DAY THIRTEEN

Electrochemistry

Learning & Revision for the Day

- Metallic and Electrolytic Conduction
- Electrolysis
- Kohlrausch's Law
- Electrochemical Cell
- Electrochemical Series
- Nernst Equation and its Applications
- Batteries
- Fuel Cells
- Corrosion and its Prevention

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.

Metallic and Electrolytic Conduction

The substance which can conduct electricity are called conductors. On the basis of species that conduct electricity (current), conductors are of two types :

(i) **Metallic or electronic conductors** can conduct current by transfer of free electrons. This process is known as **metallic conduction**.

(ii) **Electrolytic conductors** can conduct current by the mobility of ions. This process is known as **electrolytic conduction**.

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.
- Reciprocal of resistance is called conductance, G.

$$G=\frac{1}{\text{resistance}}=\frac{1}{R}.\ \text{Its unit is mho or } (\Omega^{-1}) \text{ or Siemens (S).}$$

Conductivity or Specific Conductance (κ)

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

  where, ρ is called the **resistivity** or **specific resistance**.

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

$$\therefore \qquad \kappa=\frac{1}{\rho}=\frac{l}{a}\times \text{conductance } (G)$$

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 specific conductance (κ) is $\text{ohm}^{-1}\ \text{cm}^{-1}$ or S cm^{-1}.

Molar Conductivity (Λ_m)

It is the conducting power of all the ions produced by one gram mole of an electrolyte in a given solution.

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

The units for molar conductivity

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

Equivalent Conductivity (Λ_{eq})

It is the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution.

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 $\text{S cm}^2\ (\text{g-eq})^{-1}$

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

Variation of Molar and Equivalent Conductivities with Concentration

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 and can be represented by Debye-Huckel-Onsager equation,

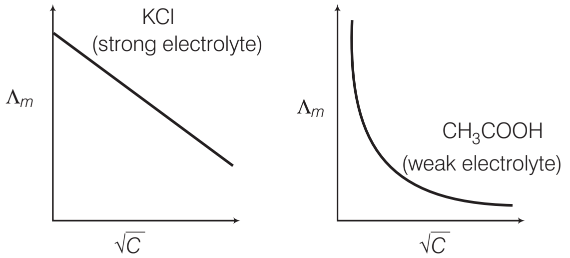
$$\Lambda_m = \Lambda_m^\circ - AC^{\frac{1}{2}}$$

where, Λ_m = molar conductivity

Λ_m° = limiting molar conductivity

A = Debye-Huckel constant

C = concentration



Variation of Λ_m with $\sqrt{C}$ for strong and weak electrolytes

- In case of 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.
- Limiting molar conductivity or infinite conductivity (Λ_m° or Λ_m°) is defined as the molar conductivity of electrolyte when concentration of electrolyte approaches zero (i.e. at infinite dilution).

Electrolysis

- Electrolysis is a process of decomposition of an electrolyte by the passage of electricity through its aqueous solution or molten state. As a result cations move towards cathode while anions towards anode.
- The reduction and oxidation changes occurs at respective electrodes during electrolysis. Oxidation occurs at anode while reduction occurs at cathode.
- An electrolytic solution usually consists of more than two ions. When electrolysis is done then all the ions are not discharged at electrodes simultaneously. Certain ions are liberated at the electrodes in prefer to other.
  For cations, which is stronger oxidising agent is discharged at cathode.

$$\xrightarrow[\text{Increasing order of decomposition}]{K^+, Ca^{2+}, Na^+, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{2+}, H^+, Cu^{2+}, Ag^+, Au^{3+}}$$

For anions, which is stronger reducing agent is liberated at anode.

$$\xrightarrow[\text{Increasing order of discharge}]{SO_4^2, NO_3^{2-}, OH^-, Cl^-, Br^-, I^-}$$

Faraday's Laws of Electrolysis

1. **According to First Law of Faraday** The amount of chemical change produced is proportional to the quantity of electric charge passing through an electrolytic cell.

$$w \propto Q, w = ZQ. \quad w = Zit$$

where, w = mass of the metal deposited/gas liberated (in grams);

Q = charge (in Coulomb)

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

Z = electrochemical equivalent.

$$= \frac{\text{equivalent wt.}}{96500\text{ C}} \left[\text{Equivalent wt.} = \frac{\text{atomic wt.}}{\text{valency}}\right]$$

- 1 Faraday = charge of one mole of electrons
  $1\text{F} = 6.022 \times 10^{23} \times 1.6 \times 10^{-19} = 96500\text{ C}$ (approx.)
- Number of gram equivalents = Number of Faradays 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 electron cause the reduction of 1 mole of monovalent cation or 1/2 mole of divalent cation.

2. **According to Second Law of Faraday** 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.

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.

$$\Lambda^\circ_m = \Lambda^\circ_a + \Lambda^\circ_c$$

e.g. $\Lambda^\circ_m CH_3COOH \longrightarrow \Lambda^\circ_m CH_3COO^- + \Lambda^\circ_m H^+$

$\Lambda^\circ_m Al_2(SO_4)_3 \longrightarrow 2 \times \Lambda^\circ_m Al^{3+} + 3 \times \Lambda^\circ_m SO_4^{2-}$

Applications of Kohlrausch's Law

- For the determination of equivalent/molar conductivity at infinite dilution.
- For the determination of degree of dissociation.

  Degree of dissociation (α)

  $$= \frac{\text{molar conductance at a given concentration}}{\text{molar conductance at infinite dilution}}$$

  $$\alpha = \frac{\Lambda^c_m}{\Lambda^\infty_m}$$

- 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

- For the determination of solubility of sparingly soluble salt.

  $$\text{Solubility} = \frac{\kappa \times 1000}{\Lambda^\circ_m}$$

Electrochemical Cell

A cell is an arrangement in which two electrodes are fitted in the same electrolyte or in which two different electrolytes are joined by a salt-bridge.

Cells are of the following two types:

1. Electrolytic Cells

It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

$$H_2SO_4(l) \underset{\text{(Acidified/dil.)}}{\overset{H^+}{\rightleftharpoons}} H_2O(g) + O_2(g) + \text{dil. } H_2SO_4$$

2. Galvanic or Voltaic Cells

It is a device in which a redox reaction used to convert chemical energy into electrical energy.

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

Electrode and Half-Cell

A strip of metal, M called electrode is immersed in a solution containing the metal ion M^{n+}, this 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.

- A metal ion M^{n+} may collide with the electrode and undergo no change.
- A metal ion M^{n+} may collide with the electrode, gain n electrons and be converted to a metal atom M. The ion is reduced.

  $$M^{n+}(aq) + ne^- \xrightarrow{\text{Reduction}} M(s)$$

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

  $$M(s) \xrightarrow{\text{Oxidation}} M^{n+}(aq) + ne^-$$

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

Some different types of electrodes are as follows :

1. **Normal hydrogen electrode** is the primary reference electrode and is used normally to know the electrode potential of a half-cell in galvanic all.
2. **Standard hydrogen electrode** is the hydrogen electrode in which the pressure of H_2 gas is maintained at 1 atm and concentration of H^+ ions is 1M.
3. **Calomel electrode** is an another generally used reference electrode but it is an secondary reference electrode. Calomel is the common name for mercury (I) chloride.

$$Hg + Cl^- \longrightarrow \frac{1}{2}Hg_2Cl_2 + e^-$$

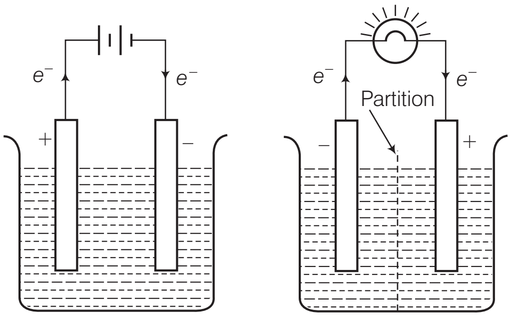
Salt-Bridge

It is a U-shaped tube containing a gel permeated with a solution of an inert electrolyte such as NH_4NO_3. 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).

Difference between Electrolytic and Electrochemical Cells

The main points of difference between these two cells are :

- The device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done is called **electrolytic cell** while **galvanic** or **voltaic** cell is a device in which **redox** reaction is used to convert chemical energy to electrical energy.
- 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)

Representation of a Cell

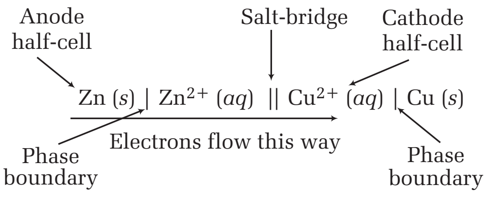
Consider the Daniell cell with following cell reaction:

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

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 $\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2e^-$	Reduction takes place $\mathrm{Cu}^{2+}(aq) + 2e^- \longrightarrow \mathrm{Cu}(s)$
Terminal	Negative	Positive
Side	LHS	RHS
Diagram	$\mathrm{Zn}(s) / \mathrm{Zn}^{2+}(aq)$	$\mathrm{Cu}^{2+}(aq) / \mathrm{Cu}(s)$

Complete cell diagram may be represented as follows:



EMF of a Galvanic Cell

In electrochemical cell, the electrodes in different half-cells have different reduction potential. This difference in electrode potential of electrodes due to which electrons flow from anode to cathode is called **electromotive force** or **cell potential of a cell**. This is the driving force for all cell reactions.

Electrode Potential and Standard 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) temperature is 298 K and concentration is 1M, electrode potential is called **standard electrode potential** denoted as E°.
- According to international convention, 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 $E^\circ_{\mathrm{ox}} = x\mathrm{V}$, then $E^\circ_{\mathrm{red}} = -x\mathrm{V}$
- E°_{cell} or E_{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.
- The SI unit of cell potential is the volt (V) and the potential of a galvanic cell is defined as the positive quantity.
$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{ox}} + E^\circ_{\mathrm{red}},$$
$$E_{\mathrm{cell}} = E_{\mathrm{ox}} + E_{\mathrm{red}}$$
- Standard Hydrogen Electrode, SHE used as a reference electrode. Its reduction potential is taken as zero. It is represented as Pt, $\mathrm{H_2}$(1 atm) | $\mathrm{H^+}$(1 M) or $\mathrm{H^+}$ (1M)|$\mathrm{H_2}$ (1 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 over voltage/over potential.

Electrochemical Series

The arrangement of metals in decreasing order of tendency to lose electrons (e^-) is called electrochemical series 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	$Li^+ + e^- \longrightarrow Li$	– 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	$Cd^+ + e^- \longrightarrow Cd$	– 0.403
Ni	$Ni^{2+} + 2e^- \longrightarrow Ni$	– 0.25
Sn	$Sn^{2+} + 2e^- \longrightarrow Sn$	– 0.14
H_2	$2H^+ + e^- \longrightarrow H_2$	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
Cr_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

Increasing tendency for reduction ↓

Increasing strength of oxidising agent ↓

Increasing strength of reducing agent ↑

Increasing tendency for oxidation ↑

Nernst Equation and its Applications

The relationship between electrode potential and concentration of solution is called Nernst equation.

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

where, n = total number of electrons lost or gained

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

Q = reaction coefficient of overall reaction $= \frac{[O.S.]}{[R.S.]}$

where, [O.S.] = concentration of oxidised state

[R.S.] = concentration of reduced state

At $T = 298$ K, the Nerst equation becomes,

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

The emf of a standard cell does not change with temperature. Weston cell is a common example of standard cell.

There are two important applications of Nernst equation are:

1. **To find equilibrium constant**

   At equilibrium, E_{cell} = zero

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

   where, K = equilibrium constant.

2. **To find Gibb's free energy change**

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

   ΔG° = standard Gibbs free energy change

Relationship between Cell Potential and Gibbs Energy Change (ΔG)

- In an electrochemical cell, maximum work done (ΔG) is given by $\Delta G = -nF \times E_{cell}$

  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

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

  For spontaneous reactions,

  $$\Delta G = -ve$$

  $$\therefore \quad E_{cell} = +ve$$

  (i) If ΔG of the system is positive then the process would be possible only if the surrounding do electrical work on the system (as in electrolysis).

  (ii) If ΔG of the system is negative then the system does electric work on the surroundings (as in galvanic cells). For a voltaic cell, the work is done on the surroundings, thus given a negative sign. Hence,

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

  and the standard free energy $(\Delta G°)$ is given by,

  $$\Delta G° = -nFE^{\circ}_{cell}$$

- The relation between cell potential (E°_{cell}), free energy $(\Delta G°)$ and equilibrium constant (K_C) is given by,

  $$\Delta G° = -2.303RT \log K_C$$

  as $\quad \Delta G° = nFE°_{cell}$

  and $\quad E^{\circ}_{cell} = \frac{2.303\,RT}{nF} \log K_C$

- If two half-reactions having potentials E_1° and E_2° are combined to give a third half-reaction having a potential E_3°, then

  $$\Delta G_3^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$$

  or $\quad -n_3FE_3^{\circ} = -n_1FE_1^{\circ} - n_2FE_2^{\circ}$

  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 1 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. The Primary Batteries

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

(i) Dry Cell or Leclanche Cell

It is also called primary voltaic cell. The electrode reactions involved in this cell are :

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

At cathode $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

The cell potential is 1.6 V.

(ii) Mercury Cell

- Mercury cell, suitable for low current devices like hearing aids, watches.
- The electrode reactions for the cell are :

At anode $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

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

The overall cell reaction is

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

2. Secondary Batteries

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

Lead Accumulator (Lead-Storage Battery)

- In lead accumulator 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 (PbO_2).
- The half-cell reactions, when the battery is being used up are:

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

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

Overall reaction $Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$

$$\longrightarrow 2PbSO_4(s) + 2H_2O$$

The reaction is reversed during charging.

During charging following reactions occur :

At anode $PbSO_4(s) + 2H_2O \longrightarrow PbO_2(\mathbf{s}) + SO_4^{2-} + 4H^+ + 2e^-$

At cathode $PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}$

Overall reaction $2PbSO_4(s) + 2H_2O$

$$\longrightarrow Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-}$$

- 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

- Fuel 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. $H_2—O_2$ 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.

The half-reactions are

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

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

Overall cell reaction $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

- The efficiency of the fuel cell is the ratio of change in Gibbs energy ΔG to the heat of combustion ΔH and mathematically can be given as,

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

where, η = thermodynamic efficiency of a fuel cell

ΔH = heat of combustion

ΔG = work done $= -nFE^\circ_{cell}$

Corrosion and its Prevention

- Corrosion is basically an electrochemical phenomenon. A metal is oxidised by loss of electrons to oxygen and form 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.

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 $[Fe_2O_3 \cdot xH_2O]$.

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

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

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 antirust solutions.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

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

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

2 Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is $1.3\ S\ m^{-1}$. If resistance of the 0.4 M solution of the same electrolyte is 260 Ω, its molar conductivity is → AIEEE 2011

(a) $6250\ Sm^2\ mol^{-1}$ (b) $6.25 \times 10^{-4}\ Sm^2\ mol^{-1}$
(c) $625 \times 10^{-4}\ Sm^2\ mol^{-1}$ (d) $62.5\ Scm^2\ mol^{-1}$

3 Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution of 0.5 M solution of same electrolyte is $1.4\ S\ m^{-1}$ and resistance of same solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in $S\ m^2\ mol^{-1}$ is → JEE Main 2014

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

4 The equivalent conductance of NaCl at concentration (C) and at infinite dilution are λ_C and λ_∞, respectively. The correct relationship between λ_C and λ_∞ is given as (Where, the constant B is positive) → JEE Main 2014

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

5 How many Faraday's are required to reduce 1 mole of BrO_3^- to Br^-?

(a) 3 (b) 5 (c) 6 (d) 4

6 Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is (atomic mass Cu = 63.5 u) → JEE Main 2015

(a) 0 g (b) 63.5 g (c) 2 g (d) 127 g

7 A solution of copper sulphate ($CuSO_4$) is electrolysed for 10 min with a current of 1.5 A. The mass of copper deposited at the cathode (Atomic mass of Cu = 63 u) is → JEE Main (Online) 2013

(a) 0.3892 g (b) 0.2938 g (c) 0.2398 g (d) 0.3928 g

8 X g of silver is plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 h at a current of 8.46 A. What is the area of the tray if the thickness of silver plating is 0.00254 cm?
[Given, density of silver = $10.5\ g\ cm^{-3}$]

(a) $10.7 \times 10^4\ cm^2$ (b) $1.02 \times 10^4\ cm^2$
(c) $4.1 \times 10^3\ cm^2$ (d) $10.2 \times 10^4\ cm^2$

9 A current of 2 A is passed for 5 h through a molten tin salt to deposit 22.2 g tin. What is the oxidation state of tin in salt ? [At. wt. of Sn = 118.69 g]

(a) +2 (b) +5 (c) +3 (d) +4

10 In the electrolytic cell, flow of electrons is from

(a) cathode to anode in solution
(b) cathode to anode through external supply
(c) cathode to anode through internal supply
(d) anode to cathode through internal supply

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

	Cathode	Anode
(a)	pure zinc	pure copper
(b)	impure zinc	pure copper
(c)	impure zinc	impure sample
(d)	pure copper	impure sample

12 $\Lambda^\circ_{m\,(NH_4OH)}$ is equal to ....

(a) $\Lambda^\circ_{m\,(NH_4OH)} + \Lambda^\circ_{m\,(NH_4Cl)} - \Lambda^\circ_{(HCl)}$
(b) $\Lambda^\circ_{m\,(NH_4Cl)} + \Lambda^\circ_{m\,(NaOH)} - \Lambda^\circ_{(NaCl)}$
(c) $\Lambda^\circ_{m\,(NH_4Cl)} + \Lambda^\circ_{m\,(NaCl)} - \Lambda^\circ_{(NaOH)}$
(d) $\Lambda^\circ_{m\,(NaOH)} + \Lambda^\circ_{m\,(NaCl)} - \Lambda^\circ_{(NH_4Cl)}$

13 For the reaction,

$$\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Cl^-(aq) + Ag(s)$$

occurs in the galvanic cell

(a) $Ag|\ AgCl(s)\ |\ KCl(aq)\ ||\ AgNO_3(aq)|Ag(s)$
(b) $Pt\ |\ H_2(g)\ |\ HCl\ (aq)\ ||\ AgNO_3(aq)\ |\ Ag(s)$
(c) $Pt\ |\ H_2(g)\ |\ HCl(aq)\ ||\ AgCl(s)|Ag(s)$
(d) $Pt\ |\ H_2(g)\ |\ KCl(aq)\ ||\ AgCl(s)|Ag(s)$

14 Which of the following is not true?

(a) Cathode is negative terminal in an electrolytic cell
(b) Anode is positive terminal in a galvanic cell
(c) Reduction occurs at cathode in either of cells
(d) Oxidation occurs at anode

15 The standard reduction potential for Fe^{2+}/Fe and Sn^{2+}/Sn electrodes are – 0.44 and – 0.14 V respectively. For the cell reaction; $Fe^{2+} + Sn \longrightarrow Fe + Sn^{2+}$, the standard emf is

(a) +0.30 V (b) – 0.58 V
(c) +0.58 V (d) – 0.30 V

16 Of the following metals that cannot be obtained by electrolysis of the aqueous solution of their salts are

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

17 The standard reduction potential values of the three metallic cations X, Y and Z are 0.52, –3.03 and –1.18 V respectively. The order of reducing power of the corresponding metals is

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

18 Given, $E^\circ_{Cl/Cl^-} = 1.36\ V; E^\circ_{Cr^{3+}/Cr} = -0.74\ V$

$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\ V; E^\circ_{MnO_4^-/Mn^{2+}} = 1.51 V$

Among the following, the strongest reducing agent is

(a) Cr (b) Mn^{2+}
(c) Cr^{3+} (d) Cl–

19 The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is ➞ JEE Main 2014

(a) Ag (b) Ca (c) Cu (d) Cr

20 Given, $E^\circ_{\frac{1}{2}Cl_2/Cl} = 1.36\ V, E^\circ_{Cr^{3+}/Cr} = -0.74\ V,$

$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\ V, E^\circ_{MnO_4^-/Mn^{2+}} = 1.51\ V$

The correct order of reducing power of the species (Cr, Cr^{3+}, Mn^{2+} and Cl^-) will be ➞ JEE Main (Online) 2013

(a) $Mn^{2+} < Cl^- < Cr^{3+} < Cr$ (b) $Mn^{2+} < Cr^{3+} < Cl^- < Cr$
(c) $Cr^{3+} < Cl^- < Mn^{2+} < Cr$ (d) $Cr^{3+} < Cl^- < Cr < Mn^{2+}$

21 Given, $E^\circ_{Cr^{3+}/Cr} = -0.74\ V; E^\circ_{MnO_4^-/Mn^{2+}} = 1.51\ V$

$E_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\ V; E^\circ_{Cl/Cl^-} = 1.36\ V$

Based on the data given above, strongest oxidising agent will be ➞ JEE Main 2013

(a) Cr^{3+} (b) Mn^{2+} (c) MnO_4^- (d) Cl^-

22 Electrode potentials (E°) are given below :

$Cu^+/Cu = +\ 0.52\ V, Fe^{3+}/Fe^{2+} = +\ 0.77\ V$

$\frac{1}{2}\ I_2(s)/I^- = +\ 0.54 V, Ag^+/Ag = +\ 0.88\ V$

Based on the above potentials strongest oxidising agent will be ➞ JEE Main (Online) 2013

(a) Cu (b) Fe^{3+} (c) Ag^+ (d) I_2

23 In the cell reaction,

$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s), E^\circ_{cell} = 0.46\ V$

by doubling the concentration of Cu^{2+}, E_{cell} is

(a) doubled
(b) halved
(c) increased but less than double
(d) decreased by a small fraction

24 For the reaction,

$$Zn(s) + Cu^{2+}(0.1 M) \longrightarrow Zn^{2+}(1 M) + Cu(s)$$

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

(a) 1.80 V (b) 1.07 V (c) 0.82 V (d) 2.14 V

25 Given, $E^\circ_{Cr^{3+}/Cr} = -0.72\ V; E^\circ_{Fe^{2+}/Fe} = -\ 0.42\ V$

The potential for the cell

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

(a) – 0.339 V (b) – 0.26 V (c) 0.26 V (d) 0.339 V

26 What will be the emf for the given cell?

$$Pt\,|\,H_2(p_1)\,|\,H^+(aq)\,|\,H_2(p_2)\,|\,Pt$$

(a) $\frac{RT}{F}\ln\frac{p_1}{p_2}$ (b) $\frac{RT}{2F}\ln\frac{p_1}{p_2}$
(c) $\frac{RT}{2F}\ln\frac{p_2}{p_1}$ (d) None of these

27 The value of the reaction quotient, Q for the cell

$Zn\ (s)|\ Zn^{2+}(0.01 M)||\ Ag^+(1.25\ M)|\ Ag(s)$ is

(a) 156 (b) 125 (c) 1.25×10^{-2} (d) 6.4×10^{-3}

28 The reduction potential of hydrogen half-cell will be negative if ➞ AIEEE 2011

(a) $p\ (H_2) = 1$ atm and $|H^+| =\ 2.0$ M
(b) $p\ (H_2) = 1$ atm and $|H^+| =\ 1.0$ M
(c) $p\ (H_2) = 2$ atm and $|H^+| =\ 1.0$ M
(d) $p\ (H_2) = 2$ atm and $|H^+| =\ 2.0$ M

29 Which of the following statement is correct?

(a) E_{cell} and $\Delta_r G$ of cell reaction both are extensive properties
(b) E_{cell} and $\Delta_r G$ of cell reaction both are intensive properties
(c) E_{cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property
(d) E_{cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property

30 The standard emf of a cell, involving one electron change is found to be 0.591V at 25°C. The equilibrium constant of the reaction is(1F = 96500 C mol^{-1})

(a) 1.0×10^1 (b) 1.0×10^5 (c) 1.0×10^{10} (d) 1.0×10^{30}

31 Given below are the half-cell reactions

$$Mn^{2+} + 2e^- \longrightarrow Mn\ ; E^\circ = -1.18\ eV$$

$$2(Mn^{3+} + e^- \longrightarrow Mn^{2+});\ E^\circ = +\ 1.51\ eV$$

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

➞ JEE Main 2014

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

32 The standard reduction potentials for Zn^{2+} / Zn, Ni^{2+}/ Ni and Fe^{2+}/Fe are – 0.76, – 0.23 and – 0.44 V respectively. The reaction $X + Y^{2+} \longrightarrow X^{2+} + Y$ will be spontaneous when ➞ AIEEE 2012

(a) $X = Ni, Y = Fe$ (b) $X = Ni, Y = Zn$
(c) $X = Fe, Y = Zn$ (d) $X = Zn, Y = Ni$

33 Given, $E^{\circ}_{Fe^{3+}/Fe} = -0.036$ V, $E^{\circ}_{Fe^{2+}/Fe} = -0.439$ V
The value of standard electrode potential for the charge, $Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ will be ➞ AIEEE 2009

(a) – 0.072 V (b) 0.385 V (c) 0.770 V (d) – 0.270 V

34 Galvanisation is applying a coating of ➞ JEE Main 2016

(a) Cr (b) Cu (c) Zn (d) Pb

35 Match the following and choose the correct option.

	Column I		Column II
A.	Lead storage battery	1.	Maximum efficiency
B.	Mercury cell	2.	Prevented by galvanisation
C.	Fuel cell	3.	Gives steady potential
D.	Rusting	4.	Pb is anode, PbO_2 is cathode

Codes

	A	B	C	D		A	B	C	D
(a)	4	3	1	2	(b)	2	1	3	4
(c)	1	4	3	2	(d)	4	1	3	2

Direction (Q. Nos. 36 and 37) *In the following questions, Assertion (A) followed by Reason (R) is given. Choose the correct answer out of the following choices.*

(a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
(c) Assertion is correct and Reason is incorrect
(d) Both Assertion and Reason are incorrect

36 **Assertion** (A) E_{cell} should have a positive value for the cell to function.

Reason (R) $E_{cathode} < E_{anode}$

37 **Assertion** (A) $E_{Ag^+/Ag}$ increases with increase in concentration of Ag^+ ions.

Reason (R) $E_{Ag^+/Ag}$ has a positive value.

Direction (Q. Nos. 38 and 39) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

38 **Statement I** For the Daniell cell, $Zn|Zn^{2+}||Cu^{2+}|Cu$ with $E_{cell} = 1.1$V, the application of opposite potential greater than1.1V results into flow of electron from cathode to anode.

Statement II Zinc is deposited at anode and Cu is deposited at cathode.

39 **Statement I** Galvanised iron does not rust.

Statement II Zinc has more negative electrode potential than iron.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal
(Atomic mass = 27u; 1F = 96500 C).
The cathode reaction is $Al^{3+} + 3e^- \longrightarrow Al$.
To prepare 5.12 kg of aluminium metal by this method required electricity will be

(a) 5.49×10^1C (b) 5.49×10^4C
(c) 1.83×10^7C (d) 5.49×10^7C

2 For a saturated solution of AgCl at 25°C, specific conductance is 3.41×10^{-6} omh^{-1} cm^{-1} and that water used for preparing the solution was 1.60×10^{-6} ohm^{-1} cm^{-1}. The solubility product of AgCl is $[\Lambda^{\infty}_{eq}(AgCl) = 138.3$ ohm^{-1} cm^{-1} equiv$^{-1}]$

(a) 1.31×10^{-5} (b) 1.74×10^{-8}
(c) 1.72×10^{-10} (d) 3.61×10^{-3}

3 The Edison storage cell is represented as

$$Fe(s)|FeO(s)|KOH(aq)|\ Ni_2O_3(s)|NiO(s)|Ni(s)$$

the half-cell reactions are

$$Ni_2O_3(s) + H_2O(l) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-; \quad E^{\circ} = +0.40\text{ V}$$

$$FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-; E^{\circ} = -0.87\text{V}$$

What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3?

(a) 127 kJ (b) 245.11 kJ (c) 90.71 kJ (d) 122.55 kJ

4 An inaccurate ammeter and silver coulometer is connected in series in an electric circuit through which a constant direct current flows. If ammeter reads 0.6 ampere throughout one hour, the silver deposited on coulometer was found to be 2.16 g. What per cent error is in the reading of ammeter ? [Assume 100% current efficiency].

(a) 1% (b) 0.54% (c) 0.06 % (d) 10%

5 An aqueous solution of NaCl on electrolysis gives $H_2(g)$, $Cl_2(g)$ and NaOH. According to reaction,

$$2Cl^-(aq) + 2H_2O \longrightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$$

A direct current of 25 A with a current efficiency of 62% is passed through 20 L of NaCl solution (20% by weight). How long it take to produce 1 kg of Cl_2?

(a) 30.20 h (b) 12.17 h (c) 48.71 h (d) 14.61 h

6 $Zn|Zn^{2+}(a = 0.1\ M)||Fe^{2+}(a = 0.01\ M)|Fe$.

The emf of the above cell is 0.2905 V.

Equilibrium constant for the cell reaction is

(a) $10^{0.32/0.0591}$ (b) $10^{0.32/0.0295}$

(c) $10^{0.26/0.0295}$ (d) $10^{0.32/0.295}$

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

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s); \quad -0.762\ V$$

$$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s); \quad -0.740\ V$$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g); \quad 0.00\ V$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq); \quad 0.770\ V$$

Which is the strongest reducing agent?

(a) Zn (*s*) (b) Cs (*s*) (c) $H_2(g)$ (d) $Fe^{3+}(aq)$

8 Same quantity of charge is being used to liberate iodine (at anode) and a metal *M* (at cathode). The mass of metal *M* liberated is 0.617 g and the liberated iodine is completely reduced by 46.3 mL of 0.124 M sodium thiosulphate. What is the total time to bring this change if 10 A current is passed through solution of metal iodide?

(a) 55.4 s (b) 25.2 s (c) 5.54 s (d) 16.8 s

9 If λ^{∞}_{eq} (NaCl), λ^{∞}_{eq} (KCl) and $\lambda^{\infty}_{eq}\ K_2SO_4$ are 123.7, 147.0 and 152.1 $\Omega^{-1}\ cm^2\ eq^{-1}$ then $\lambda^{\infty}_{eq}(Na_2SO_4)$ would be

(a) $128.8\ \Omega^{-1}\ cm^2 eq^{-1}$ (b) $257.6\ \Omega^{-1}\ cm^2 eq^{-1}$

(c) $105.5\ \Omega^{-1}\ cm^2 eq^{-1}$ (d) $118\ \Omega^{-1}\ cm^2 eq^{-1}$

10 A gas *X* at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the order of reduction potentials is $Z > Y > X$, then

(a) *Y* will oxidise *X* and not *Z* (b) *Y* will oxidise *Z* and not *X*

(c) *Y* will oxidise both *X* and *Y* (d) *Y* will reduce both *X* and *Y*

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

$$\Lambda^\circ_{CH_3COONa} = 91.0\ S\ cm^2/equiv$$

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

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

(a) Λ° of NaCl

(b) Λ° of CH_3COOK

(c) The limiting equivalent conductance of H^+ $[\lambda^\circ_{H^+}]$

(d) Λ° of chloroacetic acid ($ClCH_2COOH$)

12 The rusting of iron takes place as follows:

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

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

Calculate ΔG° for the net process.

(a) $-322\ kJ\ mol^{-1}$ (b) $-161\ kJ\ mol^{-1}$

(c) $-152\ kJ\ mol^{-1}$ (d) $-76\ kJ\ mol^{-1}$

13 Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half-cell reactions and their standard potentials are given below:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l); \quad E^\circ = 1.51\ V$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l); \quad E^\circ = 1.38\ V$$

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq); \ E^\circ = 0.77\ V$$

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq); \quad E^\circ = 1.40\ V$$

Identify the incorrect statement regarding the quantitative estimation of gaseous $Fe(NO_3)_2$.

(a) MnO_4^- can be used in aqueous HCl

(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl

(c) MnO_4^- can be used in aqueous H_2SO_4

(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

14 The cell, $Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu$ ($E^\circ_{cell} = 1.10$ V), was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is

(a) antilog (24.08) (b) 37.2

(c) $10^{37.2}$ (d) 9.65×10^4

15 How long (approximate) should water be electrolysed by passing through 100 A current so that the oxygen released can completely burn 27.66 g of diborane? (Atomic weight of $B = 10.8\mu$) ➞ **JEE Main 2018**

(a) 6.4 h (b) 0.8 h (c) 3.2 h (d) 1.6 h

16 Given the data at 25°C,

$$Ag + I^- \longrightarrow AgI + e^-; \ E^\circ = 0.152\ V$$

$$Ag \longrightarrow Ag^+ + e^-; \ E^\circ = -0.800\ V$$

What is the value of $\log K_{sp}$ for AgI ?

$$\left(2.303\frac{RT}{F} = 0.059\ V\right)$$

(a) -8.12 (b) $+8.612$ (c) -37.83 (d) -16.14

ANSWERS

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

Hints and Explanations

SESSION 1

1 Conductance $= \kappa \times \dfrac{\text{area} \times \text{conc.}}{\text{length}}$

or $\kappa = \dfrac{\text{Conductance} \times \text{length}}{\text{area} \times \text{conc.}}$

$$= \frac{\text{S} \times \text{m}}{\text{m}^2 \times \text{mol m}^{-3}} = \text{S m}^2\text{mol}^{-1}$$

2 Specific conductance

$$= \text{conductance} \times \text{cell constant}$$

$$1.3 = \frac{1}{50} \times \text{cell constant}$$

$\therefore$ Cell constant $= 1.3 \times 50 \text{ m}^{-1}$

$$= 65 \text{ m}^{-1} = \left(\frac{65}{100}\right) \text{cm}^{-1}$$

Molar conductivity

$$= \frac{1000 \times \text{conductance} \times \text{cell constant}}{\text{molarity}}$$

$$= \frac{1000}{0.4} \times \frac{1}{260} \times \frac{65}{100}$$

$$= 6.25 \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

3 For first solution,

$$k = 1.4 \text{ Sm}^{-1}, R = 50\ \Omega, M = 0.2$$

Specific conductance $(\kappa) = \dfrac{1}{R} \times \dfrac{l}{A}$

$$\Rightarrow 1.4 \text{ Sm}^{-1} = \frac{1}{50} \times \frac{l}{A}$$

$$\frac{l}{A} = 50 \times 1.4 \text{ m}^{-1}$$

For second solution,

$$R = 280, \frac{l}{A} = 50 \times 1.4 \text{ m}^{-1}$$

$$\kappa = \frac{1}{280} \times 1.4 \times 50 = \frac{1}{4}$$

Now, molar conductivity

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

$$= \frac{1/4}{1000 \times 0.5} = \frac{1}{2000}$$

$$= 5 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

4 The correct relationship between λ_C and λ_∞ is given by to Debye-Huckel Onsager equation,

$$\lambda_C = \lambda_\infty - B\sqrt{C}$$

where, λ_C = limiting equivalent conductivity at concentration C

λ_∞ = limiting equivalent conductivity at infinite dilution

C = concentration

5 $BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$

$\therefore$ Number of Faraday required = 6

6 Given, $Q = 2F$

Atomic mass of Cu = 63.5 u

Valency of the metal $Z = 2$

$$W = ZQ = \frac{E}{F} \cdot 2F = 2E$$

$$= \frac{2 \times 63.5}{2} = 63.5 \text{ g}$$

7 From Faraday's first law,

Mass of Cu deposited, $w = Zit$

$$= \frac{E}{96500} \cdot i \cdot t$$

$$= \frac{63}{2 \times 96500} \times 1.5 \text{ A} \times 10 \times 60 \text{ s}$$

$$= 0.2938 \text{ g}$$

8 $\dfrac{w_{Ag}}{\text{eq.wt.}_{Ag}} = \dfrac{i \cdot t}{96500}$

or $w_{Ag} = \dfrac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500}$

or $w_{Ag} = 272.18$ g.

Volume of Ag $= \dfrac{272.18}{10.5} = 25.92 \text{ cm}^3$

$\therefore$ Surface area

$$= \frac{25.92}{0.00254} = 1.02 \times 10^4 \text{ cm}^2$$

9 Equivalents of tin $= \dfrac{i \cdot t}{96500}$

or $\dfrac{22.2}{\text{eq.wt.}} = \dfrac{2 \times 5 \times 60 \times 60}{96500}$

Eq. wt. = 59.5

$\therefore$ Valency of tin

$$= \frac{\text{at. wt.}}{\text{eq. wt.}} = \frac{118.69}{59.5} \approx 2 \quad \text{(an integer)}$$

Therefore, $Sn^{2+} + 2e^- \longrightarrow Sn$

Thus, oxidation state of tin (Sn) in salt is +2.

10 In electrolytic cell, flow of electron is possible from anode to cathode through internal supply.

11 Impure sample is made the anode and pure copper acts as the cathode.

12 According to Kohlrausch's law,

$$\Lambda^\circ_{m(NH_4Cl)} + \Lambda^\circ_{m(NaOH)} = \Lambda^\circ_{m\,(NH_4OH)} + \Lambda^\circ_{m(NaCl)}$$

or $\Lambda^\circ_{m(NH_4OH)} = \Lambda^\circ_{m\,(NH_4Cl)} + \Lambda^\circ_{m(NaOH)} - \Lambda^\circ_{m(NaCl)}$

13 H_2 undergoes oxidation and AgCl (Ag^+) undergoes reduction. Therefore, cell may be represent, as

$$Pt \mid H_2(g) \mid HCl(aq) \parallel AgCl(s) \mid Ag(s).$$

14 In galvanic cell, cathode is positive terminal whereas anode is negative terminal.

15 Given, $E^\circ_{Fe^{2+}/Fe} = -0.44$ V

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

$$E^\circ_{cell} = E^\circ_{oxi}(Sn) + E^\circ_{red}(Fe)$$

$$= +0.14 + (-0.44) = -0.30 \text{ V}$$

16 Mg and Al have lower reduction potentials than H_2O. Hence, H_2O is reduced more easily to give H_2 gas at the cathode.

17 Greater the reduction potential, less is the reducing power.

The decreasing order of reduction potential is $X > Z > Y$.

Therefore, order of reducing power of corresponding metals is $Y > Z > X$.

18 The substances which have lower reduction potentials are stronger reducing agents. Therefore, $Cr(E^\circ_{Cr^{3+}/Cr}\ -0.74V)$ is the strongest reducing agent among all the other given options.

19 Higher the position of element in the electrochemical series more difficult is the reduction of its cations.

If $Ca^{2+}(aq)$ is electrolysed, water is reduced in preference to it. Hence, it cannot be reduced electrolytically from their aqueous solution.

$$Ca^{2+}(aq) + H_2O \longrightarrow Ca^{2+} + OH^- + H_2\uparrow$$

20 More the negative value of reduction potential, higher the reducing power. Thus, the correct order of reducing tendency is

$$\underset{(1.51\ V)}{Mn^{2+}} < \underset{(1.36\ V)}{Cl^-} < \underset{(1.33\ V)}{Cr^{3+}} < \underset{(-0.74\ V)}{Cr}$$

21 As per data mentioned MnO_4^- is strongest oxidising agent as it has maximum SRP (Standard Reduction Potential) value.

22 More positive value of electrode potential represents that Ag^+ is the strongest oxidising agent.

23 Applying Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[Cu^{2+}]}{[Ag^+]^2}$$

Doubling (Cu^{2+}) decreases the emf by a small fraction.

24 $$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.10 - \frac{0.0591}{2}\log\frac{1}{0.1} = 1.07\ V$$

25 $E^\circ_{cell} = -0.42 - (-0.72) = 0.30\ V$

The cell reaction is

$2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe, n = 6$

Using Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{6}\log\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$= 0.30 - \frac{0.0591}{6}\log\frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.0591}{6}\times 4$$

$$= 0.30 - 0.04 = 0.26\ V$$

26 RHS, $\quad 2H^+ + 2e^- \rightleftharpoons H_2(p_2)$

LHS, $\quad H_2(p_1) \rightleftharpoons 2H^+ + 2e^-$

Overall reaction, $\quad H_2(p_1) \rightleftharpoons H_2(p_2)$

$$E = E^\circ - \frac{RT}{nF}\ln\frac{p_2}{p_1}$$

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

27 The cell reaction is

$$\begin{array}{r} Zn(s) \longrightarrow Zn^{2+}(0.01M) + 2e^- \\ [Ag^+(1.25\ M) + e^- \longrightarrow Ag(s)] \times 2 \\ \hline Zn(s) + 2Ag^+(1.25M) \longrightarrow Zn^{2+}(0.01M) + 2Ag(s) \end{array}$$

$$Q = \frac{[Zn^{2+}]}{[Ag^+]^2} = \frac{0.01}{(1.25)^2} = 6.4\times10^{-3}$$

28 Reduction hydrogen half-cell is

$H^+(xM) \mid Pt(H_2)$

Half-cell reaction is

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

Reaction quotient $= Q = p_{H_2}/[H^+]^2$,

$n = 2$

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

$$= 0 - \frac{0.0591}{2}\log Q$$

	p_{H_2}	$[H^+]$	$Q = \frac{p_{H_2}}{[H^+]^2}$	E_{red}
(a)	1 atm	2.0 M	0.25	+ve
(b)	1 atm	1.0 M	1.0	0
(c)	2 atm	1.0 M	2.0	–ve
(d)	2 atm	2.0 M	0.50	+ve

29 E_{cell} is an intensive property because it does not depend on the system size or the amount of material in the system while $\Delta_r G$ of a cell reaction is an extensive property because it depends on the amount of material in the system.

30 Relation between K_{eq} and E°_{cell} is

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

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_{eq} \qquad \text{(at 298 K)}$$

$$0.591 = \frac{0.0591}{1}\log K_{eq}$$

$\therefore \log K_{eq} = 10$

$\therefore \quad K_{eq} = 1\times10^{10}$

31 $$\begin{array}{lccccc} & Mn^{2+} & \longrightarrow & Mn & + & Mn^{3+} \\ \text{O.N.} & +2 & & 0 & & +3 \end{array}$$

Reduction

Oxidation

Mn^{2+} is oxidised as well as reduced. Thus, it is a disproportionation reaction.

$$\begin{array}{ll} 2\times[Mn^{2+} \longrightarrow Mn^{3+} + e^-] & \\ & E^\circ = -1.51\ V \\ Mn^{2+} + 2e^- \longrightarrow Mn, & E^\circ = -1.18\ V \\ \hline \therefore \quad 3Mn^{2+} \longrightarrow 2Mn^{3+} + Mn & \\ & E^\circ = -2.69V \end{array}$$

Since, $E^\circ < 0$, hence reaction will not occur.

32 A cell reaction is spontaneous, if $\Delta G^\circ < 0$.

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

Thus, $\quad E^\circ_{cell} > 0$

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$

(a) If $X = Ni$, $Y = Fe$

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

$E^\circ_{Ni/Ni^{2+}} = 0.23V$

$E^\circ_{Fe^{2+}/Fe} = -0.44V$

Thus, $\quad E^\circ_{cell} = E^\circ_{Ni/Ni^{2+}} + E^\circ_{Fe^{2+}/Fe}$

$= +\ 0.23\ V - 0.44V$

$= -\ 0.21V$

$E^\circ_{cell} < 0$

(b) If $X = Ni$, $Y = Zn$

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

$E^\circ_{Ni/Ni^{2+}} = 0.23\ V$

$E^\circ_{Zn^{2+}/Zn} = -\ 0.76\ V$

$\therefore \quad E^\circ_{cell} = -\ 0.53\ V$

$E^\circ_{cell} < 0$

(c) $X = Fe$, $Y = Zn$

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

$E^\circ_{Fe/Fe^{2+}} = 0.44\ V$

$E^\circ_{Zn^{2+}/Zn} = -0.76\ V$

$E^\circ_{cell} = E^\circ_{Fe/Fe^{2+}} + E^\circ_{Zn^{2+}/Zn}$

$= 0.44 - 0.76 = -\ 0.32\ V$

$E^\circ_{cell} < 0$

(d) $X = Zn$, $Y = Ni$

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

$E^\circ_{Zn/Zn^{2+}} = 0.76\ V$

$E^\circ_{Ni^{2+}/Ni} = -\ 0.23$

$$E^\circ_{\text{cell}} = E^\circ_{\text{Zn/Zn}^{2+}} + E^\circ_{\text{Ni}^{2+}/\text{Ni}}$$
$$= 0.76 - 0.23 = 0.53\ \text{V}$$
$$E^\circ_{\text{cell}} > 0\ \text{(spontaneous)}$$

33 Given,

$\text{Fe}^{3+} + 3e^- \longrightarrow \text{Fe};\ E^\circ_1 = -0.036\ \text{V}$ …(i)

$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe};\ E^\circ_2 = -0.439\ \text{V}$ …(ii)

We need to calculate

$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+};\ E^\circ_3 = ?$ …(iii)

We can obtain (iii) by subtracting (ii) from (i) but we cannot obtain E°_3 that way because electrode potential is intensive property. That's why we determine E°_3 calculating

$$\Delta G_3 = \Delta G_1 - \Delta G_2$$
(ΔG is an extensive property)
$$\Delta G_3 = 3 \times 0.036 - 2 \times 0.439$$
$$-nFE^\circ_3 = (0.108 - 0.878)\,\text{F}$$
$$\Rightarrow -1 \times F \times E^\circ_3 = -0.770$$
$$E^\circ_3 = 0.770\ \text{V}$$

34 Zinc metal is the most stable metal to cover iron surfaces. The process of coating the iron surface by zinc is called galvanisation.

35 A→ 4, B→ 3, C→1, D→ 2

In lead storage, Pb is anode, PbO_2 is cathode. As, mercury cell is primary battery it gives steady potential. Fuel has maximum efficiency which is given as,

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

Rusting of iron can be prevented by the process of galvanisation.

36 As for spontaneous reaction,

$$\Delta G = -\text{ve}$$
$$\therefore \quad E_{\text{cell}} = +\text{ve}$$

Correct reason :

$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$. E_{cell} is +ve when, $E_{\text{cathode}} > E_{\text{anode}}$.

37 Correct explanation: $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$,

$$E_{\text{Ag}^+/\text{Ag}} = E^\circ_{\text{Ag}^+/\text{Ag}} - \frac{RT}{nF}\log\frac{1}{[\text{Ag}^+]}$$

38 In a Daniell cell, $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$

$$E_{\text{cell}} = 1.1\ \text{V}$$

The reaction of oxidation half-cell is

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

The reaction of reduction half-cell is

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

So, $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

because Zn is oxidised, it is deposited at anode and Cu is reduced, so it is deposited at cathode. If the opposite potential is greater than 1.1 V, then the electrons flow from cathode to anode. So, both the statements are true and correct explanation.

39 Galvanised iron, i.e. iron coated with zinc does not rust easily as zinc has more negative electrode potential (– 0.76 V) than iron.

SESSION 2

1 $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$

From Faraday's first law,

$$w = ZQ$$

where, w = amount of metal

$$= 5.12\ \text{kg} = 5.12 \times 10^3\,\text{g}$$

Q = charge

Z = electrochemical equivalent

$$= \frac{\text{equivalent weight}}{96500}$$
$$= \frac{\text{atomic mass}}{\text{number of electrons} \times 96500}$$
$$= \frac{27}{3 \times 96500}$$
$$5.12 \times 10^3 = \frac{27}{3 \times 96500} \times Q$$
$$Q = \frac{5.12 \times 10^3 \times 3 \times 96500}{27}\,\text{C}$$
$$= 5.49 \times 10^7\,\text{C}$$

2 For AgCl, molarity = normality

Actual specific conductance = (specific conductance of AgCl – specific conductance of water)

$$= (3.41 - 1.60) \times 10^{-6}$$
$$= 1.81 \times 10^{-6}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

For saturated solution of sparingly soluble salt,

$$\Lambda_{\text{eq}} = \Lambda^\infty_{\text{eq}},$$

and solubility = concentration

$$\Lambda^\infty_{\text{eq}} = \frac{1000 \times \text{specific conductance}}{\text{solubility}}$$
$$\therefore \quad 138.3 = \frac{1000 \times 1.81 \times 10^{-6}}{S}$$
$$S\ (\text{mol L}^{-1}) = \frac{1000 \times 1.81 \times 10^{-6}}{138.3}$$
$$= 1.31 \times 10^{-5}\ \text{mol L}^{-1}$$
$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$$
$$\therefore \quad K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = S^2$$
$$= (1.31 \times 10^{-5})^2$$
$$= 1.72 \times 10^{-10}\ \text{mol}^2\ \text{L}^{-2}$$

3 Given, $E^\circ_{\text{FeO/Fe}} = -0.87\,\text{V}$

and $E^\circ_{\text{Ni}_2\text{O}_3/\text{NiO}} = 0.40\,\text{V}$

$\therefore \quad E^\circ_{\text{Fe/FeO}} = +0.87\ \text{V}$

At anode

$$\text{Fe} + 2\text{OH}^- \longrightarrow \text{FeO}(s) + \text{H}_2\text{O}(l) + 2e^-$$

At cathode

$$\text{Ni}_2\text{O}_3(s) + \text{H}_2\text{O}(l) + 2e^- \longrightarrow 2\text{NiO}(s) + 2\text{OH}^-$$

Overall reaction

$$\text{Fe}(s) + \text{Ni}_2\text{O}_3(s) \longrightarrow \text{FeO}(s) + 2\text{NiO}(s)$$

Hence,

$$E^\circ_{\text{cell}} = 0.40 + 0.87 = 1.27\,\text{V}$$

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

$$= 2 \times 1.27 \times 96500$$
$$= -245110\ \text{J} = -245.11\ \text{kJ}$$
$$\Delta G^\circ = -W_{\text{max}}$$
$$w_{\text{max}} = 245.11\,\text{kJ}$$

4 $$\frac{\text{wt.}}{\text{eq. wt.}} = \frac{i \cdot t}{96500}$$

or $$\frac{2.16}{108} = \frac{i \times 60 \times 60}{96500}$$

or $$i = 0.54\,\text{A}$$

Error in reading of ammeter

$$= 0.60 - 0.54 = 0.06\,\text{A}$$
$$\therefore \quad \%\,\text{error} = \frac{0.06}{0.60} \times 100 = 10\%$$

5 The redox changes are :

At anode $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2e^-$

At cathode

$$2e^- + 2\text{H}_2\text{O} \longrightarrow 2\text{OH}^- + \text{H}_2$$

Now, $$\frac{w}{\text{eq.wt.}} = \frac{i \cdot t}{96500}$$

Given, $w_{\text{Cl}_2} = 10^3\,\text{g}$, eq. $\text{wt.}_{\text{Cl}_2} = 35.5$

and $$i = \frac{25 \times 62}{100} = 15.5\ \text{A}$$

Hence, $$t = \frac{10^3 \times 96500}{35.5 \times 15.5}$$
$$= 175374.83\,\text{s}$$
$$= 48.71\,\text{h}$$

6 For cell,

$\text{Zn}|\text{Zn}^{2+}(a = 0.1\text{M})||\text{Fe}^{2+}(a = 0.01\text{M})|\text{Fe}$

The half-cell reactions are:

(i) $\text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2e^-$

(ii) $\text{Fe}^{2+}(aq) + 2e^- \longrightarrow \text{Fe}(s)$

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

On applying Nernst equation,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log_{10}\frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]}$$

$$0.2905 = E^{\circ}_{\text{cell}} - \frac{0.0591}{2}\log_{10}\frac{0.1}{0.01}$$

$$0.2905 = E^{\circ}_{\text{cell}} - 0.0295 \times 1$$

$$\therefore \quad E^{\circ}_{\text{cell}} = 0.2905 + 0.0295 = 0.32\ \text{V}$$

At equilibrium, ($E_{\text{cell}} = 0$)

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log_{10} K_C$$

$$\text{or} \quad E^{\circ}_{\text{cell}} = \frac{0.0591}{2}\log_{10} K_C$$

$$0.32 = \frac{0.0591}{2}\log_{10} K_C$$

$$\text{or} \quad K_C = 10^{0.32/0.0295}$$

7 Less the reduction potential, weaker is the oxidising agent or stronger is the reducing agent.
Therefore, Zn is the strongest reducing agent.

8 Eq. of metal = Eq. of iodine
= Eq. of hypo

$$I_2 + 2e^- \longrightarrow 2I^-$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$

$$\therefore \quad \frac{0.617}{\text{eq. wt.}} = \frac{46.3}{1000} \times 0.124 \times 1$$

$$\text{Hence,} \quad \frac{0.617}{107.47} = \frac{10 \times t}{96500}$$

$$\text{or} \quad t = 55.4\ \text{s}$$

9 According to Kohlrausch's law,

$$\lambda^{\infty}_{\text{eq}}\ Na_2SO_4 = \lambda^{\infty}_{\text{eq}}\ (NaCl) + \lambda^{\infty}_{\text{eq}}\ K_2SO_4 - \lambda^{\infty}_{\text{eq}}\ KCl$$

$$= (123.7 + 152.1 - 147.0)\,\Omega^{-1}\text{cm}^2\,\text{eq}^{-1}$$

$$= 128.8\ \Omega^{-1}\text{cm}^2\,\text{eq}^{-1}$$

10 Greater the reduction potential, stronger is the oxidising agent. Hence, *Y* is stronger oxidising agent than *X* but weaker than *Z*.

11 Molar conductivity of aqueous CH_3COOH solution can be calculated from Kohlrausch law as

$$\lambda^{\circ}_{CH_3COOH} = \lambda^{\circ}_{CH_3COONa} + \lambda^{\circ}_{HCl} - \lambda^{\circ}_{NaCl}$$

Hence, for determining the molar conductivity of CH_3COOH solution, λ°_{NaCl} is required.

12 Reactions,

(i) $\text{Fe}(s) \longrightarrow \text{Fe}^{2+} + 2e^-;\ E^{\circ} = +0.44\ \text{V}$

and $\Delta G^{\circ}_1 = -nE^{\circ}\text{F} = -2 \times 0.44 \times \text{F}$

(ii) $2\text{H}^+ + 2e^- + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}(l);$

$$E^{\circ} = +1.23\ \text{V}$$

and $\Delta G^{\circ}_2 = -2 \times (+1.23) \times \text{F}$

Net reaction,

$$\text{Fe}(s) + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \longrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}(l);$$

$$\Delta G^{\circ}_3 = \Delta G^{\circ}_1 + \Delta G^{\circ}_2$$

$$= [-2 \times (+0.44) + (-2 \times 1.23)]$$

$$= [-0.88 - 2.46]$$

$$= -3.34\ \text{F} = -3.34 \times 96500\ \text{J}$$

$$= -322.31\ \text{kJ/mol} \approx -322\ \text{kJ mol}^{-1}$$

13 The reaction between MnO_4^- and HCl may be represented as follows :

$$2MnO_4^-(aq) + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Cl_2(g)$$

Thus, on the basis of this reaction following electrochemical cell will be represented

$$\text{Pt}\ Cl^-(aq)\,|\,Cl_2\ (g)(1\ \text{atm})\,||\,MnO_4^-(aq)\,|\,Mn^{2+}(aq)$$

Since, $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$

From given data,

$$E^{\circ}_{\text{cell}} = 1.51 - 1.40 = 0.11\ \text{V}$$

E°_{cell} is positive, hence ΔG° is negative. Thus, above cell reaction is feasible but MnO_4^- ion can oxidise, Fe^{2+} to Fe^{3+} and Cl^- to Cl_2 in aqueous medium also. Therefore, for quantitative estimation of aqueous $Fe(NO_3)_2$ it is not a suitable reagent.

14 Cell is completely discharged. It means equilibrium gets established, $E_{\text{cell}} = 0$

$$\text{Zn}\,|\,\text{Zn}^{2+}\ (1\ \text{M})\ ||\ \text{Cu}^{2+}\ (1\ \text{M})\ |\ \text{Cu}$$

Cell reaction :

$$\text{Zn} + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}$$

$$K_{\text{eq}} = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

We know that,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log K_{\text{eq}}$$

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{n}\log K_{\text{eq}}$$

$$\text{or} \quad 1.10 = \frac{0.0591}{2}\log K_{\text{eq}}$$

$$K_{\text{eq}} = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \text{antilog}\,\frac{2.20}{0.0591}$$

$$= \text{antilog } 37.2 \text{ or } 10^{37.2}$$

15 Given that, $i = 100$ amp. also, 27.66 g of diborane (B_2H_6)

Molecular mass of B_2H_6

$$= 10.8 \times 2 + 6 = 27.6$$

Number of moles of B_2H_6 in 27.66 g

$$= \frac{\text{Given mass}}{\text{Molar mass}} = \frac{27.66}{27.6} = 1$$

Now, consider the question,

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

From the equation we can interpret that 3 moles of oxygen is required to burn 1 mole (i.e. 27.6 g) B_2H_6 completely.

Also consider the electrolysis reaction of water, i.e.

$$H_2O \rightleftharpoons 2H^+ + O^{--}$$

$$2H^+ \xrightarrow[\text{Cathode}]{+2e^-} 2H \longrightarrow H_2 \uparrow$$

$$O^{--} \xrightarrow[-2e^-]{\text{Anode}} O \xrightarrow[\text{atoms}]{\text{2 such}} O_2 \uparrow$$

From the above equation it can be easily interpreted that in electrolysis of water for the production of 1 mole of oxygen from 1 mole of H_2O at anode 4 moles electrons are required.

Likewise for the production of 3 moles of O_2 12(3×4) moles of electrons will be needed. So, the total amount of charge required to produce 3 moles of oxygen will be $12 \times F$ or 12×96500

We know $Q = it$

So, $12 \times 96500 = 100 \times t$ in seconds

$$\text{or} \quad \frac{12 \times 96500}{100 \times 3600} = t \text{ in hours} = 3.2 \text{ hours}$$

16. $\text{AgI}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{I}^-;$

$$E^{\circ}_1 = -0.152$$

$$\underline{\text{Ag}(s) \longrightarrow \text{Ag}^+ + e^-\ ;\ E^{\circ}_2 = -0.8}$$

$$\text{AgI}(s) \longrightarrow \text{Ag}^+ + \text{I}^-;\ E^{\circ} = -0.952$$

$$\left[\begin{array}{l}\because \Delta G^{\circ} = \Delta G^{\circ}_1 + \Delta G^{\circ}_2 \\ \text{or } E^{\circ} = E^{\circ}_1 + E^{\circ}_2\end{array}\right]$$

$$E^{\circ}_{\text{cell}} = \frac{0.059}{n}\log K_{\text{sp}}$$

$$-0.952 = \frac{0.059}{1}\log K_{\text{sp}}$$

$$\log K_{\text{sp}} = \frac{-0.952}{0.059}$$

$$= -16.14$$