., e.g. dry cells like Leclanche cell, mercury cell etc.

- **Dry cell** or **Leclanche cell** is also called primary voltaic cell. In it, the electrode reactions are

  At anode $\quad \text{Zn}\,(s) \longrightarrow \text{Zn}^{2+}(aq) + 2e^-$

  At cathode $\quad \text{MnO}_2 + \text{NH}_4^+ + e^- \longrightarrow \text{MnO(OH)} + \text{NH}_3$

  The cell potential is 1.6 V.

- Another type of dry cell is **mercury cell**.

  The electrode reactions for the cell are:

  At anode $\quad \text{Zn(Hg)} + 2\text{OH}^- \longrightarrow \text{ZnO}(s) + \text{H}_2\text{O} + 2e^-$

  At cathode $\quad \text{HgO} + \text{H}_2\text{O} + 2e^- \longrightarrow \text{Hg}(l) + 2\text{OH}^-$

  The overall cell reaction is

  $$\text{Zn(Hg)} + \text{HgO}(s) \longrightarrow \text{ZnO}(s) + \text{Hg}(l)$$

## 2. Secondary Batteries

These are also called **reversible galvanic** or **voltaic cell**. These are rechargeable because on charging, reaction becomes reverse, e.g. lead storage battery, nickel-cadmium cell etc.

- In lead storage battery, a solution of sulphuric acid surrounds the plates and acts as an electrolyte. The battery consists of 6 cells, each contains lead anode and lead oxide cathode. The cell potential is 12 V. The half-cell reactions, when the battery is being used up are

  At anode, $\text{Pb}(s) + \text{SO}_4^{2-} \longrightarrow \text{PbSO}_4(s) + 2e^-$

  At cathode, $\text{PbO}_2(s) + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \longrightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}$

  Overall reaction,

  $$\text{Pb}(s) + \text{PbO}_2(s) + 4\text{H}^+ + 2\text{SO}_4^{2-} \longrightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}$$

  During charging, following reactions occur

  At anode,

  $$\text{PbSO}_4(s) + 2\text{H}_2\text{O} \longrightarrow \text{PbO}_2(s) + \text{SO}_4^{2-} + 4\text{H}^+ + 2\,e^-$$

  At cathode, $\text{PbSO}_4(s) + 2e^- \longrightarrow \text{Pb}(s) + \text{SO}_4^{2-}$

  Overall reaction,

  $$2\text{PbSO}_4(s) + 2\text{H}_2\text{O} \longrightarrow \text{Pb}(s) + \text{PbO}_2(s) + 4\text{H}^+ + 2\text{SO}_4^{2-}$$

# Lead Accumulator

- In these the electrodes are made of lead and the electrolyte consists of dilute sulphuric acid.

  The electrodes are usually cast from a lead alloy containing 7-12% of antimony (to give increased hardness and corrosion resistance) and a small amount of tin (for better casting properties).
- The electrodes are coated with a paste of lead (II) oxide (PbO) and finely divided lead; after insertion into the electrolyte, a 'forming' current is passed through the cell to convert the PbO on the negative plate into a sponge of finely divided lead. On the positive plate, the PbO is converted to lead (IV) oxide ($\text{PbO}_2$).
- The equation for the overall reaction during discharge is

  $$\text{PbO}_2 + 2\,\text{H}_2\text{SO}_4 + \text{Pb} \longrightarrow 2\ \text{PbSO}_4 + 2\ \text{H}_2\text{O}$$
- The reaction is reversed during charging. Each cell gives an emf of about 2 V and in motor vehicles, a 12 V battery of six cells is usually used. The lead-acid battery produces 80-120 kJ per kilogram.

# Fuel Cells

These cells are another means by which chemical energy may be converted into electrical energy. Energy can be obtained indefinitely from a fuel cell as long as outside supply of fuel is maintained, e.g. $\text{H}_2$- $\text{O}_2$ fuel cell.

The half-reactions are :

At anode, $\quad 2\text{H}_2(g) + 4\text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(l) + 4\,e^-$

At cathode,

$$\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4\,e^- \longrightarrow 4\text{OH}^-(aq)$$

Overall cell reaction,

$$2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l)$$

The **efficiency of the fuel cell** is the ratio of change in Gibbs energy ($\Delta G$) to the heat of combustion ($\Delta H$) and mathematically can be given as,

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

where,

$\eta$ = thermodynamic efficiency of a fuel cell

$\Delta H$ = heat of combustion

$\Delta G$ = work done = $-\,nFE^\circ_{\text{cell}}$

### Uses of Fuel Cell

This cell was used as a primary source of electrical energy on the moon flights. The overall cell reaction produces water, which was used for drinking by the astronauts.

## Corrosion

- It is basically an electrochemical phenomenon. A metal is oxidised by loss of electrons to oxygen and forms metal oxide. e.g. conversion of iron to rust [$Fe_2O_3 \cdot xH_2O$], the tarnishing of silver (due to formation of $Ag_2S$), development of a green coating on copper and bronze.
- Corrosion of iron, known as rusting, occurs in the presence of water and oxygen The reactions are:

  At anode, $2Fe\,(s) \longrightarrow 2Fe^{2+}(aq) + 4e^-$

  At cathode, $O_2\,(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O\,(l)$

The overall reaction,

$$2Fe\,(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O\,(l)$$

$Fe^{2+}$ ions further oxidised by atmospheric oxygen to $Fe^{3+}$ ions and form hydrated ferric oxide [$Fe_2O_3 \cdot xH_2O$].

$$4Fe^{2+} + O_2 + 4H_2O \longrightarrow 2Fe_2O_3(s) + 8H^+(aq)$$

$$Fe_2O_3 + xH_2O \longrightarrow \underset{\text{Hydrated ferric oxide (Rust)}}{Fe_2O_3 \cdot xH_2O}$$

### Prevention

Rusting of iron can be prevented by the following methods:

(i) Barrier protection through coating of paints or electroplating.

(ii) Galvanisation or coating of surface with tin metal.

(iii) By the use of anti-rust solutions.

## DAY PRACTICE SESSION 1

# FOUNDATION QUESTIONS EXERCISE

**1** 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 → **NEET 2016, Phase II**

(a) 2.88 S $cm^2$/mol
(b) 11.52 S $cm^2$/mol
(c) 0.086 S $cm^2$/mol
(d) 28.8 S $cm^2$/mol

**2** Which of the following electrolytic solutions has the least specific conductance?

(a) 0.02 N (b) 0.2 N (c) 2 N (d) 0.002 N

**3** Which of the following statements about solutions of electrolytes is not correct?

(a) Conductivity of solution depends upon size of ions
(b) Conductivity depends upon viscosity of solution
(c) Conductivity does not depend upon solvation of ions present in solution
(d) Conductivity of solution increases with temperature

**4**

| Electrolyte | KCl | $KNO_3$ | HCl | NaOAc | NaCl |
|---|---|---|---|---|---|
| $\Lambda^\infty$(S $cm^2$ $mol^{-1}$) | 149.9 | 145.0 | 426.2 | 91.0 | 126.5 |

Calculate $\Lambda^\infty_{AcHO}$ using appropriate molar conductances of the electrolytes listed above at infinite dilution in $H_2O$ at 25°C.

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

**5** An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to → **CBSE-AIPMT 2010**

(a) increase in ionic mobility of ions
(b) 100% ionisation of electrolyte at normal dilution
(c) increase in both, i.e. number of ions and ionic mobility of ions
(d) increase in number of ions

**6** The specific conductance of a 0.1 N KCl solution at 23°C is 0.012 $\Omega$ $cm^{-1}$. The resistance of cell containing the solution at the same temperature was found to be 55 $\Omega$. The cell constant will be

(a) 0.142 $cm^{-1}$
(b) 0.66 $cm^{-1}$
(c) 0.918 $cm^{-1}$
(d) 1.12 $cm^{-1}$

**7** Limiting molar conductivity of $NH_4OH$, (i.e. $\Lambda^\circ_m(NH_4OH)$ is equal to → **CBSE-AIPMT 2012**

(a) $\Lambda^\circ_m(NH_4Cl) + \Lambda^\circ_m(NaCl) - \Lambda^\circ_m(NaOH)$
(b) $\Lambda^\circ_m(NaOH) + \Lambda^\circ_m(NaCl) - \Lambda^\circ_m(NH_4Cl)$
(c) $\Lambda^\circ_m(NH_4OH) + \Lambda^\circ_m(NH_4Cl) - \Lambda^\circ_m(HCl)$
(d) $\Lambda^\circ_m(NH_4Cl) + \Lambda^\circ_m(NaOH) - \Lambda^\circ_m(NaCl)$

**8** If $\Lambda^\infty_{ClCH_2\,COONa} = 224\ \Omega^{-1}\ cm^2\ g\ equiv^{-1}$

$\Lambda^\infty_{NaCl} = 38.5\ \Omega^{-1}\ cm^2\ g\ equiv^{-1}$

$\Lambda^\infty_{HCl} = 203\ \Omega^{-1}\ cm^2\ g\ equiv^{-1}$

What is the value of $\Lambda^\infty_{ClCH_2COOH}$?

(a) 288.5 $\Omega^{-1}$ $cm^2$ g $equiv^{-1}$ (b) 188.5 $\Omega^{-1}$ $cm^2$ g $equiv^{-1}$
(c) 388.5 $\Omega^{-1}$ $cm^2$ g $equiv^{-1}$ (d) 59.5 $\Omega^{-1}$ $cm^2$ g $equiv^{-1}$

**9** The standard emf of a galvanic cell involving cell reaction with $n = 2$ is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be

(a) $2.0 \times 10^{11}$
(b) $4.0 \times 10^{12}$
(c) $1.0 \times 10^2$
(d) $1.0 \times 10^{10}$

**10** In a $H_2$-$O_2$ fuel cell, combustion of hydrogen occurs to

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

**11** A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as **→ CBSE-AIPMT 2015**

(a) fuel cell (b) electrolytic cell
(c) dynamo (d) Ni-Cd cell

**12** The pressure of $H_2$ required to make the potential of $H_2$-electrode zero in pure water at 298 K is **→ NEET 2016, Phase I**

(a) $10^{-12}$ atm (b) $10^{-10}$ atm
(c) $10^{-4}$ atm (d) $10^{-14}$ atm

**13** A button cell used matches, functions as following

$$Zn(s) + Ag_2O(s) + H_2O(l) \rightleftharpoons 2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq)$$

if half-cell potentials are :

Given, $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s); E^\circ = -0.76$ V

$Ag_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Ag(s) + 2OH^-(aq);$ $E^\circ = 0.34$ V

The cell potential will be **→ NEET 2013**

(a) 0.42 V (b) 0.84 V
(c) 1.34 V (d) 1.10 V

**14** What amount of $Cl_2$ gas is liberated at anode, if 1A current is passed for 30 min in NaCl solution?

(a) 0.66 mole (b) 0.33 mole
(c) 0.66 g (d) 0.33 g

**15** What is the time (in s) required 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)

(a) 10 (b) 50 (c) 1000 (d) 100

**16** The standard reduction potentials at 298 K for the following half-cell reactions are given

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s); -0.762 \text{ V}$$
$$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s); -0.74 \text{ V}$$
$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g); +0.00 \text{ V}$$
$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq); +0.77 \text{ V}$$

Which one of the following is the strongest reducing agent?

(a) Zn($s$) (b) Cr ($s$)
(c) $H_2(s)$ (d) $Fe^{2+}(aq)$

**17** Standard electrode potential for $Sn^{4+}|Sn^{2+}$ couple is + 0.15 V and that for the $Cr^{3+}|Cr$ couple is − 0.74 . These two couples in their standard state are connected to make a cell. The cell potential will be **→ CBSE-AIPMT 2011**

(a) + 0.89 V (b) + 0.18 V
(c) + 1.83 V (d) + 1.199 V

**18** The $E^\circ_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are −0.41, +1.57, + 0.77 and + 1.97 V respectively. For which one of the following metal, the change in oxidation state for + 2 to + 3 is easiest?

(a) Co (b) Mn
(c) Cr (d) Fe

**19** If $E^\circ_{Fe^{2+}/Fe} = 0.441$ V and $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$ V, the standard emf of the reaction

$$Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+} \text{ will be}$$

(a) 0.330 V (b) 1.653 V
(c) 1.212 V (d) 0.111 V

**20** A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by hydrogen gas around the platinum wire at one atm. Pressure the oxidation potential of electrode would be **→ NEET 2013**

(a) 0.59 V (b) 0.118 V
(c) 1.18 V (d) 0.059 V

**21** The quantity of electricity required to oxidise 0.1 mole of $MnO_4^{2-}$ completely to $MnO_4^-$, is **→ CBSE-AIPMT 2014**

(a) 96500 C (b) 2 × 96500 C
(c) 9650 C (d) 196.50 C

**22** Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn.

(a) Mg > Zn > Al > Fe > Cu (b) Mg > Fe > Al > Zn > Cu
(c) Mg > Al > Zn > Fe > Cu (d) Mg > Al > Fe > Zn > Cu

**23** In the electrochemical cell, Zn|| $ZnSO_4$ (0.01 M)|| $CuSO_4$(1.0M) Cu, the emf of this Daniell cell is $E_1$. When the concentration $ZnSO_4$ is changed to 1.0 M and that of $CuSO_4$ changed to 0.01 M, the emf changes to $E_2$. From the followings, which one is the relationship between $E_1$ and $E_2$? ( Given, $\frac{RT}{F} = 0.059$) **→ NEET 2017**

(a) $E_1 = E_2$ (b) $E_1 < E_2$
(c) $E_1 > E_2$ (d) $E_2 = 0 \neq E_1$

**24** Time required to deposit one millimole of aluminium metal by the passed of 9.65A current through molten electrolyte containing aluminium ion is

(a) 30 s (b) 10 s
(c) 30000 s (d) 10000 s

**25** What is the current efficiency of an electrode deposition of Cu metal from $CuSO_4$ solution in which 9.80 g copper is deposited by the passage of 5A current for 2 h?

(a) 41.4% (b) 50%
(c) 75% (d) 82.8%

**26** For the reduction of silver ions with copper metal, the standard cell potential was found to be +0.46 V at 25°C. The value of standard Gibbs energy, $\Delta G^\circ$ will be ($F = 96500$ C mol$^{-1}$) **→ CBSE-AIPMT 2010**

(a) −89.0 kJ (b) −89.0 J
(c) −44.5 kJ (d) −98.0 kJ

**27** Efficiency of a cell with cell reaction under standard conditions is 80%. The standard electrode potential of the cell $A(s) + B^{n+} \longrightarrow A^{n+} + B(s)$; $\Delta H^\circ = -300$ kJ and $n = 2$, is

(a) 1.24 V (b) 2.48 V (c) zero (d) 0.62 V

**28** Standard electrode potentials of $Fe^{2+} + 2e^- \longrightarrow Fe$ and $Fe^{3+} + 3e^- \longrightarrow Fe$ are $-0.440\,V$ and $-0.036\,V$ respectively. The standard electrode potential ($E°$) for $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ is

(a) $-0.476\,V$ (b) $-0.404\,V$
(c) $0.404\,V$ (d) $+0.772\,V$

**29** Which statement is true about a spontaneous cell reaction in galvanic cell?

(a) $E°_{cell} > 0$; $\Delta G° = -$ ve; $Q < K_C$
(b) $E°_{cell} > 0$; $\Delta G° = +$ ve; $Q < K_C$
(c) $E°_{cell} > 0$; $\Delta G° = -$ ve; $Q > K_C$
(d) $E°_{cell} > 0$; $\Delta G° = +$ ve; $Q = K_C$

**30** The charge required for the reduction of 1 mole of $MnO_4^-$ to $MnO_2$ is

(a) 1 F (b) 3 F
(c) 5 F (d) 6 F

**31** When lead storage battery is charged

(a) lead dioxide dissolves
(b) sulphuric and is regenerated
(c) the lead electrode becomes coated with lead sulphate
(d) the amount of sulphuric acid decreases

**32** Which of the following is widely used in the manufacture of lead storage battery?

(a) Arsenic (b) Lithium
(c) Bismuth (d) Antimony

**33** The equilibrium constant of the reaction

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

(Given, $E° = 0.46\,V$ at 298 K) is

(a) $2.4 \times 10^{10}$ (b) $2.0 \times 10^{10}$
(c) $4.0 \times 10^{10}$ (d) $4.0 \times 10^{15}$

**34** Zinc can be coated on iron to produce galvanised iron but the reverse is not possible. It is because

→ **NEET 2016, Phase II**

(a) zinc is lighter than iron
(b) zinc has lower melting point than iron
(c) zinc has lower negative electrode potential than iron
(d) zinc has higher negative electrode potential than iron

**35** The weight of silver (at. wt. = 108) displaced by a quantity of electricity, which displaces 5600 mL of $O_2$ at STP will be → **CBSE-AIPMT 2014**

(a) 5.4 g (b) 10.8 g
(c) 54.0 g (d) 108.0 g

**36** The emf of the cell, $Zn|Zn^{2+}\,(0.01M)||Fe^{2+}\,(0.001M)|Fe$ at 298 K is 0.2905. The value of equilibrium constant for the cell reaction is

(a) $10^{0.32/0.0295}$ (b) $e^{0.32/0.0295}$
(c) $10^{0.32/0.0591}$ (d) $10^{0.26/0.0295}$

**37** The rusting of iron takes place as.

$$2H^+ + 2e^- + \frac{1}{2}O_2 \longrightarrow H_2O(l); \quad E° = +1.23\,V$$

$$Fe^{2+} + 2e^- \longrightarrow Fe(s); \quad E° = -0.44\,V$$

Thus, $\Delta G°$ for the net process is

(a) $-322$ kJ/mol (b) $-161$ kJ/mol
(c) $-1522$ kJ/mol (d) $-76$ kJ/mol

**38** Standard electrode potential of three metals $X, Y$ and $Z$ are $-1.2$ V, $+0.5$ V and $-3.0$ V respectively. The reducing power of these metals will be → **CBSE-AIPMT 2011**

(a) $Y > X > Z$ (b) $Z > X > Y$
(c) $X > Y > Z$ (d) $Y > Z > X$

**39** If the $E°_{cell}$ for a given reaction has a negative value, then which of the following gives the correct relationships for the values of $\Delta G°$ and $K_{eq}$? → **CBSE-AIPMT 2011**

(a) $\Delta G° < 0$; $K_{eq} > 1$ (b) $\Delta G° < 0$; $K_{eq} < 1$
(c) $\Delta G° > 0$; $K_{eq} < 1$ (d) $\Delta G° > 0$; $K_{eq} > 1$

**40** Consider the change in oxidation state of bromine corresponding to different emf values as shown in the diagram below. → **NEET 2018**

$$BrO_4^- \xrightarrow{1.82\,V} BrO_3^- \xrightarrow{1.5\,V} HBrO$$
$$\xrightarrow{1.595\,V} Br_2 \xrightarrow{1.0652\,V} Br^-$$

Then the species undergoing disproportionation is

(a) $Br_2$ (b) $BrO_4^-$
(c) $BrO_3^-$ (d) HBrO

## DAY PRACTICE SESSION 2

# PROGRESSIVE QUESTIONS EXERCISE

**1** 4.5 g of aluminium (atomic mass 27 u) is deposited at cathode from a molten electrolyte containing $Al^{3+}$ ions by a certain quantity of electric charge. The volume of hydrogen produced at STP from $H^+$ ions in a solution by the same quantity of electric charge will be

(a) 44.8 L (b) 11.2 L (c) 22.4 L (d) 5.6

**2** At 25°C the molar conductance of 0.007M hydrofluoric acid is 150 mho $cm^2\,mol^{-1}$ and its $\Lambda°_m = 500$ mho $cm^2\,mol^{-1}$. The value of dissociation constant of the acid at a given concentration is

(a) $7 \times 10^{-4}$ M (b) $7 \times 10^{-5}$ M
(c) $9 \times 10^{-3}$ M (d) $9 \times 10^{-4}$M

**3** 0.04 N solution of a weak acid has specific conductance $4.23 \times 10^{-4}$ mho $cm^{-1}$ and degree of dissociation is 0.0612. The equivalent conductance ($ohm^{-1}cm^{2}equiv^{-1}$) of weak acid at infinite dilution is

(a) 1.72 (b) 17.29 (c) 142.27 (d) 172.79

**4** The standard reduction potentials of the three electrodes *P*, *Q* and *R* are respectively –1.76 V, 0.34 V and 0.8 V. Then

(a) metal *Q* will displace the cation of *P* from its aqueous solution and deposit the metal *P*
(b) metal *P* will displace the cation of R from its aqueous solution and deposit the metal *R*
(c) metal *R* will displace the cation of *P* from its aqueous solution and deposit the metal *R*
(d) Both metals *Q* and *R* will displace the cation the cation of *P* from its aqueous solution and deposit the metal *P*

**5** 9.65 C of electric current is passed through fused anhydrous $MgCl_2$. The magnesium metal thus obtained is completely converted into a Grignard reagent. The number of moles of Grignard reagent obtained is

(a) $5 \times 10^{-4}$ (b) $1 \times 10^{-4}$ (c) $5 \times 10^{-5}$ (d) $1 \times 10^{-5}$

**6** The ionic conductance of $Ba^{2+}$ and $Cl^-$ are respectively 127 and 76 $\Omega^{-1}$ $cm^2$ at infinite dilution. The equivalent conductance (in $\Omega^{-1}$ $cm^2$) of $BaCl_2$ at infinite dilution will

(a) 279 (b) 203 (c) 101.5 (d) 139.5

**7** Consider the following half-cell reactions,

$Cu^{2+} + 2e^- \longrightarrow Cu$, $E° = 0.34V$
$Zn^{2+} + 2e^- \longrightarrow Zn$, $E° = -0.76V$
$SO_4^{2-} + 4H^+ + 2e^- \longrightarrow SO_2 + 2H_2O$, $E° = 1.17V$

Hence, select the correct statement(s)

(a) Cu reacts with dil. $H_2SO_4$ forming $H_2$ and $SO_2$
(b) Cu reacts with concentrated $H_2SO_4$ forming $SO_2$
(c) Zn reacts with concentrated $H_2SO_4$ forming $SO_2$
(d) Both (b) and (c)

**8** A current of 12 A is passed through an electrolytic cell containing aqueous $NiSO_4$ solution. Both Ni and $H_2$ gas are formed at the cathode. The current efficiency is 60%. What is the mass of nickel deposited on the cathode per hour?

(a) 7.883 g (b) 3.941 g (c) 5.91 g (d) 2.645 g

**9** For the following cell with hydrogen electrodes at two different pressures $p_1$ and $p_2$.

$\underset{p_1}{Pt(H_2)} | \underset{1M}{H^+(aq)} | \underset{p_2}{Pt(H_2)}$, emf is given by

(a) $\frac{RT}{F} \log_e \frac{p_1}{p_2}$ (b) $\frac{RT}{2F} \log_e \frac{p_1}{p_2}$
(c) $\frac{RT}{F} \log_e \frac{p_2}{p_1}$ (d) $\frac{RT}{2F} \log_e \frac{p_2}{p_1}$

**10** 1 Faraday of electricity is passed through the solution containing 1 mole each of $CuSO_4$, $AlCl_3$ and $SiCl_4$. Number of moles of Cu, Al and Si forms will be in the ratio

(a) 1 : 1 : 1 (b) 2 : 3 : 4
(c) 6 : 4 : 3 (d) 3 : 4 : 6

**11** Which statement is true and about a galvanic cell employing Pb, Cu, $Pb^{2+}$ and $Cu^+$?

$$E°_{Pb^{2+}/Pb} = -0.127\ V; E°_{Cu^+/Cu} = +0.518\ V$$

.

(a) Spontaneous cell-reaction will be in the ce

$$Pb | Pb^{2+} || Cu^+ | Cu$$

(b) $E°_{cell} = 0.645$ V
(c) Both (a) and (b) are correct
(d) None of the above is correct

**12** At 25°C temperature, the cell potential of a given electrochemical cell is 1.92 V. Find the value of *x*.

$Mg(s) | Mg^{2+}(aq), x\ M || Fe^{2+}(aq)\ 0.01\ M | Fe(s)$
$E°$ for $Mg | Mg^{2+}(aq) = 2.37$ V,
$E°$ for $Fe | Fe^{2+}(aq) = 0.45$ V

(a) $x = 0.01$ M
(b) $x < 0.01$ M
(c) $x > 0.01$ M
(d) *x* cannot be predicted

**13** Aluminium displaces hydrogen from acids, but copper does not. A galvanic cell prepared by combining $Cu/Cu^{2+}$ and $Al/Al^{3+}$ has an emf of 2.0V at 298K. If the potential of copper electrode is 0.34V, that of aluminium electrode is

(a) –2.3 V (b) +2.34 V
(c) –1.66 V (d) +1.66 V

**14** Given, the following reaction involving *A*, *B*, *C* and *D*.

(i) $C + B^+ \longrightarrow C^+ + B$
(ii) $A^- + D \longrightarrow$ No reaction
(iii) $C^+ + A \longrightarrow$ No reaction
(iv) $D + B^+ \longrightarrow D^+ + B$

The correct arrangement of *A, B, C, D* in order of their decreasing ability as reducing agent.

(a) $D > B > C > A$ (b) $A > C > D > B$
(c) $C > A > B > D$ (d) $C > A > D > B$

**15** When $Al_2O_3$ is electrolysed, aluminium is produced at one electrode and oxygen gas at the other electrode. For a given quantity of electricity, ratio of number of moles of aluminium to the number of moles of oxygen gas is

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

# ANSWERS

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

# Hints and Explanations

## SESSION 1

**1** The relation between molar conductivity ($\lambda_m$) and electrolytic conductivity ($\kappa$) is given as

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

where, $M$ is molarity of solution.

Given, concentration of solution,

$$M = 0.5 \text{ mol/dm}^3$$

Electrolytic conductivity,

$$\kappa = 5.76 \times 10^{-3} \text{ S cm}^{-1}$$

Temperature, $T = 298$ K

$\therefore$ Molar conductivity,

$$\lambda_m = \frac{\kappa \times 1000}{M} = \frac{5.76 \times 10^{-3} \times 1000}{0.5} = 11.52 \text{ S cm}^2\text{/mol}$$

**2** Specific conductance $\propto$ concentration of electrolytes, hence specific conductance is least for the solution which has 0.002 N concentration.

**3** Statement 'C' is incorrect. Conductivity also depends upon the solvation of ions.

**4** $$\Lambda^\infty_{AcOH} = \Lambda^\infty_{AcONa} + \Lambda^\infty_{HCl} - \Lambda^\infty_{NaCl} = 91.0 + 426.2 - 126.5 = 390.7$$

**5** $$\Lambda_{eq} = \kappa \times V = \frac{\kappa \times 1000}{\text{normality}}$$

On dilution, the number of current carrying particles per $cm^3$ decreases but the volume of solution increases. Consequently, the ionic mobility increases, which in turn, increases the equivalent conductance of strong electrolyte.

**6** Specific conductivity,

$$\kappa = 0.012\,\Omega^{-1}\text{ cm}^{-1};$$

Resistance = 55 Ω

$$\kappa = \frac{1}{\text{resistance}} \times \frac{l}{a}\left[G = \frac{1}{R}\right]$$

$$\frac{l}{a} = \text{cell constant}$$

$$\frac{l}{a} = 55 \times 0.012 = 0.66 \text{ cm}^{-1}$$

**7** According to Kohlrausch's law,

limiting molar conductivity of $NH_4OH$

$$\overset{\circ}{\Lambda}_m(NH_4OH)$$

$$= \overset{\circ}{\Lambda}_m(NH_4Cl) + \overset{\circ}{\Lambda}_m(NaOH) - \overset{\circ}{\Lambda}_m(NaCl)$$

**8** According to Kohlrausch's law,

$$\Lambda^\infty_{ClCH_2COOH} = \Lambda^\infty_{ClCH_2COO^-} + \Lambda^\infty_{H^+}$$

Given, from Kohlrausch's law,

$$\Lambda^\infty_{ClCH_2COONa} = \Lambda^\infty_{ClCH_2COO^-} + \Lambda^\infty_{Na^+}$$

$$\text{or } \Lambda^\infty_{ClCH_2COO^-} + \Lambda^\infty_{Na^+} = 224 \qquad \ldots\text{(i)}$$

$$\Lambda^\infty_{HCl} = \Lambda^\infty_{H^+} + \Lambda^\infty_{Cl^-}$$

$$\text{or } \Lambda^\infty_{H^+} + \Lambda^\infty_{Cl^-} = 203 \qquad \ldots\text{(ii)}$$

$$\Lambda^\infty_{NaCl} = \Lambda^\infty_{Na^+} + \Lambda^\infty_{Cl^-}$$

$$\text{or } \Lambda^\infty_{Na^+} + \Lambda^\infty_{Cl^-} = 38.5 \qquad \ldots\text{(iii)}$$

Adding Eqs. (i) and (ii) and subtracting Eq. (iii), we get

$$\Lambda^\infty_{ClCH_2COO^-} + \Lambda^\infty_{H} = 224 + 203 - 38.5 = 427 - 38.5 = 388.5\,\Omega^{-1}\text{cm}^2\text{g eq}^{-1}$$

**9** $$E^\circ_{cell} = \frac{0.0591}{n}\log K$$

$$0.295 = \frac{0.0591}{2}\log K$$

$$\log K = \frac{0.295 \times 2}{0.0591} = 10$$

$$K = \text{antilog } 10 = 1 \times 10^{10}$$

**10** Fuel cell converts chemical energy into electrical energy.

**At anode** $2H_2(g) + 4OH^- \longrightarrow 4H_2O(l) + 4e^-$

**At cathode** $O_2 + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O(l);\ E^\circ = +\text{ve}$$

**11** Fuel cell is a device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy. Electrolytic cell converts electrical energy into chemical energy. Dynamo is an electrical generator that produces direct current with the use of a commutator.

Ni-Cd cell is a type of rechargeable battery which consists of a cadmium anode and a metal grid containing $NiO_2$, acting as a cathode.

**12** From the question, we have an equation

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

According to Nernst equation,

$$E = E^\circ - \frac{0.0591}{2}\log\frac{p_{H_2}}{[H^+]^2}$$

$$= 0 - \frac{0.0591}{2}\log\frac{p_{H_2}}{(10^{-7})^2}$$

$$[\because\ [H^+] = 10^{-7}]$$

$\therefore$ For potential of $H_2$ electrode to be zero, $p_{H_2}$ should be equal to $[H^+]^2$, i.e. $10^{-14}$ atm.

$$\therefore \qquad \log\frac{10^{-14}}{(10^{-7})^2} = 0$$

**13** $E^\circ_{\text{cell}} = E^\circ_{\text{OP}} + E^\circ_{\text{RP}}$

$= 0.76 + 0.34 = 1.10\text{ V}$

**14** $\underset{1\text{ mole}}{2\text{Cl}^-} \longrightarrow \text{Cl}_2 + \underset{2\times 96500\ \text{C}}{2e^-}$

$Q = it = 1 \times 30 \times 60 = 1800\text{ C}$

The amount of chlorine liberated by passing 1800 C of electric charge

$$= \frac{1 \times 1800 \times 71}{2 \times 96500} = 0.66\text{ g}$$

**15** Given, 125 mL of 1 M $\text{AgNO}_3$ solution. It means that

$\because$ 1000 mL of $\text{AgNO}_3$ solution contains = 108 g Ag

$\therefore$ 125 mL of $\text{AgNO}_3$ solution contains

$$= \frac{108 \times 125}{100}\text{ g Ag} = 13.5\text{ g Ag}$$

$\because$ 108 g of Ag is deposited by electricity 96500 C

$\therefore$ 13.5 g of Ag is deposited by

$$= \frac{96500}{108} \times 13.5 = 12062.5\text{ C electricity}$$

$\because \quad Q = it$

$\therefore \quad t = \frac{Q}{i} = \frac{12062.5}{241.25} = 50\text{ s}$

**16** The metals having higher negative value of standard reduction potential are placed above hydrogen in electrochemical series. The metals placed above the hydrogen has a great tendency to donate electrons or oxidising power.

The metals having high oxidising power are strongest reducing agent. Zn has higher negative value of standard reduction potential. Therefore, it is the strongest reducing agent.

**17** $E^\circ_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0.15\text{ V}$

$E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74\text{ V}$

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode(RP)}} - E^\circ_{\text{anode(RP)}}$

$= 0.15 - (-0.74)$

$= +\ 0.89\text{ V}$

**18** $E^\circ_{M^{3+}/M^{2+}}$ for Cr is minimum (i.e. $-$ 0.41) hence, $\text{Cr}^{2+}$ is easily oxidised to $\text{Cr}^{3+}$.

**19** Cell reaction

$\text{Fe} \longrightarrow \text{Fe}^{2+} + 2e^-;\quad E^\circ = 0.441\text{ V}$

$2\text{Fe}^{3+} + 2e^- \longrightarrow 2\text{Fe}^{2+};$

$E^\circ = 0.771\text{ V}$

$\text{Fe} + 2\text{Fe}^{3+} \longrightarrow 3\text{Fe}^{2+};$

$E^\circ_{\text{cell}} = 1.212\text{ V}$

**20** $\underset{1\text{ atm}}{\text{H}_2} \longrightarrow \underset{10^{-10}}{2\text{H}^+} + 2e^-$

$$E_{\text{H}_2/\text{H}^+} = 0 - \frac{0.059}{2}\log\frac{(10^{-10})^2}{1}$$

$= +\ 0.59\text{ V}$

**21** The reaction is

$\text{MnO}_4^{2-} \longrightarrow \text{MnO}_4^-$

i.e. $\quad \text{Mn}^{+6} \xrightarrow[+e^-]{} \text{Mn}^{+7}$

Quantity of electricity required for 1 mole of $\text{MnO}_4^{2-} = 1\text{F}$

$\therefore$ For 0.1 mole, 0.1 F is required.

because 1 F = 96500 C hence, 0.1 F means 9650 C.

**22** Mg > Al > Zn > Fe > Cu

It means that every metal on the left side can displace the next one(s) from its salt solution.

**23** Calculate the value of $E_{\text{cell}}$, i.e. $E_1$ and $E_2$ by substituting the respective given values in the Nernst equation,

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

Compare the calculated values of $E_1$ and $E_2$ and find the correct relation.

For the electrochemical cells,

$\text{Zn}\,|\,\text{ZnSO}_4\ (0.01\text{M})\,||\,\text{CuSO}_4(1\text{M})\,|\,\text{Cu}$

Cell reaction :

$\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu};\ n = 2$

$$E_1 = E^\circ - \frac{0.059}{2}\log\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}}$$

$$= E^\circ - \frac{0.059}{2}\log\frac{0.01}{1}$$

$$E_1 = E^\circ - \frac{0.059}{2}\log\frac{1}{100} = (E^\circ + 0.059)$$

For cell,

$\text{Zn}\,|\,\text{ZnSO}_4(1\text{M})\,||\,\text{CuSO}_4(0.01\text{M})\,|\,\text{Cu}$

$$E_2 = E^\circ - \frac{0.059}{2}\log\frac{1}{0.01}$$

$$E_2 = E^\circ - \frac{0.059}{2}\log 100$$

$\therefore \quad = (E^\circ - 0.059)$

$\Rightarrow \quad E_1 > E_2$

**24** 1 mole of Al requires = $3 \times 96500$ C

$10^{-3}$ mole of Al requires

$= 3 \times 96500 \times 10^{-3}$ C

$= 3 \times 96.5$ C

$$\therefore \text{Time (s)} = \frac{3 \times 96.5\text{ A-s}}{9.65\text{ A}} = 30\text{ s}$$

**25** $$\frac{\text{Weight}}{\text{Equivalent weight}} = \frac{it}{96500}$$

$$\frac{9.8}{63.512} = \frac{i \times 2 \times 60 \times 60}{96500}$$

$i = 2.06$

$\therefore$ Current efficiency

$$= \frac{\text{Theoretical value of } i}{\text{Practical value of } i} \times 100$$

$$= \frac{2.06}{5} \times 100$$

$= 41.36 = 41.4\,\%$

**26** We know that,

standard Gibbs energy,

$\Delta G^\circ = -\,nFE^\circ_{\text{cell}}$

For the cell reaction,

$2\text{Ag}^+ + \text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{Ag}$

$E^\circ_{\text{cell}} = +\ 0.46\text{ V}$

$\Delta G^\circ = -2 \times 96500 \times 0.46$

$= -88780\text{ J} = -88.7\text{ kJ} \approx -\ 89.0\text{ kJ}$

**27** $\text{Efficiency} = \frac{\Delta G^\circ}{\Delta H^\circ} = \frac{nFE^\circ}{\Delta H}$

$$E^\circ = \frac{\Delta H^\circ \times 80}{-nF \times 100}$$

$$= \frac{-\ 300 \times 10^3 \times 80}{-2 \times 96500 \times 100} = 1.24\text{V}$$

**28** $\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe};$

$\Delta G_1 = 2 \times (-0.44) \times F$

$\text{Fe}^{3+} + 3e^- \longrightarrow \text{Fe};$

$\Delta G_2 = 3 \times (-0.036) \times F$

$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-,$

$\Delta G_3 = -\ 0.88 + 0.108$

$= -\ 0.772$

$\therefore$ From, $G^\circ = -\,nFE^\circ$

or $\quad -0.772 = -\,1 \times E^\circ \times F$

$\therefore\ \text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+};\ E^\circ = 0.772\text{ V}$

**29** For spontaneous cell reaction, $E^\circ_{\text{cell}} = +\text{ ve}$, $\Delta G^\circ = -\text{ ve}$ and $Q_C < K_C$.

**30** $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^- \longrightarrow$

$\text{MnO}_2 + 4\text{OH}^-$

$\overset{+7}{\text{Mn}} \xrightarrow[+\ 3e^-]{} \overset{+4}{\text{Mn}}$

$\therefore$ It required 3F of charge for 3 moles of electrons.

Quantity of charge required for 1 mole of electron = 1 F.

**31** During the charging of a lead storage battery, the reaction at the anode and cathode are :

**Anode** $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$

**Cathode** $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + e^-$

In both the reaction, $H_2SO_4$ is regenerated.

**32** Antimony is used in making lead storage batteries because lead containing antimony is harder and more resistant to the action of acids than ordinary lead.

**33** $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

$E° = 0.46$ V at 298 K

.

$$\therefore \quad 0.46 = \frac{0.059}{2} \log K_C$$

$$\log K_C = \frac{0.46}{0.0295} = 15.59$$

$$K_C = 3.92 \times 10^{15}$$

$$\approx 4 \times 10^{15}$$

**34** The metal with higher negative standard reduction potential, have higher tendency to get reduced.

$Zn^{2+} + 2e^- \longrightarrow Zn;\ E° = -0.76\,V$

$Fe^{2+} + 2e^- \longrightarrow Fe;\ E° = -0.44\,V$

Here, in galvanised iron, Zn has higher negative reduction potential means Zn takes electrons given by iron and itself gets reduced.

Thus, Zn works as anode and protects iron from rusting by making iron as cathode.

**35** $W_{O_2} = \frac{5600}{22400} \times 32 = 8\,g = 1$ equivalent

$= 1$ equivalent of Ag $= 108$ g

**36** For the given cell, reaction is

$$Zn + Fe^{2+} \longrightarrow Zn^{2+} + Fe$$

$$E = E° - \frac{0.0591}{n} \log \frac{C_1}{C_2}$$

$$\text{or } E° = E + \frac{0.0591}{n} \log \frac{C_1}{C_2}$$

$$= 0.2905 + \frac{0.0591}{2} \log \frac{10^{-2}}{10^{-3}}$$

$$= 0.32\ V$$

$$E° = \frac{0.0591}{2} \log K_C$$

$$\therefore \quad \log K_C = \frac{0.32 \times 2}{0.0591} = \frac{0.32}{0.0295}$$

$$K_C = 10^{\frac{0.32}{0.0295}}$$

**37** $E°_{\text{cell}} = E°_C - E°_A$

$= 1.23 - (-0.44) = 1.67$ V

$\Delta G° = -nFE° = -2 \times 96500 \times 1.67$

$= -322.31$ kJ/mol

**38** $E°_x = -1.2\,V$

$E°_y = -0.5\,V$

$E°_z = -3.0\,V$

$\therefore \quad Z > X > Y$

[∵ Higher the reduction potential, lesser the reducing power]

**39** $\Delta G° = -nFE°$

When $E°$ is negative, then $\Delta G° > 0$

$\Delta G° = -RT \ln K_{eq}$

When $\Delta G° = 0$, $K_{eq} = 10^{-x}$ which is less than one, i.e. $K_{eq} < 1$.

**40** The reaction in which same species is oxidised as well as reduced is called disproportionation reaction. Firstly, calculate the value of $E°_{\text{cell}}$ of each species undergoing disproportionation reaction. The reaction whose $E°_{\text{cell}}$ value is positive will be feasible (spontaneous).

(i) Given, $BrO_3^- \longrightarrow HBrO$ ; $E°_{BrO_3^-/HBrO} = 1.5$ V

$BrO_3^- \longrightarrow BrO_4^-$; $E°_{BrO_3^-/BrO_4^-} = -1.82$ V

$$\therefore 2\overset{+5}{Br}O_3^- \longrightarrow HBrO + \overset{+7}{Br}O_4^-$$

$$E°_{\text{cell}} = E°_{\text{red}} + E°_{\text{oxi}}$$

$$= E°_{BrO_3^-/HBrO} + E°_{BrO_3^-/BrO_4^-}$$

$$= 1.5 - 1.82 = -0.32\ V$$

[Non-spontaneous]

(ii) $H\overset{+1}{Br}O \longrightarrow \overset{0}{Br_2}$;

$E°_{HBrO/Br_2} = 1.595$ V

$H\overset{+1}{Br}O \longrightarrow \overset{+5}{Br}O_3^-$;

$E°_{HBrO/BrO_3^-} = -1.5$ V

$$2H\overset{+1}{Br}O \longrightarrow \overset{0}{Br_2} + \overset{+5}{Br}O_3^-$$

$$E°_{\text{cell}} = E°_{HBrO/Br_2} + E°_{HBrO/BrO_3^-}$$

$$= 1.595 - 1.5 = 0.095\ V$$

[Spontaneous]

(iii) $\overset{0}{Br_2} \longrightarrow \overset{-1}{Br^-}$; $E°_{Br_2/Br^-} = 1.0652$ V

$\overset{0}{Br_2} \longrightarrow H\overset{+1}{Br}O$; $E°_{Br_2/HBrO} = -1.595$ V

$$2\overset{0}{Br_2} \longrightarrow \overset{-1}{Br^-} + H\overset{+1}{Br}O$$

$$E°_{\text{cell}} = E°_{Br_2/Br^-} + E°_{Br_2/HBrO}$$

$$= 1.0652 - 1.595$$

$$= -0.5298\ V$$

∴ Among the given options, only HBrO undergoes disproportionation.

## SESSION 2

**1** Equivalent mass of Al $= \frac{27}{3} = 9$

Equivalent mass of H = 1

$$\frac{W_{Al}}{W_{H_2}} = \frac{\text{eq. mass of Al}}{\text{eq. mass of } H_2}$$

$$\frac{4.5}{W_{H_2}} = \frac{9}{1}$$

$$W_{H_2} = 0.5\,g$$

∵ 2 g of $H_2$ at STP occupy volume

$= 22.4$ L

∴ 0.5 g of $H_2$ at STP will occupy volume

$$= \frac{22.4 \times 0.5}{2} = 5.6\,L$$

**2** Degree of dissociation,

$$\alpha = \frac{\Lambda^c}{\lambda_\alpha} = \frac{150}{500} = 0.3$$

Given, $C = 0.007$ M

Hydrofluoric acid dissociates in the following manner

| | HF | ⟶ | $H^+$ | + | $F^-$ |
|---|---|---|---|---|---|
| Initial | $C$ | | 0 | | 0 |
| At time, $t$ | $C(1-\alpha)$ | | $C\alpha$ | | $C\alpha$ |

Dissociation constant,

$$K_a = \frac{[H^+]\ [F^-]}{[HF]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

On substituting values, we get

$$K_a = \frac{0.007 \times (0.3)^2}{(1-0.3)} = \frac{6.3 \times 10^{-3} \times 10^{-2}}{0.7}$$

$$= 9 \times 10^{-4}\ M$$

**3** Equivalent conductance of 0.04 N weak acid

$$= \frac{1000 \times 423 \times 10^{-4}}{0.04}$$

$$= 10.575\ \Omega^{-1}\,cm^2\ equiv^{-1}$$

Also, $x$ (degree of ionisation)

$$0.0612 = \frac{10.575}{\Lambda_\infty}$$

$$\Lambda_\infty = 172.79\ \Omega^{-1}\,\text{cm}^2\ \text{equiv}^{-1}$$

**4** The metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential. Hence, metal $P$ will displace the cation of $R$ from its aqueous solution and deposit the metal $R$.

**5** 96500 C current produces $= 12$ g Mg.

9.65 C current produces

$$= \frac{12 \times 9.65}{96500} = 1.2 \times 10^{-3} \text{ g Mg}$$

$$= \frac{1.2 \times 10^{-3}}{24} = 5 \times 10^{-5} \text{ mol Mg}$$

$$R\text{—}X + \underset{\substack{5\times10^{-5}\\ \text{mol}}}{\text{Mg}} \longrightarrow \underset{\substack{5\times10^{-5}\\ \text{mol}}}{R\text{Mg}X}$$

(Grignard reagent)

Hence, number of moles of $R$Mg$X$ produced $= 5 \times 10^{-5}$

**6** $\because \text{BaCl}_2 \rightleftharpoons \text{Ba}^{2+} + 2\text{Cl}^-$

$$\therefore \lambda^{\alpha}_{\text{BaCl}_2} = \frac{1}{2}\lambda^{\alpha}_{\text{Ba}^{2+}} + \lambda^{\alpha}_{\text{Cl}^-} = \frac{127}{2} + 76$$

$$= 139.5\,\Omega^{-1}\,\text{cm}^2$$

**7** $\text{Cu} + 2\text{H}^+(\text{dil. H}_2\text{SO}_4) \longrightarrow \text{Cu}^{2+} + \text{H}_2$

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu/Cu}^{2+}} + E^\circ_{\text{SHE}}$$

$$= -0.34 \text{ V}$$

Thus, (a) is not feasible

$$\text{Cu} + \text{SO}_4^{2-} + 4\text{H}^+ \longrightarrow \text{Cu}^{2+} + \text{SO}_2 + 2\text{H}_2\text{O}$$

$$E^\circ_{\text{cell}} = -0.34 + 1.17 = 0.83 \text{ V}$$

$$E^\circ_{\text{cell}} > 0$$

Thus, (b) is feasible.

Similarly, (c) is feasible.

**8** $\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$ (at cathode)

Equivalent weight of Ni

$$= \frac{\text{molecular weight}}{\text{electrons gain}}$$

$$= \frac{58.7}{2} = 29.35$$

$i = 12$ A, $t = 1\text{h} = 60 \times 60$ s,

$$Z = \frac{\text{equivalent weight}}{96500}$$

Weight of Ni deposit

$$= \frac{Zit \times \text{efficiency}}{100}$$

$$= \frac{29.35 \times 12 \times 60 \times 60 \times 60}{96500 \times 100}$$

$$= 7.883 \text{ g}$$

**9** LHS half-cell,

$$\underset{p_1}{\text{H}_2(g)} \longrightarrow 2\text{H}^+(1\text{ M}) + 2e^-$$

RHS half-cell,

$$2\text{H}^+(1\text{ M}) + 2e^- \longrightarrow \underset{p_2}{\text{H}_2(g)}$$

$$\underset{p_1}{\text{H}_2(g)} \longrightarrow \underset{p_2}{\text{H}_2(g)}$$

$$E^\circ_{\text{cell}} = 0.00\text{ V}, K = \frac{p_2}{p_1}, n = 2$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\log_e K$$

$$= 0 - \frac{RT}{2F}\log_e\frac{p_2}{p_1}$$

$$E_{\text{cell}} = \frac{RT}{2F}\log_e\frac{p_1}{p_2}$$

**10**

| Reaction | Number of moles formed by 1F |
|---|---|
| $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$ | 1/2 |
| $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$ | 1/3 |
| $\text{Si}^{4+} + 4e^- \longrightarrow \text{Si}$ | 1/4 |

Ratio $\frac{1}{2} : \frac{1}{3} : \frac{1}{4}$

6 : 4 : 3

**11**

$$\text{Pb} \longrightarrow \text{Pb}^{2+} + 2e^-$$

$$\underline{2\text{Cu}^+ + 2e^- \longrightarrow 2\text{Cu}}$$

$$\underline{2\text{Cu}^+ + \text{Pb} \longrightarrow \text{Pb}^{2+} + \text{Cu}}$$

Also,

$$E^\circ_{\text{cell}} = E_{\text{C}} - E_{\text{A}} = E^\circ\text{C}_{\text{Cu}^+/\text{Cu}} - E^\circ_{\text{Pb}^{2+}/\text{Pb}}$$

$$= 0.518 + 0.127 = 0.645 \text{ V}$$

Thus both '*a*' and 'b' are correct.

**12** $E^\circ_{\text{cell}} = E_C - E_A = -0.45 - (-2.37)$

$$= 1.92 \text{ V}$$

$$\text{Mg}(s)|\text{Mg}^{2+}(aq), x\text{M}||\text{Fe}^{2+}(aq), 0.01\text{ M}|\text{Fe}(s)$$

The cell reaction is

$$\text{Mg} + \text{Fe}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Fe}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n}\log\frac{[\text{Mg}^{2+}]}{[\text{Fe}^{2+}]}$$

$$1.92 = 1.92 - \frac{0.059}{2}\log\frac{x}{0.01}$$

$$0 = \frac{-0.059}{2}\log\frac{x}{0.01}$$

$$\therefore \quad x = 0.01 \text{ M}$$

**13** $\because E_R = \text{Cu}/\text{Cu}^{2+}, E_L = \text{Al}/\text{Al}^{3+}$

We know that, $E_{\text{cell}} = E_R - E_L$

$$2 = +0.34 - x$$

$$x = -1.66 \text{ V}$$

**14** $C + B^+ \longrightarrow C^+ + B$ So, reducing power of $C > B$

$A^- + \infty \longrightarrow$ No reaction. So, reducing power of $A > D$.

$C^+ + A \longrightarrow$ No reaction, so, reducing power of $C > A$.

$D + B^+ \longrightarrow D^+ + B$ So, reducing power of $D > B$.

Hence, $C > A > D > B$.

**15** $\text{Al}_2\text{O}_3 \longrightarrow 2\text{Al} + \frac{3}{2}\text{O}_2$

Ratio of Al to $\text{O}_2 = 2 : \frac{3}{2} = 4 : 3$