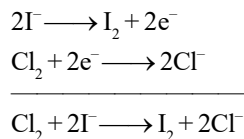# SOLVED EXAMPLES

Ex. 1 Colour of KI solution containing starch turns blue when Cl_2 water is added. Explain.

Sol. Chlorine placed below iodine in electrochemical series having more reduction potential and thus shows reduction whereas I^- undergoes oxidation. The I_2 so formed get absorbed in starch to give blue colour.

$$2I^- \longrightarrow I_2 + 2e^-$$
$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$
$$\overline{Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-}$$

Ex. 2 The resistance of a 0.01 N solution of an electrolyte was found to 210 ohm at 298 K using a conductivity cell with a cell constant of 0.88 cm^{-1}. Calculate specific conductance and equivalent conductance of solution.

Sol. Given for 0.01 N solution.

$$R = 210 \text{ ohm}$$

$$\frac{l}{A} = 0.88 \text{ cm}^{-1}$$

Specific conductance

$\therefore$ $$\kappa = \frac{1}{R} \times \frac{\lambda}{A}$$

$$\kappa = \frac{1}{210} \times 0.88 = \textbf{4.19} \times \textbf{10--3 mho cm--1}$$

$$\lambda_{eq} = \frac{k \times 1000}{N}$$

$$\lambda_{eq} = \frac{4.19 \times 10^{-3} \times 1000}{0.01}$$

$$\lambda_{eq.} = 419 \text{ mho cm}^2 \text{ eq}^{-1}.$$

Ex. 3 The conductivity of pure water in a conductivity cell with electrodes of cross-sectional area 4 cm^2 placed at a distance 2 cm apart is 8×10^{-7} S cm^{-1}. Calculate :

(A) the resistance of water.

(B) the current that would flow through the cell under the applied potential difference of 1 volt.

Sol. Cell constant $= \frac{l}{A} = \frac{2}{4} = \frac{1}{2}$ cm^{-11}

(A) Also $$\kappa = \frac{1}{R} \times \frac{1}{A}$$

$$R = \frac{1}{\kappa} \times \frac{1}{A} = \frac{1}{8 \times 10^{-7}} \times \frac{1}{2} = 6.25 \times 10^5 \text{ ohm}$$

(B) From Ohm's law, $\frac{V}{I} = R$ $\therefore$ $I = \frac{1}{6.25 \times 10^5} = 1.6 \times 10^{-6}$ ampere

Ex. 4   How many moles of electrons are needed for the reduction of 20 mL of 0.5M solution of $KMnO_4$ in acid medium ?

Sol.   Moles of $KMnO_4 = M \times V(L) = 0.5 \times 20 \times 10^{-3} = 10^{-2}$ $\qquad [\rightarrow Mn^{7+} + 5e^- \longrightarrow Mn^{2+}]$

$\qquad \rightarrow \qquad$ 1 mol $KMnO_4$ required $\qquad\qquad = 5$ mol e^-

$\qquad \therefore \qquad 10^{-2}$ mol $KMnO_4$ required $\qquad\qquad = 5 \times 10^{-2}$ mol e^-

Ex. 5   An aqueous solution of NaCl is electrolysed with inert electrodes. Write the equations for the reactions taking place at cathode and anode. What happens if $NaNO_{3(aq.)}$ is used instead of NaCl ?

Sol.   **For NaCl(aq.)** $\quad$ anode $\qquad : \qquad 2Cl^- \longrightarrow Cl_2 + 2e^-$

$\qquad\qquad\qquad\qquad$ cathode $\qquad : \qquad 2H^+ + 2e^- \longrightarrow H_2$

$\qquad$ **For NaNO3(aq.)** $\quad$ anode $\qquad : \qquad 2OH^- \longrightarrow H_2O + 1/2\ O_2 + 2e^-$

$\qquad\qquad\qquad\qquad$ cathode $\qquad : \qquad 2H^+ + 2e^- \longrightarrow H_2$

Ex. 6   On electrolysing $CuSO_4$ solution in presence of Pt, the solution becomes colourless, blue colour of solution disappears. Why ?

Sol. $\qquad$ At cathode $\qquad\qquad : \qquad Cu^{2+} + 2e^- \longrightarrow Cu$

$\qquad\qquad$ At anode $\qquad\qquad : \qquad 2OH^- \longrightarrow H_2O + 1/2\ O_2 + 2e^-$

Cu^{2+} ions are reduced and blue colour is due to Cu^{2+}.

Ex. 7   The specific conductivity of a solution containing 1.0 g of anhydrous $BaCl_2$ in 200 cm^3 of the solution has been found to be 0.0058 S cm^{-1}. Calculate the molar and equivalent conductivity of the solution. Molecular wt. of $BaCl_2$ = 208.

Sol. $\qquad$ Molarity of $BaCl_2 = \dfrac{1 \times 1000}{208 \times 200} = 0.024$ M

$\qquad$ Also $\quad$ normality of $BaCl_2 \qquad = 0.024 \times 2 = 0.048$ N $\qquad (\rightarrow$ N = M $\times$ V. f)

$\qquad$ Now $\qquad\qquad\qquad\qquad \mu = k \times \dfrac{1000}{C_M} = \dfrac{0.0058 \times 1000}{0.024} = 241.67$ S $cm^2\ mol^{-1}$

$\qquad$ Also $\qquad\qquad\qquad\qquad \lambda = k \times \dfrac{1000}{C_N} = \dfrac{0.0058 \times 1000}{0.048} = 120.83$ S cm^2 equivalent^{-1}

Ex. 8   The resistance of a solution 'A' is 50 ohm and that of solution 'B' is 100 ohm, both solution being taken in the same conductivity cell. If equal volumes of solutions A and B are mixed, what will be the resistance of the mixture using the same cell ?

$\qquad$ (Assume that there is no increase in the degree of dissociation of A and B on mixing.)

Sol.   Let k_1 and k_2 be the specific conductance of the solution A and B respectively and the cell constant of the cell be X.

$\qquad$ **For solution A :** $\quad$ Sp. conductance = Conductance $\times$ Cell constant

$$k_1 = \frac{1}{50} \times X \qquad .... \qquad (i)$$

$\qquad$ **For solution B :** $\quad$ Sp. conductance, $k_2 = \dfrac{1}{100} \times X \qquad .... \qquad (ii)$

$\qquad$ When equal volumes of A and B are mixed, both the solutions get doubly diluted, hence their individual contribution towards the sp. conductance of the mixture will be $\dfrac{k_1}{2}$ and $\dfrac{k_2}{2}$ respectively and the sp. conductance of the mixture will be $\dfrac{1}{2}(k_1 + k_2)$.

$\qquad \therefore \qquad$ For the mixture : $\dfrac{1}{2}(k_1 + k_2) = \dfrac{1}{R} \times X \qquad .... \qquad (iii)$

$\qquad$ (R is the resistance of mixture)

$\qquad$ From equation (i), (ii) and (iii) ; $\qquad$ R = 66.67 ohm

Ex. 9 The value of μ^∞ for NH_4Cl, $NaOH$ and $NaCl$ are 129.8, 248.1 and 126.4 ohm^{-1} cm^2 mol^{-1} respectively. Calculate μ^∞ for NH_4OH solution.

Sol.
$$\mu^\infty_{NH_4OH} = \mu^\infty_{NH_4Cl} + \mu^\infty_{NaOH} - \mu^\infty_{NaCl}$$

$$= 129.8 + 248.1 - 126.4$$

$$\mu^\infty_{NH_4OH} = 251.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Ex. 10 Given the standard electrode potentials ;

$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V, $Hg^{2+}/Hg = 0.79$ V, $Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$V.

Arrange these metals in their increasing order of reducing power.

Sol. More is E°_{RP}, more is the tendency to get reduced or more is the oxidising power or lesser is reducing power.

$$Ag < Hg < Cr < Mg < K$$

Ex. 11 Answer of following :

(i) In a cell, anode is represented by –ve sign and cathode by +ve sign. What is the type of the cell?

(ii) Write the reaction taking place at anode in the following cell :

Pt, H_2 (1atm) | HCl (1M) Cl_2 , Pt.

(iii) With the help of the following possible reactions, arrange Mg, Zn, Cu and Ag in decreasing order of their reduction potentials.

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

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

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

(iv) Cl_2 can displace I_2 from KI solution but I_2 does not displace.

(v) The E° (standard oxidation potentials) values of the elements A, B, C and D are + 0.76, – 0.34, + 0.25 and – 0.85 volt respectively. Arrange these in decreasing order of reactivity.

Sol. (i) The cell is an electrochemical cell i.e. galvanic cell.

(ii) Reaction taking place at anode is : $H_2 \longrightarrow 2H^+ + 2e^-$

(iii) The decreasing order of reduction potentials in : Ag > Cu > Zn > Mg

(iv) I^- is stronger reducing agents than Cl^-. Therefore, I^- can reduce Cl_2 to Cl^- ions whereas Cl^- cannot reduct I_2 to I^-. Thus, only the following reaction is feasible.

$$Cl_2 + 2I^- (2KI) \longrightarrow 2KCl (2Cl^-) + I_2$$

(v) The reactivity of an elements is directly porportional to its standard oxidation potential (E°). The decreasing order of reactivity of elements is : A > C > B > D.
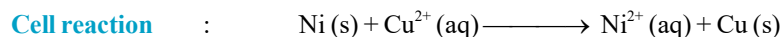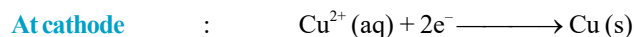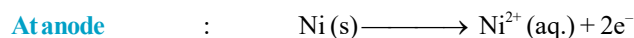
Ex. 12 A cell is prepared by dipping a copper rod in 1 M $CuSO_4$ solution and a nickel rod in 1M $NiSO_4$. The standard reduction potentials of copper and nickel electrodes are + 0.34 V and –0.25 V respectively.

(i) Which electrode will work as anode and which as cathode ?

(ii) What will be the cell reaction ?

(iii) How is the cell represented ?

(iv) Calculate the EMF of the cell.

Sol. (i) The nickel electrode with smaller E° value (–0.25 V) will work as anode while copper electrode with more E° value (+0.34V) will work as cathode.

(ii) The cell reaction may be written as :

At anode : $Ni(s) \longrightarrow Ni^{2+}(aq.) + 2e^-$

At cathode : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Cell reaction : $Ni(s) + Cu^{2+}(aq) \longrightarrow Ni^{2+}(aq) + Cu(s)$

(iii) The cell may be represented as :

$$Ni(s)/Ni^{2+}(aq) \| Cu^{2+}(aq)/Cu(s)$$

(iv) EMF of cell $= E^{\circ}_{cathode} - E^{\circ}_{anode} = (+0.34) - (-0.25) = 0.59 \text{ V}$

Ex. 13 Calculate molar conductance for NH_4OH, given that molar conductances for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 523.28, 280.0 and 129.8 ohm^{-1} cm^2 mol^{-1} respectively.

Sol. $\mu^{\infty}_{Ba(OH)_2} = \lambda^{\infty}_{Ba^{2+}} + 2\lambda^{\infty}_{OH^-} = 523.28$ .... (i)

$\mu^{\infty}_{BaCl_2} = \lambda^{\infty}_{Ba^{2+}} + 2\lambda^{\infty}_{Cl^-} = 280.00$ .... (ii)

$\mu^{\infty}_{NH_4Cl} = \lambda^{\infty}_{NH_4^+} + \lambda^{\infty}_{Cl^-} = 129.80$ .... (iii)

$\mu^{\infty}_{NH_4OH} = \lambda^{\infty}_{NH_4} + \lambda^{\infty}_{OH^-} = ?$

$Eq.(iii) + \dfrac{Eq.(i)}{2} - \dfrac{Eq.(ii)}{2}$ will gives

$\lambda^{\infty}_{NH_4^+} + \lambda^{\infty}_{OH^-} = \lambda^{\infty}_{NH_4OH^-} = \dfrac{502.88}{2} = 251.44 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Ex. 14 The equivalent conductivities of acetic acid at 298 K at the concentrations of 0.1 M and 0.001 M are 5.20 and 49.2 S cm^2 eq.$^{-1}$ respectively. Calculate the degree of dissociation of acetic acid at these concentrations. Given that, $\lambda^{\infty}(H^+)$ and $\lambda^{\infty}(CH_3COO^-)$ are 349.8 and 40.9 ohm^{-1} cm^2 mol^{-1} respectively.

Sol. Degree of dissociation is given by $\alpha = \dfrac{\lambda^c}{\lambda^{\infty}}$

(i) Evaluation of $\lambda^{\infty}_{CH_3COOH}$

$$\lambda^{\infty}_{CH_3COOH} = \lambda^{\infty}_{CH_3COO^-} + \lambda^{\infty}_{H^+}$$

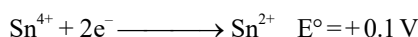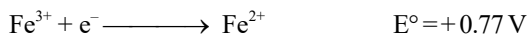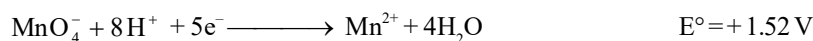$$= 40.9 + 349.8 = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq.}^{-1}$$

(ii) Evaluation of degree of dissociation

At C = 0.1 M $\quad \alpha = \dfrac{\lambda^c}{\lambda^{\infty}} = \dfrac{5.20}{390.7} = 0.013$ i.e. 1.3%

or $\quad \alpha = 1.3\%$

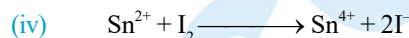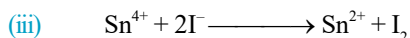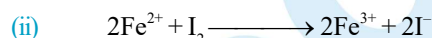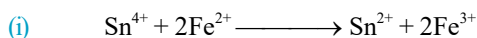At C = 0.001 M $\quad \alpha = \dfrac{\lambda^c}{\lambda^{\infty}} = \dfrac{49.2}{390.7} = 0.125$ i.e. 12.5%

Ex. 15   E° of some oxidants are given as :

$$I_2 + 2e^- \longrightarrow 2I^- \qquad\qquad E° = +0.54\,V$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \qquad\qquad E° = +1.52\,V$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad\qquad E° = +0.77\,V$$

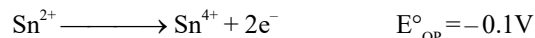$$Sn^{4+} + 2e^- \longrightarrow Sn^{2+} \quad E° = +0.1\,V$$

(A) Select the strongest reductant and oxidant in these.

(B) Select the weakest reductant and oxidant in these.

**(C)** Select the spontaneous reaction from the changes given below.

(i) $\quad Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$ $\qquad$ (ii) $\quad 2Fe^{2+} + I_2 \longrightarrow 2Fe^{3+} + 2I^-$

(iii) $\quad Sn^{4+} + 2I^- \longrightarrow Sn^{2+} + I_2$ $\qquad$ (iv) $\quad Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$

Sol.   **(A)**   More the $E°_{OP}$, more is the tendency for oxidation. Therefore, since maximum $E°_{OP}$ stands for :

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^- \qquad\qquad E°_{OP} = -0.1V$$

∴ $\qquad$ strongest reductant $\qquad$: $\qquad$ **Sn^{2+}**

$\qquad$ and weakest oxidant $\qquad$: $\qquad$ **Sn^{4+}**

(B)   More or +ve is $E°_{RP}$, more is the tendency for reduction. Therefore, since maximum $E°_{RP}$ stands for :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \qquad\qquad E°_{RP} = +1.52\,V$$
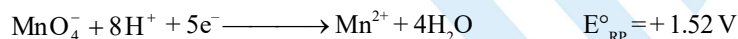
∴ $\qquad$ strongest oxidant $\qquad$: $\qquad$ **MnO_4^-**

$\qquad$ and weakest reductant $\qquad$: $\qquad$ **Mn^{2+}**

Note : Stronger is oxidant, weaker is its conjugate reducant and vice-versa.

(C) $\qquad$ For (i) $\quad E°_{Cell} = E°_{OP_{Fe^{2+}/Fe^{3+}}} + E°_{RP_{Sn^{4+}/Sn^{2+}}} = -0.77 + 0.1$

Fe^{2+} oxidizes and Sn^{4+} reduces in change.

∴ $\qquad E°_{Cell} = -0.67\,V$

$E°_{Cell}$ is negative.

∴ $\qquad$ **(i)** $\qquad$ **Is non-spontaneous change.**

For (ii) $\quad E°_{Cell} = E°_{OP_{Fe^{2+}/Fe^{3+}}} + E°_{RP_{I_2/I^-}} = -0.77 + 0.54$ **= – 0.23 V**

∴ $\qquad$ **(ii)** $\qquad$ **Is non-spontaneous change.**

For (iii) $\quad E°_{Cell} = E°_{OP_{I^-/I_2}} + E°_{RP_{Sn^{4+}/Sn^{2+}}} = -0.54 + 0.1$ **= – 0.44 V**

∴ $\qquad$ **(iii)** $\qquad$ **Is non-spontaneous change.**

For (iv) $\quad E°_{Cell} = E°_{OP_{Sn^{2+}/Sn^{4+}}} + E°_{RP_{I_2/I^-}} = -0.1 + 0.54$ **= + 0.44 V**
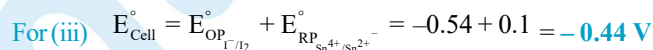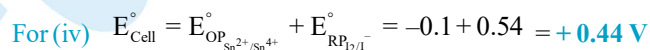
(iv) $\qquad$ **Is spontaneous change.**

Ex. 16 Predict whether the following reaction can occur under standard conditions or not.

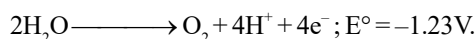$$Sn^{2+}(aq) + Br_2(\bullet) \longrightarrow Sn^{4+}(aq) + 2Br^-(aq)$$
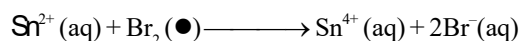
Given $E^\circ_{Sn^{4+}/Sn^{2+}} = +0.15, E^\circ_{Br_2/Br^-} = 1.06V.$

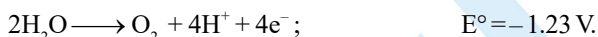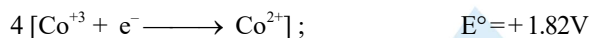**Sol.** $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.06 - 0.15 = 0.91V.$

Since, E°_{cell} comes out be positive, this means that the reaction can occur.

Ex. 17 Given that, $\qquad Co^{3+} + e^- \longrightarrow Co^{2+} \quad E^\circ = +1.82V$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-; E^\circ = -1.23V.$$

Explain why Co^{3+} is not stable in aqueous solutions.

Sol. The E°_{cell} can be calculated as follows :

$$4[Co^{+3} + e^- \longrightarrow Co^{2+}]; \qquad\qquad E^\circ = +1.82V$$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-; \qquad\qquad E^\circ = -1.23 V.$$

Add : $\quad 4Co^{3+} + 2H_2O \longrightarrow 4Co^{2+} + 4H^+ + O_2; E^\circ = 1.82 - 1.23 = +0.59V.$

Since E°_{cell} is positive, the cell reaction is spontaneous. This means that Co^{3+} ions will take part in the reaction. Therefore, Co^{3+} is not stable.

Ex. 18 The measured e.m.f. at 25°C for the cell reaction,

$$Zn(s) + Cu^{2+}(1.0M) \longrightarrow Cu(s) + Zn^{2+}(0.1 M)$$
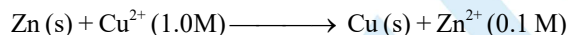
is 1.3 volt Calculate E° for the cell reaction.

Sol. Using Nernst equation (at 298 K),

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

Here $\quad E_{cell} = 1.3\ V, [Cu^{2+}(aq)] = 1.0\ M, \qquad [Zn^{2+}(aq)] = 0.1\ M, E^\circ_{cell} = ?$

Substituting the values,

$$1.3\ V = E^\circ_{cell} - \frac{0.0591V}{2} \log \frac{0.1}{1.0}$$

$$1.3\ V = E^\circ_{cell} - 0.02955\ V \log 10^{-1}$$

$$1.3\ V = E^\circ_{cell} + 0.02955\ V \log 10$$

$$E^\circ_{cell} = 1.3\ V - 0.02955\ V = 1.27\ V$$

Ex. 19 A Solution of copper (II) sulphate is electrolysed between copper electrodes by a current of 10.0 amperes passing for one hour. What changes occur at the electrodes and in the solution ?

**Sol.** According to Faraday's first law of electrolysis :

The reaction at cathode : Cu^{2+} + $2e^-$ $\longrightarrow$ Cu

$\qquad\qquad\qquad\qquad$ 63.5 $\qquad$ 2×96500 C
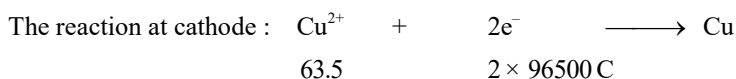
The quantity of charge passed $= I \times t = (10 \text{ amp}) \times (60 \times 60s) = 36000$ C.

2×96500 C of charge deposit copper $= 63.5$ g

36000 C of charge deposit copper $= \dfrac{(63.5 \text{ g})}{(2 \times 96500 \text{ C})} \times (36000 \text{ C}) = 11.84$ g

Thus, 11.84 g of copper will dissolve from the anode and the same amount from the solution will get deposited on the cathode. The concentration of the solution will remain unchanged.

Ex. 20 Calculate the equilibrium constant for the reaction at 298 K

$$Zn \text{ (s)} + Cu^{2+} \text{ (aq)} \; \hat{\ddagger} \; \hat{} \; \hat{\ddagger} \quad Zn^{2+}\text{(aq)} + Cu \text{ (s)}$$
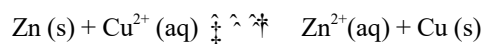
Given $E^{\circ}_{Zn^{2+}/Zn} = -0.76$ V and $E^{\circ}_{Cu^{2+}/Cu} = +0.34$ V

Sol. We know that, $\log K_c = \dfrac{nE^{\circ}_{cell}}{0.0591}$

$$E^{\circ}_{cell} = \left[E^{\circ}_{Cathode} - E^{\circ}_{Anode} \right]$$

$$= [(+0.34 \text{ V}) - (-0.76 \text{ V})] = 1.10 \text{ V}, n = 2,$$

$\therefore \qquad\qquad \log K_c = \dfrac{2 \times (1.10 \text{ V})}{(0.0591 \text{ V})} = 37.29$

$$K_c = \text{Antilog } 37.29 = 1.95 \times 10^{37}$$

Ex. 21 Calculate the cell e.m.f. and ΔG for the cell reaction at 298 K for the cell.

$$Zn \text{ (s)} \,|Zn^{2+} (0.0004M) \,\|Cd^{2+} (0.2M)\,|\, Cd(s)$$

Given $E^{\circ}_{Zn^{2+}/Zn} = -0.763$ V ; $E^{\circ}_{Cd^{+2}/Cd} = -0.403$ V at 298 K.

$\qquad F = 96500 \text{ C mol}^{-1}$.

Sol. **Step I.** Calculation of cell e.m.f.

According to Nernst equation

$$E = E^{\circ} - \dfrac{0.0591}{n} \log \dfrac{[Zn^{2+}(aq)]}{[Cd^{2+}(aq)]}$$

$$E^{\circ}_{cell} = E^{\circ}_{(Cd^{2+}/Cd)} - E^{\circ}_{(Zn^{2+}/Zn)} = (-0.403) - (-0.763) = 0.36 \text{ V}$$

$$[Zn^+ (aq)] = 0.0004 \text{ M}, [Cd^{2+} (aq)] = 0.2 \text{ M}, n = 2$$

$$E = (0.36) - \dfrac{(0.0591 \text{ V})}{2} \log \dfrac{0.0004}{0.2}$$

$$= 0.36 - \frac{(0.0591 \text{ V})}{2} \times (-2.69990)$$

$$= 0.36 \text{ V} + 0.08 = 0.44 \text{ V}$$

Step II. Calculation of ΔG

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

$$E_{cell} = 0.44 \text{ V}, n = 2 \text{ mol}, F = 96500 \text{ C mol}^{-1}$$

$\therefore$ $\Delta G = -(2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.44 \text{ V})$

$$= -84920 \text{ CV} = -84920 \text{ J}$$

Ex.22 Calculate $\Delta G°$ for the reaction : $Cu^{2+} (aq) + Fe (s) \rightleftharpoons Fe^{2+} (aq) + Cu (s)$. Given that $E°_{Cu^{2+}/Cu} = +0.34 \text{ V}$, $E°_{Fe^{+2}/Fe} = -0.44 \text{ V}$

Sol. The cell reactions are :

$$Fe (s) \longrightarrow Fe^{2+} (aq) + 2e^- \qquad .... \text{At (anode)}$$

$$Cu^{2+} (aq) + 2e^- \longrightarrow Cu (s) \qquad .... \text{At (cathode)}$$

We know that : $\Delta Gh° = -nF \, E°_{cell}$; $n = 2$ mol,

$$E°_{cell} = \left[E°_{(Cu^{2+}/Cu)} - E°_{(Fe^{2+}/Fe)} \right]$$

$$= (+0.34 \text{ V}) - (-0.44 \text{ V}) = +0.78 \text{ V}$$

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

$\therefore$ $\Delta G° = -nF \, E°_{cell}$

$$= -(2 \text{mol}) \times (96500 \text{ C mol}^{-1}) \times (+0.78 \text{ V})$$

$$= -150540 \text{ CV} = -150540 \text{ J} \qquad (\rightarrow \qquad 1 \text{ CV} = 1\text{J})$$

Ex. 23 How will show that Faraday's second law of electrolysis is simply corollary of the first law.

Sol. Accroding to Faraday's first law of electrolysis.

$$w = Z \times Q$$

If same quantity of electricity is passed through two electolytes, i.e., $Q_1 = Q_2 = Q$, then

In case of first electrolyte, $w_1 = Z_1 \times Q$ and

In case of second electrolyte, $\qquad w_2 = Z_2 \times Q$

On dividing , $\dfrac{w_1}{w_2} = \dfrac{Z_1}{Z_2} = \dfrac{E_1 / 96500}{E_2 / 96500} = \dfrac{E_1}{E_2}$

where E_1 and E_2 are their equivalent masses.

Ex. 24 Iron does not rust even if zinc coating on its surface is broken but the same is not true when coating is of tin.

Sol. The zinc is more reactive than iron. This means that if a crack appears on the surface of iron coated with zinc even then zinc will take part in the redox reaction and not iron. In other words, zinc will be corroded in preference to iron. But same is not in the case with tin. it is less reactive than iron. If a crack appears on the surface of iron coated with tin, then iron will take part in the redox reaction and not tin. Therefore, iron will be corroded under these circumstances.

## Exercise # 1 [Single Correct Choice Type Questions]

1. The standard reduction potentials E° of the following systems are

System		E° (volts)
(i)	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	1.51
(ii)	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	0.15
(iii)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	1.33
(iv)	$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	1.61

The oxidising power of the various species decreases in the order

(A) $Ce^{4+} > Cr_2O_7^{2-} > Sn^{4+} > MnO_4^-$

(B) $Ce^{4+} > MnO_4^- > Cr_2O_7^{2-} > Sn^{4+}$

(C) $Cr_2O_7^{2-} > Sn^{4+} > Ce^{4+} > MnO_4^-$

(D) $MnO_4^- > Ce^{4+} > Sn^{4+} > Cr_2O_7^{2-}$

2. Consider the reaction : (T = 298 K)

$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq.)$
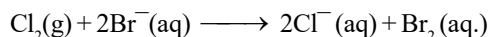
The emf of the cell, when $[Cl^-] = [Br_2] = [Br^-] = 0.01M$ and Cl_2 gas is at 1 atm pressure, will be :

(E° for the above reaction is = 0.29 volt)

(A) 0.54 volt   (B) 0.35 volt   (C) 0.24 volt   (D) –0.29 volt

3. $2Ce^{4+} + Co \longrightarrow 2Ce^{3+} + Co^{2+}$ $E^o_{cell} = 1.89$ V, $E^o_{Co^{2+}/Co} = -0.277$ V hence, $E^o_{Ce^{4+}/Ce^{3+}}$ is :

(A) 0.805 V   (B) 1.62 V   (C) –0.805 V   (D) –1.61 V

4. Given : $E^o(Cu^{2+}|Cu) = 0.337$ V and $E^o(Sn^{2+}|Sn) = -0.136$ V. Which of the following statements is correct?
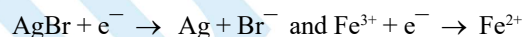
(A) Cu^{2+} ions can be reduced by $H_2(g)$

(B) Cu can be oxidized by H^+

(C) Sn^{2+} ions can be reduced by $H_2(g)$

(D) Cu can reduce Sn^{2+}

5. Red hot carbon will remove oxygen from the oxide AO and BO but not from MO, while B will remove oxygen from AO. The activity of metals A, B and M in decreasing order is

(A) A > B > M   (B) B > A > M   (C) M > B > A   (D) M > A > B

6. What is the emf at 25° C for the cell, $Ag \begin{vmatrix} AgBr(s), Br^- \\ a = 0.34 \end{vmatrix}, \begin{vmatrix} Fe^{3+} & , & Fe^{2+} \\ a = 0.1 & a = 0.02 \end{vmatrix} Pt$

The standard reduction potentials for the half-reactions

$AgBr + e^- \rightarrow Ag + Br^-$ and $Fe^{3+} + e^- \rightarrow Fe^{2+}$

are + 0.0713 V and + 0.770 V respectively.

(A) 0.474 volt   (B) 0.529 volt   (C) 0.356 volt   (D) 0.713 volt

7. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$; $E^o = 1.51$ V ; $\Delta G^0_1 = -5 \times 1.51 \times F$

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$; $E^o = 1.23$ V ; $\Delta G^0_2 = -2 \times 1.23 \times F$
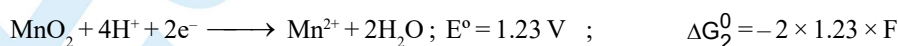
$E^o_{MnO_4^-|MnO_2}$ is

(A) 1.70 V   (B) 0.91 V   (C) 1.37 V   (D) 0.548 V

8. A hydrogen electrode placed in a buffer solution of CH_3COONa and CH_3COOH in the ratios of x : y and y : x has electrode potential values E_1 volts and E_2 volts, respectively at 25ºC. The pK_a values of acetic acid is (E_1 and E_2 are oxidation potentials)

(A) $\dfrac{E_1 + E_2}{0.118}$ (B) $\dfrac{E_2 - E_1}{0.118}$ (C) $-\dfrac{E_1 + E_2}{0.118}$ (D) $\dfrac{E_1 - E_2}{0.118}$

9. The electrode potential of electrode

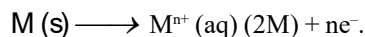$$M\,(s) \longrightarrow M^{n+}\,(aq)\,(2M) + ne^-.$$

at 298 K is E_1. When temperature is doubled and concentration is made half, then the electrode potential becomes E_2. Which of the following represents the correct relationship between E_1 and E_2 ?

(A) $E_1 > E_2$ (B) $E_1 < E_2$ (C) $E_1 = E_2$ (D) Can't be predicted

10. During the preparation of $H_2S_2O_8$ (per disulphuric acid) O_2 gas also releases at anode as byproduct, When 9.72 L of H_2 releases at cathode and 2.35 L O_2 at anode at STP, the weight of $H_2S_2O_8$ produced in gram is

(A) 87.12   (B) 43.56   (C) 83.42   (D) 51.74

11. The equivalent conductivity of KCl at infinite dilution is 130 S cm² eq⁻¹. The transport number of Cl^{-1} ion in KCl at the same temperature is 0.505. The limiting ionic mobility of K^+ ion, is

(A) 6.67×10^{-4} cm² sec⁻¹ volt⁻¹   (B) 5.01×10^{-3} cm² sec⁻¹ volt⁻¹

(C) 3.22×10^{-4} cm² sec⁻¹ volt⁻¹   (D) 2.00×10^{-4} cm² sec⁻¹ volt⁻¹

12. When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrode are

(A) pure zinc as cathode and pure copper as anode

(B) impure sample as cathode and pure copper as anode

(C) impure zinc as cathode and impure sample as anode

(D) pure copper as cathode and impure sample as anode

13. Two weak acid solutions HA_1 and HA_2 each with the same concentration and having pK_a values 3 and 5 are placed in contact with hydrogen electrode (1 atm, 25ºC) and are interconnected through a salt bridge. The emf of the cell is :
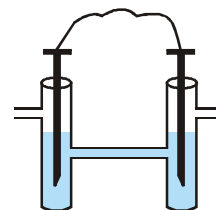
(A) 0.21 V   (B) 0.059 V   (C) 0.018 V   (D) 0.021 V

14. ΔG is the available energy (energy produced) during the electrochemical reaction in galvanic cell which can be converted into useful work. In the light of second law of thermodynamics in the cell the change in electrode potential with temperature will be equal to

(A) $\dfrac{\Delta S}{nF}$ (B) $\dfrac{nF}{\Delta S}$ (C) $-2.303\, RT \log K_C$ (D) $\dfrac{-2.303\, RT}{nF}$

15. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2. Passing a current of 27A for 24 hours gives 1kg of MnO_2. The current efficiency in this process is :

(A) 100%   (B) 95.185%   (C) 80%   (D) 82.951%

16. The reduction potential of hydrogen electrode when placed in a buffer solution is found to be – 0.413V. The pH of the buffer is -
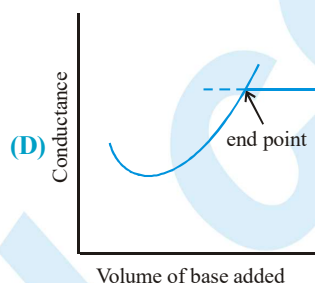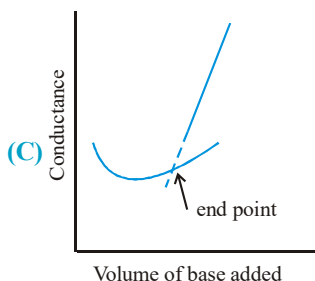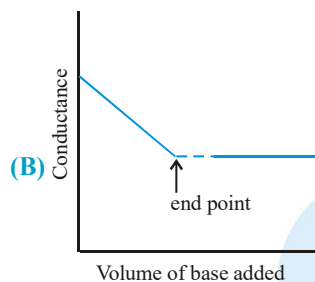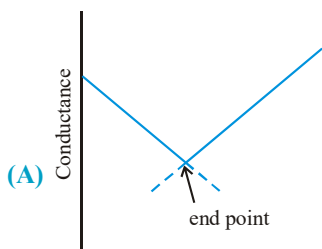
(A) 10   (B) 4   (C) 7   (D) 12

17. A galvanic cell is composed of two hydrogen electrodes, one of which is a standard one. In which of the following solutions should the other electrode be immersed to get maximum emf ?

$K_a(CH_3COOH) = 2 \times 10^{-5}, K_a(H_3PO_4) = 10^{-3}$.

(A) 0.1 M HCl (B) 0.1 M CH_3COOH (C) 0.1 M H_3PO_4 (D) 0.1 M H_2SO_4

18. A gas Cl_2 at 1 atm is bubbled through a solution containing a mixture of 1 M Br^{-1} and 1 M F^{-1} at 25ºC. If the reduction potential is F > Cl > Br, then :

(A) Cl will oxidise Br and not F (B) Cl will oxidise F and not Br.
(C) Cl will oxidise both Br and F (D) Cl will reduce both Br and F

19. Pure water is saturated with pure solid AgCl, a silver electrode is placed in the solution and the potential is measured against normal calomel electrode at 25°C. This experiment is then repeated with a saturated solution of AgI. If the difference in potential in the two cases is 0.177V. What is the ratio of solubility product (solubility) of AgCl and AgI at the temperature of the experiment ?

(A) 10^3 (B) 10^6 (C) 10^2 (D) 10^2

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

(A) increase in A and decrease in B (B) decrease in both
(C) increase in both (D) decrease in A and increase in B.

21. When iron is rusted, it is :

(A) reduced (B) oxidised (C) evaporated (D) decomposed

22. The oxidation potentials of Zn, Cu, Ag, H_2 and Ni are 0.76, –0.34, –0.80, 0.00, 0.25 volt, respectively. Which of the following reactions will provide maximum voltage ?

(A) $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$ (B) $Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$
(C) $H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu$ (D) $H_2 + Ni^{2+} \longrightarrow 2H^+ + Ni$

23. The reduction potential of a half-cell consisting of a Pt electrode immersed in 1.5 M Fe^{2+} and 0.015 M Fe^{3+} solution

at 25°C is $\left(E^0_{Fe^{3+}/Fe^{2+}} = 0.770 \text{ V}\right)$.

(A) 0.652 V (B) 0.88 V (C) 0.710 V (D) 0.850 V

24. $Zn + Cu^{2+}(aq) \rightleftharpoons Cu + Zn^{2+}(aq)$ Reaction quotient is $Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$. $E^o_{cell} = 1.10$ V. E_{cell} will be 1.1591 V when:
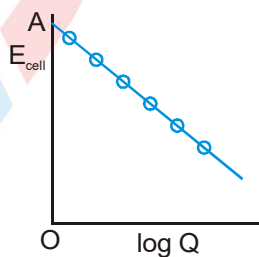
(A) $[Cu^{2+}]/[Zn^{2+}] = 0.01$ (B) $[Zn^{2+}]/[Cu^{2+}] = 0.01$
(C) $[Zn^{2+}]/[Cu^{2+}] = 0.1$ (D) $[Zn^{2+}]/[Cu^{2+}] = 1$

25. Which statement is correct.

(A) In SHE, the pressure of dihydrogen gas should be low and pH of solution should be zero.
(B) In the reaction $H_2O_2 + O_3 \longrightarrow 2H_2O + 2O_2$, H_2O_2 is oxidised to H_2O.
(C) The absolute value of electrode potential cannot be determined.
(D) According to IUPAC conventions, the standard electrode potential pertains to oxidation reactions only.

26. Conductance measurements can be used to detect the end point of acid-base titrations. Which of the following plots correctly represent the end point of the titration of strong acid and a strong base ?

(A)

Conductance vs Volume of base added

(B)

Conductance vs Volume of base added

(C)

Conductance vs Volume of base added

(D)

Conductance vs Volume of base added

27. Using the standard potential values given below, decide which of the statements I, II, III, IV are correct. Choose the right answer from **(A)**, **(B)**, **(C)** and **(D)**

$Fe^{2+} + 2e^- = Fe$, $E^o = -0.44$ V

$Cu^{2+} + 2e^- = Cu$, $E^o = +0.34$ V

$Ag^+ + e^- = Ag$, $E^o = +0.80$ V

I. Copper can displace iron from $FeSO_4$ solution

II. Iron can displace copper from $CuSO_4$ solution

III. Silver can displace Cu from $CuSO_4$ solution

IV. Iron can displace silver from $AgNO_3$ solution

(A) I and II   (B) II and III   (C) II and IV   (D) I and IV

28. Four moles of electrons were transferred from anode to cathode in an experiment on electrolysis of water. The total volume of the two gases (dry and at STP) produced will be approximately (in litres)

(A) 22.4   (B) 44.8   (C) 67.2   (D) 89.4

29. The standard reduction potential of a silver chloride electrode is 0.2 V and that of a silver electrode is 0.79 V. The **maximum amount of AgCl that can dissolve in 10^6** L of a 0.1 M $AgNO_3$ solution is

(A) 0.5 mmol   (B) 1.0 mmol   (C) 2.0 mmol   (D) 2.5 mmol

30. A cell $Cu | Cu^{++} || Ag^+ | Ag$ initially contains $2M\ Ag^+$ and $2M\ Cu^{++}$ ions in 1L electrolyte. The change in cell potential after the passage of 10 amp current for 4825 sec is :

(A) -0.00738 V   (B) -1.00738 V   (C) -0.0038 V   (D) none

31. When the electric current is passed through a cell having an electrolyte, the positive ions move towards cathode and negative ions towards the anode. If the cathode is pulled out of the solution

(A) the positive and negative ions will move towards anode

(B) the positive ions will start moving towards the anode while negative ions will stop moving

(C) the negative ions will continue to move towards anode while positive ions will stop moving

(D) the positive and negative ions will start moving randomly

32. Which one of the following will increase the voltage of the cell ? (T = 298 K)

$$Sn + 2Ag^+ \longrightarrow Sn^{2+} + 2Ag$$

(A) increase in the size of silver rod   (B) increase in the concentration of Sn^{+2} ions

(C) increase in the concentration of Ag^+ ions   (D) none of the above

33. In a $H_2 - O_2$ fuel cell, 6.72 L of hydrogen at NTP reacts in 15 minutes, the average current produced in amperes is

(A) 64.3 amp   (B) 643.3 amp   (C) 6.43 amp   (D) 0.643 amp

34. With t taken in seconds and I taken in Amp, the variation of I follows the equation
$$t^2 + I^2 = 25$$
what amount of Ag will be electrodeposited with this current flowing in the interval 0–5 second ? (Ag – 108)

(A) 22 mg   (B) 66 mg   (C) 77 mg   (D) 88 mg

35. Acetic acid is titrated with NaOH solution. Which of the following statement is correct for this titration?

(A) conductance increases upto equivalence point, then it decreases

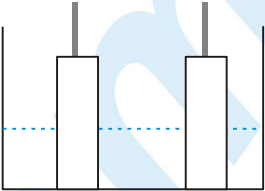(B) conductance increases upto equivalence point, then it increases

(C) first conductance increases slowly upto equivalence point and then increases rapidly

(D) first conductance increases slowly upto equivalence point and then drops rapidly .

36. Which statement is correct.

(A) A solution of copper (II) sulphate can be stored in iron vessel.

(B) An oxide layer on zinc vessel can be easily removed by washing with dilute HCl.

(C) Molten $PbBr_2$ is good conductor of electricity because it contains free ions.

(D) In the reaction, $Li + \dfrac{1}{2} H_2 \longrightarrow LiH$, hydrogen is a reducing agent.

37. During the electrolysis of 0.1 M $CuSO_4$ solution using copper electrodes, a depletion of $[Cu^{++}]$ occurs near the cathode with a corresponding excess near the anode, owing to inefficient stirring of the solution. If the local concentrations of $[Cu^{++}]$ near the anode & cathode are respectively 0.12 M & 0.08 M, calculate the back e.m.f. developed . Temperature = 298 K .

(A) 22 mV   (B) 5.2 mV   (C) 29 mV   (D) 59 mV

38. How much the potential of a hydrogen electrode will change when its solution initially at pH = 0 is neutralised to pH = 7?

(A) Increase by 0.059 V   (B) Decrease by 0.059 V

(C) Increase by 0.41 V   (D) Decrease by 0.41 V

39. The standard electrode potentials (reduction) of Pt/Fe^{2+} , Fe^{3+} and Pt/Sn^{4+}, Sn^{2+} are + 0.77 V and 0.15 V respectively at 25° C. The standard EMF of the reaction $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$ is

(A) – 0.62 V   (B) – 0.92 V   (C) + 0.31 V   (D) + 0.85 V

40. An acidic solution of copper (II) sulphate containing some contaminations of zinc and iron (II) ions was electrolysed till all the copper is deposited. If electrolysis is further continued for sometime, the product liberated at cathode would be :

(A) Fe   (B) Zn   (C) H_2 (D) Alloy of Zn and Fe.

41. Consider the following Galvanic cell as shown in figure.
By what value the cell voltage change when concentration of ions in anode and cathodic compartments both increased by factor of 10 at 298 K

(A) + 0.591   (B) – 0.0591

(C) – 0.1182   (D) 0
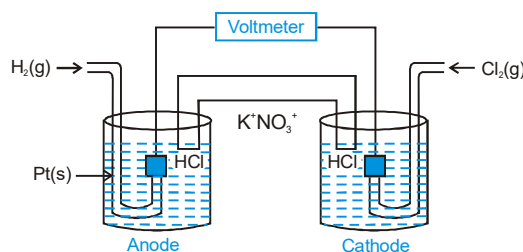
42. $Pt \mid Cl_2 (P_1 \text{ atm}) \mid HCl (0.1 \text{ M}) \mid Cl_2 (P_2 \text{ atm}) \mid Pt$, cell reaction will be spontaneous if
    (A) $P_1 = P_2$ (B) $P_1 > P_2$ (C) $P_2 > P_1$ (D) $P_1 = P_2 = 1$ atm

43. $Pt (H_2) \mid pH = 2 \mid pH = 3 \mid Pt (H_2)$
      1 atm   1 atm
    The cell reaction for the given cell is

    (A) spontaneous   (B) non-spontaneous   (C) equilibrium   (D) None of these

44. Equivalent conductance of 1M CH_3COOH is 10 ohm^{-1} cm^2 equiv^{-1} and that at infinite dilution is 200 ohm^{-1} cm^2, equiv^{-1}. Hence % ionisation of CH_3COOH is :
    (A) 5%   (B) 2%   (C) 4%   (D) 1%

45. Adding powdered Pb and Fe to a solution containing 1.0 M is each of Pb^{2+} and Fe^{2+} ions would result into the formation of
    (A) More of Pb and Fe^{2+} ions   (B) More of Fe and Pb^{2+} ions
    (C) More of Fe and Pb   (D) More of Fe^{2+} and Pb^{2+} ions

46. Cost of electricity for the production of 'X' litre H_2 at NTP at cathode is Rs. X, then cost of electricity for the production 'X' litre O_2 gas at NTP at anode will (assume 1 mole of electrons as one unit of electricity)
    (A) 2X   (B) 4X   (C) 16X   (D) 32X

47. In the given figure the electrolytic cell contains 1 L of an aqueous 1 M Copper (II) sulphate solution. If 0.4 mole of electrons passed through of cell, the concentration of copper ion after passage of the charge will be

    (A) 0.4 M   (B) 0.8 M

    (C) 1.0 M   (D) 1.2 M

48. By how much will the potential of half cell Cu^{2+} / Cu change if the solution is diluted to 100 times at 298 K
    (A) Increases by 59 mV   (B) Decreases by 59 mV
    (C) Increases by 29.5 mV   (D) Decreases by 29.5 mV

49. Which of the following facts is not true ?
    (A) If $E^o (M^{n+} / M)$ is negative, H^+ will be reduced to H_2 by the metal M
    (B) If $E^o (M^{n+} / M)$ is positive, M^{n+} will be reduced to M by H_2
    (C) In a cell M^{n+} / M electrode is attached to hydrogen-half cell. To produce spontaneous cell reaction, metal M will act as negative electrode.
    (D) Compounds of active metals (Zn, Na, Mg) are reducible by H_2 whereas those of noble metals (Cu, Ag, Au) are not reducible.

50. The reaction $Zn(s) + 2AgCl(g) \longrightarrow ZnCl_2(aq) + 2Ag(s)$ occurs in the cell $Zn \mid ZnCl_2$ (1M solution), $AgCl(s) \mid Ag$. The number of Faradays required from the external source for this reaction to occur in the cell is
    (A) 2   (B) 3   (C) 1   (D) zero

51. If the pressure of hydrogen gas is increased from 1 atm. to 100 atm, keeping the hydrogen ion concentration constant at 1M, the reduction potential of the hydrogen half cell is at 25°C will be
    (A) 0.059 V   (B) -0.059 V   (C) 0.295 V   (D) 0.118 V

52. The equilibrium $Cu^{++} (aq) + Cu(s) \rightleftharpoons 2Cu^+$ established at 20°C corresponds to $\dfrac{[Cu^{++}]}{[Cu^+]^2} = 2.02 \times 10^{4+}$. The standard potential, $E^0_{Cu^{++},Cu} = 0.33$ volt at this temperature. What is the standard potential, E^0_{Cu/Cu^+} ?
    (A) -0.457 V   (B) -0.125 V   (C) -0.66 V   (D) -0.250 V
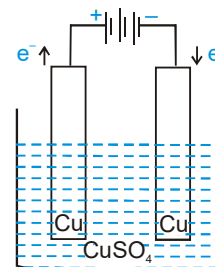
53. Zn Amalgam is prepared by electrolysis of aqueous $ZnCl_2$ using Hg cathode (9gm). How much current is to be passed through $ZnCl_2$ solution for 1000 seconds to prepare a Zn Amalgam with 25% Zn by wt. (Zn = 65.4)

(A) 5.6 amp   (B) 7.2 amp   (C) 8.85 amp   (D) 11.2 amp

54. A solution containing one mol per litre each of $Cu(NO_3)_2$, $AgNO_3$, $Hg(NO_3)_2$ and $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The values of the standard oxidation potentials in volts are $Ag/Ag^+ = -0.8$ V ; $Hg/Hg^{2+} = -0.79$ V; $Cu/Cu^{2+} = -0.34$ V ; $Mg/Mg^{2+} = 2.37$ V. The order in which metals will be formed at cathode will be -

(A) Ag, Cu, Hg, Mg   (B) Ag, Hg, Cu, Mg   (C) Ag, Hg, Cu   (D) Cu, Hg, Ag

55. At 298K the standard free energy of formation of $H_2O(\bullet)$ is –237.20 kJ/mole while $\Delta G°$ of its ionisation into H^+ ion and hydroxyl ions is 80 kJ/mole, then the emf of the following cell at 298 K will be

$$H_2(g, 1 \text{ bar}) \,|\, H^+ (1M) \,\|\, OH^- (1M) \,|\, O_2 (g, 1 bar)$$

(A) 0.40 V   (B) 0.81 V   (C) 1.23 V   (D) –0.40 V

56.

The E° in the given figure is, $E°$

(A) 0.5   (B) 0.6   (C) 0.7   (D) 0.8

57. What is cell entropy change of the following cell ?

$$Pt(s) \,|\, H_2(g) \,|\, CH_3COOH, HCl \,\|\, KCl (aq) \,|\, Hg_2Cl_2 (s) \,|\, Hg$$
$$P = 1 \text{ atm} \qquad 0.1M \qquad 0.1M$$

Emf of the cell is found to be 0.045 V at 298 K and temperature coefficient is 3.4×10^{-4} V K^{-1}

Given $K_{a\,(CH_3COOH)} = 10^{-5}$ M

(A) 60   (B) 65.2   (C) 69.2   (D) 63.5

58. Na-amalgam is prepared by electrolysis of NaCl solution using liquid Hg as cathode. How long should the current of 10 amp. is passed to produce 10% Na – Hg on a cathode of 10 gm Hg. (atomic mass of Na = 23).

(A) 7.77 min   (B) 9.44 min.   (C) 5.24 min.   (D) 11.39 min.

59. Which of following cell can produce more electrical work.

(A) Pt, H_2 |0.1M NH_4Cl || 0.1 M CH_3COOH | H_2, Pt
(B) Pt, H_2 | 0.1 M HCl || 0.1 M NaOH | H_2, Pt
(C) Pt, H_2 | 0.1 M HCl || 0.1 M CH_3COOK | H_2, Pt
(D) Pt, H_2 | 0.1 M CH_3COOK || 0.1 M HCl | H_2, Pt

60. A hydrogen electrode is immersed in a solution with pH = 0 (HCl). By how much will the potential (reduction) change if an equivalent amount of NaOH is added to the solution. (Take $P_{H_2} = 1$ atm) T = 298 K.

(A) increase by 0.41V   (B) increase by 59 mV   (C) decrease by 0.41V   (D) decrease by 59 mV

61. A current of 0.1A was passed for 2hr through a solution of cuprocyanide and 0.3745 g of copper was deposited on the cathode. Calculate the current efficiency for the copper deposition. (Cu – 63.5)

(A) 79%   B) 39.5 %   (C) 63.25%   (D) 63.5%

62. A current is passed through 2 voltameters connected in series. The first voltameter contains XSO_4 (aq.) and second has Y_2SO_4 (aq.). The relative atomic masses of X and Y are in the ratio of 2 : 1. The ratio of the mass of X liberated to the mass of Y liberated is

(A) 1 : 1   (B) 1 : 2   (C) 2 : 1   (D) None of the above

63. Which of the following is not true about e.m.f. of a cell ?

(A) work calculated from it is not the maximum work obtainable from the cell
(B) it is maximum voltage obtainable from the cell
(C) it is the potential difference between two electrodes when no current is flowing in circuit
(D) it is responsible for the flow of steady current in the cell.

64. How many electrons are delivered at the cathode during electrolysis by a current of 1amp in 60 seconds?
(A) 3.74×10^{20} (B) 6.0×10^{23} (C) 7.48×10^{21} (D) 6.0×10^{20}

65. A resistance of 50Ω is registered when two electrodes are suspended into a beaker containing a dilute solution of a strong electrolyte such that exactly half of the them are submerged into solution as shown in figure. If the solution is diluted by adding pure water (negligible conductivity) so as to just completely submerge the electrodes, the new resistance offered by the solution would be

(A) $50\,\Omega$ (B) $100\,\Omega$ (C) $25\,\Omega$ (D) $200\,\Omega$

66. Calculate the cell EMF in mV for
$$Pt \mid H_2(1atm) \mid HCl\,(0.01\,M) \mid AgCl(s) \mid Ag(s) \qquad at\ 298\ K$$
if ΔG_f° values are at 25°C $-109.56\ kJ/mol$ for AgCl(s) and $-130.79\ kJ/mol$ for $(H^+ + Cl^-)\,(aq)$
(A) 456 mV   (B) 654 mV   (C) 546 mV   (D) None of these

67. Calculate the value of Λ_m^{∞} for $SrCl_2$ in water at 25ºC from the following data :

Conc. (mol/lt)	0.25	1
$\Lambda_m\ (\Omega^{-1}\,cm^2\,mol^{-1})$	260	250

(A) 270   (B) 260   (C) 250   (D) 255

68. BY the electrolysis of aqueous solution of $CuSO_4$, the products obtained at both the electrodes are
(A) O_2 at anode and H_2 at cathode
(B) H_2 at anode and Cu at cathode
(C) O_2 at anode and Cu at cathode
(D) $H_2S_2O_8$ at anode and O_2 at cathode

69. How many gm of silver will be displaced from a solution of $AgNO_3$ by 4 gm of magnesium?
(A) 18 gm   (B) 4 gm   (C) 36 gm   (D) 16 gm

70. The moles of electrons required to deposit 1 gm equivalent aluminium (at. wt. = 27) from a solution of aluminium chloride will be :
(A) 3   (B) 1   (C) 4   (D) 2

71. A certain current liberated 0.504 g of hydrogen in 2 hours. How many grams of copper can be liberated by the same current flowing for the same time in copper sulphate solution
(A) 31.8 g   (B) 16.0 g   (C) 12.7 g   (D) 63.5 g

72. The specific conductance of a N/10 KCl at 25°C is $0.0112\ ohm^{-1}\ cm^{-1}$. The resistance of cell containing solution at the same temperature was found to be 55 ohms. The cell constant will be
(A) $6.16\ cm^{-1}$ (B) $0.616\ cm^{-1}$ (C) $0.0616\ cm^{-1}$ (D) $616\ cm^{-1}$

73. Which of the following statements is true for an electrochemical cell of $Cu-H_2$.
(A) H_2 is anode and Cu is cathode   (B) H_2 is cathode and Cu is anode
(C) reduction occurs at H_2 electrode   (D) oxidation occurs Cu electrode

74. How many electrons flow when a current of 5 amperes is passed through a conductor for 200 seconds?
(A) 6.214×10^{21} (B) 6.0241×10^{21} (C) 6.241×10^{22} (D) 6.0241×10^{22}

75. A current of 9.95 amp following for 10 minutes, deposits 3 gm of a metal. Equivalent weight of the metal is
(A) 12.5   (B) 18.5   (C) 21.5   (D) 48.5

76. Which of the following has been universally accepted as a reference electrode at all temperatures and has been assigned a value of zero volt?
(A) platinum electrode   (B) copper electrode   (C) graphite electrode   (D) standard hydrogen electrode

77. What is the amount of chlorine evolved, when 2 amp of current is passed for 30 minutes in an aqueous solution of NaCl?

    (A) 9.81 g   (B) 1.32 g   (C) 4.56 g   (D) 12.6 g

78. A spoon to be electroplated with gold it should be :

    (A) cathode   (B) anode   (C) electrolyte   (D) none of these

79. Time required to deposit one millimole of aluminium metal by the passage of 9.65 amperes through aqueous solution of aluminium ion is :

    (A) 30 s   (B) 10 s   (C) 30,000 s   (D) 10,000 s

80. During an electrolysis of conc. H_2SO_4, perdisulphuric acid $(H_2S_2O_8)$ and O_2 form in equimolar amount. The amount of H_2 that will form simultaneously at other electrode will be $(2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-)$

    (A) thrice that of O_2 in moles   (B) twice that of O_2 in moles

    (C) equal to that of O_2 in moles   (D) half of that of O_2 in moles

81. The electric charge for electrode deposition of one gram equivalent of a substance is :

    (A) one amp /sec   (B) 96,500 C / sec   (C) one amp / hour   (D) 96,500 C

82. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively.

    (A) H_2, O_2 (B) O_2, H_2 (C) O_2, Na (D) O_2, SO_2

83. Which of the following statements is true for the electrochemical, Daniel cell ?

    (A) Electrons flows from copper electrode to zinc electrode.

    (B) Current flows from zinc electrode to copper electrode.

    (C) Cations moves toward copper electrode.

    (D) Cations moves toward zinc electrode

84. The chemical reaction
    $$2AgCl(s) + H_2(g) \longrightarrow 2HCl(aq) + 2Ag(s)$$
    taking place in a galvanic cell is represented by the notation.
    (A) $Pt(s) | H_2(g), 1 \text{ bar} | 1 \text{ M KCl (aq)} | AgCl(s) | Ag(s)$
    (B) $Pt(s) | H_2(g), 1 \text{ bar} | 1 \text{ M HCl (aq)} | 1 \text{ M Ag}^+(aq) | Ag(s)$
    (C) $Pt(s) | H_2(g), 1 \text{ bar} | 1 \text{ M HCl (aq)} | AgCl(s) | Ag(s)$
    (D) $Pt(s) | H_2(g), 1 \text{ bar} | 1 \text{ M HCl (aq)} | Ag(s) | AgCl(s)$

85. For the cell (at 298 K) $Ag(s) | AgCl(s) | Cl^-(aq) || AgNO_3(aq) | Ag(s)$
    Which of following is correct -
    (A) The cell emf will be zero when $[Ag^+]_a = [Ag^+]_c$ ($[Ag^+]$ in anodic compartment $= [Ag^+]$ in cathodic compartment)
    (B) The amount of AgCl(s) precipitate in anodic compartment will decrease with the working of the cell.
    (C) The concentration of $[Ag^+]$ = constant, in anodic compartment during working of cell.

    (D) $E_{cell} = E^0_{Ag^+|Ag} - E^0_{Cl^- | AgCl | Ag} - \dfrac{0.059}{1} \log \dfrac{1}{[Cl^-]_a}$

86. The standard oxidation potentials, E°, for the half reactions are as
    $$Zn \longrightarrow Zn^{2+} + 2e^-; E^0 = +0.76 \text{ V} \quad Fe \longrightarrow Fe^{2+} + 2e^-; E^0 = +0.41 \text{ V}$$
    The EMF for the cell :
    (A) –0.35 V   (B) +0.35 V   (C) +1.17 V   (D) –1.17 V

Exercise # 2 **Part # I** [Multiple Correct Choice Type Questions]

1. Mark out the correct statement(s)

   (A) Copper metal cannot reduce iron (II) ions in acidic solutions.

   (B) Sodium can be obtained by the electrolysis of aqueous solution of NaCl using Pt electrodes.

   (C) The current carrying ions in an electrolytic cell are not necessarily discharged at the electrodes.

   (D) Cations having more negative oxidation potential than -0.828 V are reduced in preference to water.

2. Mark out the correct statement(s) regarding electrolytic molar conductivity.

   (A) It increase as temperature increases.

   (B) It experiences resistance due to vibration of ion at the mean position.

   (C) Increase in concentration decreases the electrolytic molar conductivity of both the strong as well as the weak electrolyte.

   (D) Greater the polarity of solvent, greater is the electrolytic molar conduction.

3. If same quantity of electricity is passed through three electrolytic cells containing $FeSO_4$, $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$, then

   (A) the amount of iron deposited in $FeSO_4$ and $Fe_2(SO_4)_3$ are equal

   (B) the amount of iron deposited in $FeSO_4$ is 1.5 times of the amount of iron deposited in $Fe(NO_3)_3$.

   (C) the amount of iron deposited in $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$ are equal

   (D) the same amount of gas is evolved in all three cases at the anode.

4. When a cleaned strip of zinc metal is placed in a solution of $CuSO_4$, a spontaneous reaction occurs . Which of the following observation(s) is/are made ?

   (A) the mass of zinc metal decreases gradually

   (B) the copper metal starts depositing on either zinc plate or settles down to the vessel

   (C) the solution remains electrically neutral

   (D) the temperature of the solution decreases as it is an endothermic reaction.

5. In the electrolysis of aqueous $CuBr_2$ using Pt electrodes :

   (A) Br_2 gas is evolved at the anode

   (B) $Cu(s)$ is deposited at the cathode

   (C) Br_2 gas is evolved at anode and H_2 gas at cathode

   (D) H_2 gas is evolved at anode.

6. A current of 2.68 A is passed for one hour through an aqueous solution of $CuSO_4$ using copper electrodes . Select the correct statement(s) from the following :

   (A) increase in mass of cathode = 3.174 g

   (B) decrease in mass of anode = 3.174 g

   (C) no change in masses of electrodes

   (D) the ratio between the change of masses of cathode and anode is 1 : 2 .

7. Which of the following statements is / are correct ?

   (A) The conductance of one cm^3 (or 1 $unit^3$) of a solution is called conductivity.

   (B) Specific conductance increases while molar conductivity decreases on progressive dilution.

   (C) The limiting equivalent conductivity of weak electrolyte cannot be determine exactly by extrapolation of the plot of Λ_{eq} against $\sqrt{c}$.

   (D) The conductance of metals is due to the movement of free electrons.

8. When galvanic cell started, with passage of time
    (A) spontaneity of the cell reaction decreases; E_{cell} decreases
    (B) reaction quotient Q decreases; E_{cell} increases
    (C) reaction quotient Q increases; E_{cell} decreases
    (D) at equilibrium $Q = K_c$; $E_{cell} = 0$.

9. Standard electrode potential are $E^o_{Fe^{2+}\,|\,Fe} = -0.44$ V, $E^o_{Fe^{3+}\,|\,Fe^{2+}} = 0.77$ V. If Fe, Fe^{2+} and Fe^{3+} are kept together, then
    (A) Fe^{3+} increases   **(B)** Fe^{3+} decreases   **(C)** Fe^{2+} increases   **(D)** Fe^{2+} decreases

10. In which of the following cell (s) : $E_{cell} = E_{cell}^0$?

    (A) $Cu(s)\big|Cu^{2+}(0.01M)\big\|Ag^+(0.1M)\big|Ag(s)$ **(B)** $Pt(H_2)\big|pH=1\big\|Zn^{2+}(0.01\,M)\big|Zn(s)$

    (C) $Pt(H_2)\big|pH=1\big\|Zn^{2+}(1M)\big|Zn(s)$ **(D)** $Pt(H_2)\big|H^+=0.1M\big\|Zn^{2+}(0.01M)\big|Zn(s)$

11. The reaction : $1/2H_2(g)+AgCl(s)\longrightarrow H^+(aq)+Cl^-(aq)+Ag(s)$

    occurs in the galvanic cell –
    (A) $Ag\,|\,AgCl(s)\,|\,KCl\,(soln)\,|\,AgNO_3\,(soln)\,|\,Ag$ **(B)** $Pt\,|\,H_2(g)\,|\,HCl\,(soln)\,|\,AgNO_3\,(soln)\,|\,Ag$
    (C) $Pt\,|\,H_2(g)\,|\,HCl\,(soln)\,|\,AgCl(s)\,|\,Ag$ **(D)** $Pt\,|\,H_2(g)\,|\,KCl\,(soln)\,|\,AgCl(s)\,|\,Ag$

12. Choose the correct statement(s).
    (A) At the anode, the species having minimum reduction potential is formed from the oxidation of corresponding oxidizable species.
    (B) In highly alkaline medium, the anodic process during the electrolytic process is

        $4OH^-\longrightarrow O_2+2H_2O+4e^-$.

    (C) The standard potential of $Cl^-\,|AgCl|\,Ag$ half-cell is related to that of $Ag^+\,|\,Ag$ through the expression

        $E^o_{Ag^+|Ag} = E^o_{Cl^-|AgCl|Ag} + \dfrac{RT}{F}\ln K_{sp}(AgCl)$

    (D) Compounds of active metals (Zn, Na, Mg) are reducible by H_2 whereas those of noble metals (Cu, Ag, Au) are not reducible.

13. $M(s)\longrightarrow M^{n+}(aq)+ne^-$
    Choose the correct statement(s).
    (A) $E_{M\,|\,M^{n+}}$ decreases with increase in $[M^{n+}]$ **(B)** $E_{M^{n+}\,|\,M}$ increases on increasing temperature.

    (C) $E_{M^{n+}\,|\,M}$ increases on increasing $[M^{n+}]$ **(D)** $E_{M\,|\,M^{n+}}$ increases on increasing temperature.

14. Which is/are correct among the following ?
    Given, the half cell emf's $E^0_{Cu^{+2}|Cu}=0.337$, $E^0_{Cu^{+1}|Cu}=0.521$
    (A) Cu^{+1} disproportionates   **(B)** Cu and Cu^{2+} comproportionates.

    (C) $E^0_{Cu\,|\,Cu^{+2}}+E^0_{Cu^{+1}\,|\,Cu}$ is positive   **(D)** All of these

Part # II ▸▸ **[Assertion & Reason Type Questions]**

Each question has 5 choices (A), (B), (C), (D) and (E) out of which only one is correct.
(A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1
(B) Statement-1 is true, Statement-2 is true and Statement-2 is not correct explanation for Statement-1
(C) Statement-1 is true, Statement-2 is false
(D) Statement-1 is false, Statement-2 is true
(E) Both Statements are false

1. **Statement-1 :** If $\left(\dfrac{dE_{cell}}{dT}\right)_p > 0$ for a cell reaction then ΔS is positive.

    Statement-2 : $\Delta S = nFT\left(\dfrac{dE}{dT}\right)_p$.

2. **Statement-1 :** If an aqueous solution of NaCl is electrolysed, the product obtained at the cathode is H_2 gas and not Na.

    Statement-2 : Gases are liberated faster than the metals during the electrolysis of an electrolyte.

3. **Statement-1 :** When 2 faraday of electricity is passed through 0.1 M H_2SO_4 (aq), 11.2 litre O_2 evolved at STP.

    Statement-2 : Molecular weight of oxygen is 32.

4. **Statement-1 :** The electrode potential of SHE is zero only at 25° C and not on other temperature.

    Statement-2 : SHE is a standard reference electrodes.

5. **Statement-1 :** Absolute value of E^0_{red} of an electrode cannot be determined.

    Statement-2 : Neither oxidation nor reduction can take place alone.

6. **Statement-1 :** $E^o_{cell} = 0$ for a chloride ion concentration cell.

    Statement-2 : For this concentration cell where $E_{cell} = \dfrac{RT}{nF} \ln \dfrac{[Cl^-]_{LHS}}{[Cl^-]_{RHS}}$

7. **Statement-1 :** Molar conductivity increases with decreases in concentration for weak electrolytes.

    Statement-2 : No. of ions per unit volume decreased due to dilution.

8. **Statement-1 :** Conductivity always decreases with the decreased in concentration both the weak and strong electrolytes.

    Statement-2 : No. of ions per unit volume linearly decreases in both electrolytes.

9. **Statement-1 :** Gold chloride ($AuCl_3$) solution cannot be stored in a vessel made of copper, iron, nickel chromium, zinc or tin.

    Statement-2 : Gold is very precious metal.

10. **Statement-1 :** Copper is dissolved at anode and deposited at cathode when Cu electrodes are used and electrolyte is 1 M $CuSO_4$ (aq) solution.

    Statement-2 : SOP of Cu is less than SOP of water and SRP of Cu is greater than SRP of water.

11. **Statement-1 :** Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.

    Statement-2 : Kohlrausch law help to find the molar conductivity of a weak electrolyte at infinite dilution.

Exercise # 3 ▷ Part # I ▷ [Matrix Match Type Questions]

1. Match Matrix ($E^0_{Ag^+/Ag} = 0.8$, $K_{SP}(AgCl) = 10^{-10}$).

Column – I

(A) $Pt \,|\, H_2 \,(0.1 \text{ bar}) \,|\, H^+ \,(0.1 \text{ M}) \,||\, H^+ \,(1 \text{ M}) \,|\, H_2 \,(0.01 \text{ bar}) \,|\, Pt$

(B) $Ag \,|\, AgCl \,(KCl, 0.1M) \,||\, Ag^+ \,(0.01M) \,|\, Ag$

(C) $Cu \,|\, Cu^{2+} \,(0.1 \text{ M}) \,||\, Cu^{2+} \,(0.01 \text{ M}) \,|\, Cu$

(D) $Pt \,|\, Cl_2 \,(1bar) \,|\, HCl \,(0.1 \text{ M}) \,||\, NaCl \,(0.1M) \,|\, Cl_2 \,|\, Pt \,(1 \text{ bar})$

Column – II

(p) Concentration cell

(q) $E_{cell} > 0$

(r) $E^o_{cell} = 0$ but cell is working.

(s) non working condition

2. Match the column

Column I

(A) $Zn \,/\, Zn^{+2} \,||\, Mg^{2+} \,/\, Mg$
$\quad c_1 \qquad c_2 \quad (c_1 = c_2)$

(B) $Zn \,/\, Zn^{+2} \,||\, Ag^+ \,/\, Ag$
$\quad$ at. equilibrium

(C) $Ag \,/\, Ag^+ \,||\, Ag^+ \,/\, Ag$
$\quad c_1 \qquad c_2 \quad (c_1 = c_2)$

(D) $Fe \,/\, Fe^{+2} \,||\, Ag \,/\, Ag^+$
$\quad c_1 \qquad c_2 \quad (c_1 = c_2)$

Column II

(p) $E_{cell} = 0$

(q) $E^0_{cell} = 0$

(r) $E^0_{cell} = +ve$

(s) $E^0_{cell} = -ve$

3. **Column-I** and **Column-II** contains four entries each. Entries of **Column-I** are to be matched with some entries of **Column-II**. One or more than one entries of **Column-I** may have the matching with the same entries of **Column-II**.

Column-I

(A) Very dilute solution of HCl

(B) Very dilute solution of NaCl

(C) Concentrate solution of NaCl

(D) Fairly concentrate solution of $AgNO_3$

Column-II

(p) O_2 evolved at anode

(q) H_2 evolved at cathode

(r) Cl_2 evolved at anode

(s) Ag deposition at cathode

4. **Column-I**

(A) Cathode

(B) 1 Coulomb

(C) Dry cell

(D) Lead strong cell

(E) $Zn|Zn^{2+}(0.01M)|Zn^{2+}(0.1M)|Zn$

Column-II

(p) Primary cell

(q) Secondary cell

(r) 6.24×10^{18} electrons

(s) Concentration cell

(t) Positive terminal of electrochemical cell

5. **Column-I**

(A) Cell constant

(B) Anode

(C) Conductance

(D) Electrochemical equivalent

(E) E^0_{cell}

Column-II

(p) $E^0_{cathode} + E^0_{anode}$

(q) $\bullet/A$

(r) Mass of product deposited by 1 coulomb of electricity.

(s) $(Resistance)^{-1}$

(t) Involve oxidation

6.

Column-I	Column-II
(A) Conductance	**(p)** Cm^{-1}
(B) Specific conductance	**(q)** $Ohm^{-1} cm^2 mol^{-1}$
(C) Cell constant	**(r)** Ohm^{-1}
(D) Equivalent conductance	**(s)** $Ohm^{-1} cm^{-1}$
(E) Molar conductance	**(t)** $Ohm^{-1} cm^2 equivalent^{-1}$

7.

Column-I	Column-II
(A) Electrolytic cell	**(p)** $-\Delta G°$
(B) nFE^0_{Cell}	**(q)** Concentration cell
(C) $E_{cell} = \dfrac{0.059}{n} \log \dfrac{C_{cathode}}{C_{anode}}$	**(r)** 96500 Coulombs
(D) Diffusion of ions	**(s)** Device converting electrical energy into chemical energy
(E) 1 Faraday	**(t)** Salt bridge

Part # II **[Comprehension Type Questions]**

Comprehension # 1

1 L, 2 M ZnSO₄   1 L, 0.2 M CuSO₄
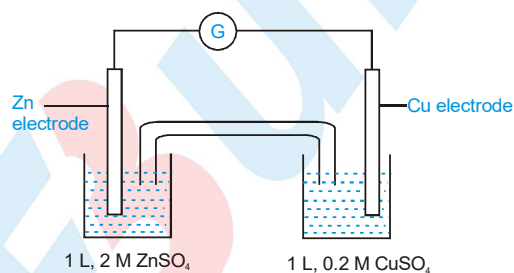
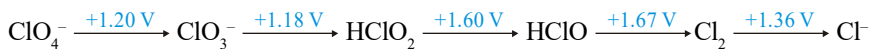Given $E°_{Zn^{+2}|Zn} = -0.76\, V$ $K_f [Cu(NH_3)_4]^{+2} = 4 \times 10^{11}$

$E°_{Cu^{+2}|Cu} = 0.34\, V$

Answer the following.

1. The emf of cell at 200 k is [Given : $\dfrac{2.303 \times R}{F} = 2 \times 10^{-4}$ and assume that E^0 values are independent on temperature.]

(A) 1.7 V (B) 1.08 V (C) 1.09 V (D) 1.10 V

2. When 1 mole NH_3 added to cathode compartment than emf of cell is (at 298K)

(A) 0.81 V (B) 1.91 V (C) 1.1 V (D) 0.72 V

3. At what conc of Cu^{+2} emf of the cell will be zero (at 298K) and conc. of Zn^{+2} is remain same

(A) 1.19×10^{-37} (B) 1.19×10^{-20} (C) 3.78×10^{-4} (D) 0.0068

Comprehension # 2

If an element can exist in several oxidation states, it is convenient to display the reduction potentials corresponding to the various half reactions in diagrammatic form, known as Latimer diagram. The Latimer diagram for chlorine in acid solution is

$$ClO_4^- \xrightarrow{+1.20 \text{ V}} ClO_3^- \xrightarrow{+1.18 \text{ V}} HClO_2 \xrightarrow{+1.60 \text{ V}} HClO \xrightarrow{+1.67 \text{ V}} Cl_2 \xrightarrow{+1.36 \text{ V}} Cl^-$$

in basic solution.

$$ClO_4^- \xrightarrow{0.37 \text{ V}} ClO_3^- \xrightarrow{0.30 \text{ V}} ClO_2^- \xrightarrow{0.68 \text{V}} ClO^- \xrightarrow{0.42 \text{V}} Cl_2 \xrightarrow{1.36 \text{V}} Cl^-$$
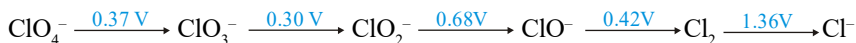
The standard potentials for two nonadjacent species can also be calculated by using the concept that $\Delta G°$ as an additive property but potential is not an additive property and $\Delta G° = - nFx^0$. If a given oxidation state is a stronger oxidising agent than in the next higher oxidation state, disproportionation can occur. The reverse of disproportionation is called comproportionation. The relative stabilities of the oxidation state can also be understood by drawing a graph of $\Delta G°/F$ against oxidation state, known as Frost diagram, choosing the stability of zero oxidation state arbitrarily as zero. The most stable oxidation state of a species lies lowest in the diagram. Disproportionation is spontaneous if the species lies above a straight line joining its two product species.

1. Which of the following couple have same value of potential at pH = 0 and pH = 14?

   (A) $\dfrac{ClO_4^-}{ClO_3^-}$ (B) $\dfrac{ClO_2^-}{Cl_2}$ (C) $\dfrac{ClO^-}{Cl_2}$ (D) $\dfrac{Cl_2}{Cl^-}$

2. What is the potential of couple $\dfrac{ClO^-}{Cl^-}$ at pH = 14 ?

   (A) 1.78 V   (B) – 0.94 V   (C) 0.89 V   (D) – 0.89 V

3. Which of the following statement is correct ?
   (A) Cl_2 undergoes disproportionation into Cl^- and ClO^- both at pH = 0 and pH = 14.
   (B) Cl_2 undergoes disproportionation into Cl^- and ClO^- at pH = 14 but not at pH = 0.
   (C) Cl_2 undergoes disproportionation into Cl^- and ClO^- at pH = 0 but not at pH = 14.
   (D) None of these

4. For a hypothetical element, the Frost diagram is shown in figure?
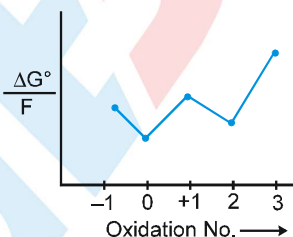
   Which of the following oxidation state is least stable?
   (A) – 1   (B) 0   (C) +2   (D) +3

5. Which of the following statement is correct ?
   (A) A^{+1} undergoes disproportionation into A and A^{2+}.
   (B) A^{2+} undergoes disproportionation in A and A^{3+}.
   (C) A undergoes comproportionation in A^{+1} and A^{-1}.
   (D) All of the above.

Comprehension # 3

Strong Acid Versus Strong Base

The principle of conductometric titrations is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that the conductivity of the solution varies during the course of the titration. Take, for example, the titration between a strong acid, say HCl, and a strong base, say NaOH. Before NaOH is added, the conductance of HCl solution has a high value due to the presence of highly mobile hydrogen ions. As NaOH is added, H^+ ions are replaced by relatively slower moving Na^+ ions. Consequently, the conductance of the solution decreases and this continues right upto the equivalence point where the solution contains only NaCl. Beyond the equivalence point, if more of NaOH is added, then the solution contains an excess of the fast moving OH^- ions with the result that its conductance is increased and it continues to increase as more and more of NaOH is added.

If we plot the conductance value versus the amount of NaOH added, we get a curve of the type shown in **Fig**.

The descending portion AB represents the conductances before

the equivalence point (solution contains a mixture of acid HCl and the salt NaCl) and the ascending portion CD represents the conductances after the equivalence point (solution contains the salt NaCl and the excess of NaOH). The point E which represents the minium conductance is due to the solution containing only NaCl with no free acid or alkali and thus represents the equivalence point. This point can, however, be obtained by the extrapolation of the lines AB and DC, and therefore, one is not very particular in locating this point experimentally as it is in the case of ordinary acid-base titrations involving the acid-base indicators.
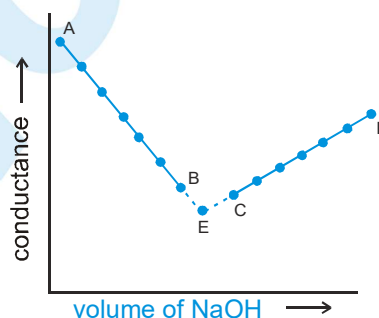
Weak Acid versus Strong Base

Let us take the specific example of acetic acid being titrated against NaOH. Before the addition of alkali, the solution shows poor conductance due to feeble ionization of acetic acid. Initially the addition of alkali cause not only the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to the common ion Ac^- and thus the conductance of the solution decreases in the beginning. But very soon the conductance starts increasing as addition of NaOH neutralizes the undissociated HAc to Na^+Ac^- thus causing the replacement of non-conducting HAc with strong-conducting electrolyte $Na^+ Ac^-$. The increase in conductance continues right up to the equivalence point. Beyond this point conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions. The graph near the equivalence point is curved due to the hydrolysis of the salt NaAc. The actual equivalence point can, as usual, be obtained by the extrapolation method.

In all these graphs it has been assumed that the volume change due addition of solution from burette is negligible, hence volume change of the solution in beaker the conductance of which is measured is almost constant throughout the measurement.
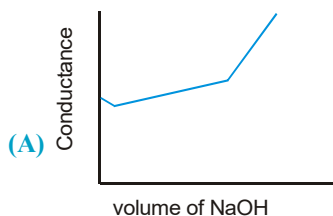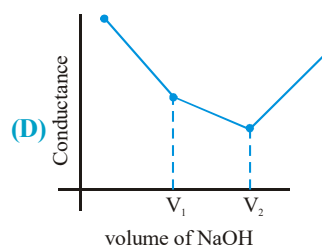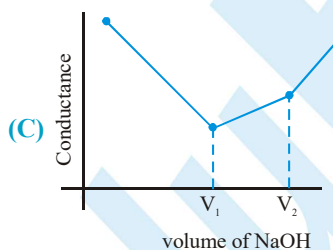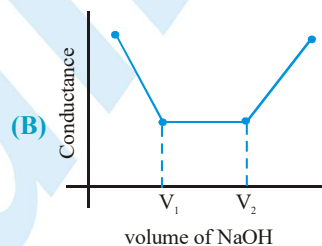
1. The nature of curve obtained for the titration **between weak acid versus strong base as described in the above passage will be :**

(A)

(B)

(C)

(D)
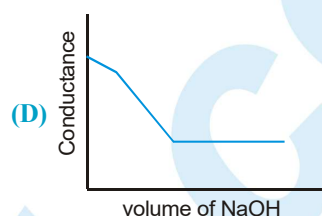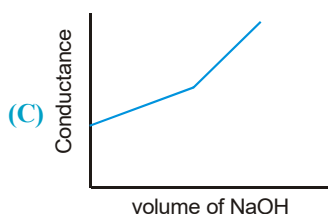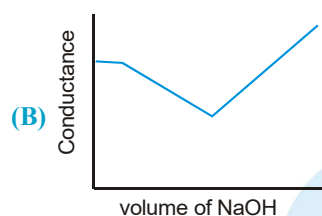
2. The most appropriate titration curve obtained when a mixture of a strong acid (say HCl) and a weak acid (say CH_3COOH) is titrated with a strong base(say NaOH) will be

(A)

(B)

(C)

(D)
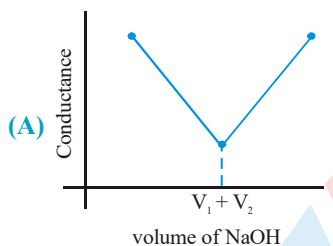
3. If a 100 mL solution of 0.1M HBr is titrated using a very concentrated solution of NaOH, then the conductivity (specific conductance) of this solution at the equivalence point will be (assume volume change is negligible due to addition of NaOH). Report your answer after multiplying it with 10 in Sm^{-1}.

[Given $\lambda^{\circ}_{(Na^+)} = 8 \times 10^{-3}\ Sm^2\,mol^{-1}$, $\lambda^{\circ}_{(Br^-)} = 4 \times 10^{-3}\ S\,m^2\,mol^{-1}$]

(A) 6   (B) 12   (C) 15   (D) 24

Comprehension # 4

The molar conductance of NaCl varies with the concentration as shown in the following table .

and all values follows the equation

$$\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$$

Where λ_m^C = molar specific conductance

λ_m^∞ = molar specific conductance at infinite dilution

C = molar concentration

Molar Concentration of NaCl	Molar Conductance in ohm^{-1} cm^2 mole^{-1}
4×10^{-4}	107
9×10^{-4}	97
16×10^{-4}	87

When a certain conductivity cell (C) was filled with 25×10^{-4} (M) NaCl solution. The resistance of the cell was found to be 1000 ohm. At Infinite dilution, conductance of Cl$^-$ and SO$_4^{-2}$ are 80 ohm^{-1} cm^2 mole^{-1} and 160 ohm^{-1} cm^2 mole^{-1} respectively.

1. What is the molar conductance of NaCl at infinite dilution ?
(A) 147 ohm^{-1} cm^2 mole^{-1}
(B) 107 ohm^{-1} cm^{2}s mole^{-1}
(C) 127 ohm^{-1} cm^2 mole^{-1}
(D) 157 ohm^{-1} cm^2 mole^{-1}

2. What is the cell constant of the conductivity cell (C)
(A) 0.385 cm^{-1}
(B) 3.85 cm^{-1}
(C) 38.5 cm^{-1}
(D) 0.1925 cm^{-1}

3. If the cell (C) is filled with 5×10^{-3} (N) Na$_2$SO$_4$ the observed resistance was 400 ohm. What is the molar conductance of Na$_2$SO$_4$.
(A) 19.25 ohm^{-1} cm^2 mole^{-1}
(B) 96.25 ohm^{-1} cm^2 mole^{-1}
(C) 385 ohm^{-1} cm^2 mole^{-1}
(D) 192.5 ohm^{-1} cm^{2}s mole^{-1}

Comprehension # 5

Copper reduces NO$_3^-$ into NO and NO$_2$ depending upon conc. of HNO$_3$ in solution. Assuming [Cu^{2+}] = 0.1 M, and P$_{NO}$ = P$_{NO_2}$ = 10^{-3} atm and using given data answer the following questions :

$E^\circ_{Cu^{2+}/Cu}$ = +0.34 volt   ; $E^\circ_{NO_3^-/NO}$ = +0.96 volt

$E^\circ_{NO_3^-/NO_2}$ = +0.79 volt   ;   at 298 K $\dfrac{RT}{F}$ (2.303) = 0.06 volt

1. E$_{Cell}$ for reduction of NO$_3^-$ $\longrightarrow$ NO by Cu(s), when [HNO$_3$] = 1 M is [At T = 298]
(A) ~0.61
(B) ~0.71
(C) ~0.51
(D) ~0.81

2. At what HNO$_3$ concentration thermodynamic tendency for reduction of NO$_3^-$ into NO and NO$_2$ by copper is same?
(A) $10^{1.23}$ M
(B) $10^{0.56}$ M
(C) $10^{0.66}$ M
(D) $10^{0.12}$ M

Comprehension # 6

Accidentally chewing on a stray fragment of aluminium foil can causes a sharp tooth pain if the aluminium comes in contact with an amalgam filling. The filling, an alloy of silver, tin and mercury, acts as the cathode of a tiny galvanic cell, the aluminium behaves as the anode, and saliva serves as the electrolyte. When the aluminium and the filling come in contact, an electric current passage from the aluminium to the filling which is sensed by a nerve in the tooth. Aluminium is oxidized at the anode, and O_2 gas is reduced to water at the cathode.

$$E^{\circ}_{Al^{3+}/Al} = -1.66 \text{ V}, \ E^{\circ}_{O_2, H^+/H_2O} = 1.23 \text{ V}$$

1. Net reaction taking place when amalgam is in contact with aluminium foil :

   (A) $Al + O_2 + OH^- \rightarrow Al(OH^-) + H_2O$

   (B) $4Al + 3O_2 + 12H^+ \rightarrow 4Al^{3+} + 6H_2O$

   (C) $4Al + 3O_2 \rightarrow 4Al_2O_3$

   (D) $2H_2 + O_2 \rightarrow 2H_2O$
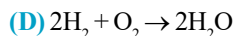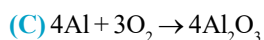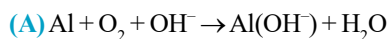
2. Standard E.M.F. experienced by the person with dental filling is :

   (A) $+2.89$ V   **(B)** -2.89 V   **(C)** -0.93 V   **(D)** $+0.43$ V

3. The standard reduction potential of the reaction,

   $$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^- \text{ at 298 K is :}$$
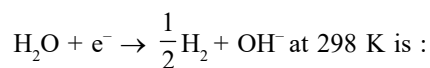
   (A) $E^{\circ} = \dfrac{RT}{2F} \ln K_w$ **(B)** $E^{\circ} = \dfrac{RT}{F} \ln \left[P_{H_2} \right]^{1/2} [OH^-]$

   (C) $E^{\circ} = \dfrac{RT}{F} \ln \dfrac{\left[P_{H_2} \right]^{1/2}}{[H^+]}$ **(D)** $E^{\circ} = \dfrac{RT}{F} \ln K_w$

Exercise # 4 — [Subjective Type Questions]

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

2. Consider the cell $Ag|AgBr(s)|Br^- \parallel Cl^-|AgCl(s)|Ag$ at 25°C. The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10}. For what ratio of the concentrations of Br^- & Cl^- ions would the e.m.f. of the cell be zero ?

3. Calculate the first dissociation constant of H_3PO_4 if the e.m.f. of the cell,

$Hg \,|\, Hg_2Cl_2(s) \,|\, KCl\,(salt)\,(conc. = 4N) \parallel H_3PO_4\,(0.1M),\, NaH_2PO_4\,(0.1M)\,|\,H_2\,(1\,atm)\,|\,Pt,\, -0.3665$ V. E_{red}° of SCE = 0.2412 V. ($10^{-2.12} = 131.82$)

4. From the standard potentials shown in the following figure, calculate the potentials E^o_1 and E^o_2.
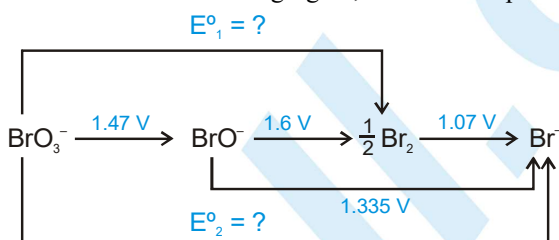
5. Consider the following redox reaction :

$$2IrCl_6^{3-} + 3HCOOH \longrightarrow 2Ir + 3CO_2 + 12Cl^- + 6H^+$$

Given : $CO_2 + 2H_3O^+ + 2e \longrightarrow HCOOH + 2H_2O \quad E^o = -0.20$ V

$IrCl_6^{3-} + 3e \longrightarrow Ir + 6Cl^- \qquad\qquad\qquad E^o = 0.77$ V

(a) Determine standard state emf of cell.
(b) Is this reaction thermodynamically spontaneous as written ? Briefly explain.

6. The overall formation constant for the reaction of 6 mole of CN^- with cobalt (II) is 1×10^{19}. The standard reduction potential for the reaction $[Co(CN)_6]^{3-} + e^- \longrightarrow Co(CN)_6^{4-}$ is -0.83V.

Calculate the formation constant of $[Co(CN)_6]^{3-}$. Given $Co^{3+} + e^- \longrightarrow Co^{2+}$; $E^\circ = 1.82$ V

7. Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained 0.1M MnO_4^- and 0.8M H^+ and which was treated with Fe^{2+} to reduce 90% of the MnO_4^- to Mn^{2+}.
$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + H_2O$, $E^o = 1.51$V

8. Calculate the emf of the cell in mV (atleast first two digits must match with correct answer)

$$Ag\,(s),\, AgIO_3\,(s)\,\left|\,Ag^+\,(xM),\, HIO_3\,(1M)\,\right|\,\left|\,Zn^{+2}\,(1M)\right|\,Zn(s)$$

If $K_{sp} = 3 \times 10^{-8}$ for $AgIO_3$ and $K_a = \dfrac{1}{6}$ for HIO_3 and E^0_{cell} for $2Ag + Zn^{+2} \longrightarrow 2Ag^+ + Zn$ is -1.56 V.

($\log 3 = 0.48$) (Take $\dfrac{RT}{F} = 0.059$) **(giving your answer in magnitude only)**

9. Calculate the voltage, E, of the cell at 25°C

$Mn(s) | Mn(OH)_2(s) | Mn^{2+} (x M), OH^- (1.00 \times 10^{-4} M) || Cu^{2+} (0.675M) | Cu(s)$

given that $K_{sp} = 1.9 \times 10^{-13}$ for $Mn(OH)_2$ (s) $E^o (Mn^{2+}/Mn) = -1.18$ V, $E^o (Cu^{+2}/Cu) = +0.34$ V

10. An external current source giving a current of 5.0 A was joined with Daniel cell arrangement opposing the normal current flow and was removed after 10 hrs. Before passing the current the LHE and RHE contained 1L each of 1M Zn^{2+} and Cu^{2+} respectively. Find the EMF supplied by the Daniel cell after removal of the external current source. E° of Zn^{2+}/Zn and Cu^{2+}/Cu at 25°C is –0.76 and + 0.34V respectively.

11. A big irregular shaped vessel contained water, the conductivity of which was 2.56×10^{-5} mho cm^{-1}. 500 g of NaCl was then added to the water and the conductivity after the addition of NaCl, was found to be 3.10×10^{-5} mho cm^{-1}. Find the capacity of the vessel if it is fulfilled with water. ($\lambda^{\infty} NaCl = 149.9$ Scm^2 mole^{-1}). Assume negligible conductivity of H_2O.

12. 100ml $CuSO_4$(aq) was electrolyzed using inert electrodes by passing 0.965 A till the pH of the resulting solution was 1. The solution after electrolysis was neutralized, treated with excess KI and titrated with 0.04M $Na_2S_2O_3$. Volume of $Na_2S_2O_3$ required was 35 ml. Assuming no volume change during electrolysis, calculate: (a) duration of electrolysis if current efficiency is 80%.

(b) initial concentration (M) of $CuSO_4$.

13. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g.ml^{-1}. H_2SO_4 of density 1.294 gmL^{-1} is 39% and that of density 1.139 gmL^{-1} is 20% by weight. The battery holds 3.5L of acid and the volume practically remains constant during discharge. Calculate the number of ampere hours for which the battery must have been used. The discharging and charging reactions are :

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^- \text{ (Anodic reaction)}$$
$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O \text{ (Cathode reaction)}$$

14. A silver coulomb meter is in series with a cell electrolyzing water. In a time of 1 minute at a constant current, 1.08 g silver got deposited on the cathode of the coulometer. What total volume (in mL) of the gases would have produced in other cell if in this cell the anodic and cathodic efficiencies were 90% and 80% respectively. Assume STP conditions and the gases collected are dry. (Ag – 108) (Molar volume of any ideal gas at STP = 22.4 L)

15. K_d for dissociation of $[Ag(NH_3)_2]^+$ into Ag^+ and NH_3 is 6×10^{-8}. Calculate E° for the following half reaction;

$[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2NH_3$

Given $Ag^+ + e^- \longrightarrow Ag$, $E^o = 0.799V$

16. The resistance of an aqueous solution containing 0.624 g of $CuSO_4 \cdot 5H_2O$ per 100 cm^3 of the solution in a conductance cell of cell constant 153.7 per metre is 520 ohms at 298 K. Calculate the molar conductivity. ($CuSO_4 \cdot 5H_2O = 249.5$)

17. Calculate the e.m.f. of the cell

$Pt | H_2(1.0 \text{ atm}) | CH_3COOH (0.1M) || NH_3 (aq, 0.01 M) | H_2 (1.0 \text{ atm}) | Pt$

$K_a (CH_3COOH) = 1.8 \times 10^{-5}, K_b, (NH_3) = 1.8 \times 10^{-5}$.

18. When a solution of conductivity 1.342 mho metre^{-1} was placed in a conductivity cell with parallel electrodes, the resistance was found to be 170.5 ohm. The area of the electrodes is 1.86×10^{-4} sq. metre. Calculate the distance between the two electrodes in metre ?

19. The pK_{SP} of AgI is 16.07. If the E° value for Ag^+ / Ag is 0.7991V, find the E° for the half cell reaction

$AgI (s) + e^- \longrightarrow Ag + I^-$.

20. Voltage of the cell Pt, H_2 (1 atm) | HOCN (1.3×10^{-3} M) || Ag^+ (0.8 M) | Ag (s) is 0.982 V. Calculate the K_a for HOCN. Neglect [H^+] because of oxidation of H_2(g).

21. Calculate the equilibrium concentrations of all ions in an ideal solution prepared by mixing 25 mL of 0.1M T●$^+$ with 25mL of 0.2M Co^{3+} which undergoes chemical change as -
T●$^+$ + Co^{3+} ⟶ T●$^{+3}$ + Co^{+2}
E^o (T●$^+$ / T●$^{3+}$) = – 1.25 V ; E^o (Co^{3+}/Co^{2+}) = 1.84 V

22. The experimental setup for a typical Zn-Ni galvanic cell as shown below in figure :
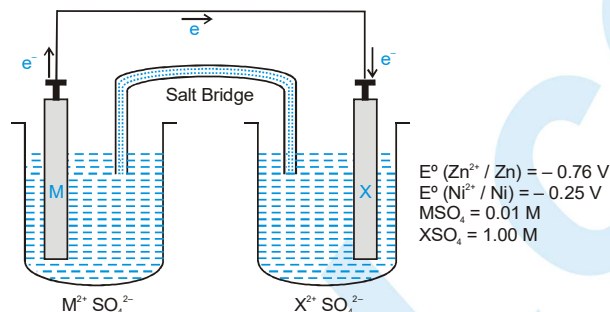
(A) Identify M and X and determine cell potential at 25°C.
(B) If concentration of M^{2+} ion changes to 1.0 M during its usage, what would be the new cell voltage ?
(C) Describe, what would happen to cell voltage if salt bridge was removed.

23. At 18°C the mobilities of NH_4^+ and ClO_4^- ions are 6.6 x 10^{-4} and 5.7 x 10^{-4} cm^2 $volt^{-1}$ sec^{-1} at infinite dilution. Calculate equivalent conductance of ammonium chlorate solution.

24. Same quantity of electricity is being used to liberate iodine (at anode) and a metal x (at cathode). The mass of x liberated is 0.617g and the iodine liberated is completely reduced by 46.3 cc of 0.124M sodium thiosulphate. Find the equivalent mass of metal x.

25. The resistances of two strong electrolytes X and Y were found to be 45 and 100 respectively. When equal volumes of both the solutions were taken in the same cell in two different experiments. If equal volumes of these solutions are mixed in the same cell, what will be the conductance of the mixture?

26. For 0.0128 N solution of acetic acid at 25°C, equivalent conductance of the solution is 1.4 mho cm^3 eq^{-1} and Λ^∞ = 391 mho cm^2 eq^{-1}. Calculate dissociation constant (K_a) of acetic acid.

27. 10 g fairly concentrated solution of $CuSO_4$ is electrolyzed using 0.01F of electricity. Calculate :
(a) The mass of resulting solution. (b) Equivalents of acid or alkali in the solution.

28. An electric current is passed through electrolytic cells in series one containing $AgNO_3$ (aq.) and other H_2SO_4(aq).
What volume of O_2 measured at 25°C and 750mm Hg pressure would be liberated from H_2SO_4 if
(a) one mole of Ag^+ is deposited from $AgNO_3$ solution
(b) 8×10^{22} ions of Ag^+ are deposited from $AgNO_3$ solution.

29. After electrolysis of NaCl solution with inert electrodes for a certain period of time 600 mL of the solution was left. Which was found to be 1N in NaOH. During the same time, 31.75 g of Cu deposited in the copper voltameter in series with the electrolytic cell. Calculate the percentage yield of NaOH obtained.

30. A $T\bullet^+ / T\bullet$ couple was prepared by saturating 0.1 M KBr with $T\bullet$Br and allowing the $T\bullet^+$ from the relatively insoluble bromide to equilibrate. This couple was observed to have a potential of -0.443 V with respect to Pb^{2+} / Pb couple in which Pb^{2+} was 0.1 M. What is K_{sp} of $T\bullet$Br.

(Report answer in multiplication of 10^{-8}) ($E^0_{Pb^{2+}/Pb} = -0.126$, $E^0_{T\lambda^+/T\lambda} = -0.336$ V)

(Take antilog $(0.5509) = 3.55$, $\dfrac{2.303\ RT}{F} = 0.059$)

31. The following two cells with initial concentration as given are connected in parallel with each other.
(1) $Fe(s) | Fe(NO_3)_2(aq.)\ (1M) \| SnCl_2(aq.)\ (1M) | Sn(s)$
(2) $Zn(s) | ZnSO_4(aq.)\ (1M) \| Fe(NO_3)_2(aq.)\ (1M) | Fe(s)$
After sufficient time equilibrium is established in the circuit. What will be the concentrations (in mmoles/L) of Fe^{2+} ions in first and second cells respectively.

[Take $E^0_{Sn^{2+}/Sn} = -0.14V$, $E^0_{Zn^{2+}/Zn} = -0.76V$, $E^0_{Fe^{2+}/Fe} = -0.44$ V, $2.3 \times RT = 6433$, $\log 2 = 0.3$]

32. For the cell (at 1 bar H_2 pressure) $Pt/H_2(g)\ HX\ (m_1),\ NaX(m_2),\ NaCl(m_3) / AgCl / Ag / Pt$ it is found that the value of

$E - E° + RTF^{-1} \bullet n \left[\dfrac{m_{HX} \cdot m_{Cl^-}}{m_{X^-}} \right]$ approaches 0.2814 in the limit of zero concentration. Calculate K_a for the acid HX

at 25°C expressing your answer as $10^7\ K_a$.

33. Specific conductance of pure water at 25°C is 0.58×10^{-7} mho cm^{-1}. Calculate ionic product of water (K_w) if ionic conductances of H^+ and OH^- ions at infinite dilution are 350 and 198 mho cm^2 respectively at 25°C.

34. The reduction potential diagram for Cu in acid solution is

$$Cu^{2+} \xrightarrow{+\ 0.15\ volt} Cu^+ \xrightarrow{0.50\ Volt} Cu$$
$$E° = x\ volt$$

Calculate x. Does Cu^+ disproportionate in the solution ?

35. For the cells in opposition,
$$Zn(s) | ZnCl_2(sol.) | AgCl(s) | Ag | AgCl(s) | ZnCl_2(sol.) | Zn(s)$$
$$C_1 = 0.02\ M \qquad\qquad\qquad C_2 = 0.5\ M$$

Find out the emf (in millivolt) of the resultant cell ? (Take $\log 2 = 0.3$, $\dfrac{RT}{F}$ at 298 K = 0.060)

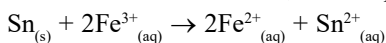**Exercise # 5**   **Part # I**   [Previous Year Questions] [AIEEE/JEE-MAIN]

1. Consider the following E^0 values :

$$E^0_{Fe^{3+}/Fe^{2+}} = +0.77\,V\,; \qquad E^0_{Sn^{2+}/Sn} = -0.14\,V$$

Under standard conditions, the cell potential for the reaction given below is :   **[AIEEE–2004]**

$$Sn_{(s)} + 2Fe^{3+}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$$

(A) 1.68 V   (B) 1.40 V   (C) 0.91 V   (D) 0.63 V

2. The limiting molar conductivities Λ^o for NaCl, KBr and KCl are 126, 152 and 150 S cm^2 mol^{-1} respectively. The value of Λ^o for NaBr is :   **[AIEEE–2004]**

(A) 128 S cm^2 mol^{-1} (B) 176 S cm^2 mol^{-1} (C) 278 S cm^2 mol^{-1} (D) 302 S cm^2 mol^{-1}

3. In a cell that utilizes the reaction $Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$,

addition of H_2SO_4 to cathode compartment will :   **[AIEEE–2004]**

(A) lower the E and shift equilibrium to the left.

(B) lower the E and shift the equilibrium to the right.

(C) increase the E and shift the equilibrium to the right.

(D) increase the E and shift the equilibrium to the left.

4. The $E^0_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are -0.41, $+1.57$, $+0.77$ and $+1.97$ V respectively. For which one of these metals, the change in oxidation state from +2 to +3 is easiest :   **[AIEEE–2004]**

(A) Cr   (B) Mn   (C) Fe   (D) Co

5. The highest electrical conductivity among the following aqueous solutions is of :   **[AIEEE–2005]**

(A) 0.1 M acetic acid   (B) 0.1 M chloroacetic acid

(C) 0.1 M fluoroacetic acid   (D) 0.1 M difluoroacetic acid

6. Aluminium oxide may be electrolysed at 1000ºC to furnish aluminium metal (At. Mass of Al = 27 amu ; 1 Faraday = 96,500 Coulombs). The cathode reaction is $Al^{3+} + 3e^- \rightarrow Al^0$. To prepare 5.12 kg of aluminium metal by this method, one would require :   **[AIEEE–2005]**

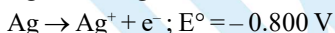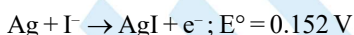(A) 5.49×10^7 C of electricity   (B) 1.83×10^7 C of electricity

(C) 5.49×10^4 C of electricity   (D) 5.49×10^{10} C of electricity

7. The molar conductivities Λ^0_{NaOAc} and Λ^0_{HCl} at infinite dilution in water at 25°C are 91.0 and 426.2 Scm^2/mol respectively. To calculate Λ^0_{HOAc}, the additional value required is :   **[AIEEE–2006]**

(A) $\Lambda^0_{H_2O}$ (B) Λ^0_{KCl} (C) Λ^0_{NaOH} (D) Λ^0_{NaCl}

8. Given data is at 25°C :

$Ag + I^- \rightarrow AgI + e^-$; $E° = 0.152$ V

$Ag \rightarrow Ag^+ + e^-$; $E° = -0.800$ V

What is the value of log K_{sp} for AgI :   (Take $\dfrac{0.474}{0.059} = 8.065$)   **[AIEEE–2006]**

(A) -8.12 (B) $+8.612$ (C) -37.83 (D) -16.13

9. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 Sm^{-1}. Resistance of the same cell when filled with 0.02 M of the same solution is 520 Ω. The molar conductivity of 0.02 M solution of the electrolyte will be : (Take $\dfrac{129}{520} = 0.248$) **[AIEEE–2006]**

(A) 124×10^{-4} Sm^{2}mol^{-1} (B) 1240×10^{-4} Sm^{2}mol^{-1} (C) 1.24 Sm^{2}mol^{-1} (D) 12.4×10^{-4} Sm^{2}mol^{-1}

10. 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 : **[AIEEE–2007]**

$$\Lambda^0_{CH_3COONa} = 91.0 \text{ Scm}^2/\text{equiv} \quad \text{and} \quad \Lambda^0_{HCl} = 426.2 \text{ Scm}^2/\text{equiv}$$

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

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

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

(C) Λ° of NaCl

(D) Λ° of CH_3COOK

11. The cell $Zn \,|\, Zn^{2+}(1M) \,\|\, Cu^{2+}(1M) \,|\, Cu$: ($E^\circ_{cell} = 1.10V$) was allowed to completely discharge at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\dfrac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}\right)$ is : (Take $\dfrac{1.1}{0.059} = 18.65$) **[AIEEE–2007]**

(A) $10^{37.3}$ (B) 9.65×10^4 (C) antilog (24.08)   (D) 37.3

12. Given : $E^0_{Cr^{3+}/Cr} = -0.72$, $E^0_{Fe^{2+}/Fe} = -0.42$ V

The potential for the cell $Cr \,|\, Cr^{3+}(0.1 \text{ M}) \,\|\, Fe^{2+}(0.01 \text{ M}) \,|\, Fe$ at 298 K is : (Take $\dfrac{2.303 \, R \, (298)}{F} = 0.06$)

[AIEEE–2008]

(A) 0.339 V   (B) –0.339 V   (C) –0.26 V   (D) 0.26 V

13. Given : $E^0_{Fe^{3+}/Fe} = -0.036$ V, $E^0_{Fe^{2+}/Fe} = -0.439$ V

The value of standard electrode potential for the change, $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$ will be :

(A) 0.385V   (B) 0.770V   (C) –0.270V   (D) –0.072V

14. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows : **[AIEEE–2010]**

$\dfrac{2}{3} Al_2O_3 \rightarrow \dfrac{4}{3} Al + O_2$; $\Delta_r G = +966$ kJmol^{-1}. The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least :

(A) 4.5 V   (B) 3.0 V   (C) 2.5 V   (D) 5.0 V

15. The reduction potential of hydrogen half-cell will be negative, if : **[AIEEE–2011(1)]**

(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

16. 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 $X + Y^{2+} \rightarrow X^{2+} + Y$ 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

17. Given : **[JEE-MAIN 2013]**

$E^0_{Cr^{3+}/Cr} = -0.74$ V ; $E^0_{MnO_4^-/Mn^{2+}} = 1.51$ V

$E^0_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V ; $E^0_{Cl/Cl^-} = 1.36$ V

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

(A) Cl   (B) Cr^{3+} (C) Mn^{2+} (D) MnO_4^-

18. Given $\qquad$ **[JEE-MAIN 2017]**

$E^0_{Cl_2/Cl^-} = 1.36\,V,\ E^0_{Cr^{3+}/Cr} = -0.74\,V$

$E^0_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\,V,\ E^0_{MnO_4^-/Mn^{2+}} = 1.51\,V$.

Among the following, the strongest reducing agent is :

(A) Cr　　　　**(B)** Mn^{2+}　　　　**(C)** Cr^{3+}　　　　**(D)** Cl^-

19. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane ? (Atomic weight of B = 10.8 u) **[JEE-MAIN 2018]**

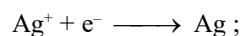**(A)** 0.8 hours　　　　**(B)** 3.2 hours　　　　**(C)** 1.6 hours　　　　**(D)** 6.4 hours

Part # II ▷▷ [Previous Year Questions][IIT-JEE ADVANCED]

1. The emf of the cell, $Zn\,|\,Zn^{2+}(0.01\,M)\,\|\,Fe^{2+}(0.001\,M)\,|\,Fe$

at 298 K is 0.2905 V. Then the value of equilibrium constant for the cell reaction is : **[JEE 2004]**

(A) $e^{\frac{0.32}{0.0295}}$　　　　**(B)** $10^{\frac{0.32}{0.0295}}$　　　　**(C)** $10^{\frac{0.26}{0.0295}}$　　　　**(D)** $10^{\frac{0.32}{0.059}}$

2. Find the equilibrium constant at 298 K for the reaction : **[JEE 2004]**

$$Cu^{2+}(aq) + In^{2+}(aq) \rightleftharpoons Cu^+(aq) + In^{3+}(aq)$$

Given that $E^o_{Cu^{2+}/Cu^+} = 0.15\,V,\ E^o_{In^{3+}/In^+} = -0.42\,V,\ E^o_{In^{2+}/In^+} = -0.40\,V$.

3. The half cell reactions for rusting of iron are :

$$2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O;\ E^o = +1.23\,V\ \&\ Fe^{2+} + 2e^- \longrightarrow Fe\,;\ E^o = -0.44\,V$$

ΔG^o (in kJ/mol) for the overall reaction is : **[JEE 2005]**

(A) –76　　　　**(B)** –322　　　　**(C)** –122　　　　**(D)** –176

4. **(a)** Calculate ΔG^o_f of the following reaction :

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

Given : $\Delta G^o_f(AgCl) = -109\,kJ/mole,\ \Delta G^o_f(Cl^-) = -129\,kJ/mole,\ \Delta G^o_f(Ag^+) = 77\,kJ/mole$.

Represent the above reaction in form of a cell.

Calculate E^o of the cell. Find $\log_{10}K_{sp}$ of AgCl at 25ºC.

(b) 6.539×10^{-2} g of metallic Zn (atomic mass = 65.39 amu) was added to 100 mL of saturated solution of AgCl.

Calculate $\log_{10}\dfrac{[Zn^{2+}]}{[Ag^+]^2}$ at equilibrium at 25ºC, given that :

$$Ag^+ + e^- \longrightarrow Ag \qquad\qquad E^o = 0.80\,V$$

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

Also find how many moles of Ag will be formed. (Take $\dfrac{114}{193} = 0.59,\ \dfrac{1.56}{0.059} = 26.44$) **[JEE 2005]**

Comprehension # 1

Tollen's reagent is used for the detection of aldehyde. When a solution of $AgNO_3$ is added to glucose with NH_4OH, then gluconic acid is formed.

$$Ag^+ + e^- \longrightarrow Ag ; \qquad\qquad E^o_{red} = 0.8 \, V$$

$$C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7 \, (\text{Gluconic acid}) + 2H^+ + 2e^- ; \qquad E^o_{oxd} = -0.05 \, V$$
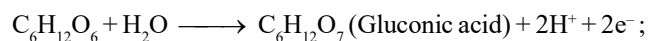
$$Ag(NH_3)_2{}^+ + e^- \longrightarrow Ag(s) + 2NH_3 ; \qquad\qquad E^o = -0.337 \, V$$

[Use $2.303 \times \dfrac{RT}{F} = 0.0592$ and $\dfrac{F}{RT} = 38.92$ at 298 K]

Now answer the following three questions :

5. $2Ag^+ + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$
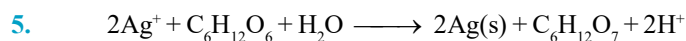
Find ln K of this reaction : **[JEE 2006]**

(A) 66.13　　　　(B) 58.38　　　　(C) 28.30　　　　(D) 46.29

6. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much : **[JEE 2006]**

(A) E_{oxd} will increase by a factor of 0.65 for E^o_{oxd} 　　(B) E_{oxd} will decrease by a factor of 0.65 for E^o_{oxd}

(C) E_{red} will increase by a factor of 0.65 for E^o_{red} 　　(D) E_{red} will decrease by a factor of 0.65 for E^o_{red}

7. Ammonia is always is added in this reaction. Which of the following must be INCORRECT :

(A) NH_3 combines with Ag^+ to form a complex. **[JEE 2006]**

(B) $Ag(NH_3)_2{}^+$ is a weaker oxidising reagent than Ag^+.

(C) In absence of NH_3, silver salt of gluconic acid is formed.

(D) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode.

8. We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution, find conductivity (specific conductance) of this solution in terms of 10^{-7} Sm^{-1}.

Given : $\lambda^o_{(Ag^+)} = 6 \times 10^{-3}$ Sm^2mol^{-1}, $\lambda^o_{(Br^-)} = 8 \times 10^{-3}$ Sm^2mol^{-1}, $\lambda^o_{(NO_3{}^-)} = 7 \times 10^{-3}$ Sm^2mol^{-1}. **[JEE 2006]**

Comprehension # 2

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

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes.

(Given : Atomic masses : Na = 23, Hg = 200 ; 1 Faraday = 96500 coulombs)

Now answer the following three questions :

9. The total number of moles of chlorine gas evolved is : **[JEE 2007]**

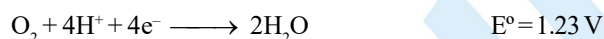(A) 0.5　　　　(B) 1.0　　　　(C) 2.0　　　　(D) 3.0

10. If the cathode is Hg electrode, the maximum weight (in g) of amalgam formed from this solution is : **[JEE 2007]**

(A) 200   (B) 225   (C) 400   (D) 446

11. The total charge (in coulombs) required for complete electrolysis is : **[JEE 2007]**

(A) 24125   (B) 48250   (C) 96500   (D) 193000

Comprehension # 3

Redox reactions play a pivoted role in chemistry and biology. The values of standard redox potential (E°) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below is a set of half-cell reactions (acidic medium) along with their E° values with respect to normal hydrogen electrode. Using this data, obtain the correct explanations to questions 15 - 16.

$$I_2 + 2e^- \longrightarrow 2I^- \qquad\qquad E^\circ = 0.54\ V$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \qquad\qquad E^\circ = 1.36\ V$$

$$Mn^{3+} + e^- \longrightarrow Mn^{2+} \qquad\qquad E^\circ = 1.50\ V$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad\qquad E^\circ = 0.77\ V$$

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \qquad\qquad E^\circ = 1.23\ V$$

12. Among the following, identify the correct statement : **[JEE 2007]**

(A) Chloride ion is oxidised by O_2

(B) Fe^{2+} is oxidised by iodine

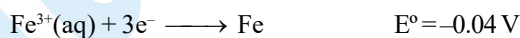(C) Iodine ion is oxidised by chlorine

(D) Mn^{2+} is oxidised by chlorine

13. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution, because : **[JEE 2007]**

(A) O_2 oxidises Mn^{2+} to Mn^{3+}

(B) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}

(C) Fe^{3+} oxidises H_2O to O_2

(D) Mn^{3+} oxidises H_2O to O_2

14. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milliampere current. The time required to liberate 0.01 mole of H_2 gas at the cathode is : (1 Faraday = 96500 C) **[JEE 2008]**

(A) 9.65×10^4 sec   (B) 19.3×10^4 sec   (C) 28.95×10^4 sec   (D) 38.6×10^4 sec

15. For the reduction of NO_3^- ion in an aqueous solution, E° is +0.96 V. Values of E° for some metal ions are given below

$$V^{2+}(aq) + 2e^- \longrightarrow V \qquad\qquad E^\circ = -1.19\ V$$

$$Fe^{3+}(aq) + 3e^- \longrightarrow Fe \qquad\qquad E^\circ = -0.04\ V$$

$$Au^{3+}(aq) + 3e^- \longrightarrow Au \qquad\qquad E^\circ = +1.40\ V$$

$$Hg^{2+}(aq) + 2e^- \longrightarrow Hg \qquad\qquad E^\circ = +0.86\ V$$

The pair(s) of metals that is(are) oxidized by NO_3^- in aqueous solution is(are) : **[JEE 2009]**

(A) V and Hg   (B) Hg and Fe   (C) Fe and Au   (D) Fe and V
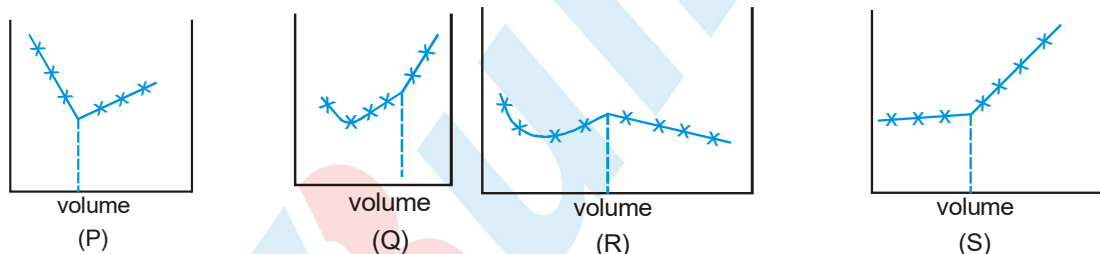
Comprehension # 4

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

$$M(s) \,|\, M^+(aq \,;\, 0.05 \text{ molar}) \,\|\, M^+(aq \,;\, 1 \text{ molar}) \,|\, M(s)$$
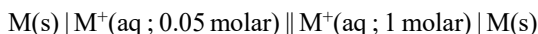
For the above electrolytic cell, the magnitude of the cell potential is $|\, E_{cell} \,| = 70$ mV.

Now answer the following two questions :

16. For the above cell : **[JEE 2010]**

    (A) $E_{cell} < 0 \,;\, \Delta G > 0$ (B) $E_{cell} > 0 \,;\, \Delta G < 0$ (C) $E_{cell} < 0 \,;\, \Delta G^\circ > 0$ (D) $E_{cell} > 0 \,;\, \Delta G^\circ < 0$

17. If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be : **[JEE 2010]**

    (A) 35 mV   (B) 70 mV   (C) 140 mV   (D) 700 mV

18. $AgNO_3$(aq.) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) versus the volume of $AgNO_3$ is : **[JEE 2011]**

    volume (P)   volume (Q)   volume (R)   volume (S)

    (A) (P)   (B) Q   (C) (R)   (D) (S)

19. Consider the following cell reaction : **[JEE 2011]**

    $$2Fe\,(s) + O_2\,(g) + 4H^+\,(aq) \longrightarrow 2Fe^{2+}\,(aq) + 2H_2O\,(l) \qquad E^\circ = 1.67 \text{ V}$$
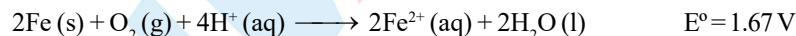
    At $[Fe^{2+}] = 10^{-3}$ M, $P(O_2) = 0.1$ atm and pH = 3, the cell potential at 25ºC is : (Take $\dfrac{2.303\,R\,(298)}{F} = 0.06$)

    (A) 1.47 V   (B) 1.77 V   (C) 1.87 V   (D) 1.57 V

Comprehension # 5

The electrochemical cell shown below is a concentration cell.

$$M\,|\,M^{2+} \text{ (saturated solution of a sparingly soluble salt, } MX_2) \,\|\, M^{2+} \text{ (0.001 mol dm}^{-3}) \,|\,M$$
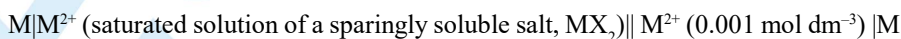
The emf of the cell depends on the difference in concentration of M^{2+} ions at the two electrodes. The emf of the cell at 298 is 0.059 V

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20. The solubility product $(K_{sp}$; in $mol^3\ dm^{-9})$ of MX_2 at 298 K based on the information available in the given concentration cell is : (Take $2.303 \times R \times 298/F = 0.059\ V$) **[IIT-JEE 2012]**

(A) 1×10^{-15} (B) 4×10^{-15} (C) 1×10^{-12} (D) 4×10^{-12}

21. The value of ΔG (in $kJ\ mol^{-1}$) for the given cell is : (Take $1F = 96500\ C\ mol^{-1}$) **[IIT-JEE 2012]**

(A) -5.7 (B) 5.7 (C) 11.4 (D) -11.4

22. An aqueous solution ox **X** is added slowly to an aqueous solution of **Y** as shown in list I. The variation in conductivity of these reactions is given in List II. Match List I with List II and select the correct answer using the code given below the lists : **[JEE(ADVANCE 2013]**

	List I		List II
P.	$(C_2H_5)_3N + CH_3COOH$ X Y	**1.**	Conductivity decreases and then increases
Q.	$KI\ (0.1M) + AgNO_3(0.01M)$ X Y	**2.**	Conductivity decreases and then does not change much
R.	$CH_3COOH + KOH$ X Y	**3.**	Conductivity increases and then does not change much
S.	$NaOH$ + HI	**4.**	Conductivity does not change much

Codes :

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

23. The standard reduction potential data at 25ºC is given below. **[JEE(ADVANCE)- 2013]**

$E^o\ (Fe^{3+}.Fe^{2+}) = +0.77\ V$;

$E^o\ (Fe^{2+}.Fe) = -0.44\ V$;

$E^o\ (Cu^{2+}.Cu) = +0.34\ V$;

$E^o\ (Cu^+.Cu) = +0.52\ V$;

$E^o\ (O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O) = +1.23\ V$;

$E^o\ (O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-) = +0.40\ V$

$E^o\ (Cr^{3+}.Cr) = -0.74\ V$;

$E^o\ (Cr^{2+}.Cr) = -0.91\ V$

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

	List I / I		List II / II
P.	$E^o\ (Fe^{3+,}\ Fe)$	1.	$-0.18\ V$
Q.	$E^o\ (4H_2O \rightleftharpoons 4H^+ + 4OH^-)$	2.	$-0.4\ V$
R.	$E^o\ (Cu^{2+} + Cu \rightarrow 2Cu^+)$	3.	$-0.04\ V$
S.	$E^o(Cr^{3+},\ Cr^{+2})$	4.	$-0.83\ V$

Codes :

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

24. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm². The conductance of this solution was found to be 5×10^{-7} S. The pH of the solution is 4. The value of limiting molar conductivity (Λ_m°) of this weak monobasic acid in aqueous solution is $Z \times 10^2 \, S \, cm^{-1}$. The value of Z is **[JEE(ADVANCE)- 2017]**

25. For the following cell,

$$Zn(s) \,|\, ZnSO_4(aq) \,\|\, CuSO_4(aq) \,|\, Cu(s)$$

when the concentration of Zn^{2+} is 10 times the concentration fo Cu^{2+}, the expression for ΔG (in J mol^{-1}) is

[F is Faraday constant ; R is gas constant ; T is temperature ; E° (cell) = 1.1 V] **[JEE(ADVANCE)- 2017]**

(A) 2.303 RT – 2.2 F (B) –2.2 F (C) 2.303 RT + 1.1 F (D) 1.1 F

26. For the electrochemical cell. **[JEE(ADVANCED) 2018]**

$$Mg(s) \,|\, Mg^{2+} \, (aq, 1 \, M) \,\|\, Cu^{2+} \, (aq, 1 \, M) \,|\, Cu(s)$$

the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{+2} is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of x is _____.

(given, $\dfrac{F}{R} = 11500 \, K \, V^{-1}$, where F is the Faraday constant and R is the gas constant, ln(10) = 2.30)

27. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below : **[JEE(ADVANCED) 2018]**
$$2Cu(s) + H_2O \, (g) \longrightarrow Cu_2O(s) + H_2(g)$$

pH_2 is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H_2})$ is _____.
(Given : total pressure = 1 bar, R (universal gas constant) = 8 J K^{-1} mol^{-1}, ln(10) = 2.3, Cu(s) and Cu$_2$O(s) atr mutually immiscible.

At 1250 K : $2Cu(s) + \dfrac{1}{2}O_2(g) \longrightarrow Cu_2O(s)$; $\Delta G^\circ = -78{,}000 \, J \, mol^{-1}$

$H_2(g) + \dfrac{1}{2}O_2(g) \longrightarrow H_2O(g)$; $\Delta G^\circ = -1{,}78{,}000 \, J \, mol^{-1}$; G is the Gibbs energy

28. Consider an electrochemical cell : A(s) | A^{n+} (aq, 2M) || B^{2n+} (aq, 1 M) | B(s). The value of ΔH° for the cell reaction is twice that of ΔG° at 300K. If the emf of the cell is zero, ΔS° (in J K^{-1} mol^{-1}) of the cell reaction per mole of B formed at 300 K is_____.
(Given : ln (2) = 0.7, R (universal gas constant) = 8.3 J K^{-1} mol^{-1}. H, S and G are enthalpy, entropy and Gibbs energy, respectively.) **[JEE(ADVANCED) 2018]**

MOCK TEST

SECTION - I : STRAIGHT OBJECTIVE TYPE

1.

$$ClO_3^- \longrightarrow ClO^- \xrightarrow{\ 0.45\ V\ } \frac{1}{2}Cl_2 \xrightarrow{\ 1.07\ V\ } Cl^-$$

$$0.71\ V$$

$$E^0$$
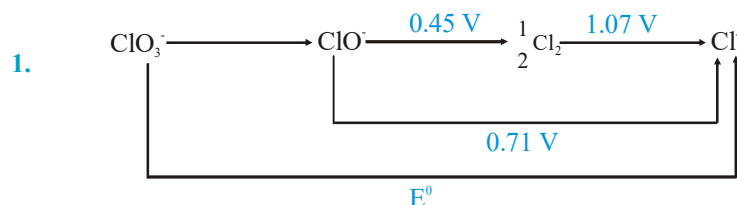
The E^0 in the given diagram is,

(A) 0.5   (B) 0.6   (C) 0.7   (D) 0.8

2. What is cell entropy change of the following cell ?

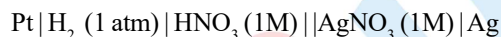$$Pt(s)\,|\,H_2(g)\,|\,CH_3COOH,\,HCl\,||\,KCl\,(aq)\,|\,Hg_2Cl_2\,(s)\,|\,Hg$$

$$P = 1\ atm \qquad 0.1\ M \qquad 0.1\ M$$

Emf of the cell ius found to be 0.045 V at 298 K and temperature coefficient is 3.4×10^{-4} V K^{-1}

Given $K_{a(CH_3COOH)} = 10^{-5}\,M$

(A) 60   (B) 65.2   (C) 69.2   (D) 63.5

3. Following cell has EMF 0.7995 V.

$$Pt\,|\,H_2\ (1\ atm)\,|\,HNO_3\,(1M)\,||\,AgNO_3\,(1M)\,|\,Ag$$

If we add enough KCl to the Ag cell so that the final Cl$^-$ is 1M. Now the measured emf of the cell is 0.222 V. The Ksp of AgCl would be :

(A) $1 \times 10^{-9.8}$ (B) $1 \times 10^{-19.6}$ (C) 2×10^{-10} (D) 2.64×10^{-14}

4. The solubility of $[Co(NH_3)_4Cl_2]ClO_4$ if the $\lambda_{Co(NH_3)_4Cl_2^+} = 50$, $\lambda_{ClO_4^-} = 70$ and the measured resistance was 33.5 Ω in a cell with cell constant of 0.20 is _____

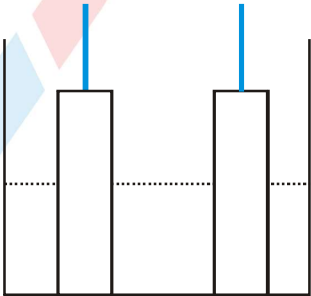(A) 59.7 mmol/L   (B) 49.7 mmol/L   (C) 39.7 mmol/L   (D) 29.7 mmol/L

5. At 298K the standard free energy of formation of $H_2O(\bullet)$ is –237.20 kJ/mole while that of its ionisation into H$^+$ ion and hydroxyl ions is 80 kJ/mole, then the emf of the following cell at 298 K will be

(Take F = 96500 C]

$$H_2\,(g,\,1\ bar)\,|\,H^+\,(1M)\,|\,|\,OH^-\,(1M)\,|\,O_2\,(g,\,1\ bar)$$
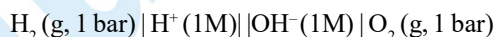
(A) 0.40 V   (B) 0.81 V   (C) 1.23 V   (D) –0.40 V

6. A hydrogen electrode X was placed in a buffer solution of sodium acetate and acetic acid in the ratio a : b and another hydrogen electrode Y was placed in a buffer solution of sodium acetate and acetic acid in the ratio b : a. If reduction potential values for two cells are found to be E_1 and E_2 respectively w.r.t. standard hydrogen electrode, the pK_a value of the acid can be given as

(A) $\dfrac{E_1 - E_2}{0.118}$ (B) $-\dfrac{E_1 - E_2}{0.118}$ (C) $\dfrac{E_1}{E_2} \times 0.118$ (D) $\dfrac{E_2 - E_1}{0.118}$

7. Which of the following cell can produce more electrical work.

(A) pt, H_2 |NH_4Cl| | 0.1 M CH_3COOH | H_2, pt   **(B)** pt, H_2 |0.1 M HCl| | 0.1 M NaOH | H_2, pt

(C) pt, H_2 |0.1 M HCl| | 0.1 M CH_3COOK | H_2, pt   **(D)** pt, H_2 | 0.1 M CH_3COOK | |0.1 M HCl| H_2, pt

8. A hydrogen electrode is immersed in a solution with pH = 0 (HCl). By how much will the potential (reduction) change if an equivalent amount of NaOH is added to the solution. (Take $p_{H_2} = 1$ atm) T = 298 K.

(A) increase by 0.41 V   **(B)** increase by 59 mV

(C) decrease by 0.41 V   **(D)** decrease by 59 mV

9. Calculate the EMF of the cell at 298 K

pt, H_2 |(1 atm)| NaOH (xM), NaCl (xM)|AgCl **(s)**|Ag

If $E^0_{Cl^-/AgCl/Ag} = +0.222V$

(A) 1.048 V   **(B)** –0.04 V   **(C)** –0.604 V

(D) emf depends on x and cannot be determined unless value of x is given

10. A current of 0.1A was passed for 2hr through a solution of cuprocyanide and 0.3745 g of copper was deposited on the cathode. Calculate the current efficiency for the copper deposition. (Cu – 63.5)

(A) 79%   **(B)** 39.5%   **(C)** 63.25%   **(D)** 63.5%

11. A flashlight cell has the cathodic reaction

$$2MnO_2 (s) + Zn^{+2} + 2e^- \longrightarrow Zn\,Mn_2\,O_4(s)$$

If the flashlight cell is to give out 4.825 mA, how long could it run if initially 8.7 g of the limiting reagent MnO_2 is present ? [Mn = 55, O = 16]

(A) 2×10^6 sec   **(B)** 4×10^6 sec   **(C)** 6×10^6 sec   **(D)** 8×10^6 sec

12. A resistance of 50Ω is registered when two electrodes are suspended into a beaker containing a dilute solution of a strong electrolyte such that exactly half of the them are submerged into solution. If the solution is diluted by adding pure water (negligible conductivity) so as to just completely submerge the electrodes, the new resistance offered by the solution would be

(A) 50 Ω   **(B)** 100 Ω   **(C)** 25 Ω   **(D)** 25 Ω

13. The standard reduction potential of a silver chloride electrode is 0.2 V and that of a silver electrode is 0.79 V. The maximum amount of AgCl that can dissolve in 10^6 L of a 0.1 M $AgNO_3$ solution is

(A) 0.5 mmol   **(B)** 1.0 mmol   **(C)** 2.0 mmol   **(D)** 2.5 mmol

14. It is observed that the voltage of a galvanic cell using the reaction $M(s) + xH^+ \longrightarrow M^{x+} + \dfrac{x}{2}H_2$ varies linearly with the log of the square root of the hydrogen pressure and the cube root of the M^{x+} concentration. The value of x is

15. Acetic acid has $K_a = 1.8 \times 10^{-5}$ while formic acid has $K_a = 2.1 \times 10^{-4}$. What would be the magnitude of the emf of the cell

$$Pt(H_2) \left| \begin{matrix} 0.1 \text{ M acetic acid} + \\ 0.1\text{M sodium acetate} \end{matrix} \right| \left| \begin{matrix} 0.1 \text{ M formic acid} + \\ 0.1\text{M sodium formate} \end{matrix} \right| Pt(H_2) \text{ at } 25°\text{ C ?}$$

(A) 0.0315 volt   **(B)** 0.0629 volt   **(C)** 0.0455 volt   **(D)** 0.545 volt

16. Consider the cell $Ag(s)|AgBr(s)|Br^-(aq)||AgCl(s)|Cl^-(aq)|Ag(s)$ at 25° C. The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10}. For what ratio of the concentrations of Br^- & Cl^- ions would the emf of the cell be zero ?

(A) 1 : 200   **(B)** 1 : 100   **(C)** 1 : 500   **(D)** 200 : 1

17. Value of Λ_m^∞ for $SrCl_2$ in water at 25°C from the following data :

Conc. (mol/lt)	0.25	1
$\Lambda_m (\Omega^{-1}cm^2mol^{-1})$	260	250

(A) 270   **(B)** 260   **(C)** 250   **(D)** 255

18. Which of these ions Cu^+, Co^{3+}, Fe^{2+} is stable in aqueous medium.

Given : $E^0_{Cu^{2+}/Cu^+} = 0.15$ volt ; $E^0_{Cu^+/Cu} = 0.53$ V ; $E^0_{Co^{3+}/Co^{2+}} = 1.82$ V ; $E^0_{Fe^{3+}/Fe^{2+}} = 0.77$ V

$E^0_{Fe^{2+}/Fe} = -0.44$ V ; $E^0_{O_2,H^+/H_2O} = 1.23$ V

(A) Cu^+, Co^{3+} **(B)** Co^{3+} **(C)** Cu^+ **(D)** Co^{3+}, Cu^+, Fe^{2+}

19. What is the value of pK_b (CH_3COO^-) if $\lambda_m^\infty = 390$ & $\lambda_m = 7.8$ for 0.04 of a CH_3COOH at 25°C

(A) 9.3   **(B)** 9.2   **(C)** 4.7   **(D)** 4.8

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

20. In which the following cell (s) : $E_{cell} = E^0_{cell}$?

(A) $Cu(s)|Cu^{2+}(0.01M)||Ag^+(0.1M)|Ag(s)$

(B) $Pt(H_2)|pH = 1||Zn^{2+}(0.01M)|Zn(s)$

(C) $Pt(H_2)|pH = 1||Zn^{2+}(1M)|Zn(s)$

(D) $Pt(H_2)|H^+ = 00.1M||Zn^{2+}(0.01M|Zn(s)$

21. Which one is/are correct among the followings ?

Given, the half cell emf's $E^0_{Cu^{+2}|Cu} = 0.337, E^0_{Cu^{+1}|Cu} = 0.521$

(A) Cu^{+1} disproportionates

(B) Cu and Cu^{2+} comproportionates (reverse of disproportionation into Cu^+).

(C) $E^0_{Cu|Cu^{+2}} + E^0_{Cu^{+1}|Cu}$ is positive

(D) All of these

22. For the cell (at 298 K)

$$Ag(s)\,|AgCl(s)\,|\,Cl^-\,(aq)|\,|AgNO_3\,(aq)\,|\,Ag(s)$$
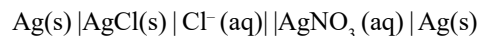
Which of the following is correct -

(A) The cell emf will be zero when $[Ag^+]_a = [Ag^+]_c$ ($[Ag^+]$ in anodic compartment $= [Ag^+]$ in cathodic compartment)

(B) The amount of AgCl(s) precipitate in anodic compartment will decrease with the working of the cell.

(C) The concentration of $[Ag^+]$ = constant, in anodic compartment during working of cell.

(D) $E_{cell} = E^0_{Ag^+|Ag} - E^0_{Cl^-|AgCl|Ag} - \dfrac{0.059}{1}\log\dfrac{1}{[Cl^-]_a}$

23. The standard redox potentials E^0 of the following systems are

System	E°(volts)
(i) $\quad MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	1.51
(ii) $\quad Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$	–0.15
(iii) $\quad Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	1.33
(iv) $\quad Ce^{3+} \longrightarrow Ce^{4+} + e^-$	–1.61

The oxidising power of the various species are related as

(A) $Cr_2O_7^{2-} > MnO_4^-$ **(B)** $Ce^{4+} > Sn^{4+}$ **(C)** $Ce^{4+} > MnO_4^-$ **(D)** $MnO_4^- > Sn^{4+}$

24. Acetic acid is titrated with NaOH solution. Which of the following statement is correct for this titration ?

(A) conductance increase upto equivalence point, then it decreases

(B) conductance decreases upto equivalence point, then it increases

(C) first conductance increases slowly upto equivalence point and then increases rapidly

(D) first conductance increases slowly upto equivalence point and then drops rapidly

25. During an electrolysis of conc. H_2SO_4, perdisulphuric acid ($H_2S_2O_8$) and O_2 from in equimolar amount. The amount of H_2 that will form simultaneously will be ($2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$)

(A) thrice that of O_2 in moles

(B) twice that of O_2 in moles

(C) equal to that of O_2 in moles

(D) Half of that of O_2 in moles

SECTION - III : ASSERTION AND REASON TYPE

26.   **Statement - 1 :** Zinc protect the iron better than tin even after it cracks.

Statement - 2 : $E^0_{OP_{Zn}} < E^0_{OP_{Fe}}$ But $E^0_{OP_{Sn}} < E^0_{OP_{Fe}}$

(A) Statement-1 is True, Statement-2 is True and Statement-2 is correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True and Statement-2 is not correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

27.   **Statement - 1 :** For the reaction :

$$Ni^{++} + 2e^- \longrightarrow Ni$$

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

$\Rightarrow$ $E^0_{Fe^{++}|Fe} < E^0_{Ni^{++}|Ni}$ and $E^0_{red} > 0$

$\Rightarrow$ So Fe electrode is cathode and Ni electrode is anode

Statement - 2 : Because DG° < 0 and E°$_{Cell}$ > 0, so cell is possible.

(A) Statement-1 is True, Statement-2 is True and Statement-2 is correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True and Statement-2 is not correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

28. $KMnO_4$ liberates O_2 from water in presence of an acid.

Given, $E^0_{MnO_4^-, Mn^{+2}, H^+|Pt} = 1.51V$

$E^0_{H^+|O_2|Pt} = 1.223V$

29.   The standard potentials of some metal-insoluble salt-anion electrode are as given below

$Ag - AgCl$ $E^0_{red} = 0.222$

$Ag - AgBr$ $= 0.03$

$Ag - AgI$ $= -0.151$

$Ag - Ag_2S$ $= -0.69$

Then the K_{SP} values must follow :

$K_{SP}(AgCl) > K_{SP}(AgBr) > K_{SP}(AgIP) > K_{SP}(Ag_2S)$

30.   At 300 K specific conductivity of ethanol is 4×10^{-10} mho cm^{-1} . The ionic conductances of H$^+$, C$_2$H$_5$O$^-$ at this temperature is 300 and 100 mho cm^2 equivalent^{-1} respectively. Then the negative logarithm of ionic product of alcohol will be 18.

**31.**   The process of $AgCn + KCN \longrightarrow K[Ag(CN)_2]$ involves the oxidation of Ag.

SECTION - IV : COMPREHENSION TYPE

Read the following comprehensions carefully and answer the questions.

Comprehension # 1

Strong Acid Versus Strong Base

The principle of conductometric titrations is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that the conductivity of the solution varies during the course of the titration. Take, for example, the titration between as strong acid, say HCl, and a strong base 2, say NaOH. Before NaOH is added, the conductance added, H^+ ions are replaced by relatively slower moving Na^+ ions. Consequently, the conductance of the solution decreases and this continues right upto the equivalence point where the solution contains only NaCl. Beyond the equivalence point, if more of NaOH is added, then the solution contains in excess of the fast moving OH^- ions with the result that its conductance is increased and it continues to increase as more and more of NaOH is added. If we plot the conductance value versus the amount of NaOH added, we get a curve of the type shown in Fig.
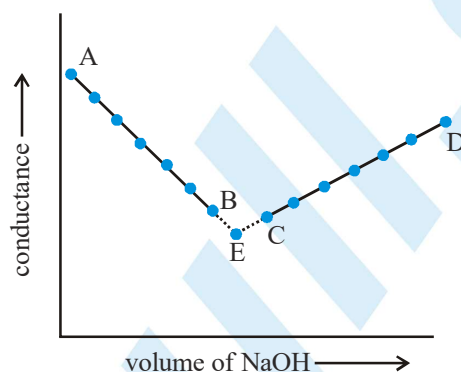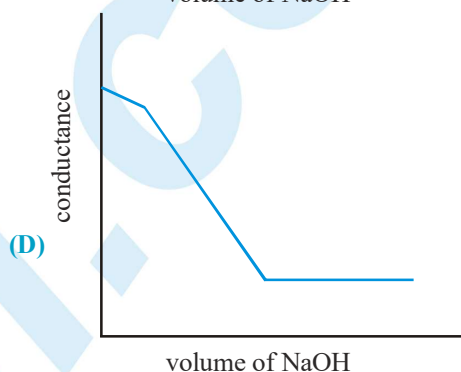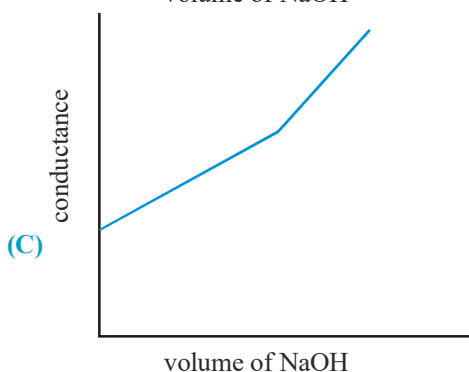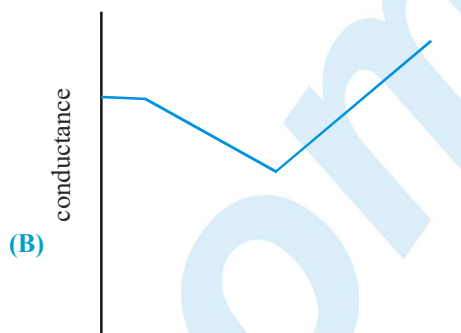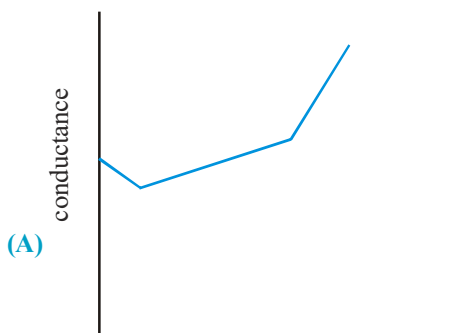

The descending portion AB represents the conductances before the equivalence point (solution contains as mixture of acid HCl and the salt NaCl) and the ascending portion CD represents the conductances after the equivalence point (solution contains the salt NaCl and the excess of NaOH). The point E which represents the minimum conductance is due to the solution containing only NaCl with not free acid or alkali and thus represents the equivalence point. This point can, however, be obtained by the extrapolation of the lines AB and DC, and therefore, one is not very particular in locating this point experimentally as it is in the case of ordinary acid-base titrations involving the acid-base indicators.

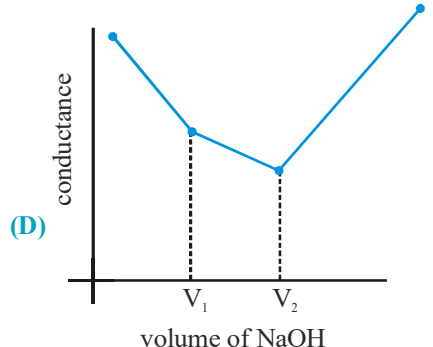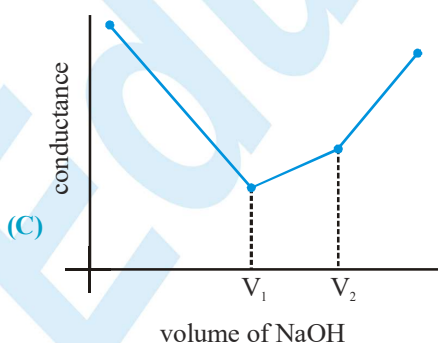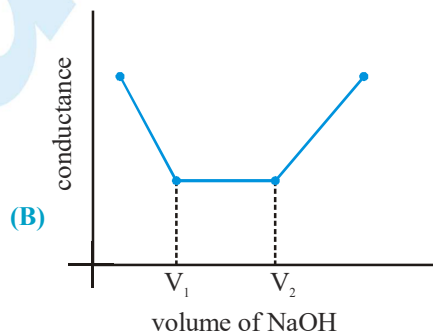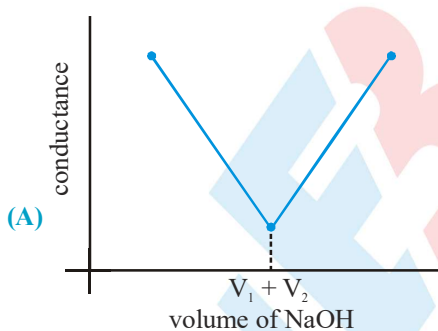#### Weak Acid versus Strong Base

Let us take the specific example of acetic acid being titrated against NaOH. Before the addition of alkali, the solution shows poor conductance due to feeble ionization of acetic and. Initially the addition of alkali causes not only the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to the common ion Ac^- and thus the conductance of the solution decreases in the beginning. But very soon the conductance starts increasing as addition of NaOH neutralized the undissociated HAc to Na^+Ac^+ thus causing the replacement of non-conduction HAc with strong-conducting electrolyte Na^+Ac^-. The increase in conductance continues right up to the equivalence point. Beyond this point conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions. The graph near the equivalence point is curved due the hydrolysis of the salt NaAc. The actual equivalence point can, as usual, be obtained by the extrapolation method.

In all these graphs it has been assumed that the volume change due addition of solution from burette is negligible, hence volume change of the solution in beaker the conductance of which is measured is almost constant throughout the measurement.

32. The nature of curve obtained for the titration between weak acid versus strong base as described in the above passage will be

(A)

conductance / volume of NaOH

(B)

conductance / volume of NaOH

(C)

conductance / volume of NaOH

(D)

conductance / volume of NaOH

33. The most appropriate titration curve obtained when a mixture of a strong acid (say HCl) and weak acid (say CH_3COOH) is titrated with a strong base (say NaOH) will be

(A)

conductance / $V_1 + V_2$ / volume of NaOH

(B)

conductance / V_1 V_2 / volume of NaOH

(C)

conductance / V_1 V_2 / volume of NaOH

(D)

conductance / V_1 V_2 / volume of NaOH

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34. If a 100 mL solution of 0.1 M HBr is titrated using a very concentrated solution of NaOH, then the conductivity (specific conductance) of this solution at the equivalence point will be (assume volume change is negligible due to addition of NaOH). Calculate your answer in terms of 10^{-1} Sm^{-1}.

[Given $\lambda^0_{(Na^+)} = 8 \times 10^{-3}$ Sm^2 mol^{-1} $\lambda^0_{(Br^-)} = 4 \times 10^{-3}$ S m^{-1} mol^{-1}]

(A) 6   (B) 12   (C) 15   (D) 24

Comprehension # 2

Redox titrations

Titrations are one of the methods we can use to discover the precise concentrations of solution. A typical titration involves adding a solution from a buretic to another solution in a flask. The endpoint of the titration is found by watching a colour change taking place. However, a problem arises when a suitable indicator cannot be found or when the colour changes involved are unclear. In these cases redox potentials may sometimes come to the rescue.
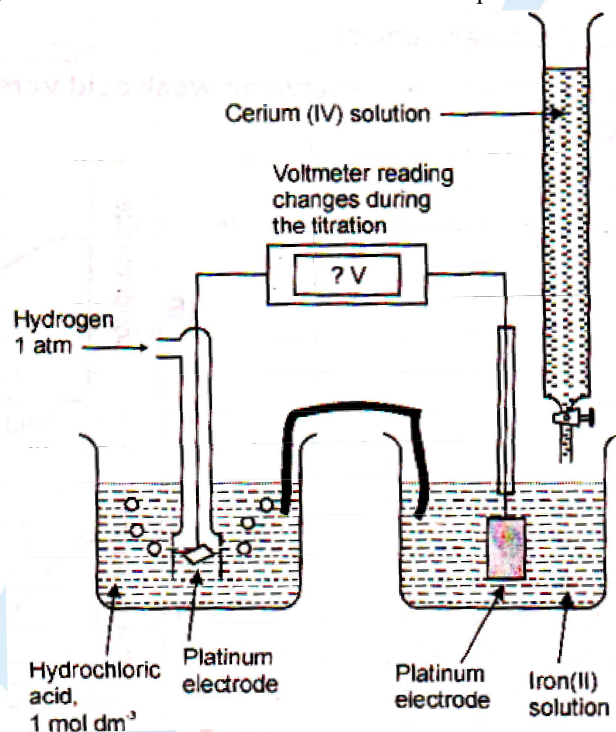
A particularly well known example (Fig.) is a method of discovering the concentration of iron (II) ions in a solution by titrating them with a solution of cerium (IV). The redox potentials that are of interest here are $E^0_{Fe^{3+}/Fe^{2+}} = + 0.77$

V and $E^0_{Ce^{4+}/Ce^{3+}} = + 1.61$ V. These tell us that cerium (IV) ions are the oxidising agents, and iron (II) ions are the reducing agents. They should react according to the equation.

$Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$

Now imagine that we know the concentration of the cerium (IV) ions solution in the burette. We want to measure the concentration of the iron (II) solution. If we add just one drop of the cerium (IV) solution from the burette, some of the iron (II) ions will be oxidised. As a consequence the beak would now contain a large number of unreacted iron (II) ions, but also some iron (III) ions as well. All of the cerium (III). The solution in the beaker now represents an iron (III) / iron (II) half cell, although not at standard conditions. Thus the e.m.f. of the cell will be near, but not equal, to
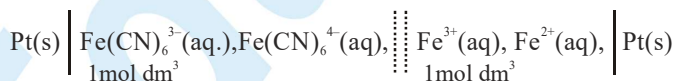
$E^\phi_{Fe^{3+}/Fe^{2+}}$.

	Ions Present				Cell	E.m.f/V
	Fe^{2+}	Fe^{3+}	Ce^{3+}	Ce^{4+}		
After the first few drops of Ce4+ (aq)	Many	Some	Some	None	Fe^{3+}/Fe^{2+}	A little less than 0.77
Near the endpoint	Some	Many	Many	None	Fe^{3+}/Fe^{2+}	A little more than 0.77
Just after	None	Many	Many	Some	Fe^{4+}/Fe^{3+}	A little more than 1.61

If we continue to add cerium (IV) solution, the number of iron (II) ions is gradually reduced and eventually only a very few are left (Table). At this stage the next few drops of cerium (IV) solution convert all the remaining iron (II) ions into iron (III) and some of the cerium (IV) ions are left unreacted. Once this happens we no longer have an iron (III) / Iron (II) half-cell. Instead we have a solution in which there is a large number of cerium (III) ions and a smaller number of cerium (IV) ions. The solution in the beaker now behaves as a cerium (IV)/ cerium (III) half-cell (although no a standard one).
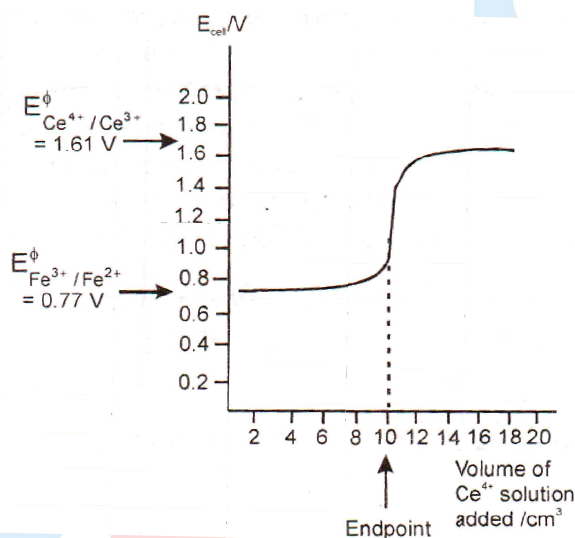
Just before all the iron (II) ions are converted into iron (III) we have a cell with an e.m.f. of around + 0.77V. After all the iron (II) ions are oxidised, we have a cell with an e.m.f. of about +1.61 V. This rapid rise in e.m.f. occurs with the addition of just one drop of cerium (IV) solution. You should be able to understand why a graph of cell e.m.f. against volume of cerium (IV) solution added looks like that of Fig. The end point of the titration can be read from the graph and the concentration of the iron (II) solution calculated in the usual way
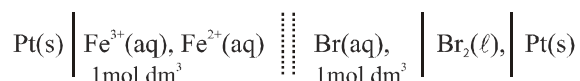
35. When an ion is converted into a complex ion, the redox potential changes. You can see this in the case of the e.m.f. of the iron (III) / iron (II) system (+0.77V) and the hexacyanoferrate (III) /hexacyanoferrate(II) system (+0.36V). The cyanide ion is said to stabilise the oxidation stale of the iron. If you were to make up a cell

$$Pt(s) \left| \begin{matrix} Fe(CN)_6^{3-}(aq.), Fe(CN)_6^{4-}(aq), \\ 1mol\ dm^3 \end{matrix} \right. \vdots \left| \begin{matrix} Fe^{3+}(aq), Fe^{2+}(aq), \\ 1mol\ dm^3 \end{matrix} \right| Pt(s)$$

What would be the e.m.f. and what would be the cell reaction?

(A) 0.41 V, $Fe(CN)_6^{4-}(aq.) + Fe^{3+}(aq.) \longrightarrow Fe(CN)_6^{3-}(aq.) + Fe^{2+}(aq.)$

(B) 0.13 V, $Fe(CN)_6^{4-}(aq.) + Fe^{3+}(aq.) \longrightarrow Fe(CN)_6^{3-}(aq.) + Fe^{2+}(aq.)$

(C) 0.41 V, $Fe(CN)_6^{3-}(aq.) + Fe^{2+}(aq.) \longrightarrow Fe(CN)_6^{4-}(aq.) + Fe^{3+}(aq.)$

(D) 0.13 V, $Fe(CN)_6^{3-}(aq.) + Fe^{2+}(aq.) \longrightarrow Fe(CN)_6^{4-}(aq.) + Fe^{3+}(aq.)$

36. The cell shown below was set up

$$Pt(s) \left| \begin{array}{c} Fe^{3+}(aq), Fe^{2+}(aq) \\ 1\,mol\ dm^3 \end{array} \right| \left| \begin{array}{c} Br(aq), \\ 1\,mol\ dm^3 \end{array} \right| Br_2(\ell), \left| Pt(s) \right.$$

What would be the cell e.m.f. ? If potassium cyanide solution were added to the left hand half cell (with due care!), what would you expect to happen to the e.m.f. of the cell?

$E^0_{Br_2Br} = 1.07\ V$ and use data of previous question, if required.

(A) 0.30 V, emf will increase from 0.30 V to 0.41 V   (B) 1.84 V, emf will decrease from 1.84 V to 1.43 V

(C) 0.30 V, emf will increase from 0.30 V to 0.71 V   (D) 0.30 V, emf will increase from 0.30 V to 0.43 V

37. Imagine you were given a solution of potassium dichromate (VI) in a beaker and a solution of iron (II) sulphate in a burette. You do not know the concentration of dichromate (VI) ions but the concentration of the iron (II) solution is known. You take is to carry out a redox titration using the two solutions in order to determine the above titration.

$E^0_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\ V$, $E^0_{Fe^{3+}/Fe^{2+}} = 0.77\ V$.
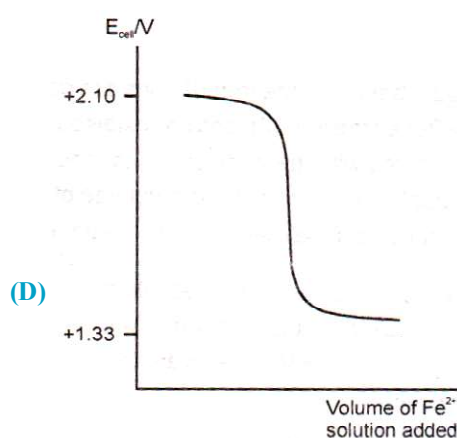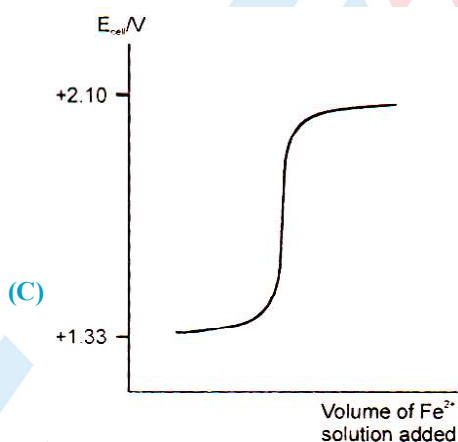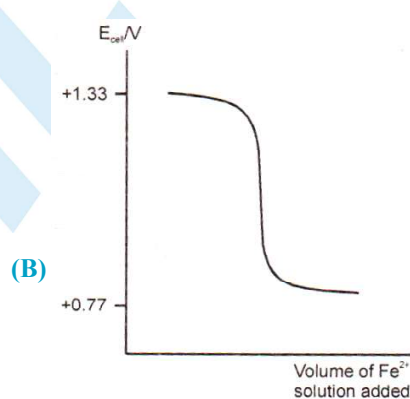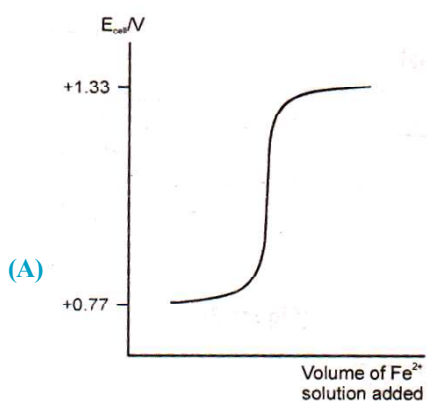
Comprehension # 3

A fuel cell is a cell that is continuously supplied with an oxidant and a reductant so that it can deliver a current indefinitely. Fuel cells offer the possibility of achieving high thermodynamic efficiency in the conversion of Gibbs energy into mechanical work. Internal combustion engines at best convert only the fraction $(T_2 - T_1)/T_2$ of the heat

of combustion into mechanical work. While the thermodynamic efficiency of the fuel cell is given by, $\eta = \dfrac{\Delta G}{\Delta H}$, where ΔG is the Gibbs energy change for the cell reaction and ΔH is the enthalpy change of the cell reaction. This efficiency can be upto 80% also in contrast to normal heat engine efficiencies which are generally about 40%.
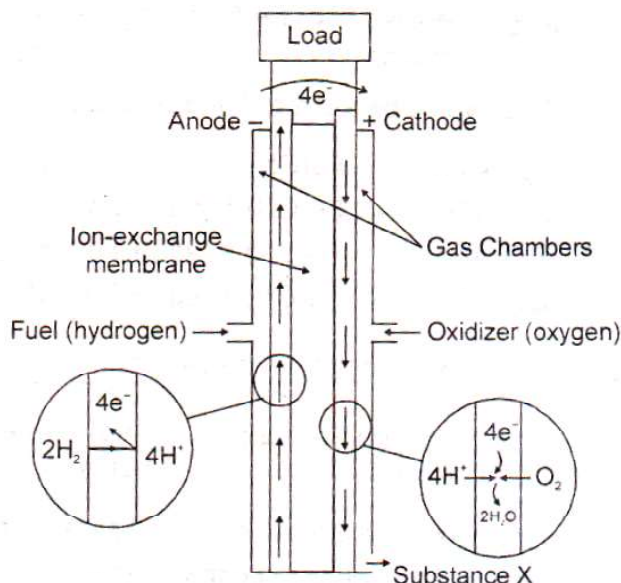
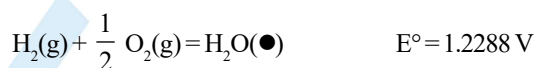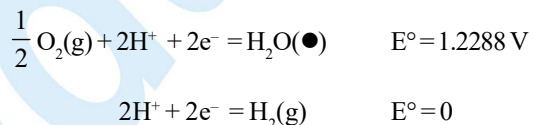Fuel cells may be classified according to the temperature range in which they operate : low temperature (25 – 100°C), medium temperature (100 to 500°C), high temperature (500 to 1000°C) and very high temperature (above 1000°C). The advantage of using high temperature is that catalysts for the various steps in the process are not so necessary. Polarization of a fuel cell reduces the current. Polarization is the result of slow reaction or processes such as diffusion in the cell.

The figure, indicates the construction of a hydrogen-oxygen fuel cell with a solid electrolyte, which is an ion exchange membrane. The membranes is impermeable to the reactant gases, but is permeable to hydrogen ions, which carry the current between the electrodes. To facilitate the operation of the cell at 40 to 60°C, the electrodes are covered with finely divided platinum that function as a catalyst. Water is drained out of the cell during operation. Fuel cells of this general type have been used successfully in the space program and are quite efficient. Their disadvantages for large-scale commercial application are that hydrogen presents storage problems and platinum is an expensive catalyst. Cheaper catalysts have been found for higher temperature operation of hydrogen-oxygen fuel cells.

Fuel cells that use hydrocarbons and air have been developed, but their power per unit weight is too low to make them practical in ordinary automobiles. Batter catalysts are needed.

A hydrogen-oxygen fuel cell may have an acidic or alkaline electrolyte. The half-cell reactions are

$$\frac{1}{2}O_2(g) + 2H^+ + 2e^- = H_2O(\bullet) \qquad E° = 1.2288\,V$$

$$2H^+ + 2e^- = H_2(g) \qquad E° = 0$$

$$\overline{\rule{6cm}{0.4pt}}$$

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(\bullet) \qquad E° = 1.2288\,V$$

or

$$\frac{1}{2} O_2(g) + H_2O(\bullet) + 2e^- = 2OH^- \qquad E° = 0.4009 \text{ V}$$

$$2H_2O(\bullet) + 2e^- = H_2(g) + 2OH^- \qquad E° = -0.8279 \text{ V}$$

$$H_2(g) + \frac{1}{2} O_2(g) = H_2O(\bullet) \qquad E° = 1.2288 \text{ V}$$
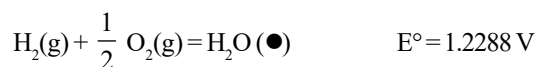
To maximize the power per unit mass of an electrochemical cell, the electronic and electrolytic resistances of the cell must be minimized. Since fused salts have lower electrolytic resistances than aqueous solutions, high-temperature electrochemical cells are of special interest for practical applications.

High temperature also allow the use of liquid metal electrode, which make possible higher current densities than solid electrodes.

38. If 560 mL of H_2 gas at STP is fed into and is consumed by the fuel cell in 10 minutes, then what is the current output of the fuel cell?

(A) 4 A   (B) 8 A   (C) 16 A   (D) 12 A

39. For a Hydrogen – Oxygen fuel cell if $\Delta H_f^0(H_2O, \bullet) = 285$ kJ/mol, then what will be thermodynamic efficiency under standard conditions (use data given in the passage if required)

(A) 0.91   (B) 0.41   (C) 0.63   (D) 0.83

.40. Why are fuel cells not being used in daily life despite their very high efficiency.

(A) The fuels needed for their operation are rarely found in nature

(B) Their operation always needs very high temperature

(C) The catalyst used in fuel cells at normal temperature are very expensive

(D) The design of fuel cells is so complicated that it is not feasible to construct these for daily applications.

41. What is the substance X taken out of the bottom of the fuel cell shown in the figure.

(A) H_2O (B) H_2O_2 (C) Both (A) and (B)   (D) neither

42. The advantage of using fuel cell in a motorcar could be

(A) emissionless operation   (B) light weight

(C) freedom from refueling   (D) low initial cost

Comprehension # 4

Metallurgy of copper

Electrolytic purification of copper is required since the product of the Bessemer converter is impure. Sheets of pure copper are made the cathodes and blister copper is used as the anodes. The bath contains $CuSO_4$, H_2SO_4 and NaCl Metallic copper goes into solution as Cu^{+2} ions at the anode and deposit at the cathode. Zinc and iron go into solution and do not deposit at the cathode along with copper. Silver goes into solution as Ag^+ ions, but forms a sludge in the electrolysis cell. The noble metals such as gold and platinum do not dissolve, they fall to the bottom when released from the copper anode. They help to pay for the copper refining process.

43. In what form will silver be recovered from the plating bath?

(A) Ag^+ (B) AgCl   (C) Ag   (D) Ag – Cu alloy

44. The different chemical behaviour of various metal ions (for example only Cu is deposited on the cathode) involved are explainable best using

(A) their amounts in impure copper   (B) the electrochemical series

(C) their ionization potentials   (D) their hydration energies

45. The voltage is kept low enough during the operation. This is to ensure that

(A) Fe^{+2} and Zn^{+2} ions are kept in solution only

(B) there is no risk of electric shock to the plant operators

(C) gold and platinum do not dissolve in solution and are recovered as solids.

(D) temperature control is maintained to effect reaction rate control

46. The most important role of various electrolytes added to the electrorefining bath in this case is

(A) to reduce the temperature of bath

(B) to result in good electrical connectivity so as to have high production rates

(C) so that the anode acts as an attackable electrode

(D) to enhance the viscosity of electrolyte thus preventing leakage from bath.

SECTION - V : MATRIX - MATCH TYPE

47. Match the column

      Column I   **Column II**

(A) $Zn / Zn^{+2} |$ $|Mg^{2+} / Mg$ (p) $E^0_{Cell} = 0$

        c_1 c_2 $(c_1 = c_2)$

(B) $Zn / Zn^{+2} | | Ag^+ / Ag$ (q) $E^0_{Cell} \neq 0$

        at. equilibrium

(C) $Ag / Ag^+ |$ $|Ag^+ / Ag$ (r) $E^0_{Cell} = +ve$

        c_1 c_2 $(c_1 = c_2)$

(D) $Fe / Fe^{+2} |$ $|Ag / Ag^+$ (s) $E^0_{Cell} = 0$

        c_1 c_2 $(c_1 = c_2)$
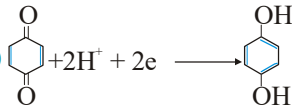
48. Match the following (1 to 1 matching) :

      Column I   **Column II**

(A) Concentration cell   (p) $+2H^+ + 2e \longrightarrow$

(B) Electrode reversible with respect to anion   (q) $Pt | Ce^{+4}, Ce^{+3}$

(C) Quin hydrone electrode   (r) $Hg | Hg_2Cl_2, KCl$

(D) Redox-electrode   (s) $Na(Hg) | NaCl | Na (Hg)$

SECTION - VI : SUBJECTIVE TYPE

49. The $E^\circ_{cell} = 1.18$ V for

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

Determine the value of x if when excess granulated zinc is added to 1 M Cu^{+2} solution the $[Cu^{+2}]_{eq.}$ becomes 10^{-x} M.

$(T = 298 \, K, \dfrac{2.303RT}{F} = 0.059)$

50. For the cell in opposition,

$\qquad Zn(s) \mid ZnCl_2(sol.) \mid AgCl(s) \mid Ag \mid AgCl(s) \mid ZnCl_2 (sol.) \mid Zn(s) \mid$

$\qquad\qquad C_1 = 0.02$ M $\qquad\qquad\qquad\qquad C_2 = 0.5$ M

Find out the emf (in millivolt) of the resultant cell? (Take $\log 2 = 0.3$, $\dfrac{RT}{F}$ at $= 298 \, K = 0.060$)

51. The following two cells with initial concentration as given are connected in parallel with each other.

(1) $Fe(s) \mid Fe(NO_3)_2 (aq.) (1 M) \parallel SnCl_2(1M) \mid Sn(s)$

(2) $Zn(s) \mid ZnSO_4(aq.) (1M) \parallel Fe(NO_3)_2(aq.) (1M) \mid Fe(s)$

After sufficient time equilibrium is established in the circuit. What will be the concentrations (in mmoles/L) of Fe^{2+} ions in first and second cells respectively.

[Take $E^0_{sn^{2+}/Sn} = -0.14$ V, $E^0_{Zn^{2+}/Zn} = -0.76$V, $E^0_{Fe^{2+}/Fe} = -0.44$ V, $2.3 \times RT = 6433$, $\log 2 = 0.3$]

52. For the cell (at 1 bar H_2 pressure) $Pt/H_2(g) \, H \, X(m_1), NaX(m_2), NaCl(m_3) / AgCl / Ag / Pt$ it is found that the value of

$E - E^\circ + RTF^{-1} \bullet n \left[\dfrac{m_{HX}.m_{cl^-}}{m_{x^-}} \right]$ approaches 0.2814 in the limit of zero concentration.

Calculate K_a for the acid HX at 25°C expressing your answer as 10^7 Ka.

53. The standard EMF of the cell

$\qquad Pt \mid H_2(g) \mid H^+ (A) \parallel OH^- (aq) \mid O_2 (g) \mid Pt$ is

0.3900 V at 27°C and 0.4000 V at 7°C.

If entropy change during formation of $H_2O(\bullet)$ from $H_2(g)$ and $O_2(g)$ is $- 193$ J/K, then find the ΔS° (magnitude only, in mJ/K) for

$H^+ (aq) + OH^- (aq) \longrightarrow H_2O (\bullet)$.

54. Calculate the emf of the cell in mV (atleast in fist two digit must match with correct answer) (giving your answer in magnitude only)

$\qquad Ag (s), AgIO_3 (s) \mid Ag^+ (xM), HIO_3 (1M) \mid\mid Zn^{+2} (1M) \mid Zn(s)$

If $K_{ap} = 3 \times 10^{-8}$ for $AgIO_3$ and $K_a = \dfrac{1}{6}$ for HIO_3 and E^0_{cell} for $2Ag + Zn^{+2} \longrightarrow 2Ag^+ + Zn$ is $- 1.56$ V.

$(\log 3 = 0.48)$ (Take $\dfrac{RT}{F} = 0.059$)

ANSWER KEY

EXERCISE - 1

1. B **2.** B **3.** B **4.** A **5.** C **6.** D **7.** A **8.** A **9.** B **10.** B **11.** A **12.** D **13.** B

14. A **15.** B **16.** C **17.** B **18.** A **19.** A **20.** D **21.** B **22.** B **23.** A **24.** B **25.** C **26.** A

27. C **28.** C **29.** B **30.** A **31.** D **32.** C **33.** A **34.** A **35.** C **36.** C **37.** B **38.** D **39.** A

40. C **41.** C **42.** C **43.** B **44.** A **45.** A **46.** A **47.** C **48.** B **49.** D **50.** D **51.** B **52.** A

53. C **54.** C **55.** A **56.** B **57.** B **58.** A **59.** D **60.** C **61.** A **62.** A **63.** A **64.** A **65.** A

66. A **67.** A **68.** C **69.** C **70.** A **71.** C **72.** C **73.** A **74.** A **75.** D **76.** D **77.** B **78.** A

79. B **80.** A **81.** D **82.** A **83.** C **84.** B **85.** A **86.** B

EXERCISE - 2 : PART # I

1. A,C,D **2.** A,C,D **3.** B,C,D **4.** A,B,C **5.** A,B **6.** A,B **7.** A,C,D **8.** A,C,D **9.** B,C **10.** A,B,D

11. C,D **12.** A,B **13.** A,B,C **14.** A,C

PART # II

1. D **2.** B **3.** B **4.** C **5.** C **6.** B **7.** B **8.** C **9.** B **10.** A **11.** C

EXERCISE - 3 : PART # I

1. $A \rightarrow p, q, r, B \rightarrow q, C \rightarrow p, s, D \rightarrow p, s$

2. $A \rightarrow s, B \rightarrow p, r, C \rightarrow p, q, D \rightarrow r$

3. $A \rightarrow p, q, B \rightarrow p, q, C \rightarrow q, r, D \rightarrow p, s$

4. $A \rightarrow u, B \rightarrow r, C \rightarrow p, D \rightarrow q, E \rightarrow s$

5. $A \rightarrow q, B \rightarrow u, C \rightarrow s, D \rightarrow r, E \rightarrow p$

6. $A \rightarrow r, B \rightarrow s, C \rightarrow p, D \rightarrow u, E \rightarrow r$

7. $A \rightarrow s, B \rightarrow p, C \rightarrow q, D \rightarrow u, E \rightarrow r$

PART # II

Comprehension # 1 : **1.** B **2.** A **3.** A

Comprehension # 2 : **1.** D **2.** C **3.** B **4.** D **5.** A

Comprehension # 3 : **1.** A **2.** C **3.** B

Comprehension # 4 : **1.** C **2.** D **3.** D

Comprehension # 5 : **1.** B **2.** C

Comprehension # 6 : **1.** A **2.** C **3.** A

EXERCISE - 5 : PART # I

1. C **2.** A **3.** C **4.** A **5.** D **6.** A **7.** D **8.** D **9.** D **10.** C **11.** A **12.** D **13.** B

14. C **15.** C **16.** D **17.** D **18.** A **19.** B

PART # II

1. B **2.** $K_C = 10^{10}$ **3.** B **4.** **(A)** $E^o = 0.59\,V, \log_{10}K_{sp} = -10$; **(B)** $52.88, 10^{-6}$ mole. **5.** B **6.** A **7.** D

8. $55\,S\,m^{-1}$ **9.** B **10.** D **11.** D **12.** C **13.** D **14.** B **15.** A, D **16.** B **17.** C **18.** D **19.** D

20. B **21.** D **22.** A **23.** D **24.** 6 **25.** A **26.** 10 **27.** –14.6 **28.** $-11.62\,JK^{-1}\,mol^{-1}$

MOCK - TEST

1. B **2.** B **3.** A **4.** B **5.** A **6.** B **7.** D **8.** C **9.** A **10.** A **11** A **12.** A **13.** B

14. B **15.** B **16.** A **17.** A **18.** B **19.** B **20.** A, B, D **21.** A, C **22.** A **23.** B, C, D **24.** C **25.** A

26. C **27.** D **28.** True **29.** True **30.** True **31.** False **32.** A **33.** C **34.** B **35.** A **36.** C **37.** B

38. B **39.** D **40.** C **41.** A **42.** A **43.** B **44.** B **45.** A **46.** B **47.** A→q,s ; B→ p ; C→ p ; D→q,r

48. A→s ; B→ r ; C→ p ; D→ q