

S.No.		Description
13	Nernst Equation	$E_{\text{half-cell}} = E^{\circ}_{\text{half-cell}} - \frac{2.303 RT}{nF} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$ <p>At 298 K, the Nernst equation can be written as,</p> $E_{\text{half-cell}} = E^{\circ}_{\text{half-cell}} - \frac{0.0591}{n} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$

## Solved Examples

### JEE Main/Boards

**Example 1:** Zn and iron can replace Cu in a solution but Pt and Au cannot. Why?

**Sol:** Both Zn and iron have more  $E^{\circ}_{\text{OP}}$  than Cu, whereas Pt and Au have less  $E^{\circ}_{\text{OP}}$

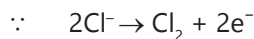
**Example 2:** Which of the following metals cannot be obtained by the electrolysis of their aqueous salt solution and why?

Al, Na, Cu, Ag.

**Sol:** Al and Na cannot be obtained because they have higher  $E^{\circ}_{\text{OP}}$  than H and thus, reduction of  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  will give Cu and Ag.

**Example 3:** Calculate the no. of electron lost or gained during electrolysis of 2 g  $\text{Cl}^-$  from NaCl (aq) to give  $\text{Cl}_2$  at anode.

**Sol:** First calculate the equivalent of  $\text{Cl}^-$  used during the reaction and on multiplying it with avogadro number will give us the no of electron lost during the reaction



Eq. of  $\text{Cl}^-$  used =  $2/35.5$

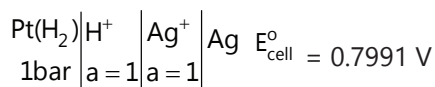
$\therefore$  1 eq. of an element involves 1 faraday charge or N electrons

$\therefore$   $(2/35.5)$  eq. of an element involves

$$= \frac{N \times 2}{35.5} \text{ electrons} = \frac{6.023 \times 10^{23} \times 2}{35.5}$$

$$= 3.4 \times 10^{22} \text{ electrons}$$

**Example 4:** Evaluate the  $E^{\circ}_{\text{Ag}^+/\text{Ag}}$  and  $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}$  from the given values:



**Sol:** Since platinum electrode has zero reduction potential the standard electrode potential will be equal to the standard electrode potential of the cell.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{H}^+/\text{H}^+} + E^{\circ}_{\text{RP}_{\text{Ag}^+/\text{Ag}}}$$

$$\text{Or } 0.7991 = 0 + E^{\circ}_{\text{RP}_{\text{Ag}^+/\text{Ag}}} \quad \therefore E^{\circ}_{\text{RP}_{\text{Ag}^+/\text{Ag}}} = 0.7991 \text{ V}$$

**Example 5:** Standard reduction potential of the  $\text{Ag}^+/\text{Ag}$  electrode at 298 K is 0.799 V. Given that for AgI,  $K_{\text{sp}} = 8.7 \times 10^{-17}$ , evaluate the potential of the  $\text{Ag}^+/\text{Ag}$  electrode in a saturated solution of AgI. Also calculate the standard reduction potential of  $\text{I}^-/\text{AgI}/\text{Ag}$  electrode.

**Sol:** Here solubility product is given from this calculate the concentration of silver ions. Now substituting this value in Nernst equation determine  $E_{\text{Ag}^+/\text{Ag}}$

As we have found out  $E_{\text{Ag}^+/\text{Ag}}$ ,  $E^{\circ}_{\text{I}^-/\text{AgI}/\text{Ag}}$  can find out by using the value of solubility product.

$$E_{\text{Ag}^+/\text{Ag}} = E^{\circ}_{\text{Ag}^+/\text{Ag}} + (0.059/1) \log [\text{Ag}^+] \quad \dots \text{(i)}$$

$$\text{Also, } K_{\text{spAgI}} = [\text{Ag}^+][\text{I}^-]$$

$$\therefore [\text{Ag}^+] = [\text{I}^-] \quad (\text{for a saturated solution})$$

$$\therefore [\text{Ag}^+] = \sqrt{K_{\text{spAgI}}} = \sqrt{(8.7 \times 10^{-17})}$$

$$= 9.32 \times 10^{-19} \quad \dots \text{(ii)}$$

$\therefore$  By Eq. (i),

$$E_{\text{Ag}^+/\text{Ag}} = 0.799 + (0.059/1) \log (9.32 \times 10^{-9})$$

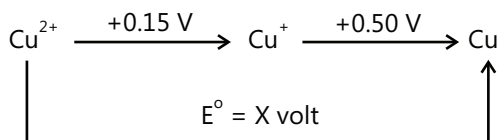
$$= 0.799 - 0.474 = 0.32 \text{ V}$$

$$\text{Also, } E_{\text{I}^-/\text{AgI}/\text{Ag}} = E_{\text{Ag}^+/\text{Ag}}^\circ + (0.059/1) \log K_{\text{spAgI}}$$

$$= 0.799 + (0.059/1) \log [8.7 \times 10^{-17}]$$

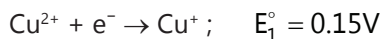
$$= 0.799 - 0.948 = -0.149 \text{ V}$$

**Example 6:** The reduction potential diagram for Cu in acid solution is:

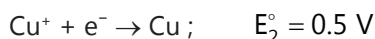


Calculate X. Does  $\text{Cu}^+$  disproportionate in solution?

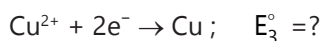
**Sol:** Given;



$$-\Delta G_1^\circ = 1 \times E_1^\circ \times F \quad \dots \text{ (i)}$$

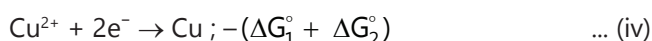


$$-\Delta G_2^\circ = 1 \times E_2^\circ \times F \quad \dots \text{ (ii)}$$



$$-\Delta G_3^\circ = 2 \times E_3^\circ \times F \quad \dots \text{ (iii)}$$

Adding Eqs. (i) and (ii)



$$\text{i.e., } -\Delta G_3^\circ = -(\Delta G_1^\circ + \Delta G_2^\circ)$$

$$2 \times E_3^\circ \times F = [1 \times 0.15 \times F + 1 \times 0.5 \times F]$$

$$\therefore E_3^\circ = 0.325 \text{ V}$$

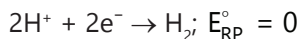
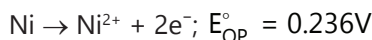
**Example 7:** The standard oxidation potential of  $\text{Ni}/\text{Ni}^{2+}$  electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured e.m.f. be zero at 25°C?

(Assume  $[\text{Ni}^{2+}] = 1 \text{ M}$ )

**Sol:** Here we are provided with standard oxidation potential of nickel electrode and we all know that reduction potential of hydrogen electrode is always zero so first the standard electrode potential of the cell is equal the oxidation potential of nickel electrode. Here it we are also with e.m.f. of the cell (zero) so substitute the values of different term in Nernst equation and

calculate the concentration of hydrogen ion. From the concentration one can easily find out the pH as using the following expression

$$\text{pH} = -\log H^+$$



$$\therefore E_{\text{Cell}}^\circ = E_{\text{OP}_{\text{Ni}}}^\circ + E_{\text{RP}_{\text{H}}}^\circ = 0.236 + 0.0 = 0.236 \text{ V}$$

$$\therefore E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{0.059}{2} \log_{10} \frac{[\text{H}^+]^2}{[\text{Ni}^{2+}]}$$

$$0 = 0.236 + \frac{0.059}{2} \log_{10} [\text{H}^+]^2$$

$$\text{or } -\log H^+ = 4$$

$$\therefore \text{pH} = 4$$

**Example 8:** A current of 3 ampere was passed for 2 hour through a solution of  $\text{CuSO}_4$ . 3g of  $\text{Cu}^{2+}$  ions were discharged at cathode. Calculate current efficiency. (At wt. of Cu = 63.5)

**Sol:** Find out current in ampere and from the calculated current passed, determine the current efficiency.

Current efficiency =

$$\frac{\text{Current passed actually}}{\text{Total current passed experimentally}} \times 100$$

$$\therefore w_{\text{Cu}} = E. i. t / 96500$$

$$\therefore 3 = \frac{63.5 \times i \times 2 \times 60 \times 60}{2 \times 96500} \text{ or } i = 1.266 \text{ ampere}$$

Current efficiency

$$= \frac{\text{Current passed actually}}{\text{Total current passed experimentally}} \times 100$$

$$= (1.266/3) \times 100 = 42.2\%$$

**Example 9:** An ammeter and copper voltmeter are connected in series in an electric circuit through which a constant direct current flows. The ammeter shows 0.525 ampere. If 0.6354 g of Cu is deposited in one hour, what is percentage error of ammeter? (At. Wt. of Cu = 63.54)

**Sol:** In order to find out the error first from the given Weight, time and other term calculate the actual current flow. The difference between the two will give us the error shown by the ammeter. As we are asked to calculate percentage error divide the error by actual current flow

Current flown = 0.525 ampere as shown by ammeter  
Actual current flown

$$(I) = \frac{W}{E \times t} \times 96500$$

$$\frac{0.6354 \times 96500}{(63.54/2) \times 60 \times 60} \quad (\because t = 60 \times 60 \text{ sec})$$

$$\therefore i = 0.536 \text{ ampere}$$

Thus, error in (I) = 0.536 – 0.525 = 0.011

$$\therefore \% \text{ error in ammeter} = \frac{0.011 \times 100}{0.536} = 2.05\%$$

**Example 10:** 3 ampere current was passed through an aqueous solution of unknown salt of Pd for 1 hour 2.977 g of Pd<sup>n+</sup> was deposited at cathode. Find n. (At. Wt. of Pd = 106.4)

**Sol:** For the reduction: Pd<sup>n+</sup> + ne<sup>-</sup> → Pd

Eq. of Pd or (w/E) = (I × t)/96500

$$\text{or } \frac{2.977}{106.4/n} = \frac{3 \times 1 \times 60 \times 60}{96500}$$

$$\therefore n = 4 \text{ (an integer).}$$

## JEE Advanced/Boards

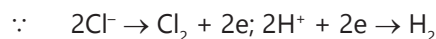
**Example 1:** Calculate the quantity of electricity that will be required to liberate 710g of Cl<sub>2</sub> gas by electrolyzing a conc. solution of NaCl. What weight of NaOH and what volume of H<sub>2</sub> at 27°C and 1 atm pressure is obtained during this process?

**Sol:** Quantity of electricity can be calculated using

Simple relationship

$$W = \frac{E \times i \times t}{96500} \quad (\because Q = i \times t)$$

Similarly calculate w<sub>NaOH</sub> and w<sub>H<sub>2</sub></sub> from the value of w<sub>H<sub>2</sub></sub> volume can be calculated using ideal gas equation.



$$\therefore \text{Eq. wt. of Cl}_2 = \text{M. Wt.}/2$$

$$\text{Now } w = \frac{E \times i \times t}{96500} = \frac{E \times Q}{96500} \quad (\because Q = i \times t)$$

$$\therefore Q = \frac{w}{E} \times 96500 = \frac{710}{71/2} \times 96500$$

$$= 1.93 \times 10^6 \text{ coulomb}$$

Also Eq. of NaOH formed

= Eq. of H<sup>+</sup> discharged = Eq. of Cl<sub>2</sub> formed

$$\therefore w_{\text{NaOH}} = \{710/[71/2]\} \times 40 = 800 \text{ g}$$

$$\text{And } w_{\text{H}_2} = \{710/[71/2]\} \times 1 = 20\text{g}$$

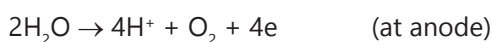
$$\therefore V_{\text{H}_2} = wRT / mp$$

$$= [20 \times 0.0821 \times 300] / [2 \times 1] = 246.3 \text{ liter}$$

**Example 2:** 50 mL 0.1 M CuSO<sub>4</sub> solution is electrolyzed using Pt electrodes with a current of 0.965 ampere for a period of 1 minute. Assuming that volume of solution does not change during electrolysis, calculate [Cu<sup>2+</sup>], [H<sup>+</sup>] and [SO<sub>4</sub><sup>2-</sup>] after electrolysis. What will be the concentration of each species, if current is passed using Cu electrodes?

**Sol:** Meq. Of CuSO<sub>4</sub> in solution = Meq. Of Cu<sup>2+</sup>  
= 50 × 0.1 × 2 = 10 (∵ Meq. Of N × V in mL)

The redox changes are:



$$\therefore w/E = i.t/96500$$

And Eq. of Cu<sup>2+</sup> lost = Equivalent of H<sup>+</sup> formed

$$= \frac{i.t.}{96500} = \frac{0.965 \times 1 \times 60}{96500} = 6 \times 10^{-4}$$

Or Meq. Of Cu<sup>2+</sup> lost = 0.6

∴ Meq. of Cu<sup>2+</sup> or Meq. of CuSO<sub>4</sub> left in solution = 10 – 0.6 = 9.4

$$\therefore [\text{Cu}^{2+}] = \frac{N_{\text{Cu}^{2+}}}{2} = \frac{\text{Meq. of Cu}^{2+}}{2 \times \text{Volume of solution (in mL)}}$$

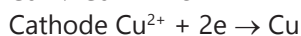
$$= \frac{9.4}{2 \times 50} = 0.094 \text{ M}$$

$$[\text{H}^+] = (N_{\text{H}^+} / 1) = (0.6/50) = 0.012 \text{ M}$$

$$[\text{SO}_4^{2-}] = 0.1\text{M}$$

(∵ SO<sub>4</sub><sup>2-</sup> is not involved in redox changes)

Also, if Cu electrodes are used, Cu<sup>2+</sup> ions are discharged at cathode and Cu<sup>2+</sup> are formed at anode and thus no changes in molarity of CuSO<sub>4</sub> solution. Anode  
Cu → Cu<sup>2+</sup> + 2e<sup>-</sup>



**Example 3:** Two students use same stock solution ZnSO<sub>4</sub> and a solution of CuSO<sub>4</sub>. The e.m.f., of one cell is 0.03 V higher than the other. The conc. of CuSO<sub>4</sub> in the cell with higher e.m.f. value is 0.5 M. Find out the conc. of CuSO<sub>4</sub> in the other cell.

$$\left( \frac{2.303RT}{F} = 0.06 \right)$$

**Sol:** First write down the half-cell reaction and nernst equation for both the half cell. By comparing both the equation, value of  $C_2$  can be calculated.

**Cell I:**  $\text{Zn} | \text{ZnSO}_4 || \text{CuSO}_4 | \text{Cu}$

$$\begin{aligned} (C_2 = 0.5 \text{ M}); E_{\text{cell}} &= E_{\text{cell}}^{\circ} + \frac{0.060}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} \\ &= E_{\text{cell}}^{\circ} + \frac{0.060}{2} \log \frac{[C_2]}{[C_1]} \quad \dots \text{(i)} \end{aligned}$$

**Cell II:**  $\text{Zn} | \text{ZnSO}_4 || \text{CuSO}_4 | \text{Cu}$   
 $\quad \quad \quad c_1 \quad \quad \quad c_2$

$$E'_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.06}{2} \log \frac{[C_2']}{[C_1']} \quad \dots \text{(ii)}$$

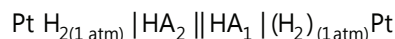
$$\text{By Eqs. (i) and (ii) } E_{\text{cell}} - E'_{\text{cell}} = \frac{0.06}{2} \log \frac{[C_2]}{[C_2']}$$

$$0.03 = \frac{0.06}{2} \log \frac{0.5}{C_2'} \quad \text{or} \quad C_2' = 0.05 \text{ M}$$

**Example 4:** Two weak acid solutions  $\text{HA}_1$  and  $\text{HA}_2$  each with the same concentration and having  $\text{pK}_a$  values 3 and 5 are placed in contact with hydrogen electrode (1 atm at  $25^\circ\text{C}$ ) and are interconnected through a salt bridge. Find e.m.f. of cell.

**Sol:** First write down the nernst equation for two half-cell as both solutions are acid we have to find out the concentration of hydrogen ion we can express it in the form of pH. As an acid undergoes dissociation, by substituting pH in terms of degree of dissociation and concentration in nernst equation, e.m.f of the cell can be easily determined.

Consider the cell



$$\text{At L.H.S. } E_{\text{H}/\text{H}^+} = E_{\text{OP}_{\text{H}/\text{H}^+}}^{\circ} - \frac{0.059}{1} \log [\text{H}^+]_2$$

$$\therefore -\log \text{H}^+ = \text{pH}$$

$$\therefore E_{\text{H}/\text{H}^+} = E_{\text{OP}_{\text{H}/\text{H}^+}}^{\circ} + 0.059(\text{pH})_2 \quad \dots \text{(i)}$$

$$\text{At R.H.S. } E_{\text{H}^+/\text{H}} = E_{\text{RP}_{\text{H}^+/\text{H}}}^{\circ} + \frac{0.059}{1} \log [\text{H}^+]_1$$

$$E_{\text{H}^+/\text{H}} = E_{\text{RP}_{\text{H}^+/\text{H}}}^{\circ} - 0.059(\text{pH})_1 \quad \dots \text{(ii)}$$



$$[\text{H}^+] = C \alpha = \sqrt{K_a \cdot C}$$

$$\therefore \text{pH}_1 = \frac{1}{2} \text{pK}_{a_1} - \frac{1}{2} \log C$$

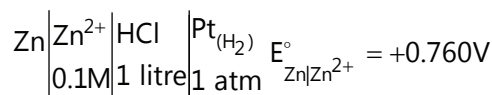
$$\text{Similarly, } \text{pH}_2 = \frac{1}{2} \text{pK}_{a_2} - \frac{1}{2} \log C$$

( $\because$  C are same) By Eqs. (i) and (ii),  $E_{\text{cell}}$

$$= E_{\text{OP}_{\text{H}/\text{H}^+}}^{\circ} + E_{\text{RP}_{\text{H}/\text{H}^+}}^{\circ} + 0.059 \left[ \frac{1}{2} \text{pK}_{a_2} - \frac{1}{2} \text{pK}_{a_1} \right]$$

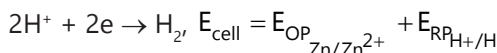
$$= 0 + 0.059 \times 5[5 - 3]/2 = + 0.059 \text{ volt}$$

**Example 5:** Calculate the minimum weight of NaOH required to added in RHS to consume all the  $\text{H}^+$  present in RHS of cell of e.m.f. +0.701 V at  $25^\circ\text{C}$  before its use. Also report the e.m.f. of cell after addition of NaOH.



**Sol:** For given cell  $\because E_{\text{OP}_{\text{Zn}/\text{Zn}^{2+}}} > E_{\text{OP}_{\text{H}/\text{H}^+}}$

$\therefore$  Redox changes will be:  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}$



$$= E_{\text{OP}_{\text{Zn}/\text{Zn}^{2+}}}^{\circ} - \frac{0.059}{2} \log_{10} [\text{Zn}^{2+}]$$

$$+ E_{\text{RP}_{\text{H}^+/\text{H}}}^{\circ} + \frac{0.059}{2} \log_{10} \frac{[\text{H}^+]^2}{(\text{P}_{\text{H}_2})}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.059}{2} \log \frac{[\text{H}^+]^2}{[\text{Zn}^{2+}](\text{P}_{\text{H}_2})}$$

$$0.701 = 0.760 + \frac{0.059}{2} \log_{10} \frac{[\text{H}^+]^2}{[\text{Zn}^{2+}](\text{P}_{\text{H}_2})}$$

$$0.701 = 0.760 + \frac{0.059}{2} \log_{10} \frac{[\text{H}^+]^2}{[0.1] \times 1}$$

$$[\text{H}^+] = 0.0316 \text{ mole liter}^{-1}$$

Since,  $\text{H}^+$  must be used by NaOH

$$\therefore \text{Meq. of NaOH} = \text{Meq. of } [\text{H}^+]$$

$$(w/40) \times 1000 = 0.0316 \times 1000 (\because V = 1 \text{ liter})$$

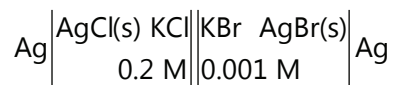
$$\therefore w = 1.265 \text{ g}$$

After addition of NaOH to cathode solution  $[\text{H}^+]$  becomes  $10^{-7}$  since both acid and base are neutralized completely. Thus, new e.m.f. of cell,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} = \frac{0.059}{2} \log_{10} \frac{[\text{H}^+]^2}{(0.1)}$$

$$= 0.760 + \frac{0.059}{2} \log_{10} \frac{(10^{-7})^2}{0.1} \quad E_{\text{cell}} = 0.3765 \text{ V}$$

**Example 6:** For the galvanic cell:



Calculate the e.m.f generated and assign correct polarity to each electrode for a spontaneous process after taking an account of cell reaction at 25°C.

[Give,  $K_{\text{spAgCl}} = 2.8 \times 10^{-10}$ ,  $K_{\text{spAgBr}} = 3.3 \times 10^{-13}$ ]

**Sol:** Write down the half-cell equation for both the cell. Here we are provided with solubility product of the two solution. From the value of solubility product first find out the concentration of silver ion in each solution. Now substitute this value in Nernst equation and calculate the e.m.f.

$$E_{\text{cell}} = E_{\text{OPAg}} + E_{\text{RPAg}}; \text{L.H.S. R.H.S.}$$

$$= E_{\text{OPAg}}^{\circ} - \frac{0.059}{1} \log [\text{Ag}^+]_{\text{L.H.S.}}$$

$$+ E_{\text{RPAg}}^{\circ} + \frac{0.059}{1} \log [\text{Ag}^+]_{\text{R.H.S.}}$$

$$E_{\text{cell}} = \frac{0.059}{1} \log \frac{[\text{Ag}^+]_{\text{R.H.S.}}}{[\text{Ag}^+]_{\text{L.H.S.}}} \quad \dots (i)$$

For L.H.S.  $K_{\text{sp}}$  of  $\text{AgCl} = 2.8 \times 10^{-10}$

$$\text{or } [\text{Ag}^+][\text{Cl}^-] = 2.8 \times 10^{-10}$$

$$\text{or } [\text{Ag}^+] = \frac{2.8 \times 10^{-10}}{[\text{Cl}^-]} = \frac{2.8 \times 10^{-10}}{0.2} = 1.4 \times 10^{-9} \text{ M}$$

For R.H.S.  $K_{\text{sp}}$  of  $\text{AgBr} = 3.3 \times 10^{-13}$

$$\text{or } [\text{Ag}^+][\text{Br}^-] = 3.3 \times 10^{-13}$$

$$\text{or } [\text{Ag}^+] = (3.3 \times 10^{-13}) / 0.001 = 3.3 \times 10^{-10} \text{ M}$$

$\therefore$  By Eq. (i),

$$E_{\text{cell}} = \frac{0.059}{1} \log \frac{3.3 \times 10^{-10}}{1.4 \times 10^{-9}} = -0.037 \text{ V}$$

Thus, to get cell reaction (i.e.  $E_{\text{cell}}$ ,  $E_{\text{cell}} = +ve$ ) polarity of cell

**Example 7:**  $E_{\text{cell}}^{\circ}$  values for

$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$  and  $\text{Fe} \rightarrow \text{Fe}^{3+} + 3e^-$  are 0.440 and 0.036 V respectively:

(a) Design and point out the number of cells showing the overall reaction  $\text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+}$

(b) Also calculate  $E_{\text{cell}}^{\circ}$  and  $\Delta G^{\circ}$  values for each cell. Also comment on the result.

**Sol:** Standard free energy can be calculated using the equation

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

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-; -\Delta G_1^{\circ} = +0.440 \times 2 \times F$$

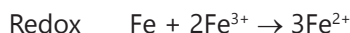
$$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}; -\Delta G_2^{\circ} = -0.036 \times 3 \times F$$

$$\therefore \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}; -\Delta G_3^{\circ} = -(\Delta G_2^{\circ} + \Delta G_1^{\circ})$$

$$-n E^{\circ} F = [2 \times 0.440 - 3 \times 0.036] \times F \quad (n = 1)$$

$$E^{\circ} = +0.772 \text{ V}$$

**Cell no. I:**  $\text{Fe} | \text{Fe}^{2+} || \text{Fe}^{3+} | \text{Fe}$



$$E_{\text{cell}}^{\circ} = E_{\text{OP}_{\text{Fe}|\text{Fe}^{2+}}}^{\circ} + E_{\text{RP}_{\text{Fe}^{3+}|\text{Fe}}}^{\circ} = 0.440 - 0.036 = 0.404 \text{ V}$$

$$\text{Also, } \Delta G^{\circ} = -6 \times 0.404 \times F = -2.424 F$$

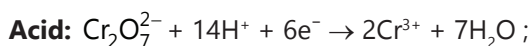
**Cell no. II:**  $\text{Fe} | \text{Fe}^{2+} || \text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$



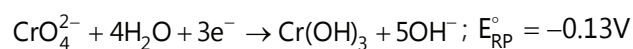
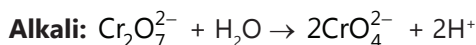
$$E_{\text{cell}}^{\circ} = E_{\text{OP}_{\text{Fe}|\text{Fe}^{2+}}}^{\circ} + E_{\text{RP}_{\text{Fe}^{3+}|\text{Fe}^{2+}}}^{\circ}$$

**Example 8:** Oxidizing power of  $\text{Cr}_2\text{O}_7^{2-}$  is more in acidic medium than in alkaline medium.

**Sol:**  $E_{\text{RP}}^{\circ}$  in acidic medium is more than  $E_{\text{RP}}^{\circ}$  in alkaline medium.

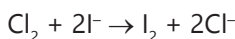
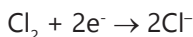
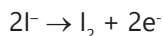


$$E_{\text{RP}}^{\circ} = +1.33 \text{ V}$$



**Example 9:** Color of KI solution containing starch turns blue when  $\text{Cl}_2$  water is added. Explain.

**Sol:** Chlorine placed below iodine in electrochemical series having lesser  $E_{\text{OP}}^\circ$  than iodine and thus, shows reduction whereas  $\text{I}^-$  undergoes oxidation. The  $\text{I}_2$  so formed gets absorbed in starch to give blue color.



**Example 10:** Calculate the e.m.f of the cell.



$$E_{\text{Ag}^+/\text{Ag}}^\circ = +0.8 \text{ volt}, E_{\text{Mg}^{2+}/\text{Mg}}^\circ = -2.37 \text{ volt}$$

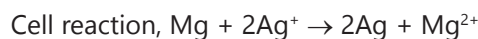
What will be the effect on e.m.f if concentration of  $\text{Mg}^{2+}$  ion is decreased to 0.1 M?

**Sol:** First calculate the standard potential for reaction which is calculated as  $E_{\text{cell}}^\circ = E_{\text{oxidation}}^\circ - E_{\text{reduction}}^\circ$

After calculating  $E_{\text{cell}}^\circ$  e.m.f of the cell can be easily calculated using following equation

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$E_{\text{Cell}}^\circ = E_{\text{Cathode}}^\circ - E_{\text{Anode}}^\circ = 0.80 - (-2.37) = 3.17 \text{ volt}$$



$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 3.17 - \frac{0.0591}{2} \log \frac{0.2}{[1 \times 10^{-3}]^2}$$

$$= 3.17 - 0.1566 = 3.0134 \text{ volt}$$

When  $\text{Mg}^{2+} = 0.1 \text{ M}$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{2} \log \frac{0.1}{(1 \times 10^{-3})^2}$$

$$= (3.17 - 0.1477) \text{ volt} = 3.0223 \text{ volt}$$

## JEE Main/Boards

### Exercise 1

**Q.1** Depict the galvanic cell in which the reaction  $\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$  takes place. Further show:

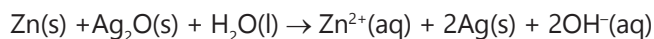
- (i) Which of the electrode is negatively charged?
- (ii) Individual reaction at each electrode.

**Q.2** Electrolytic conductivity of 0.20 mole  $\text{L}^{-1}$  solution of KCl at 298 K is  $2.48 \times 10^{-2} \text{ ohm}^{-1}\text{cm}^{-1}$ . Calculate its molar conductivity.

**Q.3** Write the Nernst equation and e.m.f of the following cells at 298K:

- (i)  $\text{Mg(s)} \mid \text{Mg}^{2+}(0.001\text{M}) \parallel \text{Cu}^{2+}(0.0001 \text{ M}) \mid \text{Cu(s)}$
- (ii)  $\text{Fe(s)} \mid \text{Fe}^{2+}(0.001\text{M}) \parallel \text{H}^+(1\text{M}) \mid \text{H}_2(\text{g})(1\text{bar}) \mid \text{Pt(s)}$
- (iii)  $\text{Sn(s)} \mid \text{Sn}^{2+}(0.050 \text{ M}) \parallel \text{H}^+(0.020 \text{ M}) \mid \text{H}_2(\text{g})(1 \text{ bar}) \mid \text{Pt(s)}$
- (iv)  $\text{Pt(s)} \mid \text{Br}_2(\text{l}) \mid \text{Br}^-(0.010 \text{ M}) \parallel \text{H}^+(0.030 \text{ M}) \mid \text{H}_2(\text{g})(1 \text{ bar}) \mid \text{Pt(s)}$

**Q.4** In the button cells widely used in watches and other devices the following reaction takes place:



Determine  $\Delta_r G'$  and  $E'$  for the reaction.

**Q.5** The conductivity of 0.20 M solution of KCl at 298 K is  $0.0248 \text{ S cm}^{-1}$ . Calculate its molar conductivity.

**Q.6** How much electricity in terms of faraday is required to produce

- (i) 20.0 g of Ca from molten  $\text{CaCl}_2$ ?
- (ii) 40.0 g of Al from molten  $\text{Al}_2\text{O}_3$ ?

**Q.7** How much electricity is required in coulomb for the oxidation of:

- (i) 1 mole of  $\text{H}_2\text{O}$  to  $\text{O}_2$ ?
- (ii) 1 mole of  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$ ?

**Q.8** The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500  $\Omega$ . What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is  $0.146 \times 10^{-3} \text{ S cm}^{-1}$ ?

**Q.9** Conductivity of 0.00241 M acetic acid is  $7.896 \times 10^{-5} \text{ S cm}^{-1}$ . Calculate its molar conductivity. If  $\Lambda_{\infty}^0$  for acetic acid is  $390.5 \text{ S cm}^2 \text{ mole}^{-1}$ , what is its dissociation constant?

**Q.10** A solution of  $\text{Ni}(\text{NO}_3)_2$  is electrolyzed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni deposited at the cathode?

**Q.11** The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

**Concentration M**

0.001      0.010      0.020      0.050      0.100

**$10^2 \times \text{k/S m}^{-1}$**

1.237      11.85      23.15      55.53      106.74

Calculate  $\Lambda_{\infty}$  for all concentrations and draw a plot between  $\Lambda_{\infty}$  and S. Find the values of  $\Lambda_{\infty}^0$

**Q.12** Three electrolytic cells A, B, C containing solution of  $\text{ZnSO}_4$ ,  $\text{AgNO}_3$  and  $\text{CuSO}_4$ , respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

**Q.13** Using the standard electrode potentials of electrochemical series, predict if the reaction between the following is feasible:

- (i)  $\text{Fe}^{3+}(\text{aq})$  and  $\text{I}^{-}(\text{aq})$       (ii)  $\text{Ag}^{+}(\text{aq})$  and  $\text{Cu}(\text{s})$   
 (iii)  $\text{Fe}^{3+}(\text{aq})$  and  $\text{Br}^{-}(\text{aq})$       (iv)  $\text{Ag}(\text{s})$  and  $\text{Fe}^{3+}(\text{aq})$   
 (v)  $\text{Br}_2(\text{aq})$  and  $\text{Fe}^{2+}(\text{aq})$ .

**Q.14** The standard electrode potentials of  $\text{Cu}^{2+}|\text{Cu}^{+}$  and  $\text{Cu}^{+}|\text{Cu}$  electrodes are +0.18 V and +0.50 V, respectively. Calculate the standard potential of  $\text{Cu}^{2+}|\text{Cu}$  electrode.

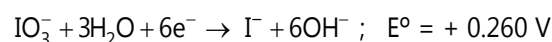
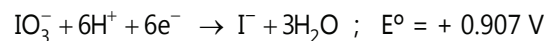
**Q.15** Arrange Zn, Pb and Al in the increasing order of their reducing power under standard conditions.

Given:  $E_{\text{Zn}^{2+}|\text{Zn}}^{\circ} = -0.76 \text{ V}$ ,  $E_{\text{Pb}^{2+}|\text{Pb}}^{\circ} = -0.13 \text{ V}$ ,  $E_{\text{Al}^{3+}|\text{Al}}^{\circ} = -1.66 \text{ V}$

**Q.16** The standard electrode potentials of  $\text{Ag}^{+}|\text{Ag}$ ,  $\text{Cl}_2|\text{Cl}^{-}$  and  $\text{O}_3|\text{O}_2$  electrodes are +0.80V, +1.36V and +2.07 V, respectively. Using these information, answer the following:

- (i) Which of the following is strongest oxidizing agent:  $\text{Ag}^{+}$ ,  $\text{Cl}_2$ , and  $\text{O}_3$ ?  
 (ii) Which of the following is the strongest oxidizing agent:  $\text{Ag}$ ,  $\text{Ag}^{+}$ ,  $\text{O}_3$ , and  $\text{O}_2$ ?  
 (iii) Which of the following is the strongest reducing agent:  $\text{Ag}$ ,  $\text{Cl}^{-}$ , and  $\text{O}_2$ ?  
 (iv) Which of the following is the strongest reducing agent:  $\text{Ag}$ ,  $\text{Ag}^{+}$ ,  $\text{O}_3$ , and  $\text{O}_2$ ?

**Q.17** The following reactions represent the reduction of  $\text{IO}_3^{-}$  ion into  $\text{I}^{-}$  ion in acidic and basic medium.



[Acid Medium]

**Q.18** Can  $\text{Fe}^{3+}$  oxidize  $\text{Br}^{-}$  to  $\text{Br}$  under standard conditions?

Given:  $E_{\text{Fe}^{3+}|\text{Fe}^{2+}}^{\circ} = + 0.77 \text{ V}$ ,  $E_{\text{Br}_2|\text{Br}^{-}}^{\circ} = + 1.09 \text{ V}$

**Q.19** Calculate the electrode potential of the following electrodes at 25°C:

(i)  $\text{Cu}^{2+} (0.001 \text{ M}) | \text{Cu} ; E_{\text{Cu}^{3+}|\text{Cu}}^{\circ} = + 0.34 \text{ V}$

(ii)  $\text{Zn} | \text{Zn}^{2+} (0.02 \text{ M}) ; E_{\text{Zn}^{2+}|\text{Zn}}^{\circ} = -0.76 \text{ V}$

(iii)  $\text{AgCl} (\text{stand. sol}) | \text{Ag} ; E_{\text{Ag}^{+}|\text{Ag}}^{\circ} = +0.80 \text{ V}$ ,  $K_{\text{sp}}$  of  $\text{AgCl} = 2 \times 10^{-10}$ .

(iv)  $\text{Pt} | \text{Cl}_2 (0.5 \text{ atm}) | \text{Cl}^{-} (0.02 \text{ M}) ; E_{\text{Cl}_2|\text{Cl}^{-}}^{\circ} = 1.36 \text{ V}$

(v)  $\text{HCl} (\text{pH} = 4.4) | \text{H}_2 (2 \text{ atm}) | \text{Pt}$

**Q.20** Calculate the reduction potential at 25°C for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  electrode if the concentration of  $\text{Fe}^{2+}$  ion is five times that of  $\text{Fe}^{3+}$  ion.

$E_{\text{Fe}^{3+}|\text{Fe}^{2+}}^{\circ} = 0.77 \text{ volt}$ .

**Q.21** Calculate electrode potential for the half-cell  $\text{Pt}|\text{H}_2 (1 \text{ atm}) | 0.357 \text{ M} - \text{CH}_3\text{COOH}$ .  $K_{\text{a}}$  for  $\text{CH}_3\text{COOH} = 1.74 \times 10^{-5}$ .

**Q.22** The standard reduction potential for  $\text{Cu}^{2+}|\text{Cu}$  is +

0.34 V. Calculate the reduction potential at pH = 13 for the above couple.  $K_{sp}$  of  $\text{Cu}(\text{OH})_2$  is  $1.0 \times 10^{-10}$ .

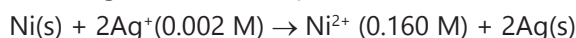
**Q.23** Calculate

(i)  $E^\circ_{\text{Cl}^+|\text{AgCl}|\text{Ag}}$  ;  $E^\circ_{\text{Ag}^+|\text{Ag}} = 0.80 \text{ V}$ ,  $K_{sp}$  of  $\text{AgCl} = 2 \times 10^{-10}$

(ii)  $E^\circ_{\text{Cl}^-(0.004\text{M})|\text{AgCl}|\text{Ag}}$  ;  $E^\circ_{\text{Ag}^+|\text{Ag}} = + 0.80 \text{ V}$ ,

$K_{sp}$  of  $\text{AgCl} = 2 \times 10^{-10}$

**Q.24** Calculate the e.m.f of the cell in which the following reaction takes place:



Given that  $E^\circ_{\text{cell}} = 1.05 \text{ V}$

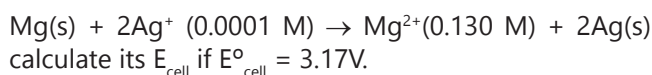
**Q.25** The molar conductivity of 0.025 mole methanoic acid is  $46.1 \text{ S cm}^2 \text{ mole}^{-1}$ . Calculate its degree of dissociation and dissociation constant.

Given  $\Lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol/L}$  and

$\lambda^\circ(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol/L}$ .

**Q.26** Suggest a list of metals that are extracted electrolytically.

**Q.27** Represent the cell in which following reaction takes place:



**Q.28** Calculate the reduction potential of the following electrodes:

(a)  $\text{Pt}_2 \text{H}_2(4 \text{ atm}) | \text{H}_2\text{SO}_4(0.01 \text{ M})$

(b)  $\text{Pt}_2 \text{H}_2(1 \text{ atm}) | \text{HCl}(0.2 \text{ M})$

(c) Calculate the potential of hydrogen electrode in contact with a solution whose

(i) pH = 5 (ii) pOH = 4

**Q.29** Calculate the equivalent conductivity of 1M  $\text{H}_2\text{SO}_4$  solution, if its conductivity is  $26 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

## Exercise 2

### Single Correct Choice Type

**Q.1** One gm. metal  $\text{M}^{+2}$  was discharged by the passage of  $1.81 \times 10^{22}$  electrons. What is the atomic weight of metal?

(A) 33.35 (B) 133.4 (C) 66.7 (D) 55

**Q.2** One mole of electron passes through each of the solution of  $\text{AgNO}_3$ ,  $\text{CuSO}_4$  and  $\text{AlCl}_3$  when Ag, Cu and Al are deposited at cathode. The molar ratio of Ag, Cu and Al deposited are:

(A) 1: 1: 1 (B) 6: 3: 2 (C) 6: 3: 1 (D) 1: 3: 6

**Q.3** Salts of A (atomic weight = 7), B (atomic weight = 27) and C (atomic weight = 48) were electrolyzed under identical conditions using the same quantity of electricity. It was found that when 2.1 g of A was deposited, the weights of B and C deposited were 2.7 and 7.2 g. The valencies of A, B and C respectively are:

(A) 3, 1 and 2 (B) 1, 3 and 2

(C) 3, 1 and 3 (D) 2, 3 and 2

**Q.4** The density of Cu is  $8.94 \text{ g cm}^{-3}$ . The quantity of electricity needed to plate an area  $10 \text{ cm} \times 10 \text{ cm}$  to a thickness of  $10^{-2} \text{ cm}$  using  $\text{CuSO}_4$  solution would be

(A) 13586 C (B) 27172 C

(C) 40758 (D) 20348 C

**Q.5** During electrolysis of an aqueous solution of sodium sulphate, 2.4L of oxygen at STP was liberated at anode. The volume of hydrogen at STP, liberated at cathode would be

(A) 1.2 L (B) 2.4 L (C) 2.6 L (D) 4.8 L

**Q.6** When an aqueous solution of lithium chloride is electrolyzed using graphite electrodes

(A)  $\text{Cl}_2$  is liberated at the anode

(B) Li is deposited at the cathode

(C) As the current flows, pH of the solution around the cathode remains constant

(D) As the current flows, pH of the solution around the cathode decreases.

**Q.7** A standard hydrogen electrode has zero electrode potential because

(A) Hydrogen is easier to oxidize

(B) This electrode potential is assumed to be zero

(C) Hydrogen atom has only one electron

(D) Hydrogen is the lightest element.

**Q.8** If the pressure of  $\text{H}_2$  gas is increased from 1 atm to 100 atm keeping  $\text{H}^+$  concentration constant at 1 M, the change in reduction potential of hydrogen half-cell at  $25^\circ\text{C}$  will be

(A) 0.059 V (B) 0.59 V (C) 0.0295 V (D) 0.118 V



**Q.9** The equilibrium constant for the reaction  $\text{Sr}(s) + \text{Mg}^{2+}(\text{aq}) \rightarrow \text{Sr}^{2+}(\text{aq}) + \text{Mg}(s)$  is  $2.69 \times 10^{12}$  at  $25^\circ\text{C}$

The  $E^\circ$  for a cell made up of the  $\text{Sr}/\text{Sr}^{2+}$  and  $\text{Mg}^{2+}/\text{Mg}$  half-cells

- (A) 0.3667 V (B) 0.7346 V  
(C) 0.1836 V (D) 0.1349 V

**Q.10** A silver wire dipped in 0.1 M HCl solution saturated with AgCl develop a potential of  $-0.25$  V. If  $E^\circ_{\text{Ag}/\text{Ag}^+} = -0.799$  V, the  $K_{\text{sp}}$  of AgCl in pure water will be:

- (A)  $2.95 \times 10^{-11}$  (B)  $5.1 \times 10^{-11}$   
(C)  $3.95 \times 10^{-11}$  (D)  $1.95 \times 10^{-11}$

**Q.11** During electrolysis of an aqueous solution of  $\text{CuSO}_4$  using copper electrodes, if 2.5 g of Cu is deposited at cathode, then at anode

- (A) 890 ml of  $\text{Cl}_2$  at STP is liberated  
(B) 445 ml of  $\text{O}_2$  at STP is liberated  
(C) 2.5 g of copper is deposited  
(D) A decrease of 2.5 g of mass takes place

**Q.12** The cost at 5 paise / KWH of operating an electric motor for 8 hours which takes 15 amp at 110 V is

- (A) Rs 66 (B) 66 paise  
(C) 37 paise (D) Rs. 6.60

**Q.13** The resistance of 0.5 M solution of an electrolyte in a cell was found to be  $50\Omega$ . If the electrodes in the cell are 2.2 cm apart and have an area of  $4.4 \text{ cm}^2$  then the molar conductivity (in  $\text{S m}^2 \text{ mole}^{-1}$ ) of the solution is

- (A) 0.2 (B) 0.02 (C) 0.002 (D) None of these

**Q.14** Equivalent conductance of 0.1 M HA (weak acid) solution is  $10 \text{ S cm}^2 \text{ equivalent}^{-1}$  and that at infinite dilution is  $200 \text{ S cm}^2 \text{ equivalent}^{-1}$  Hence pH of HA solution is

- (A) 1.3 (B) 1.7 (C) 2.3 (D) 3.7

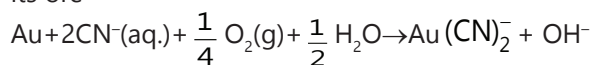
**Q.15** If  $x$  is specific resistance of the electrolyte solution and  $y$  is the molarity of the solution, then  $\Lambda_m$  is given by

- (A)  $\frac{1000x}{y}$  (B)  $1000\frac{y}{x}$   
(C)  $\frac{1000}{xy}$  (D)  $\frac{xy}{1000}$

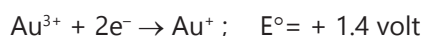
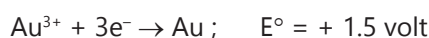
**Q.16** The dissociation constant of n-butyric acid is  $1.6 \times 10^{-5}$  and the molar conductivity at infinite dilution is  $380 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ . The specific conductance of the 0.01 M acid solution is

- (A)  $1.52 \times 10 \text{ S m}^{-1}$  (B)  $1.52 \times 10^{-2} \text{ S m}^{-1}$   
(C)  $1.52 \times 10^{-3} \text{ S m}^{-1}$  (D) None of these

**Q.17** Consider the reaction of extraction of gold from its ore

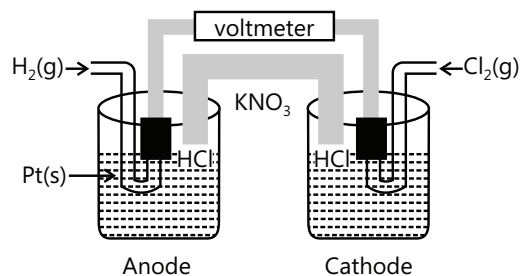


Use the following data to calculate  $\Delta G^\circ$  for the reaction,  $K_f\{\text{Au}(\text{CN})_2\} = X$



- (A)  $-RT \ln X + 1.29 F$  (B)  $-RT \ln X - 2.11 F$   
(C)  $-RT \ln \frac{1}{X} + 2.11 F$  (D)  $-RT \ln X - 1.29 F$

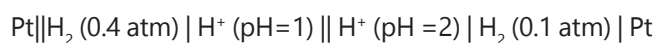
**Q.18** Consider the following Galvanic cell



By what value the voltage change when concentration of ions in anodic and cathodic compartments both increases by factor of 10 at 298 K

- (A) 0.0591 (B)  $-0.0591$  (C)  $-0.1182$  (D) 0

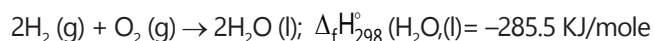
**Q.19** For the cell



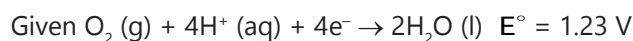
The measured potential at  $25^\circ\text{C}$  is

- (A)  $-0.1 \text{ V}$  (B)  $-0.5$  (C)  $-0.041$  (D) None of these

**Q.20** For the fuel cell reaction:



What is  $\Delta S_{298}^\circ$  for the given fuel cell reaction?



- (A)  $-0.322 \text{ J/K}$  (B)  $-0.635 \text{ kJ/K}$   
(C)  $3.51 \text{ kJ/K}$  (D)  $-0.322 \text{ kJ/K}$

**Q.21** The standard reduction potentials of  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Cu}^{2+}/\text{Cu}^+$  are 0.337 and 0.153 V respectively. The standard electrode potential of  $\text{Cu}^+/\text{Cu}$  half-cell is:

- (A) 0.184 V                      (B) 0.827 V  
(C) 0.521 V                      (D) 0.490 V

## Previous Years' Questions

**Q.1** When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are **(2002)**

Cathode	Anode
(a) Pure zinc	Pure copper
(b) Impure sample	Pure copper
(c) Impure zinc	Impure sample
(d) Pure copper	Impure sample

**Q.2** In the electrolytic cell, flow of electrons is from **(2003)**

- (A) Cathode to anode in solution  
(B) Cathode to anode through external supply  
(C) Cathode to anode through internal supply  
(D) Anode to cathode through internal supply

**Q.3** During the electrolysis of a solution of  $\text{AgNO}_3$ , 9650 coulombs of charge pass through the electroplating both, the mass of silver deposited in the cathode will be **(2003)**

- (A) 1.08 g    (B) 10.8 g    (C) 21.6 g    (D) 108 g

**Q.4** During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud.' These are **(2005)**

- (A) Sn and Ag                      (B) Pb and Zn  
(C) Ag and Au                      (D) Fe and Ni

**Q.5** Conductivity (unit Siemen's) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is **(2002)**

- (A)  $\text{S m mole}^{-1}$                       (B)  $\text{S m}^2 \text{ mole}^{-1}$   
(C)  $\text{S}^{-2} \text{ m}^2 \text{ mole}$                       (D)  $\text{S}^2 \text{ m}^2 \text{ mole}^{-2}$

**Q.6** The highest electrical conductivity of the following aqueous solution is of **(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

**Q.7** The equivalent conductance's of two strong electrolytes at infinite dilution in  $\text{H}_2\text{O}$  (where ions move freely through a solution) at  $25^\circ\text{C}$  are given below: At  $25^\circ\text{C}$  are given below: **(2007)**

$$\Lambda_{\text{CH}_3\text{COONa}}^\circ = 91.0 \text{ S cm}^2 / \text{equivalent}$$

$$\Lambda_{\text{HCl}}^\circ = 426.2 \text{ S cm}^2/\text{equivalent}$$

What additional information/quantity one needs to calculate  $\Lambda^\circ$  of an aqueous solution of acetic acid

- (A)  $\Lambda^\circ$  of NaCl  
(B)  $\Lambda^\circ$  of  $\text{CH}_3\text{COOK}$   
(C) The limiting equivalent conductance of  $\text{H}^+$  ( $\Lambda^\circ\text{H}^+$ )  
(D)  $\Lambda^\circ$  of chloroacetic acid ( $\text{Cl}/\text{CH}_2\text{COOH}$ )

**Q.8** The molar conductivities  $\lambda_{\text{NaOAc}}^\circ$  and  $\lambda_{\text{HCl}}^\circ$  at infinity dilution in water at  $25^\circ\text{C}$  are 91.0 and 426.2  $\text{S cm}^2/\text{mole}$  respectively. To calculate  $\lambda_{\text{HOAc}}^\circ$ , the additional value required is **(2006)**

- (A)  $\lambda_{\text{H}_2\text{O}}^\circ$     (B)  $\lambda_{\text{KCl}}^\circ$     (C)  $\lambda_{\text{NaOH}}^\circ$     (D)  $\lambda_{\text{NaCl}}^\circ$

**Q.9** Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100  $\Omega$ . The conductivity of this solution is  $1.29 \text{ S m}^{-1}$ . Resistance of the same cell when filled with 0.2 M of the same solution is 520  $\Omega$ . The molar conductivity of 0.02 M solution of the electrolyte will be **(2006)**

- (A)  $12.4 \times 10^{-4} \text{ S m}^2 \text{ mole}^{-1}$   
(B)  $1240 \times 10^{-4} \text{ S m}^2 \text{ mole}^{-1}$   
(C)  $1.24 \times 10^{-4} \text{ S m}^2 \text{ mole}^{-1}$   
(D)  $1.24 \times 10^{-4} \text{ S m}^2 \text{ mole}^{-1}$

**Q.10** Saturated solution of  $\text{KNO}_3$  is used to make 'salt-bridge' because **(2002)**

- (A) Velocity of  $\text{K}^+$  is greater than that of  $\text{NO}_3^-$   
(B) Velocity of  $\text{NO}_3^-$  is greater than that of  $\text{K}^+$   
(C) Velocities of both  $\text{K}^+$  and  $\text{NO}_3^-$  are nearly the same  
(D)  $\text{KNO}_3$  is highly soluble in water

**Q.11** The reduction potential of hydrogen half-cell will be negative if **(2011)**

- (A)  $P_{(H_2)} = 1 \text{ atm}$  and  $[H^+] = 2.0 \text{ M}$   
 (B)  $P_{(H_2)} = 1 \text{ atm}$  and  $[H^+] = 1.0 \text{ M}$   
 (C)  $P_{(H_2)} = 2 \text{ atm}$  and  $[H^+] = 1.0 \text{ M}$   
 (D)  $P_{(H_2)} = 2 \text{ atm}$  and  $[H^+] = 2.0 \text{ M}$

**Q.12** The cell,  $Zn|Zn^{2+} (1M) || Cu^{2+} (1M) |Cu$  ( $E_{\text{cell}}^\circ = 1.10 \text{ V}$ ) was allowed to be completely discharged at 298 K. The relative concentration of  $Zn^{2+}$  to

$Cu^{2+} \left[ \frac{Zn^{2+}}{[Cu^{2+}]} \right]$  is **(2007)**

- (A) Antilog (24.08)      (B) 37.3  
 (C)  $10^{37.3}$               (D)  $9.65 \times 10^4$

**Q.13** The standard reduction potential for  $Fe^{2+}/Fe$  and  $Sn^{2+}/Sn$  electrodes are  $-0.44$  and  $-0.14$  volt respectively, For the given cell reaction  $Fe^{2+} + Sn \rightarrow Fe + Sn^{2+}$ , the standard EMF is **(1990)**

- (A)  $+0.30 \text{ V}$       (B)  $-0.58 \text{ V}$       (C)  $+0.58 \text{ V}$       (D)  $-0.30 \text{ V}$

**Q.14** Given  $E_{Fe^{3+}/Fe}^\circ = -0.036 \text{ V}$ ,  $E_{Fe^{2+}/Fe}^\circ = -0.439 \text{ V}$   
 The value of standard electrode potential for the change,  $Fe_{(aq)}^{3+} + e^- \rightarrow Fe^{2+}(aq)$  will be

- (A)  $-0.072 \text{ V}$               (B)  $0.385 \text{ V}$   
 (C)  $0.770 \text{ V}$               (D)  $-0.270 \text{ V}$

**Q.15** For the redox reaction:

$Zn_{(s)} + Cu^{2+} (0.1M) \rightarrow Zn^{2+} (1M) + Cu_{(2)}$  taking place in a cell,  $E_{\text{cell}}^\circ$  is 1.10 volt.  $E_{\text{cell}}$  for the cell will be

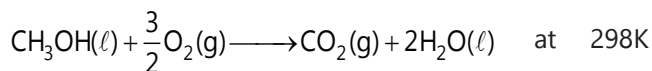
$\left( 2.303 \frac{RT}{F} = 0.0591 \right)$  **(2003)**

- (A) 2.14 volt              (B) 1.80 volt  
 (C) 1.07 volt              (D) 0.82 volt

**Q.16** Given  $E_{Cr^{3+}/Cr}^\circ = -0.72 \text{ V}$ ,  $E_{Fe^{2+}/Fe}^\circ = -0.42 \text{ V}$ .  
 The potential for the cell  $Cr|Cr^{3+} (0.1M)||Fe^{2+}(0.01M)|Fe$  is **(2008)**

- (A) 0.26 V      (B) 0.399 v      (C) -0.339 V      (D) -0.26 V

**Q.17.** In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is



standard Gibb's energies of formation for  $CH_3OH(\ell)$ ,  $H_2O(\ell)$  and  $CO_2(g)$  are  $-166.2$ ,  $-237.2$  and  $394.4 \text{ kJ mol}^{-1}$  respectively. If standard enthalpy of combustion of methanol is  $-726 \text{ kJ mol}^{-1}$ , efficiency of the fuel cell will be **(2009)**

- (A) 80 %      (B) 87%      (C) 90%      (D) 97%

**Q.18** Given:  $E_{Fe^{3+}/Fe}^\circ = -0.036 \text{ V}$ ,  $E_{Fe^{2+}/Fe}^\circ = -0.439 \text{ V}$ .  
 The value of standard electron potential for the change,  $Fe_{(aq)}^{3+} + e^- \longrightarrow Fe^{2+}(aq)$  will be: **(2009)**

- (A)  $-0.072 \text{ V}$       (B)  $0.385 \text{ V}$       (C)  $0.770 \text{ V}$       (D)  $-0.270$

**Q.19** The reduction potential of hydrogen half-cell will be negative if: **(2011)**

- (A)  $p(H_2) = 1 \text{ atm}$  and  $[H^+] = 1.0 \text{ M}$   
 (B)  $p(H_2) = 2 \text{ atm}$  and  $[H^+] = 1.0 \text{ M}$   
 (C)  $p(H_2) = 2 \text{ atm}$  and  $[H^+] = 2.0 \text{ M}$   
 (D)  $p(H_2) = 1 \text{ atm}$  and  $[H^+] = 2.0 \text{ M}$

**Q.20** The standard reduction potentials for  $Zn^{2+}/Zn$ ,  $Ni^{2+}/Ni$ , and  $Fe^{2+}/Fe$  are  $-0.76$ ,  $-0.23$  and  $-0.44 \text{ V}$  respectively. The reaction  $X + Y^{2+} \longrightarrow X^{2+} + Y$  will be spontaneous when: **(2012)**

- (A)  $X = Ni$ ,  $Y = Fe$       (B)  $X = Ni$ ,  $Y = Zn$   
 (C)  $X = Fe$ ,  $Y = Zn$       (D)  $X = Zn$ ,  $Y = Ni$

**Q.21** Given:  $E_{Cr^{3+}/Cr^{3+}}^\circ = -0.74 \text{ V}$ ;  $E_{MnO_4^-/Mn^{2+}}^\circ = 1.51 \text{ V}$

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

Based on the data given above, strongest oxidising agent will be: **(2013)**

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

**Q.22** The equivalent conductance of NaCl at concentration C and at infinite dilution are  $\lambda_c$  and  $\lambda_\infty$ , respectively. The correct relationship between  $\lambda_c$  and  $\lambda_\infty$  is given as (Where the constant B is positive) **(2014)**

- (A)  $\lambda_c = \lambda_\infty + (B)C$               (B)  $\lambda_c = \lambda_\infty - (B)C$   
 (C)  $\lambda_c = \lambda_\infty - (B)\sqrt{C}$               (D)  $\lambda_c = \lambda_\infty + (B)\sqrt{C}$

**Q.23** Given below are the half-cell reactions

(2014)



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

- (A)  $-2.69 \text{ V}$ ; the reaction will not occur  
 (B)  $-2.69 \text{ V}$ ; the reaction will occur  
 (C)  $-0.33 \text{ V}$ ; the reaction will not occur  
 (D)  $-0.33 \text{ V}$ ; the reaction will occur

**Q.24** Two Faraday of electricity is passed through a solution of  $\text{CuSO}_4$ . The mass of copper deposited at the cathode is: (at. mass of  $\text{Cu} = 63.5 \text{ amu}$ )

(2015)

- (A) 0 g      (B) 63.5 g      (C) 2 g      (D) 127 g

## JEE Advanced/Boards

### Exercise 1

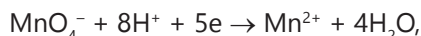
**Q.1** The standard reduction potential values,  $E^\circ (\text{Bi}^{3+}|\text{Bi})$  and  $E^\circ (\text{Cu}^{2+}|\text{Cu})$  are  $0.226 \text{ V}$  and  $0.344 \text{ V}$  respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolyzed at  $25^\circ\text{C}$ . To what value can  $[\text{Cu}^{2+}]$  be brought down before bismuth starts to deposit, in electrolysis.

**Q.2** The cell  $\text{Pt}, \text{H}_2 (1 \text{ atm}) | \text{H}^+ (\text{pH} = x) || \text{Normal calomel electrode}$  has an EMF of  $0.67 \text{ V}$  at  $25^\circ\text{C}$ . Calculate the pH of the solution. The oxidation potential of the calomel electrode on hydrogen scale is  $-0.28 \text{ V}$ .

**Q.3** Voltage of the cell  $\text{Pt}, \text{H}_2 (1 \text{ atm}) | \text{HOCN} (1.3 \times 10^{-3} \text{ M}) || \text{Ag}^+ (0.8 \text{ M}) | \text{Ag}(\text{s})$  is  $0.982 \text{ V}$ . Calculate the  $K_a$  for  $\text{HOCN}$ . Neglect  $[\text{H}^+]$  because of oxidation of  $\text{H}_2$  (g).

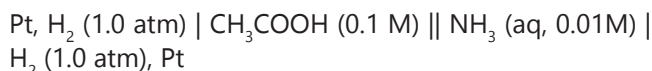


**Q.4** Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained  $0.1 \text{ M MnO}_4^-$  and  $0.8 \text{ M H}^+$  and which was treated with 90% of the  $\text{Fe}^{2+}$  necessary to reduce all the  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ .



$$E^\circ = 1.51 \text{ V}$$

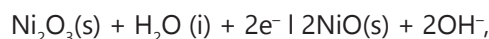
**Q.5** Calculate the e.m.f of the cell



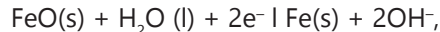
$$K_a (\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$$

$$K_b (\text{NH}_3) = 1.8 \times 10^{-5}$$

**Q.6** The Edison storage cell is represented as  $\text{Fe}(\text{s}) | \text{FeO}(\text{s}) | \text{KOH} (\text{aq}) | \text{Ni}_2\text{O}_3(\text{s}) | \text{Ni}(\text{s})$  the half-cell reaction are



$$E^\circ = +0.40 \text{ V}$$

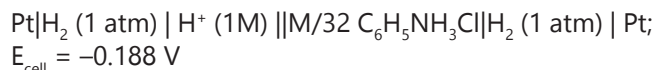


$$E^\circ = -0.87 \text{ V}$$

- (i) What is the cell reaction?  
 (ii) What is the cell e.m.f.? How does it depend on the concentration of  $\text{KOH}$ ?  
 (iii) What is the maximum amount of electrical energy that can be obtained from one mole of  $\text{Ni}_2\text{O}_3$ ?

**Q.7** The standard reduction potential for  $\text{Cu}^{2+}/\text{Cu}$  is  $0.34 \text{ V}$ . Calculate the reduction potential at  $\text{pH} = 14$  for the above couple.  $K_{sp}$  of  $\text{Cu}(\text{OH})_2$  is  $1 \times 10^{-19}$ .

**Q.8** Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride in  $M/32$  solution of salt at  $298 \text{ K}$  from the following cell data at  $298 \text{ K}$ .



**Q.9** The e.m.f of the cell,  $\text{Pt} | \text{H}_2 (1 \text{ atm}), | \text{H}^+ (0.1 \text{ M}, 30 \text{ ml}) || \text{Ag}^+ (0.8 \text{ M}) | \text{Ag}$  is  $0.9 \text{ V}$ . Calculate the e.m.f when  $40 \text{ ml}$  of  $0.05 \text{ M NaOH}$  is added.

**Q.10** The e.m.f of the cell  $\text{Ag} | \text{AgI} | \text{KI} (0.05 \text{ M}) || \text{AgNO}_3 (0.05 \text{ M}) | \text{Ag}$  is  $0.788 \text{ V}$ . Calculate the solubility product of  $\text{AgI}$ .

**Q.11** Consider the cell

Ag | AgBr(s) Br<sup>-</sup> || AgCl(s), Ag | Cl<sup>-</sup> at 25°C. The solubility product constants of AgBr & AgCl are respectively  $5 \times 10^{-13}$  &  $1 \times 10^{-10}$ . For what ratio of the concentration of Br<sup>-</sup> and Cl<sup>-</sup> ions would the e.m.f of the cell be zero?

**Q.12** The  $pK_{sp}$  of AgI is 16.07. If the  $E^\circ$  value for Ag<sup>+</sup>|Ag is 0.7991 V. Find the  $E^\circ$  for the half-cell reaction AgI (s) + e<sup>-</sup> → Ag + I<sup>-</sup>

**Q.13** For the galvanic cell: Ag AgCl(s) | KCl (0.2 M) || KBr (0.001 M) | AgBr(s) | Ag, Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C.

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

**Q.14** Given,  $E^\circ = -0.268$  V for the Cl<sup>-</sup>|PbCl<sub>2</sub>|Pb couple and  $-0.126$  V for the Pb<sup>2+</sup>|Pb couple, determine  $K_{sp}$  for PbCl<sub>2</sub> at 25°C?

**Q.15** Calculate the voltage, E, of the cell at 25°C

Mn(s) | Mn(OH)<sub>2</sub>(s) | Mn<sup>2+</sup> (xM), OH<sup>-</sup> (1.00 × 10<sup>-4</sup>M) || Cu<sup>2+</sup> (0.675 M) | Cu(s) given that  $K_{sp} = 1.9 \times 10^{-13}$  for Mn(OH)<sub>2</sub>(s)  $E^\circ$  (Mn<sup>2+</sup>/Mn) =  $-1.18$  V

**Q.16** Calculate the voltage, E, of the cell

Ag(s) | AgIO<sub>3</sub>(s) | Ag<sup>+</sup>(x M), HIO<sub>3</sub> (0.300 M) || Zn<sup>2+</sup> (0.175 M) | Zn(s) if  $K_{sp} = 3.02 \times 10^{-8}$  for AgIO<sub>3</sub>(s) and  $K_a = 0.162$  for HIO<sub>3</sub>.

**Q.17** The voltage of the cell

Pb(s) || PbSO<sub>4</sub>(s) | NaHSO<sub>4</sub> (0.600 M) || Pb<sup>2+</sup> (2.50 × 10<sup>-5</sup>M) | Pb(s) is E = +0.061 V. Calculate  $K_2 = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$ , the dissociation constant for HSO<sub>4</sub><sup>-</sup>. Given Pb(s) + SO<sub>4</sub><sup>2-</sup>(aq) → PbSO<sub>4</sub>(s) + 2e<sup>-</sup> ( $E^\circ = 0.356$ )  $E^\circ$  (Pb<sup>2+</sup>/Pb) =  $-0.126$  V

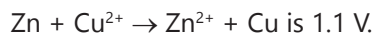
**Q.18** The voltage of the cell

Zn(s) | Zn(CN)<sub>4</sub><sup>2-</sup>(0.450M), CN<sup>-</sup>(2.65 × 10<sup>-3</sup>M) || Zn<sup>2+</sup> (3.84 × 10<sup>-4</sup>M) | Zn(s) is E = + 0.099 V. Calculate the constant  $K_f$  for

Zn<sup>2+</sup> + 4CN<sup>-</sup> → Zn(CN)<sub>4</sub><sup>2-</sup>, the only Zn<sup>2+</sup> + CN<sup>-</sup> complexation reaction of importance.

**Q.19** Given the standard reduction potentials Ti<sup>+</sup> + e<sup>-</sup> → Ti,  $E^\circ = -0.34$  V and Ti<sup>3+</sup> + 2e<sup>-</sup> → Ti<sup>+</sup>,  $E^\circ = 1.25$  V. Examine the spontaneity of the reaction, 3Ti<sup>+</sup> → 2Ti + Ti<sup>3+</sup>. Also find  $E^\circ$  for this disproportionation.

**Q.20** Estimate the cell potential of a daniel cell having 1 M Zn<sup>2+</sup> & originally having 1 M Cu<sup>2+</sup> after sufficient NH<sub>3</sub> has been added to the cathode compartment to make NH<sub>3</sub> concentration 2M.  $K_f$  for [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> =  $1. \times 10^{12}$ ,  $E^\circ$  for the reaction,



**Q.21** The normal oxidation potential of Zn referred to SHE is 0.76 and that of Cu is  $-0.34$  V at 25°C. When excess of Zn is added to CuSO<sub>4</sub>, Zn displaces Cu<sup>2+</sup> till equilibrium is reached. What is the ratio of Zn<sup>2+</sup> to Cu<sup>2+</sup> ions at equilibrium?

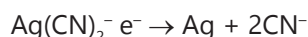
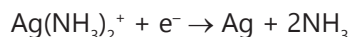
**Q.22**  $K_d$  for complete dissociation of [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> into Ag<sup>+</sup> and 2NH<sub>3</sub> is  $6 \times 10^{-8}$ . Calculate  $E^\circ$  for the following half reaction; Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> + e<sup>-</sup> → Ag + 2NH<sub>3</sub>



**Q.23** The overall formation constant for the reaction of 6 mole of CN<sup>-</sup> with cobalt (II) is  $1 \times 10^{19}$ . The standard reduction potential for the reaction

[Co(CN)<sub>6</sub>]<sup>3-</sup> + e<sup>-</sup> → Co(CN)<sub>6</sub><sup>4-</sup> is  $-0.83$  V. Calculate the formation constant of [Co(CN)<sub>6</sub>]<sup>3-</sup> Given Co<sup>3+</sup> + e<sup>-</sup> → Co<sup>2+</sup>;  $E^\circ = 1.82$  V

**Q.24** Calculate  $E^\circ$  for the following reactions at 298 K,

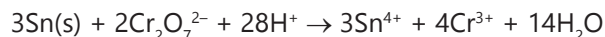


Given:  $E^\circ_{\text{Ag}^+|\text{Ag}} = 0.7991$  V,

$$K_{\text{ins}} [\text{Ag}(\text{NH}_3)_2^+] = 6.02 \times 10^{-8} \text{ and}$$

$$K_{\text{ins}} [\text{Ag}(\text{CN})_2^-] = 1.995 \times 10^{-19}$$

**Q.25** Calculate the equilibrium constant for the reaction:



$$E^\circ \text{ for Sn/Sn}^{2+} = 0.136 \text{ V } E^\circ \text{ for Sn}^{2+}/\text{Sn}^{4+} = -0.154 \text{ V}$$

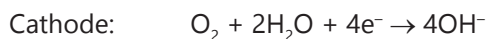
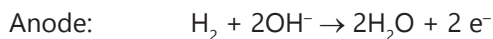
$$E^\circ \text{ for Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+} = 1.33 \text{ V}$$

**Q.26** Calculate the equilibrium concentration of all ions in an ideal solution prepared by mixing 25.00 mL of 0.100 M Ti<sup>+</sup> with 25.00 mL of 0.200M Co<sup>3+</sup>.

$$E^\circ (\text{Ti}^+/\text{Ti}^{3+}) = -1.25 \text{ V}; E^\circ (\text{Co}^{3+}/\text{Co}^{2+}) = 1.84 \text{ V}$$

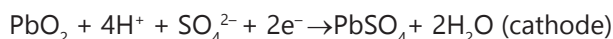
**Q.27** Same quantity of electricity is being used to liberate iodine (at anode) and a metal x (cathode). The mass of x deposited is 0.617 g and the iodine is completely reduced by 46.3 cc of 0.124 M sodium thiosulphate. Find the equivalent mass of x.

**Q.28** In a fuel cell,  $H_2$  &  $O_2$  react to produce electricity. In the process,  $H_2$  gas is oxidized at the anode &  $O_2$  at the cathode. If 67.2 liter of  $H_2$  at STP react in 15 minutes, what is the average current produced? If the entire current is used for electrode deposition of Cu from  $Cu(II)$  solution, how many grams of Cu will be deposited?



**Q.29** One of the methods of preparation of per disulphuric acid,  $H_2S_2O_8$ , involve electrolytic oxidation of  $H_2SO_4$  at anode ( $2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$ ) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of  $H_2$  and 2.35 L of  $O_2$  were generated at STP. What is the weight of  $H_2S_2O_8$  formed?

**Q.30** During the discharge of a lead storage battery the density of sulphuric acid fell from 1.294 to 1.139  $g \cdot mL^{-1}$ .  $H_2SO_4$  of density 1.294  $g \cdot mL^{-1}$  is 39% and that of density 1.139  $g \cdot mL^{-1}$  is 20% by weight. The battery holds 3.5 L of acid and the volume practically remains constant during the discharge. Calculate the number of ampere hours for which the battery must have been used. The discharging reactions are:



**Q.31** A current of 3 amp was passed for 2 hour through a solution of  $CuSO_4$ , 3g of  $Cu^{2+}$  ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.

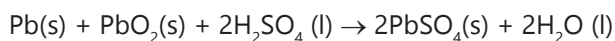
**Q.32** An acidic solution of  $Cu^{2+}$  salt containing 0.4 g of  $Cu^{2+}$  is electrolyzed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis.

**Q.33** In the refining of silver by electrolytic method what will be the weight of 100 gm. Ag anode if 5 ampere current is passed for 2 hours? Purity of silver is 95% by weight.

**Q.34** Dal Lake has water  $8.2 \times 10^{12}$  liter approximately. A power reactor produces electricity at the rate of  $1.5 \times 10^6$  coulomb per second at an appropriate voltage. How many years would it take to electrolyze the lake?

**Q.35** A lead storage cell is discharged which causes the  $H_2SO_4$  electrolyte to change from a concentration of 34.6% by weight (density 1.261  $g \cdot mL^{-1}$  at 25°C) to 27% by weight. The original volume of electrolyte is one liter. Calculate the total charge released at anode of the

battery. Note that the water is produced by the reaction as  $H_2SO_4$  is used up. Overall reaction is



**Q.36** 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 0.04 M  $Na_2S_2O_3$ . Volume of  $Na_2S_2O_3$  required was 35 ml. Assuming no volume change during electrolysis, calculate:

- Duration of electrolysis if current efficiency is 80%
- Initial concentration (M) of  $CuSO_4$ .

**Q.37** An external current source giving a current of 0.5 A was joined with Daniel cell and 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.  $E^\circ$  of  $Zn^{2+}/Zn$  and  $Cu^{2+}/Cu$  at 25°C is  $-0.76$  and  $+0.34$  V respectively.

**Q.38** Determine at 298 for cell



- Its e.m.f when pH = 5.0
- The pH when  $E_{cell} = 0$
- The positive electrode when pH = 7.5

Given  $E^\circ_{RP(RHS)} = 0.28$ ,  $E^\circ_{RP(LHS)} = 0.699$

**Q.39** At 25°C,  $\Delta H_f$  ( $H_2O, l$ ) =  $-56700$  cal/mole and energy of ionization of  $H_2O(l)$  = 19050 Cal/mol. What will be the reversible EMF at 25°C of the cell?

$Pt | H_2(g) (1 \text{ atm}) | H^+ || OH^- | O_2(g) (1 \text{ atm}) | Pt$ , if at 26°C the e.m.f increase by 0.001158 V.

**Q.40** Calculate the cell potential of a cell having reaction:  $Ag_2S + 2e^- \rightarrow 2Ag + S^{2-}$  in a solution buffered at pH = 3 and which is also saturated with 0.1 M  $H_2S$ .

For  $H_2S$ :  $K_1 = 10^{-8}$  and  $K_2 = 1.1 \times 10^{-13}$ ,  $K_{sp}(Ag_2S) = 2 \times 10^{-49}$ ,  $E^\circ_{Ag^+/Ag} = -0.8$ .

**Q.41** The equivalent conductance of 0.10N solution of  $MgCl_2$  is 97.1  $mho \cdot cm^2 \cdot equi^{-1}$  at 25°C. A cell with electrode that are 1.5  $cm^2$  in surface area and 0.5 cm apart is filled with 0.1 N  $MgCl_2$  solution. How much current will flow when potential difference between the electrodes is 5 volt?

**Q.42** A dilute aqueous solution of KCl was placed between two electrodes 10 cm apart, across which a potential of 6 volt was applied. How far would the

$K^+$  ion move in 2 hours at 25°C? Ionic conductance of  $K^+$  ion at infinite dilution at 25°C is  $73.52 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ?

**Q.43** When a solution of specific conductance  $1.342 \text{ ohm}^{-1} \text{ meter}^{-1}$  was placed in a conductivity cell with parallel electrodes, the resistance was found to be  $170.5 \text{ ohm}$ . Area of electrodes is  $1.86 \times 10^{-4} \text{ m}^2$ . Calculate separation of electrodes.

**Q.44** The specific conductance at 25°C of a saturated solution of  $\text{SrSO}_4$  is  $1.482 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$  while that of water used is  $1.5 \times 10^{-6} \text{ mho cm}^{-1}$ . Determine at 25°C the solubility in gm. per liter of  $\text{SrSO}_4$  in water. Molar ionic conductance of  $\text{Sr}^{2+}$  and  $\text{SO}_4^{2-}$  ions at infinite dilution are  $59.46$  and  $79.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  respectively. [Sr = 87.6, S = 32, O = 16]

**Q.45** Calculate the solubility and solubility product of  $\text{Co}_2[\text{Fe}(\text{CN})_6]$  in water at 25°C from the following data: Conductivity of a saturated solution of  $\text{Co}_2[\text{Fe}(\text{CN})_6]$  is  $2.06 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  and that of water used  $4.1 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ . The ionic molar conductivities of  $\text{Co}^{2+}$  and  $\text{Fe}(\text{CN})_6^{4-}$  are  $86.0 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$  and  $444.0 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ .

**Q.46** A sample of water from a large swimming pool has a resistance of  $9200 \Omega$  at 25°C when placed in a certain conductance cell. When filled with  $0.02 \text{ M}$  KCl solution, the cell has a resistance of  $85 \Omega$  at 25°C.  $500 \text{ gm}$ . of NaCl were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of  $7600 \Omega$ . Calculate the volume of water in the pool.

Given: Molar conductance of NaCl at that concentration is  $126.5 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$  and molar conductivity of KCl at  $0.02 \text{ M}$  is  $138 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ .

## Exercise 2

### Single Correct Choice Type

**Q.1** An aqueous solution containing one mole per liter each of  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{AgNO}_3$ ,  $\text{Hg}_2(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$  is being electrolyzed by using inert electrodes. The value of standard potentials are

$$E^\circ_{\text{Ag}^+|\text{Ag}} = -0.80\text{V}, \quad E^\circ_{\text{Hg}_2^{2+}|\text{Hg}} = -0.79\text{V},$$

$$E^\circ_{\text{Cu}^{2+}|\text{Cu}} = -0.34\text{V} \quad \text{and} \quad E^\circ_{\text{Mg}^{2+}|\text{Mg}} = -2.3\text{V}$$

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

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

**Q.2** The charge required for the oxidation of one mole  $\text{Mn}_3\text{O}_4$  into  $\text{MnO}_4^{2-}$  in presence of alkaline medium is

- (A)  $5 \times 96500 \text{ C}$           (B)  $96500 \text{ C}$   
(C)  $10 \times 96500 \text{ C}$       (D)  $2 \times 96500 \text{ C}$

**Q.3** A solution of sodium sulphate in water is electrolyzed using inert electrodes. The products at the cathode and anode are respectively.

- (A)  $\text{H}_2, \text{O}_2$       (B)  $\text{O}_2, \text{H}_2$       (C)  $\text{O}_2, \text{Na}$       (D) None

**Q.4** 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  $\text{pK}_a$  value of the acid can be given as

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

**Q.5** The conductivity of a saturated solution of  $\text{Ag}_3\text{PO}_4$  is  $9 \times 10^{-6} \text{ S m}^{-1}$  and its equivalent conductivity is  $1.50 \times 10^{-4} \text{ S m}^{-2} \text{ equivalent}^{-1}$ . The  $K_{sp}$  of  $\text{Ag}_3\text{PO}_4$  is:

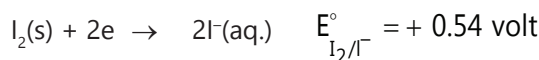
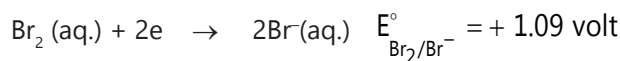
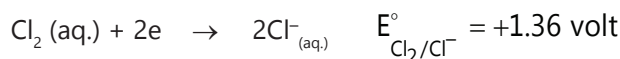
- (A)  $4.32 \times 10^{-18}$       (B)  $1.8 \times 10^{-9}$   
(C)  $8.64 \times 10^{-13}$       (D) None of these

**Q.6** Equal volumes of  $0.015 \text{ M}$   $\text{CH}_3\text{COOH}$  &  $0.015 \text{ M}$  NaOH are mixed together. What would be molar conductivity of mixture if conductivity of  $\text{CH}_3\text{COONa}$  is  $6.3 \times 10^{-4} \text{ S cm}^{-1}$ ?

- (A)  $8.4 \text{ S cm}^2 \text{ mole}^{-1}$       (B)  $84 \text{ S cm}^2 \text{ mole}^{-1}$   
(C)  $4.2 \text{ S cm}^2 \text{ mole}^{-1}$       (D)  $42 \text{ S cm}^2 \text{ mole}^{-1}$

### Multiple Correct Choice Type

**Q.7** Pick out the correct statements among the following from inspection of standard reduction potentials (Assume standard state conditions).



$$E^\circ_{\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}} = +2.00 \text{ volt}$$

- (A)  $\text{Cl}_2$  can oxidize  $\text{SO}_4^{2-}$  from solution  
 (B)  $\text{Cl}_2$  can oxidize  $\text{Br}^-$  and  $\text{I}^-$  from aqueous solution  
 (C)  $\text{S}_2\text{O}_8^{2-}$  can oxidize  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  from aqueous solution  
 (D)  $\text{S}_2\text{O}_8^{2-}$  is added slowly,  $\text{Br}^-$  can be reduce in presence of  $\text{Cl}^-$

**Q.8** Which of the following arrangement will produce oxygen at anode during electrolysis?

- (A) Dilute  $\text{H}_2\text{SO}_4$  solution with Cu electrodes.  
 (B) Dilute  $\text{H}_2\text{SO}_4$  solution with inert electrodes.  
 (C) Fused NaOH with inert electrodes.  
 (D) Dilute NaCl solution with inert electrodes.

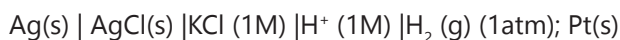
**Q.9** If 270.0 of water is electrolyzed during an experiment performed by Miss Abhilasha with 75% current efficiency then

- (A) 168 L of  $\text{O}_2$  (g) will be evolved at anode at 1 atm & 273 K  
 (B) Total 504 L gases will be produced at 1 atm & 273 K  
 (C) 336 L of  $\text{H}_2$ (g) will be evolved at anode at 1 atm & 273 K  
 (D) 45 F electricity will be consumed

**Q.10** During discharging of lead storage battery, which of the following is/are true?

- (A)  $\text{H}_2\text{SO}_4$  is produced  
 (B)  $\text{H}_2\text{O}$  is consumed  
 (C)  $\text{PbSO}_4$  is formed at both electrodes  
 (D) Density of electrolytic solution decreases

**Q.11** The EMF of the following cell is 0.22 volt.



Which of the following will decreases the EMF of cell

- (A) Increasing pressure of  $\text{H}_2$  (g) from 1 atm to 2 atm  
 (B) Increasing  $\text{Cl}^-$  concentration in Anodic compartment  
 (C) Increasing  $\text{H}^+$  concentration in cathodic compartment  
 (D) Decreasing KCl concentration in Anodic compartment.

### Assertion Reasoning Type

- (A) Statement-I is true, statement-2 is true and statement-II is correct explanation for statement-I  
 (B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I.  
 (C) Statement-I is true, statement-II is false  
 (D) Statement-I is false, statement-II is true

**Q.12 Statement-I:** The voltage of mercury cell remains constant for long period of time.

**Statement-II:** It because net cell reaction does not involve active species.

**Q.13 Statement-I:** We can add the electrode potential in order to get electrode potential of net reaction.

**Statement-II:** Electrode potential is an intensive property.

**Q.14 Statement-I:** The SRP of three metallic ions  $\text{A}^+$ ,  $\text{B}^{2+}$ ,  $\text{C}^{3+}$  are  $-0.3$ ,  $-0.5$ ,  $0.8$  volt respectively, so oxidizing power of ions is  $\text{C}^{3+} > \text{A}^+ > \text{B}^{2+}$ .

**Statement-II:** Higher the SRP, higher the oxidizing power

### Comprehension type

**Paragraph 1:** A sample of water from a large swimming pool has a resistance of  $10000 \Omega$  at  $25^\circ\text{C}$  when placed in a certain conductance cell. When filled with  $0.02 \text{ M}$  KCl solution, the cell has a resistance of  $100 \Omega$  at  $25^\circ\text{C}$ .  $585 \text{ gm.}$  of NaCl were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of  $8000 \Omega$ .

[Given: Molar conductance of NaCl at that concentration is  $125 \Omega^{-1}\text{cm}^2 \text{mole}^{-1}$  and molar conductivity of KCl at  $0.02 \text{ M}$  is  $200 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$ .]

**Q.15** Cell constant (in  $\text{cm}^{-1}$ ) of conductance cell is:

- (A) 4      (B) 0.4      (C)  $4 \times 10^{-2}$       (D)  $4 \times 10^{-5}$

**Q.16** Conductivity ( $\text{Scm}^{-1}$ ) of  $\text{H}_2\text{O}$  is:

- (A)  $4 \times 10^{-2}$       (B)  $4 \times 10^{-3}$   
 (C)  $4 \times 10^{-5}$       (D) None of these

**Q.17** Volume (in Liters) of water in the pool is:

- (A)  $1.25 \times 10^5$       (B) 1250  
 (C) 12500      (D) None of these



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

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ volt}$$

$$E^\circ_{\text{NO}_3^-/\text{NO}} = +0.96 \text{ volt}$$

$$E^\circ_{\text{NO}_3^-/\text{NO}_2} = +0.79 \text{ volt}$$

$$\text{At } 298 \text{ K } \frac{RT}{F} (2.303) = 0.06 \text{ volt}$$

**Q.18**  $E_{\text{cell}}$  for reduction of  $\text{NO}_3^- \rightarrow \text{NO}$  by  $\text{Cu(s)}$ , when  $[\text{HNO}_3] = 1 \text{ M}$  is [At  $T = 298$ ]

- (A)  $\sim 0.61$  (B)  $\sim 0.71$  (C)  $\sim 0.51$  (D)  $\sim 0.81$

**Q.19** At what  $\text{HNO}_3$  concentration thermodynamic tendency for reduction of  $\text{NO}_3^-$  into NO and  $\text{NO}_2$  by copper is same?

- (A)  $10^{1.23} \text{ M}$  (B)  $10^{0.56} \text{ M}$  (C)  $10^{0.66} \text{ M}$  (D)  $10^{0.12} \text{ M}$

### Match the Columns

**Q.20**

Column I	Column II (Electrolysis product using inert electrode)
(A) Dilute solution of HCl	(p) $\text{O}_2$ evolved at anode
(B) Dilute solution of NaCl	(q) $\text{H}_2$ evolved at cathode
(C) Concentrated Solution of NaCl	(r) $\text{Cl}_2$ evolved at anode
(D) $\text{AgNO}_3$ solution	(s) Ag deposition at cathode

### Previous Years' Questions

**Q.1** In the electrolytic cell, flow of electrons is from (2003)

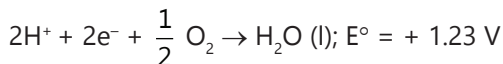
- (A) Cathode to anode in solution  
 (B) Cathode to anode through external supply  
 (C) Cathode to anode through internal supply  
 (D) Anode to cathode through internal supply

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

The e.m.f of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is (2004)

- (A)  $10^{0.32/0.059}$  (B)  $10^{0.32/0.0295}$   
 (C)  $10^{0.26/0.0295}$  (D)  $10^{0.32/0.295}$

**Q.3** The half-cell reaction for rusting of iron are:



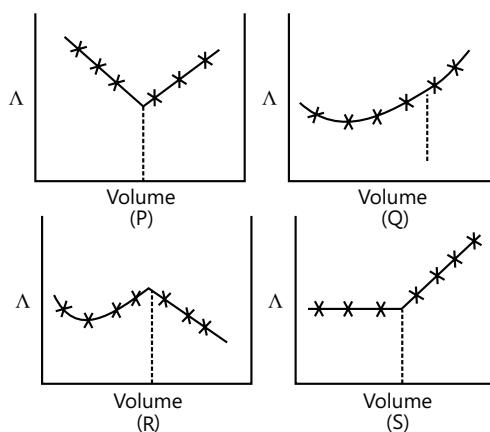
$\Delta G^\circ$  (in kJ) for the reaction is (2005)

- (A)  $-76$  (B)  $-322$  (C)  $-122$  (D)  $-176$

**Q.4** Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mole of  $\text{H}_2$  gas at the cathode is (1 F = 96500 C mole<sup>-1</sup>) (2008)

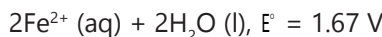
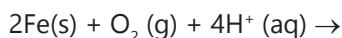
- (A)  $9.65 \times 10^4 \text{ s}$  (B)  $19.3 \times 10^4 \text{ s}$   
 (C)  $28.95 \times 10^4 \text{ s}$  (D)  $38.6 \times 10^4 \text{ s}$

**Q.5**  $\text{AgNO}_3$  (aqueous) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance ( $\Lambda$ ) versus the volume of  $\text{AgNO}_3$  is (2011)



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

**Q.6** Consider the following cell reaction,



At  $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$ ,  $P(\text{O}_2) = 0.1 \text{ atm}$  and  $\text{pH} = 3$ , the cell potential at  $25^\circ\text{C}$  is (2011)

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

**Q.7** For the reduction of  $\text{NO}_3^-$  ion in an aqueous solution  $E^\circ$  is + 0.96 V. Values of  $E^\circ$  for some metal ion are given below





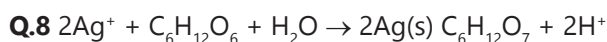
The pair (s) of metals that is (are) oxidized by  $\text{NO}_3^{-}$  in aqueous solution is (are) **(2009)**

- (A) V and Hg                      (B) Hg and Fe  
(C) Fe and Au                      (D) Fe and V

**Paragraph 1:** Tollen's reagent is used for the detection of aldehydes. When a solution of  $\text{AgNO}_3$  is added to glucose with  $\text{NH}_4\text{OH}$  then gluconic acid is formed.



[Use  $2.303 \times \frac{RT}{F} = 0.0592$  and  $\frac{F}{RT} = 38.92$  at 298 K] **(2006)**



Find in K of this reaction.

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

**Q.9** When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?

- (A)  $E^{\circ}_{\text{oxi}}$  will increase by a factor of 0.65 from  $E^{\circ}_{\text{oxi}}$   
(B)  $E^{\circ}_{\text{oxi}}$  will decrease by a factor of 0.65 from  $E^{\circ}_{\text{oxi}}$   
(C)  $E^{\circ}_{\text{red}}$  will increase by a factor of 0.65 from  $E^{\circ}_{\text{red}}$   
(D)  $E^{\circ}_{\text{red}}$  will decrease by a factor of 0.65 from  $E^{\circ}_{\text{red}}$

**Q.10** Ammonia is always added in this reaction. Which of the following must be incorrect?

- (A)  $\text{NH}_3$  combines with  $\text{Ag}^{+}$  to form a complex  
(B)  $\text{Ag}(\text{NH}_3)_2^{+}$  is a stronger oxidizing reagent than  $\text{Ag}^{+}$   
(C) In absence of  $\text{NH}_3$  silver salt of gluconic acid is formed  
(D)  $\text{NH}_3$  has no effect on the standard reduction potential of glucose/gluconic acid electrode

**Paragraph 2:** Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately  $6.023 \times 10^{23}$ ) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 M aqueous solution of NaCl is prepared and 500 mL of this solution is electrolyzed. This lead to the evolution of chlorine gas at one of the electrodes (Atomic mass: Na = 23, Hg = 200, 1 F = 96500C). **(2007)**

**Q.11** The total number of moles of chlorine gas evolved is

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

**Q.12** If the cathode is a Hg electrode, the maximum weight (in gram) of amalgam formed this solution is

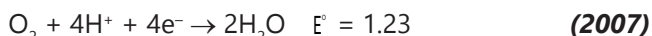
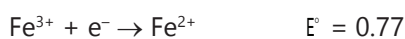
- (A) 200              (B) 255              (C) 400              (D) 446

**Q.13** The total charge (coulombs) required for complete electrolysis is

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

**Paragraph 3:** Redox reaction play a pivotal role in chemistry and biology. The values of standard redox potential ( $E^{\circ}$ ) of two half-cell

Reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reaction (acidic medium) along with their  $E^{\circ}$  (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to



**Q.14** Among the following, identify the correct statement

- (A) Chloride ion is oxidized by  $\text{O}_2$   
(B)  $\text{Fe}^{2+}$  is oxidized by iodine  
(C) Iodide ion is oxidized by chlorine  
(D)  $\text{Mn}^{2+}$  is oxidized by chlorine

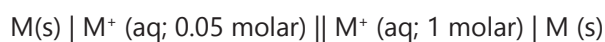
**Q.15** While  $\text{Fe}^{3+}$  is stable,  $\text{Mn}^{3+}$  is not stable in acid solution because

- (A)  $\text{O}_2$  oxidizes  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$ .  
(B)  $\text{O}_2$  oxidizes both  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$   
(C)  $\text{Fe}^{3+}$  oxidizes  $\text{H}_2\text{O}$  to  $\text{O}_2$   
(D)  $\text{Mn}^{3+}$  oxidizes  $\text{H}_2\text{O}$  to  $\text{O}_2$

**Q.16** Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and  $\text{H}_2\text{SO}_4$  in presence of air gives a Prussian blue precipitate. The blue color is due to the formation of

- (A)  $\text{Fe}_4 [\text{Fe} (\text{CN})_6]_3$       (B)  $\text{Fe}_3 [\text{Fe} (\text{CN})_6]_2$   
 (C)  $\text{Fe}_4 [\text{Fe} (\text{CN})_6]_2$       (D)  $\text{Fe}_3 [\text{Fe} (\text{CN})_6]_3$

**Paragraph 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:



For the above electrolytic cell the magnitude of the cell potential  $|E_{\text{cell}}| = 70 \text{ mV}$ . **(2010)**

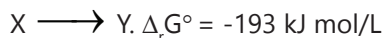
**Q.17** For the above cell

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

**Q.18** If the 0.05 molar solution of  $\text{M}^+$  is replaced by a 0.0025 molar  $\text{M}^+$  solution, then the magnitude of the cell potential would be

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

**Q.19** All the energy released from the reaction  $0 \rightarrow 1$



is used for oxidizing  $\text{M}^+$  as  $\text{M}^+ \longrightarrow \text{M}^{3+} + 2\text{e}^-$ ,

$$E^\circ = -0.25\text{V}.$$

Under standard conditions, the number of moles of  $\text{M}^+$  oxidized when one mole of X is converted to Y is

$$[F = 96500 \text{ C mol}^{-1}] \quad \textbf{(2015)}$$

**Q.20** The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M).

If  $\lambda_{\text{X}^-}^0 \approx \lambda_{\text{Y}^-}^0$ , the difference in their  $\text{pK}_a$  values, a  $\text{pK}_a$  (HX) -  $\text{pK}_a$  (HY), is consider degree of ionization of both acids to be  $\ll 1$  **(2015)**

**Q.21** For the following electrochemical cell at 298 K,



$$E_{\text{cell}} = 0.092 \text{ V when } \frac{[\text{M}^{2+}(\text{aq})]}{[\text{M}^{4+}(\text{aq})]} = 10^x.$$

$$\text{Given: } E_{\text{M}^{4+}/\text{M}^{2+}}^\circ = 0.151 \text{ V}; 2.303 \frac{RT}{F} = 0.059 \text{ V}$$

The value of x is **(2016)**

- (A) -2      (B) -1      (C) 1      (D) 2

**Q.22** In a galvanic cell, the salt bridge **(2014)**

- (A) Does not participate chemically in the cell reaction.  
 (B) Stops the diffusion of ions from one electrode to another.  
 (C) Is necessary for the occurrence of the cell reaction.  
 (D) Ensures mixing of the two electrolytic solutions.

# MASTERJEE Essential Questions

## JEE Main/Boards

### Exercise 1

Q.3	Q.4	Q.8
Q.9	Q.12	Q.16
Q.23	Q.30	

### Exercise 2

Q.3	Q.5	Q.9
Q.12	Q.15	Q.18
Q.20		

### Previous Years' Questions

Q.3	Q.8
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## JEE Advanced /Boards

### Exercise 1

Q.1	Q.6	Q.12
Q.19	Q.22	Q.30
Q.35	Q.42	Q.45

### Exercise 2

Q.4	Q.7	Q.16
Q.18		

### Previous Years' Questions

Q.5	Q.7	Q.17
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## Answer Key

## JEE Main/Boards

### Exercise 1

<b>Q.2</b>	$124 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$
<b>Q.4</b>	$\Delta_r G^\circ = -213.04 \text{ kJ}$ , $E_{\text{cell}}^\circ = +1.104 \text{ V}$
<b>Q.5</b>	$\lambda_m = 124 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
<b>Q.8</b>	$0.219 \text{ cm}^{-1}$
<b>Q.9</b>	$\wedge_m = 32.765 \text{ cm}^2 \text{ mol}^{-1}$ , $k_a = 2.2 \times 10^{-4}$
<b>Q.10</b>	$3.66 \text{ gm}$
<b>Q.14</b>	$E^\circ = 0.34 \text{ V}$
<b>Q.19</b>	(i) $0.2515 \text{ V}$ ; (ii) $0.8101 \text{ V}$ (iii) $0.226 \text{ V}$ (iv) $1.451 \text{ V}$ ; (v) $-0.268 \text{ V}$
<b>Q.20</b>	$0.7288 \text{ V}$

<b>Q.21</b>	$0.1536 \text{ V}$
<b>Q.22</b>	$-0.1615 \text{ V}$
<b>Q.23</b>	(i) $0.2278 \text{ V}$ ; (ii) $0.3692$
<b>Q.24</b>	$0.91 \text{ V}$
<b>Q.25</b>	$3.67 \times 10^{-4}$
<b>Q.26</b>	Na, Ca, Mg and Al.
<b>Q.27</b>	$2.96 \text{ V}$
<b>Q.28</b>	(a) $-0.118 \text{ V}$ ; (b) $-0.0413 \text{ V}$ ; (c) (i) $-0.0295 \text{ V}$ (ii) $-0.59 \text{ V}$
<b>Q.29</b>	$1.3 \times 10^2 \text{ ohm}^{-1} \text{ cm}^2 \text{ equi}^{-1}$

**Exercise 2****Single Correct Choice Type**

<b>Q.1</b> C	<b>Q.2</b> B	<b>Q.3</b> B	<b>Q.4</b> B	<b>Q.5</b> D	<b>Q.6</b> D
<b>Q.7</b> B	<b>Q.8</b> A	<b>Q.9</b> A	<b>Q.10</b> B	<b>Q.11</b> B	<b>Q.12</b> B
<b>Q.13</b> C	<b>Q.14</b> C	<b>Q.15</b> C	<b>Q.16</b> B	<b>Q.17</b> A	<b>Q.18</b> C
<b>Q.19</b> C	<b>Q.20</b> D	<b>Q.21</b> C			

**Previous Years Questions**

<b>Q.1</b> D	<b>Q.2</b> D	<b>Q.3</b> B	<b>Q.4</b> C	<b>Q.5</b> B	<b>Q.6</b> D
<b>Q.7</b> A	<b>Q.8</b> D	<b>Q.9</b> A	<b>Q.10</b> C	<b>Q.11</b> C	<b>Q.12</b> C
<b>Q.13</b> D	<b>Q.14</b> C	<b>Q.15</b> C	<b>Q.16</b> A	<b>Q.17</b> D	<b>Q.18</b> C
<b>Q.19</b> B	<b>Q.20</b> D	<b>Q.21</b> D	<b>Q.22</b> C	<b>Q.23</b> A	<b>Q.24</b> A

**JEE Advanced/Boards****Exercise 1**

<b>Q.1</b> $[\text{Cu}^{2+}] = 10^{-4} \text{ M}$	<b>Q.2</b> pH = 6.61
<b>Q.3</b> $K_a = 6.74 \times 10^4$	<b>Q.4</b> 1.39 V
<b>Q.5</b> -0.46 V	<b>Q.6</b> (ii) 1.27V (ii) 245.1 kJ
<b>Q.7</b> $E^\circ = -0.22 \text{ V}$	<b>Q.8</b> $h = 2.12 \times 10^{-2}$ , $K_h = 1.43 \times 10^{-5} \text{ M}$
<b>Q.9</b> 0.95 V	<b>Q.10</b> $K_{sp} = 1.1 \times 10^{-16}$
<b>Q.11</b> $[\text{Br}^-]: [\text{Cl}^-] = 1: 200$	<b>Q.12</b> $E^\circ = -0.1511 \text{ V}$
<b>Q.13</b> -0.037 V	<b>Q.14</b> $1.536 \times 10^{-5} \text{ M}^3$
<b>Q.15</b> 1.66 V	<b>Q.16</b> -1.188V
<b>Q.17</b> $10^{-2}$	<b>Q.18</b> $5.24 \times 10^{16}$
<b>Q.19</b> $E^\circ = 1.59 \text{ V}$ , non-spontaneous	<b>Q.20</b> $E^\circ = 0.71 \text{ V}$
<b>Q.21</b> $[\text{Zn}^{2+}]/[\text{Cu}^{2+}] = 1.941 \times 10^{37}$	<b>Q.22</b> 0.373 V
<b>Q.23</b> $K_f = 8.227 \times 10^{63}$	<b>Q.24</b> 0.372 V, -0.307 V
<b>Q.25</b> $K = 10^{268}$	<b>Q.26</b> $\text{Ta}^+ = 5 \times 10^{-9}$ ; $\text{Co}^{3+} = 10^{-8}$
<b>Q.27</b> Eq. wt. = 107.3	<b>Q.28</b> 643.33 amp, 190.5 g
<b>Q.29</b> 43.456 g	<b>Q.30</b> 265 Amp. Hr.
<b>Q.31</b> 42.2 %	
<b>Q.32</b> $V(\text{O}_2) = 99.68 \text{ mL}$ , $V(\text{H}_2) = 58.46 \text{ mL}$ , Total vol. = 158.1 mL	
<b>Q.33</b> 57.5894 gm.	<b>Q.34</b> 1.9 million year
<b>Q.35</b> $2.4 \times 10^5$ coulomb	<b>Q.36</b> 1250 s, 0.064 M
<b>Q.37</b> 1.143 V	<b>Q.38</b> (a) -0.124 V, (b) 7.1 (c) calomel electrode
<b>Q.39</b> 0.4414 V	<b>Q.40</b> -0.167 V
<b>Q.41</b> 0.1456 ampere	<b>Q.42</b> 3.29 cm

**Q.43**  $4.25 \times 10^{-2}$  meter**Q.44** 0.1934 gm. /liter**Q.45**  $K_{sp} = 7.682 \times 10^{-17}$ **Q.46**  $2 \times 10^5 \text{dm}^3$ 

## Exercise 2

### Single Correct Choice Type

**Q.1** C**Q.2** C**Q.3** A**Q.4** C**Q.5** A**Q.6** B

### Multiple Correct Choice Type

**Q.7** B, C**Q.8** B, C, D**Q.9** A, B**Q.10** C, D**Q.11** D, C

### Assertion Reasoning Type

**Q.12** A**Q.13** D**Q.14** A

### Comprehension Type

Paragraph - 1

**Q.15** B**Q.16** C**Q.17** A

Paragraph - 2

**Q.18** B**Q.19** C

### Match the Columns

**Q.20** A  $\rightarrow$  p, q; B  $\rightarrow$  p, q; C  $\rightarrow$  q, r; D  $\rightarrow$  p, s

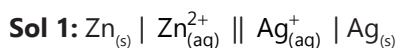
### Previous Years' Questions

**Q.1** C**Q.2** B**Q.3** B**Q.4** B**Q.5** D**Q.6** D**Q.7** A, B, D**Q.8** B**Q.9** C**Q.10** D**Q.11** B**Q.12** D**Q.13** D**Q.14** C**Q.15** D**Q.16** A**Q.17** B**Q.18** C**Q.21** D**Q.22** A

## Solutions

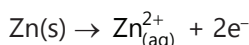
### JEE Main/Boards

#### Exercise 1

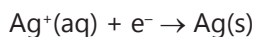


(i) Zinc electrode is negatively charged

(ii) At anode:



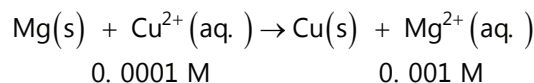
At cathode



**Sol 2:**  $\Lambda_m = \frac{k \times 1000}{M} = \frac{2.48 \times 10^{-2} \times 1000}{0.2}$

$$\Lambda_m = 124 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

**Sol 3:** (i) Reaction:



$$E = E^\circ - \frac{2.303 RT}{nF} \log \left( \frac{[\text{Cu}^{2+}]}{[\text{Mg}^{2+}]} \right)^{-1}$$

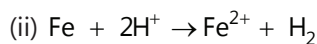
$$E = E^\circ - \frac{0.0591}{2} \log \frac{0.001}{0.0001}$$

$$E = E^\circ - 0.02955$$

$$E = E^\circ - 0.03$$

$$= 2.70 - 0.03$$

$$= 2.67 \text{ V}$$



1    0.001

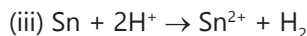
$$n = 2$$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}] P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$E = E^\circ - 0.03 \log \frac{0.001 \times 1}{1}$$

$$E = E^\circ + 0.09 = 0.44 + 0.09$$

$$\Rightarrow E = 0.53 \text{ V}$$



0.02                      0.05

$$n = 2$$

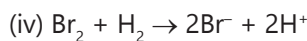
$$E = E^\circ - \frac{-0.0591}{2} \log \frac{[\text{Sn}^{2+}] P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$E = E^\circ - 0.03 \log \frac{0.05}{0.04}$$

$$E = E^\circ - 0.0029$$

$$E = 0.14 - 0.0029$$

$$\Rightarrow E = 0.1371 \text{ V}$$



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

$$= E^\circ - 0.02955 \log (0.01)^2 (0.03)^2$$

$$E = E^\circ + 0.208$$

$$E = 1.09 + 0.208$$

$$E = 1.298 \text{ V}$$

**Sol 4:** The formula of standard cell potential is

$$E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

Use this link to get all values

$$E^\circ_{\text{cell}} = 0.344 - (-0.76)$$

$$E^\circ_{\text{cell}} = 0.344 + 0.076 \text{ V}$$

$$E^\circ_{\text{cell}} = +1.104 \text{ V}$$

In balanced reaction there are 2 electron are transferring so that  $n = 2$

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

$$E^\circ_{\text{cell}} = +1.104 \text{ V}$$

Use formula

$$\Delta_r G^\circ = -n F E^\circ_{\text{cell}}$$

Plug the value we get

$$\text{Then, } = -2 \times 96500 \text{ C mol}^{-1} \times 1.104 \text{ V}$$

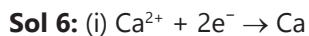
$$= -212304 \text{ CV mol}^{-1}$$

$$= -212304 \text{ mol}^{-1}$$

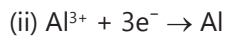
$$= -212.304 \text{ kJ mol}^{-1} = -213.04 \text{ kJ}$$

**Sol 5:**  $\wedge_m = k \times \frac{1000}{C}$

$$\wedge_m = \frac{0.0248 \times 1000}{0.2} = 124 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

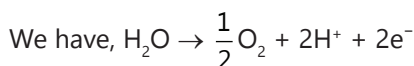
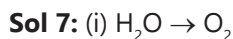


$$\text{Charge needed} = 2 \times nF = 2 \times \frac{20}{40} F = 1 F = 96500 \text{ C}$$

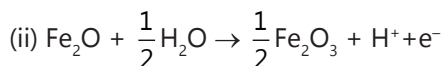


$$\text{Charge needed} = (3n_{\text{Al}}) \times 96500 \text{ C}$$

$$= 3 \times \frac{40}{27} \times 96500 \text{ C} = 4.28 \times 10^5 \text{ C}$$



$$\text{Charge required} = 2 F = 1.93 \times 10^5 \text{ C}$$



$$\text{Charge needed for 1 mole FeO} = 1 F = 96500 \text{ C}$$

**Sol 8:**  $k = 0.146 \times 10^{-3} \text{ s cm}^{-1}$

$$R = 1500 \Omega$$

$$G^* = Rk = 0.219 \text{ cm}^{-1}$$

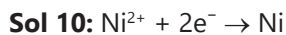
**Sol 9:**  $\wedge_m = 1000 \times \frac{k}{C} = \frac{1000 \times 7.896 \times 10^{-5}}{0.00241}$

$$\wedge_m = 32.765 \text{ cm}^2 \text{mol}^{-1}$$

$$q = \frac{\wedge_m}{\wedge_m^0} = \frac{32.76}{390.5}$$

$$\alpha = 0.084$$

$$k_a = \frac{C\alpha^2}{1-\alpha}; k_a = 2.2 \times 10^{-4}$$



$$\text{Charge supplied} = 5 \times 20 \times 60 \text{ C} = 6000 \text{ C}$$

$$\text{Moles of Ni deposited} = \frac{6000}{96500}$$

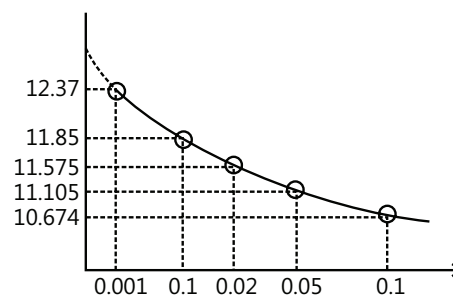
$$\text{Mass of Ni deposited} = \frac{6000}{96500} \times 59 = 3.66 \text{ gm}$$

**Sol 11:** We use the formula

$$\wedge_m = \frac{k \times 1000}{C}$$

C/M	0.001	0.010	0.02	0.05	0.100
$10^2 \times k / \text{sm}^{-1}$	12.37	11.85	23.15	55.53	106.74
$\wedge_m^0$ S cm <sup>2</sup> /mol	12.37	11.85	11.575	11.106	10.674
$\sqrt{C}$	0.03	0.1	0.14	0.22	0.31

$\wedge_m$  vs C



We have

$$\wedge_m = \wedge_m^0 - A\sqrt{C}$$

At  $C = 0.01$ ,

$$\wedge_m = 11.85 = \wedge_m^0 - A \times 0.1 \quad \dots(i)$$

At  $C = 0.02$

$$\wedge_m = 11.575 = \wedge_m^0 - A \times 0.14 \quad \dots(ii)$$

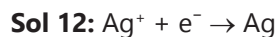
Subtracting

$$0.01 A = 0.275$$

$$A = 6.875$$

$$\wedge_m^0 = 12.5375 \text{ cm}^2 \text{mol}^{-1}$$

(putting A in (i))



$$n_{\text{Ag}} = \frac{1.45}{108} = 0.0134$$

$$\text{Charge, } Q = n_{\text{Ag}} \cdot F = 0.0134 \times 96500 \text{ C}$$

$$Q = 1295.6 \text{ C}$$

$$t = \frac{Q}{I} = \frac{1295.6}{1.5}$$

$$t = 863.735 \text{ s}$$





$$\text{Moles of Zn, } n_{\text{Zn}} = \frac{Q}{2F} = \frac{n_{\text{Ag}}}{2}$$

$$\text{Wt. of Zn} = n_{\text{Zn}} \times 65 = \frac{w_{\text{Ag}}}{m_{\text{Ag}}} \times \frac{1}{2} \times 65$$

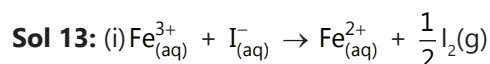
$$\text{Wt. of Zn} = 0.43 \text{ gm}$$

For Cu,



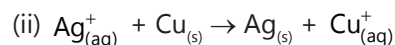
$$n_{\text{Cu}} = \frac{Q}{2F} = n_{\text{Zn}}$$

$$\text{Wt. of copper} = n_{\text{Cu}} \times 63.5 = 0.426 \text{ gm}$$



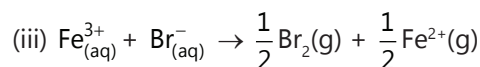
$$E^\circ = E^\circ_{\text{I}^-/\text{I}_2} + E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = -0.54 + 0.77 = +0.23 > 0$$

This is feasible.



$$E^\circ = E^\circ_{\text{Ag}^+/\text{Ag}} + E^\circ_{\text{Cu}/\text{Cu}^+} = 0.8 - 0.52 = 0.2870$$

This is feasible.

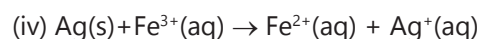


$$E^\circ = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^\circ_{\text{Br}_2/\text{Br}^-} = 0.77 - (1.09) = -0.32 < 0$$

So, this is not feasible

If  $\text{Fe}^{3+} \rightarrow \text{Fe}$ , then,  $E_{\text{Fe}^{3+}/\text{Fe}} = -0.036$

and  $E^\circ = -1.126$ , still not feasible.

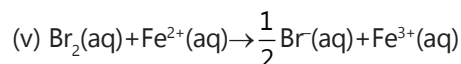


$$E^\circ = E^\circ_{\text{Ag}^+/\text{Ag}} + E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = -0.8 + 0.77 = -0.03 < 0$$

So, this is not feasible

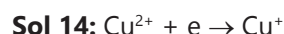
if  $\text{Fe}^{3+} \rightarrow \text{Fe}$ ,  $E_{\text{Fe}^{3+}/\text{Fe}} = -0.03$ ,

$E^\circ = -0.836$ , still not feasible.



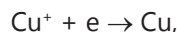
$$E^\circ = E^\circ_{\text{Br}_2/\text{Br}^+} + E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}} = 1.09 - 0.77 = 0.32 > 0$$

This reaction is feasible.



$$E^\circ = +0.18 \text{ V, } n = 1$$

$$\Delta E_1 = -nFE^\circ = -0.18 \text{ F}$$



$$E^\circ = 0.50 \text{ V, } n = 1$$

$$\Delta G_2 = -nFE^\circ = -0.5 \text{ F}$$

Adding



$$\Delta G = \Delta G_1 + \Delta G_2, n = 2$$

$$-2FE^\circ = -0.18 \text{ F} - 0.5 \text{ F}$$

$$E^\circ = 0.34 \text{ V}$$

**Sol 15:** Element with maximum oxidation potential will have highest reduction potential.

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

$$E^\circ_{\text{Pb}/\text{Pb}^{2+}} = 0.13 \text{ V}$$

$$E^\circ_{\text{Al}/\text{Al}^{2+}} = 1.66 \text{ V}$$

∴ Reducing order:  $\text{Pb} < \text{Zn} < \text{Al}$

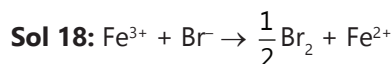
**Sol 16:** (i) Since  $\text{O}_3$  has the highest SRP, it is the strongest oxidising agent.

(ii) As Ag cannot get reduced,  $\text{O}_3$  is still the strongest oxidised agent.

(iii) Ag is the strongest reducing agent as it has the least negative oxidation potential.

(iv) Ag is still the strongest reducing agent.

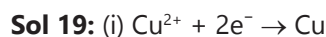
**Sol 17:**  $\text{IO}_3^-$  will act as better oxidising agent in acidic medium due to its larger SRP in acidic medium than basic medium.



$$E^\circ = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} + E^\circ_{\text{Br}^-/\text{Br}_2}$$

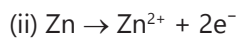
$$= 0.77 - 1.09 = -0.32 < 0$$

∴  $\text{Fe}^{3+}$  cannot oxidise  $\text{Br}^-$  to  $\text{Br}_2$ .



$$E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} = 0.34 - 0.0295 \log \frac{1}{0.001}$$

$$E = 0.2515 \text{ V}$$

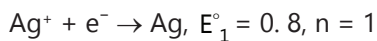
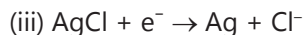


0.02

$$E_{\text{Zn}/\text{Zn}^{2+}}^{\circ} = -E_{\text{Zn}/\text{Zn}^{2+}}^{\circ} = 0.76$$

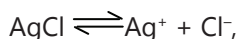
$$E = E^{\circ} - \frac{0.0591}{2} \log[\text{Zn}^{2+}] = 0.76 - 0.0295 \log(0.02)$$

$$E = 0.8101 \text{ V}$$



$$\Delta G_1 = -nFE_1^{\circ}$$

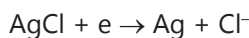
$$\Delta G_1 = -0.8 F$$



$$K_{s_1} = 2 \times 10^{-10}$$

$$\Delta G_2 = -RT \ln K_{sp}$$

Adding



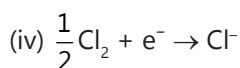
$$\Delta G = \Delta G_1 + \Delta G_2, n = 1$$

$$-FE^{\circ} = -0.8 F - 2.303RT \log(2 \times 10^{-10})$$

$$E^{\circ} = 0.8 + \frac{2.303RT}{F} \log(2 \times 10^{-10})$$

$$E^{\circ} = 0.8 - 0.57$$

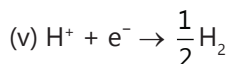
$$E^{\circ} = 0.226 \text{ V}$$



$$E_{\text{Cl}_2/\text{Cl}^-}^{\circ} = 1.36 \text{ V}$$

$$E = E^{\circ} - 0.0591 \log \frac{[\text{Cl}^-]}{(\text{P}_{\text{Cl}_2})^{1/2}}$$
$$= 1.36 - 0.0591 \log \frac{0.02}{(0.5)^{1/2}} = 1.36 - 0.0591(-1.548)$$

$$E = 1.451 \text{ V}$$



$$E^{\circ} = 0$$

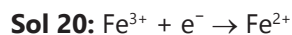
$$\text{pH} = -\log[\text{H}^+]$$

$$[\text{H}^+] = 10^{-4.4}$$

$$E = 0.0591 \log \frac{\text{P}_{\text{H}_2}^{1/2}}{[\text{H}^+]} = -0.0591(\log \sqrt{2} - \log[\text{H}^+])$$

$$= -0.0591(0.15 + 4.4)$$

$$E = -0.268 \text{ V}$$



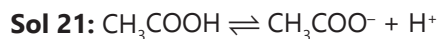
$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.77 \text{ V}$$

$$E = E^{\circ} - 0.0591 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$E = 0.77 - 0.0591 \log 5$$

$$(\because [\text{Fe}^{2+}] = 5 \times [\text{Fe}^{3+}])$$

$$E = 0.7287 \text{ V}$$



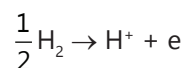
$$K_a = \frac{C\alpha^2}{1-\alpha} = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$[\text{H}^+] = C\alpha = \sqrt{CK_a}$$

$$[\text{H}^+] = \sqrt{0.357 \times 1.74 \times 10^{-5}}$$

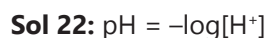
$$[\text{H}^+] = 2.492 \times 10^{-3}$$



$$E^{\circ} = 0$$

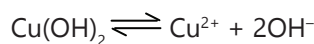
$$E = -0.0591 \log[\text{H}^+] = -0.0295 \log(2.492 \times 10^{-3})$$

$$E = 0.1536 \text{ V}$$



$$13 = -\log[\text{H}^+] \Rightarrow [\text{H}^+] = 10^{-13}$$

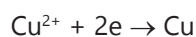
$$[\text{OH}^-] = \frac{k_w}{[\text{H}^+]} = \frac{10^{-14}}{10^{-13}} = \frac{1}{10}$$



$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2$$

$$[\text{Cu}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} = \frac{1 \times 10^{-19}}{10^{-2}}$$

$$[\text{Cu}^{2+}] = 10^{-17} \text{ M}$$



$$E^{\circ} = 0.34 \text{ V}, n = 2$$

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

$$= 0.34 - 0.0591 \log \frac{1}{10^{-17}} = 0.34 - 0.5015$$

$$E = -0.1615 \text{ V}$$

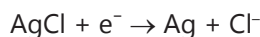
**Sol 23:** (i)  $\text{Ag}^+ + e^- \rightarrow \text{Ag}$ ;  $E_1^\circ = 0.80 \text{ V}$ ,  $n = 1$

$$\Delta G_1 = -nFE_1^\circ = -0.8F$$



$$\Delta G_2 = -RT \ln k_{sp} = -2.303 RT \log(2 \times 10^{-10})$$

Adding,



$$\Delta G = -nFE^\circ = \Delta G_1 + \Delta G_2, n = 1$$

$$-F E^\circ = -0.8F - 2.303 RT \log(2 \times 10^{-10})$$

$$E^\circ = 0.8 + \frac{2.303RT}{F} \log(2 \times 10^{-10})$$

$$E^\circ = 0.22 \text{ V}$$

$$(ii) E = E^\circ - 0.0591 \log[\text{Cl}^-] = 0.22 - 0.0591 \log(4 \times 10^{-3})$$

$$E = 0.36 \text{ V}$$

**Sol 24:**  $\text{Ni(s)} + 2\text{Ag}^+(0.002 \text{ M})$



$$n = 2$$

$$\therefore E = E_1^\circ - \frac{0.0591}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 1.05 - 0.0295 \log \frac{0.16}{(2 \times 10^{-3})^2} = 1.05 - 0.135$$

$$E = 0.91 \text{ V}$$

**Sol 25**  $\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^-$

$$\Delta_m^0(\text{HCOOH}) = \Delta_m^0(\text{HCOO}^-) + \Delta_m^0(\text{H}^+)$$

$$= 349.6 + 54.6$$

$$\Delta_m^0 = 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Delta_m}{\Delta_m^0} = \frac{46.1}{404.2}$$

$$\alpha = 0.114$$

$$k_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025(0.114)^2}{1-0.114}$$

$$k_a = 3.67 \times 10^{-4}$$

**Sol 26:** (i) Potassium

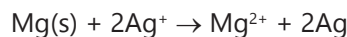
(ii) Sodium

(iii) Calcium

(iv) Magnesium

(v) Aluminium

**Sol 27:**  $\text{Mg(s)}|\text{Mg}^{2+}(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag(s)}$



$$n = 2, E^\circ = 3.17 \text{ V}$$

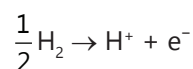
$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 3.17 - 0.0295 \log \frac{(0.13)}{(10^{-4})^2} = 3.17 - 0.209$$

$$E = 2.96 \text{ V}$$

**Sol 28:** (a)  $\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$

$$[\text{H}^+] = 2[\text{H}_2\text{SO}_4] = 0.02 \text{ M}$$



$$E^\circ = 0, n = 1$$

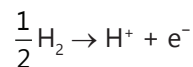
$$E = E^\circ - 0.0591 \log \frac{[\text{H}^+]}{P_{\text{H}_2}^{1/2}} = -0.0591 \log \frac{0.02}{\sqrt{4}}$$

$$E = -0.0591 \log(0.01)$$

$$E = +0.1182, E_r = -0.1182$$

(b)  $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$

$$[\text{H}^+] = [\text{HCl}] = 0.2$$



$$E^\circ = 0, n = 1$$

$$E = E^\circ - \frac{0.0591}{1} \log \frac{[\text{H}^+]}{P_{\text{H}_2}^{1/2}} = 0 - 0.0591 \log \frac{0.2}{1}$$

$$E = 0.0413 \text{ V}, E_r = -0.0413 \text{ V}$$

(c)  $E = 0, n = 1$

$$E^\circ = \frac{-0.0591}{1} \log[\text{H}^+] = 0.0591 \text{ p[H]}$$

(i)  $\text{pH} = 5$

$$E = 0.0591 \times 5 = 0.2955 \text{ V}$$

$$E_r = -0.2955 \text{ V}$$

(ii)  $\text{pOH} = 4$

$$\text{pH} = 14 - \text{pOH} = 10$$

$$E = 0.0591 \times 10 = 0.591 \text{ V}$$

$$E_r = -E = -0.591 \text{ V}$$

**Sol 29:**  $n$  for  $\text{H}_2\text{SO}_4 = 2$

$$\text{Normality} = \text{Molarity} \times n = 2 \text{ M}$$

$$\Delta_e = \frac{k \times 1000}{N} = \frac{26 \times 1000 \times 10^{-2}}{2} = 130 \text{ Scm}^2 \text{ equiv}^{-1}$$

## Exercise 2

### Single Correct Choice Type

**Sol 1: (C)**  $M^{+2} + 2e \rightarrow M$

For one mole, charge required =  $2F$

If atomic weight is  $M$ .

Then, for  $M$  gm,  $2F$  charge

For 1 gm, charge =  $\frac{2F}{M} = 1.81 \times 10^{22} \times 1.6 \times 10^{-19}$

$\Rightarrow M = 66.7$  gm

**Sol 2: (B)** Moles of  $Ag = 1$

Moles of  $Cu = \frac{1}{2}$

Moles of  $Al = \frac{1}{3}$

1:  $\frac{1}{2}$ :  $\frac{1}{3} = 6: 3: 2$

**Sol 3: (B)** Moles of  $A = \frac{2.1}{7}$

Molar ratio =  $\frac{2.1}{7} : \frac{2.7}{27} : \frac{7.2}{78} = 0.3: 0.1: 0.15$

= 3: 1: 1.5

= 6: 2: 3

= 1:  $\frac{1}{3}$ :  $\frac{1}{2}$

$\therefore$  Valency = 1, 3 and 2

**Sol 4: (B)** Volume of plate =  $10 \times 10 \times 10^{-2} \text{ cm}^3 = 1 \text{ cm}^3$

Mass = 8.94 g

Moles =  $\frac{8.94}{63.5}$

Quantity of electricity =  $\frac{8.94}{63.5} \times 2F = 27172 \text{ C}$

**Sol 5: (D)**  $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

$2H_2O \rightarrow 2H_2 + O_2$

Only water will be oxidised and reduced.

$V_{H_2} = 2 \times V_{O_2} = 4.8 \text{ L}$

**Sol 6: (D)** At cathode, water will be reduced,

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-(aq)$

pH of the solution around cathode will decrease.

**Sol 7: (B)** This is a convention.

**Sol 8: (A)**  $H^+ + e^- \rightarrow \frac{1}{2}H_2$

$E^\circ = 0$

$E = \frac{-0.0591}{1} \log \frac{(P_{H_2})^{1/2}}{[H^+]} = -0.0591 \log 10 = -0.0591 \text{ V}$

$\Delta E = 0.0591 \text{ V}$

**Sol 9: (A)** We have,

$E^\circ = \frac{0.0591}{2} \log k_c$

$E^\circ = \frac{0.0591}{2} \log(2.69 \times 10^{12}) = 0.3667 \text{ V}$

**Sol 10: (B)**  $Ag^+ + e^- \rightarrow Ag$

$E = E^\circ - 0.0591 \log \frac{1}{[Ag^+]}$

$0.25 = 0.799 + 0.059 \log [Ag^+]$

$[Ag^+] = 5.13 \times 10^{-10}$

$k_{sp} = [Ag^+][Cl^-] = 5.1 \times 10^{-11}$

**Sol 11: (B)** At cathode

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

At anode

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

Moles  $n_{O_2} = \frac{1}{2}nC_2$

$V_{O_2} = 22400 n_{O_2} = 22400 \times \frac{1}{2} \times \frac{2.5}{63.5} = 441 \text{ mL}$

$\approx 445 \text{ mL } O_2$  is liberated

**Sol 12: (B)**  $P = VI$

$P = 1.65 \text{ kW}$

$q = 1.65 \times 8 \text{ kWh} = 13.2 \text{ kWh}$

Cost =  $13.2 \times 5$  paise = 66 paise

**Sol 13: (C)**  $\wedge_m = \frac{1}{R} \cdot \frac{\ell}{a} \cdot \frac{1000}{C}$

$= \frac{1}{50} \cdot \frac{2.2}{4.4 \times 10^{-2}} \times \frac{1}{0.5} = 0.002 \text{ Sm}^2 \text{ mol}^{-1}$

**Sol 14: (C)**  $\alpha = \frac{\wedge_m}{\wedge_m^0} = \frac{10}{200} = 0.05$

$$[\text{H}^+] = C\alpha = 0.005$$

$$\text{pH} = -\log[\text{H}^+] = \log[200] = 2.3$$

$$\text{Sol 15: (C)} \quad \wedge_m = k \times \frac{1000}{C} = \frac{1000}{xy} \quad (k = \frac{1}{x}, C = y)$$

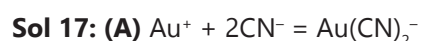
$$\text{Sol 16: (B)} \quad \alpha = \sqrt{\frac{k_a}{C}} = \sqrt{\frac{1.6 \times 10^{-5}}{0.01}} = 0.04$$

$$\alpha = \frac{\wedge_m^0}{\wedge_m}$$

$$\Rightarrow \wedge_m = 380 \times 10^{-4} \times 0.04 = 1.52 \times 10^{-3}$$

$$\wedge_m = \frac{1000 \times k}{C \times 1000}$$

$$k = 1.52 \times 10^{-2} \text{ S m}^{-1}$$



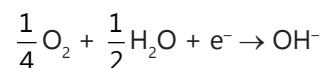
$$\Delta G_1 = -RT \ln X$$



$$\Delta G_2 = -nFE^\circ = -2.8F$$



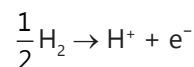
$$\Delta G_3 = -nF(-E^\circ) = 4.5F$$



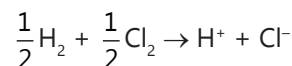
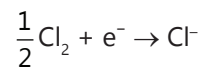
$$\Delta G_4 = -1F(E^\circ) = -0.41F$$

$$\text{Summing, } \Delta G = \sum_{i=1}^4 \Delta G_i = -RT \ln X + 1.29 F$$

**Sol 18: (C)** At anode



At cathode

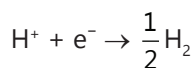


$$E = E^\circ - 0.0591 \log \frac{[\text{H}^+][\text{Cl}^-]}{P_{\text{H}_2}^{1/2} \cdot P_{\text{Cl}_2}^{1/2}}$$

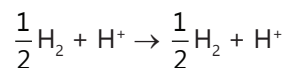
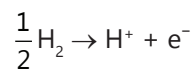
$$E_1 - E_2 = 0.0591 \log \frac{[\text{H}^+]_2 [\text{Cl}^-]_2}{[\text{H}^+]_1 [\text{Cl}^-]_1} = 0.0591 \times 2 = 0.1182$$

$$\therefore E_2 - E_1 = -0.1182$$

**Sol 19: (C)** At cathode,



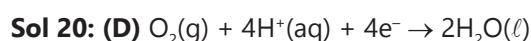
At anode



$$0.410^{-20} \rightarrow 10^{-1}$$

$$E = -0.0591 \log \frac{10^{-1} \cdot (0.1)^{1/2}}{10^{-2} \cdot (0.4)^{1/2}}$$

$$E = -0.041 \text{ V}$$



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

$$\Delta G^\circ = -nFE^\circ = -474.78 \text{ kJ}$$

$$\Delta H_f(\text{O}_2) = 0$$

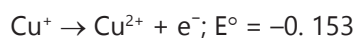
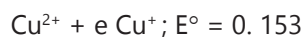
$$\Delta H_r = 2\Delta H_f(\text{H}_2\text{O}, \ell) = -2 \times 285.5 \text{ kJ} = -571 \text{ kJ}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = -0.322 \text{ kJ/k}$$



$$\Delta G_1^\circ = -nFE^\circ = -0.674 F$$



$$\Delta G_2^\circ = -nFE^\circ = +0.153 F$$

Adding,



$$\Delta G = \Delta G_1^\circ + \Delta G_2^\circ$$

$$-F E^\circ = -0.674 F + 0.153 F$$

$$E^\circ = 0.521 \text{ V}$$

## Previous Years' Questions

**Sol 1: (D)** Impure metal made anode while pure metal made cathode.

**Sol 2: (D)** In electrolytic cell, cathode acts as source of electrons.

**Sol 3: (B)**  $\text{Ag}^+ \xrightarrow{+\text{e}^-} \text{Ag}$ , 96500 C will liberate silver = 108 gm.  
9650C will liberate silver = 10.8

**Sol 4: (C)** Gold (Au) and Silver (Ag) are present in the anode mud.

$$\text{Sol 5 (B)} \quad C = \frac{K[A]A}{1}, \quad K = \frac{C \times l}{[A]A} = \frac{S \text{ m}}{\text{mol m}^{-3} \text{ m}^2}$$

$$= S \text{ m}^2 \text{ mol}^{-1}.$$

**Sol 6: (D)** 0.1 M difluoroacetic acid has highest electrical conductivity among the given solutions.

**Sol 7: (A)** From Kohlrausch's law

$$\Lambda_{\text{CH}_3\text{COOH}}^\circ = \Lambda_{\text{CH}_3\text{COONa}}^\circ + \Lambda_{\text{HCl}}^\circ - \Lambda_{\text{NaCl}}^\circ$$

Hence, (A) is the correct answer.

**Sol 8: (D)** According to Kohlrausch's law, the molar conductivity of an electrolyte at infinite dilution is the sum of conductivities of its ions. Therefore to obtain  $\Lambda_{\text{HOAc}}^\circ$  from the conductivity of  $\Lambda_{\text{NaOAc}}^\circ$  &  $\Lambda_{\text{HCl}}^\circ$ , the conductivity value of NaCl i.e.  $\Lambda_{\text{NaCl}}^\circ$  is also needed.

$$\Lambda_{\text{NaOAc}}^\circ + \Lambda_{\text{HCl}}^\circ - \Lambda_{\text{NaCl}}^\circ = \Lambda_{\text{HOAc}}^\circ$$

$$\text{i.e. } \Lambda_{\text{Na}^+}^\circ + \Lambda_{\text{OAc}^-}^\circ + \Lambda_{\text{H}^+}^\circ + \Lambda_{\text{Cl}^-}^\circ - (\Lambda_{\text{Na}^+}^\circ + \Lambda_{\text{Cl}^-}^\circ)$$

$$= \Lambda_{\text{OAc}^-}^\circ + \Lambda_{\text{H}^+}^\circ = \Lambda_{\text{HOAc}}^\circ$$

**Sol 9: (A)** Cell constant

$$= \frac{\text{Conductivity(I)}}{\text{Conductance(I)}} = \frac{\text{Conductivity(II)}}{\text{Conductance(II)}}$$

$$\text{Conductivity (II)} = \frac{129}{520} \text{ Sm}^{-1}$$

$$0.2 \text{ M} = 200 \text{ mol m}^{-3}.$$

Molar conductivity of 0.2 M solution

$$= \frac{129/520}{200} = 12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}.$$

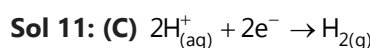
**Note:** From given data it is not possible to calculate molar conductivity of 0.02 M solution exactly. However, it is sure that its molar conductivity will be slightly greater than  $12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ . Assuming linear inverse variation of molar conductivity with concentration we can say that

$\therefore$  Molar conductivity of 0.02M solution

$$= 1.24 \times 10^{-3} \times 10$$

$$= 12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}.$$

**Sol 10: (C)** Velocities of both  $\text{K}^+$  and  $\text{NO}_3^-$  are nearly the same in  $\text{KNO}_3$  so it is used to make salt-bridge.



$$E_{\text{red}} = E_{\text{red}}^\circ - \frac{0.0591}{n} \log \frac{P_{(\text{H}_2)}}{(\text{H}^+)^2}$$

$$E_{\text{red}} = 0 - \frac{0.0591}{2} \log \frac{2}{(1)^2}$$

$$E_{\text{red}} = \frac{0.0591}{2} \log 2$$

$\therefore E_{\text{red}}$  is found to be negative for (c) option

$$\text{Sol 12: (C)} \quad E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q$$

$$\text{Where, } Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

For complete discharge,  $E_{\text{cell}} = 0$

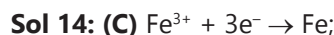
$$\text{So, } E_{\text{cell}}^\circ = \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\Rightarrow \left[ \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right] = 10^{37.3}.$$

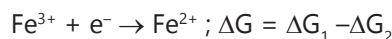
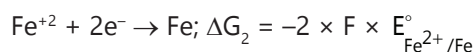
**Sol 13: (D)** For the cell reaction, Fe acts as cathode and Sn as anode. Hence,

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = -0.44 - (-0.14) = -0.30\text{V}$$

The negative EMF suggests that the reaction goes spontaneously in reverse direction.



$$\Delta G_1 = -3 \times F \times E_{\text{Fe}^{3+}/\text{Fe}}^\circ$$



$$\Delta G = 3 \times 0.036F - 2 \times 0.439 \times F$$

$$= -1 \times E_{\text{(Fe}^{3+}/\text{Fe}^{2+})}^\circ \times F$$

$$E_{\text{(Fe}^{3+}/\text{Fe}^{2+})}^\circ = 2 \times 0.439 - 3 \times 0.036$$

$$= 0.878 - 0.108 = 0.770 \text{ V}$$

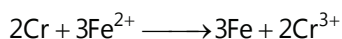
$$\text{Sol 15: (C)} \quad E = E^\circ - \frac{0.059}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 1.10 - \frac{0.059}{2} \log \frac{1}{0.1}$$

$$= 1.10 - 0.0295 \log 10 = 1.07 \text{ volt.}$$

**Sol 16: (A)**

As  $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.72\text{V}$  and  $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.42\text{V}$

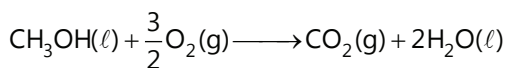


$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{6} \log \frac{(\text{Cr}^{3+})^2}{(\text{Fe}^{2+})^3}$$

$$= (-0.42 + 0.72) - \frac{0.0591}{6} \log \frac{(0.1)^2}{(0.01)^3} = 0.30 - \frac{0.0591}{6} \log \frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.0591}{6} \log \frac{10^{-2}}{10^{-6}} = 0.30 - \frac{0.0591}{6} \log 10^4$$

$$E_{\text{cell}} = 0.2606 \text{ V}$$

**Sol 17: (D)**

$$\Delta H = -726 \text{ kJ mol}^{-1}$$

$$\text{Also } \Delta G_f^\circ \text{CH}_3\text{OH}(\ell) = -166.2 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ \text{H}_2\text{O}(\ell) = -237.2 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ \text{CO}_2(\ell) = -394.4 \text{ kJ mol}^{-1}$$

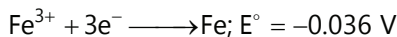
$$\therefore \Delta G = \Sigma \Delta G_f^\circ \text{ products} - \Sigma \Delta G_f^\circ \text{ reactants}$$

$$= -394.4 - 2(237.2) + 166.2$$

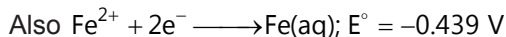
$$= -702.6 \text{ kJ mol}^{-1}$$

$$\text{now Efficiency of fuel cell} = \frac{\Delta G}{\Delta H} \times 100$$

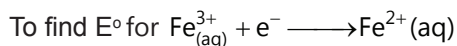
$$= \frac{702.6}{726} \times 100 = 97\%$$

**Sol 18: (C)**

$$\therefore \Delta G_1^\circ = -nFE^\circ = -3F(-0.036) = +0.108F$$



$$\therefore \Delta G_2^\circ = -nFE^\circ = -2F(-0.439) = 0.878F$$



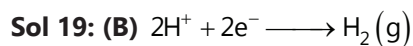
$$\Delta G_1^\circ = -nFE^\circ = -1FE^\circ$$

$$\therefore G^\circ = G_1^\circ - G_2^\circ$$

$$\therefore G^\circ = 0.108F - 0.878F$$

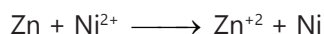
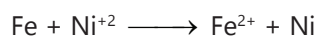
$$\therefore -FE^\circ = +0.108F - 0.878F$$

$$\therefore E^\circ = 0.878 - 0.108 = 0.77\text{v}$$



$$E = E^\circ - 0.059 \log \left( \frac{P_{\text{H}_2}}{[\text{H}^+]^2} \right) \quad (\text{here } E \text{ is } -\text{ve when } P_{\text{H}_2} > [\text{H}^+]^2)$$

$$= \frac{-0.0591}{2} \log_{10} \left( \frac{2}{1} \right) = \frac{-0.0591}{2} \times 0.3010 = \text{negative value}$$

**Sol 20: (D)**

All these are spontaneous

**Sol 21: (D)**

Higher the SRP, better is oxidising agent.

Hence,  $\text{MnO}_4^-$  is strongest oxidising agent.

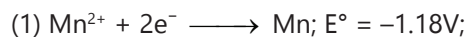
**Sol 22: (C)**

According to Debye Huckle onsager equation,

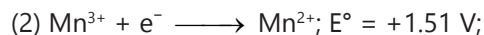
$$\lambda_c = \lambda_\infty + (A)\sqrt{C}$$

Here  $A = B$

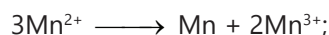
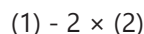
$$\therefore \lambda_c = \lambda_\infty + (B)\sqrt{C}$$

**Sol 23: (A)**

$$\Delta G_1^\circ = -2F(-1.18) = 2.36F$$



$$\Delta G_2^\circ = -F(-1.51) = -1.51F$$



$$\Delta G_3^\circ = \Delta G_1^\circ - 2\Delta G_2^\circ$$

$$= [2.36 - 2(-1.51)] F$$

$$= (2.36 + 3.02) F$$

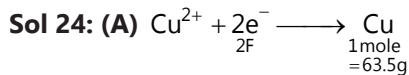
$$= 5.38 F$$

$$\text{But } \Delta G_3^\circ = 12FE^\circ$$

$$\Rightarrow 5.38F = -2FE^\circ$$

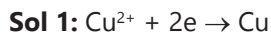
$$\Rightarrow E^\circ = -2.69 \text{ V}$$

As  $E^\circ$  value is negative reaction is non-spontaneous.



## JEE Advanced/Boards

### Exercise 1



$$E^\circ = 0.344$$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} = 0.226$$

As after  $E < 0.226$ , Bi will also start to deposit

$$0.344 - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} = 0.226$$

$$0.0295 \log [\text{Cu}^{2+}] = -0.118$$

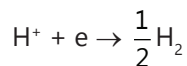
$$\log [\text{Cu}^{2+}] = -4$$

$$[\text{Cu}^{2+}] = 10^{-4} \text{ M}$$

**Sol 2:** Reduction potential of calomel electrode = 0.28 V

$$0.67 = 0.28 - E^\circ_{\text{H}^+/\text{H}_2}$$

$$E^\circ_{\text{H}^+/\text{H}_2} = -0.39$$



$$E = E^\circ - 0.059 \log \frac{1}{[\text{H}^+]}$$

$$-0.39 = -0.059 \log \frac{1}{[\text{H}^+]}$$

$$\frac{-0.039}{0.059} = \log[\text{H}^+]$$

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = 6.61$$

**Sol 3:**  $\text{Ag}^+ + e^- \rightarrow \text{Ag}$

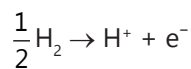
$$E_{\text{Ag}^+/\text{Ag}} = E^\circ_{\text{Ag}^+/\text{Ag}} - \frac{0.0591}{1} \log \frac{1}{[\text{Ag}^+]}$$

$$= 0.8 - 0.0591 \log \frac{1}{0.8}$$

$$E_{\text{Ag}^+/\text{Ag}} = 0.794$$

$$E_{\text{H}_2/\text{H}^+} + E_{\text{Ag}^+/\text{Ag}} = 0.982$$

$$E_{\text{H}_2/\text{H}^+} = 0.188$$



$$0.188 = 0 - 0.059 \log[\text{H}^+]$$

$$[\text{H}^+] = 6.6 \times 10^{-4}$$

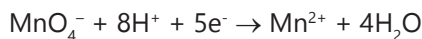
$$C\alpha = 6.6 \times 10^{-4}$$

$$\Rightarrow \alpha = \frac{6.6 \times 10^{-4}}{1.3 \times 10^{-3}} = 0.5$$

$$k_a = \frac{C\alpha^2}{1-\alpha}$$

$$k_a = 6.74 \times 10^{-4}$$

**Sol 4:**  $E = E^\circ - \frac{0.0591}{5} \log \frac{[\text{Mn}^{2+}]}{[\text{H}^+]^8 [\text{MnO}_4^-]}$



$$t = 0 \quad 0.1 \quad 0.8$$

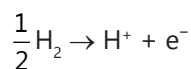
$$t = t \quad 0.01 \quad 0.08 \quad 0.09$$

$$E = 1.51 - 0.01182 \log \frac{0.09}{(0.08)^8 (0.01)} = 1.39 \text{ V}$$

**Sol 5:**  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$\alpha = \sqrt{\frac{k_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = 0.0134$$

$$[\text{H}^+] = C\alpha = 1.34 \times 10^{-3}$$

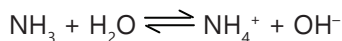


$$E_{\text{H}_2/\text{H}^+} = E^\circ_{\text{H}_2/\text{H}^+} - 0.0591 \log \frac{[\text{H}^+]}{P_{\text{H}_2}^{1/2}}$$

$$E_{\text{H}_2/\text{H}^+} = 0 - 0.0591 \log 1.34 \times 10^{-3}$$

$$E_{\text{H}_2/\text{H}^+} = 0.170 \text{ V}$$

At cathode,



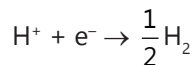
$$\alpha = \sqrt{\frac{k_b}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.01}}$$

$$\alpha = 0.042$$



$$[\text{OH}^-] = C\alpha = 4.24 \times 10^{-4}$$

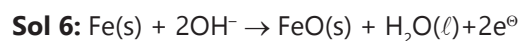
$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} = 2.35 \times 10^{-11}$$



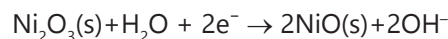
$$E_{\text{H}^+/\text{H}_2} = E_{\text{H}_2/\text{H}^+}^\circ - 0.0591 \log \frac{1}{[\text{H}^+]}$$

$$= 0.0591 \log \frac{1}{2.35 \times 10^{-11}} = -0.628 \text{ V}$$

$$E_{\text{cell}} = E_{\text{H}_2/\text{H}^+} + E_{\text{H}^+/\text{H}_2} = 0.170 - 0.628 = 0.458 \text{ V}$$

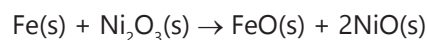


$$E^\circ = 0.87 \text{ V}$$



$$E^\circ = +0.4 \text{ V}$$

(i) Cell reaction



$$(ii) E^\circ = 0.87 + 0.4 = 1.27 \text{ V}$$

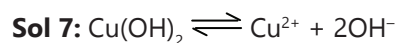
It does not depend on [KOH]

(iii) Maximum amount of electrical energy

$$= |-n F E^\circ|$$

$$= |-2 \times 96.5 \times 1.27 \text{ kJ}|$$

$$= 245.1 \text{ kJ}$$



$$\text{We have } \text{pH} = -\log[\text{H}^+] = 14$$

$$[\text{H}^+] = 10^{-14}$$

$$[\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} = 1$$

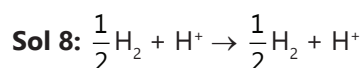
$$[\text{Cu}^{2+}] [\text{OH}^-]^2 = K_{\text{sp}}$$

$$[\text{Cu}^{2+}] = 1 \times 10^{-19}$$



$$E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} = 0.34 - 0.0295 \log \frac{1}{10^{-19}}$$

$$= 0.34 - 0.56 = -0.22 \text{ V}$$



All conditions are standard except  $[\text{H}^+]_{\text{anode}}$

$$E = E^\circ - 0.0591 \log \frac{1}{[\text{H}^+]_{\text{cathode}}}$$

$$-0.188 = 0 - 0.0591 \log \frac{1}{[\text{H}^+]}$$

$$\log [\text{H}^+] = 6.59 \times 10^{-4}$$



$$\text{Ch} = [\text{H}^+]$$

$$h = \frac{6.59 \times 10^{-4}}{(1/32)} = 2.12 \times 10^{-2}$$

$$k_h = \frac{C\alpha^2}{1.\alpha}$$

$$k_h = 1.43 \times 10^{-5}$$

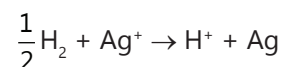
**Sol 9:** m. equivalents of  $\text{OH}^-$  added = MV

$$= 40 \times 0.05 = 2 \text{ meq.}$$

m. equivalents of  $\text{H}^+$  = MV =  $30 \times 0.1 = 3 \text{ meq.}$

$\therefore$  m. equivalents of  $\text{H}^+$  remaining = 1 meq.

$$[\text{H}^+] = \frac{1}{40+30} = 0.014$$



$$P_{\text{H}_2} = 1 \text{ atm,}$$

$$\therefore E = E^\circ - 0.0591 \log \frac{[\text{H}^+]}{[\text{Ag}^+]}$$

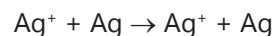
$$\therefore E_2 - E_1 = 0.0591 \log \frac{[\text{H}^+]_1}{[\text{H}^+]_2} \cdot \frac{[\text{Ag}^+]_2}{[\text{Ag}^+]_1}$$

$$E_2 - 0.9 = 0.0591 \log \frac{0.1}{0.014} \cdot 1$$

$$E_2 - 0.9 = 0.05$$

$$E_2 = 0.95 \text{ V}$$

**Sol 10:**  $E^\circ = 0$



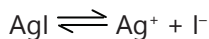
$$[\text{Ag}^+]_c = 0.05 \text{ M}$$

$$E = \frac{-0.0591}{1} \log \frac{[\text{Ag}^+]_a}{[\text{Ag}^+]_c}$$

$$0.788 = -0.0591 \log \frac{[\text{Ag}^+]_a}{0.05}$$

$$\log \frac{[\text{Ag}^+]_a}{0.05} = -13.3$$

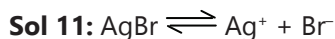
$$[\text{Ag}^+] = 2.32 \times 10^{-15}$$



$$k_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$$

$$[\text{I}^-] = [\text{KI}] = 0.05$$

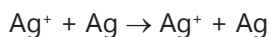
$$\therefore k_{\text{sp}} = 1.16 \times 10^{-16}$$



$$k_{\text{sp}} = [\text{Ag}^+]_a [\text{Br}^-]$$

$$[\text{Ag}^+]_a = \frac{(k_{\text{sp}})_{\text{AgBr}}}{[\text{Br}^-]}$$

$$\text{Similarly, } [\text{Ag}^+]_c = \frac{(k_{\text{sp}})_{\text{AgCl}}}{[\text{Cl}^-]}$$



cathode anode

$$E^\circ = 0$$

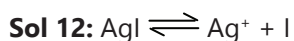
$$E = -0.0591 \log \frac{[\text{Ag}^+]_a}{[\text{Ag}^+]_c} = 0$$

$$[\text{Ag}^+]_a = [\text{Ag}^+]_c$$

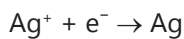
$$\frac{(k_{\text{sp}})_{\text{AgBr}}}{[\text{Br}^-]} = \frac{(k_{\text{sp}})_{\text{AgCl}}}{[\text{Cl}^-]}$$

$$\frac{[\text{Br}^-]}{[\text{Cl}^-]} = \frac{5 \times 10^{-13}}{1 \times 10^{-10}}$$

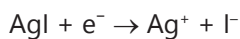
$$\frac{[\text{Br}^-]}{[\text{Cl}^-]} = 5 \times 10^{-3} = \frac{1}{200}$$



$$\Delta G^\circ = -nFE_1^\circ$$



$$\Delta G^\circ = -nFE_1^\circ$$

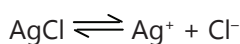


$$\Delta n = -nFE^\circ = -nFE_1^\circ - RT \ln k$$

$$E^\circ = E_1^\circ + \frac{RT}{nF} \ln k$$

$$E^\circ = E_1^\circ - \frac{2.303RT}{nF} \text{pk}_{\text{sp}}$$

$$E^\circ = -0.15$$



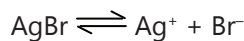
$$k_{\text{sp}} = [\text{Ag}^+]_a [\text{Cl}^-]$$

$$2.8 \times 10^{-10} = [\text{Ag}^+]_a \times 0.2$$

$$[\text{Ag}^+]_a = 1.4 \times 10^{-9}$$

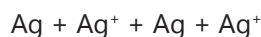


At cathode



$$k_{\text{sp}} = [\text{Ag}^+]_c [\text{Br}^-]$$

$$[\text{Ag}^+]_c = \frac{3.3 \times 10^{-13}}{10^{-3}} = 3.3 \times 10^{-10}$$



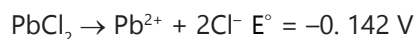
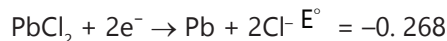
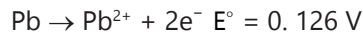
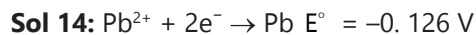
Cathode anode

$$E^\circ = 0$$

$$E = -0.591 \log \frac{[\text{Ag}^+]_a}{[\text{Ag}^+]_c} = 0.0591 \log \frac{1.4 \times 10^{-9}}{3.3 \times 10^{-10}}$$

$$E = -0.037 \text{ V}$$

For a spontaneous process, electrodes should be reversed.



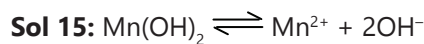
$$\Delta G^\circ = -FnE^\circ = -RT \ln k$$

$$\ln k = \frac{nF}{RT} E^\circ$$

$$\log k = \frac{nF}{RT \times 2.303} E^\circ$$

$$\log k = -4.8n = 2$$

$$k = 1.536 \times 10^{-5}$$



$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{OH}^-]^2$$

$$[\text{Mn}^{2+}] = \frac{1.9 \times 10^{-13}}{(10^{-4})^2}$$

$$[\text{Mn}^{2+}] = 1.9 \times 10^{-5}$$

Cell reaction:



$$E_{\text{Mn}^{2+}/\text{Mn}}^\circ = -1.18 \text{ V}$$

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.34 \text{ V}$$

$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Mn}^{2+}/\text{Mn}}^{\circ}$$

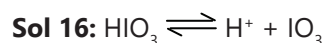
$$E^{\circ} = 0.34 - (-1.18)$$

$$E^{\circ} = 1.52 \text{ V}$$

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Mn}^{2+}]}{[\text{Cu}^{2+}]}$$

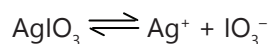
$$= 1.52 - 0.0295 \log \frac{1.9 \times 10^{-5}}{6.75 \times 10^{-2}} = 1.52 - (-0.14)$$

$$E = 1.66 \text{ V}$$



$$[\text{IO}_3^-] = C\alpha = C \sqrt{\frac{k_a}{C}} = \sqrt{Ck_a}$$

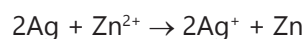
$$[\text{IO}_3^-] = 0.22 \text{ M}$$



$$k_{\text{sp}} = [\text{Ag}^+][\text{IO}_3^-]$$

$$[\text{Ag}^+] = \frac{3.08 \times 10^{-8}}{0.22}$$

$$[\text{Ag}^+] = 1.37 \times 10^{-7}$$



$$E_{\text{Ag}/\text{Ag}^+}^{\circ} = -0.80 \text{ V}$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$

$$E_{\text{cell}}^{\circ} = E_{\text{Ag}/\text{Ag}^+}^{\circ} + E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -1.56 \text{ V}$$

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Ag}^+]^2}{[\text{Zn}^{2+}]}$$

$$E = -1.56 - 0.0295 \log \frac{(1.37 \times 10^{-7})^2}{0.175}$$

$$E = -1.56 + 0.372$$

$$E = -1.188 \text{ V}$$



$$E^{\circ} = 0$$

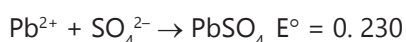
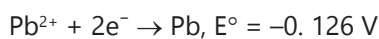
$$E = 0 - \frac{0.0591}{2} \log \frac{[\text{Pb}^{2+}]_a}{[\text{Pb}^{2+}]_c} + 0.061$$

$$= \frac{0.0591}{2} \log \frac{[\text{Pb}^{2+}]_a}{2.5 \times 10^{-3}}$$

$$\log \frac{[\text{Pb}^{2+}]_a}{2.5 \times 10^{-5}} = -2.06$$

$$[\text{Pb}^{2+}]_a = 2.13 \times 10^{-7}$$

At anode,



$$\Delta G = -nF E^{\circ} = -RT \ln k$$

$$\ln k = \frac{nF}{RT} E^{\circ}$$

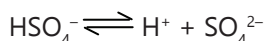
$$\log k = \frac{nF}{2.303RT} E^{\circ}$$

$$k = 1.60 \times 10^{-8}$$

$$k_{\text{sp}} = 1.6 \times 10^{-8} = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = \frac{1.6 \times 10^{-8}}{2.13 \times 10^{-7}}$$

$$[\text{SO}_4^{2-}] = 7.50 \times 10^{-2}$$



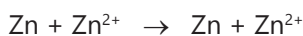
$$0.525 \quad 0.075 \quad 0.075$$

$$k_a = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

$$k_a = 9.46 \times 10^{-3}$$

$$k_a \approx 10^{-2}$$

**Sol 18:** Cell reaction



Cathode                  anode

$$E^{\circ} = 0$$

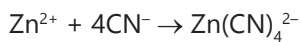
$$E = \frac{-0.0591}{2} \log \frac{[\text{Zn}^{2+}]_a}{[\text{Zn}^{2+}]_c}$$

$$0.099 = \frac{-0.0591}{2} \log \frac{[\text{Zn}^{2+}]_a}{3.84 \times 10^{-4}}$$

$$\log \left( \frac{[\text{Zn}^{2+}]_a}{3.84 \times 10^{-4}} \right) = -3.356$$

$$[\text{Zn}^{2+}]_a = 1.69 \times 10^{-7}$$

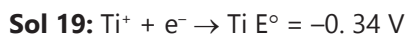
At anode



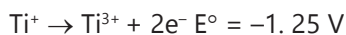
$$K_f = \frac{[\text{Zn}(\text{CN})_4^{2-}]}{[\text{Zn}^{2+}][\text{CN}^-]^4}$$

$$= \frac{0.450}{1.69 \times 10^{-7} \times (2.65 \times 10^{-3})^4}$$

$$K_f = 5.24 \times 10^{16}$$



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



$$\Delta G_1 = -nF E^\circ = -2F(-1.25)$$



$$\Delta G_2 = -2nF E^\circ = -2F(-0.34)$$



$$\Delta G = \Delta G_1 + \Delta G_2$$

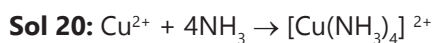
$$\Rightarrow -2FE^\circ = -2FE^\circ_1 - 2FE^\circ_2$$

$$E^\circ = E^\circ_1 + E^\circ_2$$

$$E^\circ = -0.34 - 1.25$$

$$E^\circ = -1.59 \text{ V}$$

Since,  $E^\circ < 0$ , it is non spontaneous reaction.



We have,  $A - 4x = 2$

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

$$1 \times 10^{12} = \frac{x}{(1-x) \cdot 2^4}$$

$$\frac{1-x}{x} = 6.25 \times 10^{-14}$$

$$\frac{1}{x} - 1 = 6.25 \times 10^{-14}$$

$$x = \frac{1}{1 + 6.25 \times 10^{-14}}$$

$$1 - x = \frac{6.25 \times 10^{-14}}{1 + 6.25 \times 10^{-14}} \approx 6.25 \times 10^{-14}$$



$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E = 1.1 - \frac{0.0591}{2} \log \frac{1}{1-x}$$

$$= 1.1 - 0.0295 \log \frac{1}{6.25 \times 10^{-14}}$$

$$E = 0.71 \text{ V}$$



we have,  $E^\circ = 0.76 - (-0.34) = 1.1 \text{ V}$

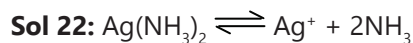
$$\Delta G = -nF E^\circ = -RT \ln k$$

$$\log k = \frac{nF}{2.303 \times RT} E^\circ$$

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

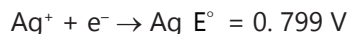
$$\log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{2}{0.0591} \times 1.1 = 37.28$$

$$\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.941 \times 10^{37}$$



$$K_0 = 6 \times 10^{-8}$$

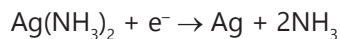
$$\Delta G_1 = -RT \ln k_0$$



$$\Delta G_2 = -nF E^\circ = -F \times 0.799$$

(n = 1)

Adding,



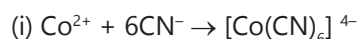
$$\Delta G = -nF E^\circ = \Delta G_1 + \Delta G_2$$

$$-n E^\circ = -RT \ln k_0 - 0.799 F$$

$$E^\circ = \frac{RT}{F} \ln k_0 + 0.799 = \frac{2.303 RT}{F} \log(6 \times 10^{-8}) + 0.799$$

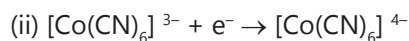
$$E^\circ = 0.373 \text{ V}$$

**Sol 23:** We have,



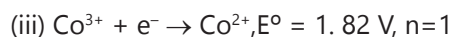
$$K_f = 1 \times 10^{14}$$

$$\Delta G_1 = -RT \ln k_f = -43.757 RT$$



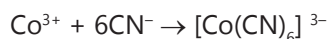
$$E^\circ = -0.83 \text{ V}, n=1$$

$$\Delta G_2 = -nF E^\circ = 0.83 F$$



$$\Delta G_3 = -nF E^\circ = -1.82 F$$

(iii) + (i). (ii) gives,



$$\Delta G = \Delta G_3 + \Delta G_1 - \Delta G_2$$

$$\Delta G = -RT \ln k_f = -1.82F - 43.757RT - 0.83 F$$

$$\Rightarrow \ln k_f = \frac{F}{RT} \times 1.82 + 43.757 + \frac{F}{RT} 0.83$$

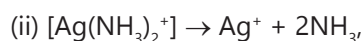
$$\log k_f = \frac{1.82 + 0.83}{0.059} + 19$$

$$k_f = 8.27 \times 10^{63}$$

**Sol 24:** we have,



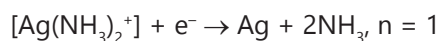
$$\Delta G_1^\circ = -nF E^\circ = -0.7991 F$$



$$k_{\text{ins}} = 6.02 \times 10^{-8}$$

$$\Delta G_2 = -RT \ln k_{\text{ins}}$$

Adding (i) and (ii),



$$\Delta G = \Delta G_1 + \Delta G_2$$

$$-F E^\circ = -0.7991 F - RT \ln k_{\text{ins}}$$

$$E^\circ = 0.7991 + \frac{2.303RT}{F} \log k_{\text{ins}}$$

$$= 0.7991 + 0.0591 \log (6.02 \times 10^{-8})$$

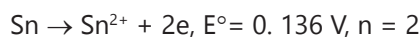
$$E^\circ = 0.372 \text{ V}$$

Similarly for  $[\text{Ag}(\text{CN})_2]^-$

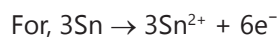
$$E^\circ = 0.7991 + 0.0591 \log (1.995 \times 10^{-19})$$

$$E^\circ = -0.307 \text{ V}$$

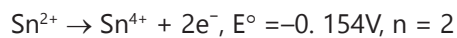
**Sol 25:** We have,



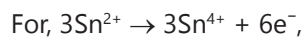
$$\Delta G_1' = -nF E^\circ = -2F \times 0.136 = -0.272 F$$



$$\Delta G_1 = 3\Delta G_1' = -0.816 F$$



$$\Delta G_2 = -nF E^\circ = -2 \times F \times (-0.154) = 0.308 F$$

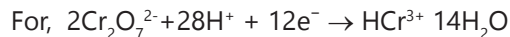


$$\Delta G_2 = 3\Delta G_2' = 0.924 F$$



$$E^\circ = 1.33 \text{ V}, n = 6$$

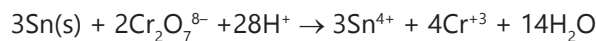
$$\Delta G_3' = -nF E^\circ = -6F(1.33) = -7.98 F$$



$$\Delta G_3 = 2\Delta G_3'$$

$$\Delta G_3 = -15.96 F$$

Now, (i) + (ii) + (iii) gives



$$\Delta G = -RT \ln k = \Delta G_1 + \Delta G_2 + \Delta G_3$$

$$-RT \ln k = -0.816 F + 0.924 F - 15.96 F$$

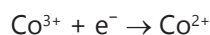
$$\ln k = \frac{F}{RT} \times 15.852$$

$$\log k = \frac{15.852}{0.0591}$$

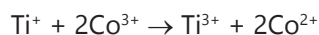
$$\log k = 268$$

$$k = 10^{268}$$

**Sol 26:**  $\text{Ti}^+ \rightarrow \text{Ti}^{3+} + 2e^-; E^\circ = -1.25 \text{ V}$



Adding,



$$E^\circ = 0.59 \text{ V}$$

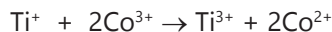
$$\Delta G = -nF E^\circ = -RT \ln k, n = 2$$

$$\log k = \frac{2F}{2.303 RT} E^\circ = \frac{0.59}{0.0295} = 20$$

$$k = 10^{20}$$

Now, if  $\text{Ti}^+ = 0.1 \times 2.5 = 25$

Initial milimoles of  $\text{Co}^{3+} = 25 \times 0.2 = 5$



$$t = 0 \quad 2.5 \quad 5 \quad 0 \quad 0$$

$$t = t \quad 2.5 - x \quad 5 - 2x \quad x \quad 2x$$

$$k = \frac{[\text{Ti}^{3+}][\text{Co}^{2+}]^2}{[\text{Co}^{3+}]^2[\text{Ti}^+]} = 10^{20}$$

$$V_{\text{final}} = 50 \text{ ml}$$

$$\frac{x \cdot 4x^2 \cdot (50)^2 \cdot (50)}{(50) \cdot (50)^2 (2.5 - x)(5 - 2x)^2} = 10^{20}$$

$$\frac{x^3}{(2.5 - x)(5 - 2x)^2} = 10^{20}$$

$$\frac{x^3}{(2.5 - x)^3} = 10^{20}$$

$$x \approx 2.5 \text{ as } k \gg \gg 1$$

Putting  $x = 2.5$

$$(2.5 - x)^3 = \frac{(2.5)^3}{10^{20}} = 1.5625 \times 10^{-3}$$

$$2.5 - x = 2.5 \times 10^{-7}$$

$$[\text{Ti}^+] = \frac{2.5 \cdot x}{50} = 5 \times 10^{-9}$$

$$[\text{Co}^{3+}] = \frac{2(2.5 - x)}{50} = 10^{-8}$$

**Sol 27:** For thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ ),  $n = 2$

Number of equivalent =  $n \cdot V \cdot M$ .

$$= 46.3 \times 0.124 \times 2 \times 10^{-9} = 11.4824 \text{ m. eq.}$$

Equivalents of  $x = \text{eq. of I}^-$

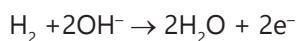
$$= 1 \times \frac{\text{eq.}}{2} \text{ of } \text{I}_2 = \frac{1}{2} \times \text{eq. of } \text{S}_2\text{O}_3^{2-}$$

$$\text{Eq. of } x = \frac{11.4824 \times 10^{-3}}{2}$$

$$\frac{0.617}{M} = \frac{11.4824 \times 10^{-3}}{2}$$

$$M = 107.3 \text{ gm}$$

**Sol 28:** At anode,



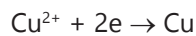
$$\text{Moles of } \text{H}_2 \text{ reacted} = \frac{67.2}{22.4} = 3$$

Charge produced by 1 mole  $\text{H}_2 = 2F$

Charge produced by 3 mole  $\text{H}_2 = 6F$

$$\text{Current, } I = \frac{6F}{t} = \frac{6 \times 96500}{15 \times 60}$$

$$I = 643.33 \text{ A}$$

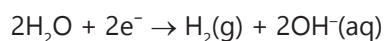


number of moles of Cu produced = 3

$$\text{wt.} = 3 \times 63.5 \text{ g}$$

$$\text{wt.} = 190.5 \text{ g}$$

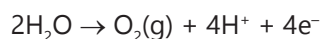
**Sol 29:** At cathode, only reduction of water takes place



$$\text{Moles of } \text{H}_2 \text{ produced} = \frac{9.722}{22.4} = 0.434$$

$$\text{Charge needed, } Q = 2 \times 0.434 = 0.868$$

At anode, for oxidation of water



$$\text{Moles of } \text{O}_2 \text{ produced, } n_{\text{O}_2} = \frac{2.35}{22.4} = 0.105$$

$$\text{Charge needed, } q = 4 \times n_{\text{O}_2} = 0.420$$

Charge utilised for production of  $\text{H}_2\text{S}_2\text{O}_8$

$$= Q \cdot q = 0.998$$

$$\text{Moles of } \text{H}_2\text{S}_2\text{O}_8 = \frac{\text{charge utilised}}{2} = 0.224$$

$$\text{Weight of } \text{H}_2\text{S}_2\text{O}_8 = 0.224 \times 194 = 43.456 \text{ gm}$$

**Sol 30:** Initially, mass of  $\text{H}_2\text{SO}_4$  solution

$$= 1.294 \times 3.5 \times 1000 \text{ gm} = 4.529 \text{ kg}$$

$$\text{Wt. of } \text{H}_2\text{SO}_4 = \frac{39}{100} \times 4.529 = 1.76631 \text{ kg}$$

$$\text{Moles of } \text{H}_2\text{SO}_4 = 18.02$$

$$[\text{H}_2\text{SO}_4] = 5.15 \text{ M}$$

$$\text{Finally, Mass } \text{H}_2\text{SO}_4 \text{ solution} = 1.139 \times 3.5 \text{ kg}$$

$$= 3.9865 \text{ kg}$$

$$\text{Mass of } \text{H}_2\text{SO}_4 = \frac{20}{100} \times 3.9865 \text{ kg} = 0.7973 \text{ kg}$$

$$\text{Moles of } \text{H}_2\text{SO}_4 = 8.136$$

$$[\text{H}_2\text{SO}_4] = 2.324 \text{ M}$$

$$\therefore \Delta n_{\text{SO}_4^{2-}} = 9.884$$

$2F$  charge consumes 2 moles of  $[\text{SO}_4^{2-}]$

According to net reaction

Charge required = 9.884 F

$$\text{Ampere hours} = \frac{9.884 \times 96500}{3600} = 265 \text{ Amp. hr.}$$

**Sol 31:**  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

$$\text{Moles of Cu deposited} = \frac{3}{63.5} = 0.047$$

$$\text{Charge utilised} = 2 \times 0.047 \times F = 0.094 F = 9071 \text{ C}$$

$$\text{Charge supplied} = 3 \times 2 \times 3600 = 21600 \text{ C}$$

$$\therefore \text{Efficiency} = \frac{\text{Charge utilised}}{\text{Charge supplied}} = \frac{9071}{21600} = 0.422$$

$$\therefore \text{Efficiency} = 42.2 \%$$

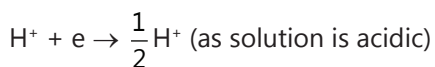
**Sol 32:** At cathode,



$$\text{Moles of Cu deposited} = \frac{0.4}{63.5} = 6.3 \times 10^{-3}$$

$$\text{Charge supplied} = 2 \times 6.3 \times 10^{-3} F = 1215.74 \text{ C}$$

After deposition of copper,



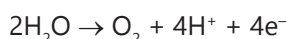
$$\text{Extra charge supplied} = 1.2 \times 7 \times 60$$

$$= 504 \text{ C} = 5.22 \times 10^{-3} F$$

$$\text{Moles of H}_2 \text{ evolved} = \frac{5.22 \times 10^{-3}}{2} = 2.61 \times 10^{-3}$$

$$\text{Volume of H}_2 \text{ evolved} = 2.61 \times 10^{-3} \times 22400 = 58.46 \text{ mL}$$

At anode,



Total charge,

$$Q = 2 \times 6.3 \times 10^{-3} \times F + 5.22 \times 10^{-2} F = 1.78 \times 10^{-2} F$$

$$\text{Moles of O}_2 \text{ evolved} = \frac{Q}{4} = 4.45 \times 10^{-3}$$

$$\text{Volume of O}_2 \text{ evolved} = 4.45 \times 10^{-3} \times 22400 = 99.68 \text{ mL}$$

$$\text{Total volume} = 158.14 \text{ mL}$$

**Sol 33:**  $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$

$$\text{Total charge supplied} = \frac{5 \times 2 \times 3600}{96500} = 0.373 F$$

Now, since purity of electrode is 95%

Here, if charge will oxidise 0.95 moles of Ag, rather than 1 mole

$$\therefore \text{Moles of Ag oxidised} = \frac{0.373}{0.95} = 0.392$$

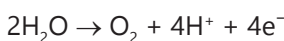
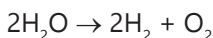
$$\text{Mass of Ag oxidised} = 0.392 \times 108 = 42.41 \text{ g}$$

$$\text{Mass of electrode} = 100 - 42.41 = 57.58 \text{ g}$$

**Sol 34:** Charge supplied per second

$$= \frac{1.5 \times 10^6}{96500} = 15.54 \text{ F}$$

Electrolysis:



4 F charges electrolysed 2 moles of H<sub>2</sub>O.

$$\therefore \text{Moles of water electrolysed per second} = \frac{15.54}{2}$$

$$= 7.77$$

$$\text{Total moles of water} = \frac{8.2 \times 10^{12} \times 10^3}{18}$$

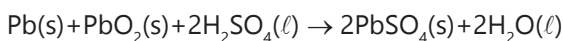
$$\text{Time required in years} = \frac{8.2 \times 10^{15}}{18 \times 7.77} \times 86400 \times 365 = 1.9 \text{ million years}$$

**Sol 35:** Initial mass of electrolyte

$$= 1.261 \times 1000 = 1261 \text{ g}$$

$$\text{Wt. of H}_2\text{SO}_4 = \frac{34.6}{100} \times 1261 = 436.306$$

$$\text{Moles of H}_2\text{SO}_4 = \frac{436.306}{98} = 4.45$$



$$t=0 \quad \quad \quad 4.45$$

$$t=t \quad \quad \quad 4.45-x \quad \quad \quad x$$

we have, wt. of H<sub>2</sub>SO<sub>4</sub> = 27

$$\therefore \frac{(4.45-x)98}{12.61 \times 436.606 + (4.45-x)98 + x.18} = 0.27$$

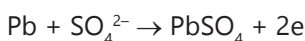
$$\Rightarrow 436.608 - 98x = 0.27(1261 - 80x)$$

$$463.608 - 98x = 340.47 - 21.6x$$

$$76.4x = 96.138$$

$$x = 1.258$$

$$\text{Change in moles of SO}_4^{2-} = x = 1.258$$

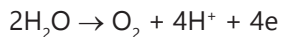


$$\text{Charge produced by 1 mole SO}_4^{2-} = 2F$$

$$\text{Charge produced by 1.258 moles SO}_4^{2-}$$

$$= 2 \times 1.258 F = 2.4 \times 10^5 \text{ C}$$

**Sol 36:** At anode,



$$\text{pH} = 1$$

$$\log[\text{H}^+] = 1$$

$$[\text{H}^+] = 0.1$$

$$n_{\text{H}^+} = [\text{H}^+] \times v = 0.1 \times 10^{-1} = 10^{-2}$$

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

$$n_{\text{H}^+} = 10^{-7} \times 10^{-1} = 10^{-8}$$

$$\text{Moles of H}^+ \text{ produced} = 10^{-2} - 10^{-8}$$

$$\approx 10^{-2}$$

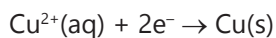
$$\text{Charge needed} = 10^{-2} F = 965 \text{ C}$$

$$\text{Theoretical time} = \frac{Q}{I} = \frac{96.5 \times 10}{0.965} = 1000 \text{ s}$$

$$\text{Current efficiency} = 80\%$$

$$\text{Therefore, actual time} = \frac{1000 \times 5}{4} \text{ s} = 1250 \text{ s}$$

Now, at cathode



$$\text{Current passed} = 10^{-2} F$$

$$\therefore \text{Moles of copper reduced} = \frac{10^{-2}}{2} = 5 \times 10^{-3}$$

After passing of current,

$$\text{Equivalent of copper} = \text{equivalents of I}_2$$

$$= 2 \text{ equivalents of S}_2\text{O}_3^{2-}$$

$$\text{Equivalent of copper}$$

$$= 2 \times 0.04 \times 35 \times 10^{-3}$$

$$\text{Moles of copper} = 31.4 \times 10^{-3}$$

$$(\because n = 2 \text{ for Cu}^{2+})$$

$$\therefore \text{Total moles of Cu}^{2+} = 6.4 \times 10^{-3}$$

$$\text{Molarity} = \frac{64 \times 10^{-3}}{100 \times 10^{-3}} = 0.064 \text{ M}$$

$$\text{Sol 37: Current passed} = \frac{5 \times 10 \times 3600}{96500} F = 1.861 F$$

At anode



$$\text{Moles of Zn}^{2+} \text{ reduced} = \frac{Q}{2} = 0.9326$$

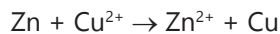
$$\text{Final, } [\text{Zn}^{2+}] = 1 - 0.9326 = 0.067$$

At cathode,



$$\text{Final, } [\text{Cu}^{2+}] = 1 + 0.9326 = 1.9326$$

Now, cell reaction,



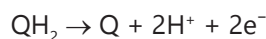
$$E^\circ = 1.1 \text{ V, } n = 2$$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.1 - 0.0295 \log \left( \frac{0.067}{1.9326} \right)$$

$$= 1.1 - (0.0295)(-1.45)$$

$$E = 1.143 \text{ V}$$

**Sol 38:** At anode, for quinhydrone electrode,



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

$$E^\circ + 0.0591 \text{ pH} = -0.699 + 0.0591 \text{ pH}$$

$$(\because E_{\text{OP}}^\circ = -E_{\text{RP}}^\circ)$$

At cathode,

$$E = E^\circ = 0.28$$

$$\therefore E_{\text{cell}} = 0.28 - 0.699 + 0.0591 \text{ pH}$$

$$E_{\text{cell}} = -0.419 + 0.0591 \text{ pH}$$

(a) At pH = 5.0,

$$E_{\text{cell}} = -0.419 + (0.0591) \times (5) = -0.124 \text{ V}$$

(b) When  $E_{\text{cell}} = 0$ ,

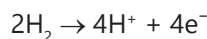
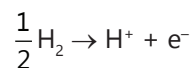
$$\text{pH} = \frac{0.419}{0.0591} = 7.1$$

(c) At pH = 7.5

$$E_{\text{cell}} = 0.0235 \text{ V}$$

Since,  $E_{\text{cell}}$  is positive, reaction takes place in the given direction and cathode (Calomel electrode) is positive electrode.

**Sol 39:** We have, at anode

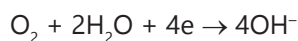


$$E^\circ = 0$$

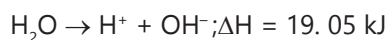
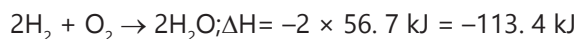
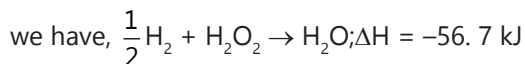
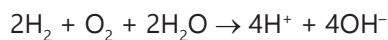
$$E = -0.0591 \log [\text{H}^+]$$



At cathode

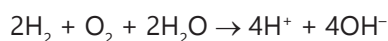


Overall cell reaction



$$\Delta H = 4 \times 19.05 \text{ kJ} = 76.2 \text{ kJ}$$

Adding,



$$\Delta H = -37.2 \text{ kJ}$$

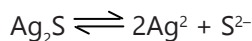
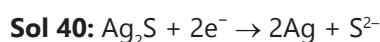
$$\Delta S = nF \left( \frac{\Delta E}{\Delta T} \right)_p = 4 \times 96500 \times 0.001058$$

$$\Delta S = 408.38$$

$$\Delta G = -nFE^\circ = \Delta H - T\Delta S$$

$$E^\circ = T \left( \frac{\Delta E}{\Delta T} \right)_p - \frac{\Delta H}{\Delta F}$$

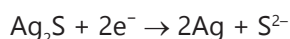
$$E^\circ = 0.4414 \text{ V}$$



$$\Delta G_1 = -RT \ln k_{sp}$$



$$\Delta G_2 = -2FE^\circ$$



$$\Delta G = \Delta G_1 + \Delta G_2 = -2FE^\circ - RT \ln k_{sp}$$

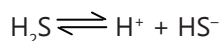
$$-nFE^\circ = -2FE^\circ - RT \ln k_{sp}$$

$$E^\circ = E^\circ + \frac{2.303 RT}{nF} \log k_{sp}$$

$$E^\circ = -0.64 \text{ V}$$

$$E = -0.64 - \frac{0.0591}{2} \log[\text{S}^{2-}]$$

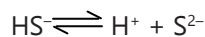
We have,



$$\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = k_1$$

$$k_1 = 10^{-8}, [\text{H}^+] = 10^{-3}, [\text{H}_2\text{S}] = 0.1$$

$$\therefore [\text{HS}^-] = 10^{-6} \text{ M}$$



$$10^{-6} \quad 10^{-3}$$

$$\frac{[\text{S}^{2-}][\text{H}^+]}{[\text{HS}^-]} = k_2$$

$$[\text{H}^+] = 10^{-3}, [\text{HS}^-] = 10^{-6}, k_2 = 1.1 \times 10^{-13}$$

$$\frac{[\text{S}^{2-}] \cdot 10^{-3}}{10^{-6}} = 1.1 \times 10^{-13}$$

$$[\text{S}^{2-}] = 1.1 \times 10^{-16} \text{ M}$$

$$E = -0.64 - 0.0295 \log(1.1 \times 10^{-16})$$

$$= -0.64 - 0.0295(-15.95)$$

$$E = -0.167 \text{ V}$$

**Sol 41:**  $\Lambda_{eq} = k \times \frac{1000}{N}$

$$k = \frac{97.1 \times 0.1}{1000} = 9.71 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$$

and,  $k = \frac{1}{R} \frac{\ell}{a}$

$$R = \frac{\ell}{ka} = \frac{0.5}{9.71 \times 10^{-3} \times 1.5}$$

$$R = 34.32 \Omega$$

$$I = \frac{V}{R} = \frac{5}{34.32} \text{ Z}$$

$$I = 0.1456 \text{ A}$$

**Sol 42:**  $E = \frac{V}{L} = \frac{6}{10/100} = 60 \text{ V/m} = 0.6 \text{ V/cm}$

Ionic mobility (drift speed) =  $\frac{\Lambda_{\infty}^0}{F} \times E$

$$= \frac{73.52}{96500} \times 0.6 \text{ cm/s} = 4.57 \times 10^{-4} \text{ cm/s}$$

$$\text{Distance in 2 hours} = 4.57 \times 10^{-4} \times 2 \times 3600 = 3.29 \text{ cm}$$

**Sol 43:**  $R = \frac{1}{k} \frac{\ell}{a}$

$$\ell = k R a = 1.342 \times 170.5 \times 1.86 \times 10^{-4} = 0.0425 \text{ m}$$

$$\ell = 4.25 \text{ cm}$$

**Sol 44:**  $\Lambda_m^0 \text{SrSO}_4 = \Lambda_m^0 \text{Sr}^{2+} + \Lambda_m^0 \text{SO}_4^{2-}$   
 $= 59.46 + 79.8 = 139.26 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$

$$\Lambda_m^0 \text{SrSO}_4 = 1000 \times \frac{k_{\text{SrSO}_4}}{C}$$

$$C = \frac{1000 \times 1.482 \times 10^{-4}}{139.26}$$

$$C = 1.064 \times 10^{-3}$$

$$C = S = 1.064 \times 10^{-3} \text{ mole/L}$$

$$= 1.064 \times 10^{-3} \times 183.6 \text{ gm/L}$$

$$S = 0.1953 \text{ gm/L}$$

**Sol 45:**  $\Lambda_m^0 (\text{Co}_2[\text{Fe}(\text{CN})_6])$

$$= 2\Lambda_m^0 (\text{Co}^{2+}) + \Lambda_m^0 ([\text{Fe}(\text{CN})_6]^{-})$$

$$= 2 \times 86 + 444 = 616 \Omega^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$$

$$k_{\text{Co}_2[\text{Fe}(\text{CN})_6]} = k_{\text{solution}} - k_{\text{water}}$$

$$= 2.06 \times 10^{-6} - 0.41 \times 10^{-6}$$

$$= 1.65 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$$

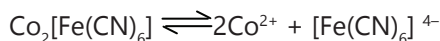
$$= 1.65 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$$

$$\Lambda_m^0 = k \times \frac{1000}{C}$$

$$C = \frac{k \times 1000}{\Lambda_m^0} = \frac{1.65 \times 10^{-6} \times 1000}{616}$$

$$C = 2.59 \times 10^{-6} \text{ mol/L}$$

$$S = C = 2.59 \times 10^{-6} \text{ mol/L}$$



$$k_{\text{sp}} = (2s)^2 \cdot S = 4S^3$$

$$k_{\text{sp}} = 7.682 \times 10^{-17}$$

**Sol 46:** For KCl,  $\Lambda_m^0 = 138 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

$$\therefore \Lambda_m = k \times \frac{1000}{C}$$

$$k = \frac{138 \times 0.02}{1000} = 2.76 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$$

$$G^* = Rk$$

$$= 2.76 \times 10^{-3} \times 85 = 0.2346 \text{ cm}^{-1}$$

$$k_{\text{water}} = \frac{G^*}{R} = \frac{0.2346}{9200}$$

$$k_{\text{water}} = 2.55 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$$

$$n_{\text{NaCl}} = \frac{500}{58.5} = 8.547$$

$$k_{\text{NaCl}+\text{H}_2\text{O}} = \frac{0.2346}{7600} = 3.08 \times 10^{-5}$$

$$k_{\text{NaCl}} = k_{\text{NaCl}+\text{H}_2\text{O}} \cdot k_{\text{H}_2\text{O}}$$

$$= (3.08 - 2.55) \times 10^{-5}$$

$$= 5.3 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$$

$$C_{\text{NaCl}} = \frac{k_{\text{NaCl}} \times 1000}{\Lambda_m}$$

$$= \frac{5.3 \times 10^{-6} \times 1000}{126.5} = 4.190 \times 10^{-5} \text{ mole/L}$$

$$C = \frac{n}{V}$$

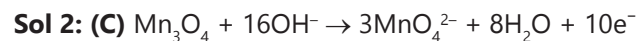
$$V = \frac{n}{C} = \frac{8.547}{4.19 \times 10^{-5}} (1 \text{ L} = 1 \text{ dm}^3)$$

$$V \approx 2 \times 10^5 \text{ dm}^3.$$

## Exercise 2

### Single Correct Choice Type

**Sol 1: (C)** As  $E_{\text{Ag}^+/\text{Ag}}^{\circ} > E_{\text{Hg}_2/\text{Hg}}^{\circ} > E_{\text{Cu}^{2+}/\text{Cu}}^{\circ}$

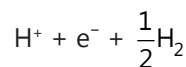


$$\therefore \text{Charge required} = 10 \text{ F}$$

**Sol 3: (A)** Only water will be oxidised and reduced at anode and cathode respectively because SRP of  $\text{SO}_4^{2-}$  is very high (magnitude).

**Sol 4: (C)** At X

$$\text{pH} = \text{pk}_a + \log \frac{[\text{A}^+]}{[\text{H}_\text{A}]} = \text{pk}_a + \log \frac{a}{b}$$



$$E_1 = 0 + 0.0591 \log [\text{H}^+] = -0.0591 \text{ pH}$$

$$\frac{E_1}{0.0591} = -\text{pk}_a - \log \frac{a}{b}$$

At Y

$$\text{pH} = \text{pk}_a + \log \frac{b}{a}$$

$$E_2 = -0.0591 \text{ pH}$$

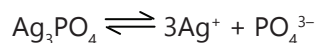
$$\frac{E_2}{0.0591} = -\text{pk}_a - \log \frac{b}{a} = -\text{pk}_a + \log \frac{a}{b}$$

$$\frac{E_1 + E_2}{0.0591} = -2pk_a$$

$$pk_a = -\frac{E_1 + E_2}{0.118}$$

$$\text{Sol 5: (A)} \quad \wedge_{\text{eq}} = \frac{k \times t}{C}$$

$$C = \frac{9 \times 10^{-6}}{1.5 \times 10^{-4}} \times 10^{-3} = 6 \times 10^{-5} \text{ M}$$



$$[\text{Ag}^+] = 3C = 1.8 \times 10^{-4} \text{ M}$$

$$[\text{PO}_4^{3-}] = 6 \times 10^{-5} \text{ M}$$

$$k_{\text{sp}} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}]$$

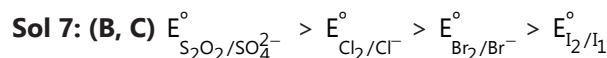
$$k_{\text{sp}} = 4.32 \times 10^{-18}$$



$$[\text{CH}_3\text{COONa}] = \frac{0.015}{2} = 0.0075$$

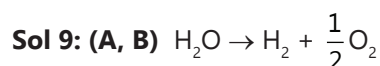
$$\begin{aligned} \wedge_m &= k \times \frac{1000}{C} \\ &= \frac{6.3 \times 10^{-4} \times 1000}{0.0075} = 84 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

### Multiple Correct Choice Type



species with higher  $E^\circ$  can oxidise a species with lower  $E^\circ$ .

**Sol 8: (B, C, D)** In all case  $\text{H}_2\text{O}$  will oxidise at anode to give  $\text{O}_2$ .



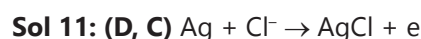
$$n_{\text{H}_2\text{O}} = \frac{270}{18} = 15$$

$$V_{\text{H}_2} = 15 \times 22.1 = 33.6 \text{ L}$$

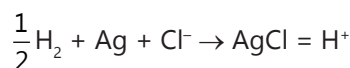
$$V_{\text{O}_2} = 168 \text{ L, evolved at anode}$$

$$V_{\text{T}} = 504 \text{ L}$$

**Sol 10: (C, D)** Refer text



Cell reaction

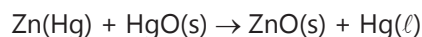


$$E = E^\circ - 0.0591 \log \frac{[\text{H}^+]}{[\text{Cl}^-][\text{P}_{\text{H}_2}]^{1/2}}$$

on increasing  $[\text{H}^+]$  or decreasing  $[\text{Cl}^-]$ ,  $E$  will decrease.

### Assertion Reasoning Type

**Sol 12: (A)** Cell Reaction:



$$\text{Sol 13: (D)} \quad E^\circ = E^\circ_{\text{left}} - E^\circ_{\text{right}}$$

$E^\circ$  is intensive.

**Sol 14: (A)** These are facts.

### Comprehension Type

#### Paragraph 1

**Sol 15: (B)**  $R = \rho G^*$

for KCl,  $\wedge_m = 200 \text{ S cm}^2 \text{ mol}^{-1}$

$$k = \frac{C \wedge_m}{1000} = \frac{0.02 \times 200}{1000}$$

$$k = 4 \times 10^{-3}$$

$$G^* = Rk = 100 \times 4 \times 10^{-3}$$

$$G^* = 0.4$$

$$\text{Sol 16: (C)} \quad k_{\text{water}} = \frac{G^*}{R} = \frac{0.4}{10^4} = 4 \times 10^{-5}$$

$$\text{Sol 17: (A)} \quad n_{\text{NaCl}} = \frac{585}{58.8} = 10$$

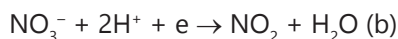
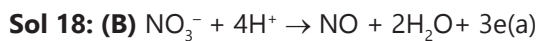
$$k_{\text{NaCl}+\text{H}_2\text{O}} = \frac{G^*}{R} = \frac{0.4}{8000} = 5 \times 10^{-5}$$

$$k_{\text{NaCl}} = k_{\text{NaCl}+\text{H}_2\text{O}} - k_{\text{H}_2\text{O}} = 10^{-5}$$

$$\begin{aligned} \therefore C_{\text{NaCl}} &= \frac{k_{\text{NaCl}} \times 1000}{\wedge_m} \\ &= \frac{10^{-5} \times 1000}{125} = 8 \times 10^{-5} \end{aligned}$$

$$C_{\text{NaCl}} = \frac{10}{V}$$

$$V = \frac{10}{8 \times 10^{-5}} = 1.25 \times 10^5 \text{ L}$$

**Paragraph 2**

For (a),

$$E = -\frac{0.06}{3} \log \frac{P_{\text{NO}}}{[\text{H}^+]^4 [\text{NO}_3^-]}$$

For (b),

$$E = E^\circ - \frac{0.06}{1} \log \frac{P_{\text{NO}_2}}{[\text{H}^+]^2 [\text{NO}_3^-]}$$

For (a),  $[\text{NO}_3^-] = [\text{H}^+] = 1\text{M}$ ,  $P_{\text{NO}} = 10^{-3}$ 

$$E_{\text{R}} = 0.96 - \frac{0.06}{3} \log 10^{-3} = 1.02$$



$$E_{\text{L}} = -0.34 - \frac{0.06}{2} \log [\text{Cu}^{2+}]$$

$$= -0.34 - 0.03 \log [\text{Cu}^{2+}]$$

$$E_{\text{L}} = -0.34 + 0.03 \log 10^{-1}$$

$$= -0.31$$

$$E = E_{\text{R}} + E_{\text{L}} \approx 0.71\text{V}$$

E for  $\text{NO}_3^- \rightarrow \text{NO}$ ,

$$E_1 = 0.65 - 0.02 \log \frac{10^{-3}}{[\text{H}^+] [\text{NO}_3^-]}$$

$$E_2 = 0.48 - 0.06 \log \frac{10^{-3}}{[\text{H}^+]^2 [\text{NO}_3^-]}$$

**Sol 19: (C)**  $E_1 = E_2$ 

$$0.65 - 0.02(-3 - 5 \log [\text{HNO}_3])$$

$$= 0.48 - 0.06(-3 - 3 \log [\text{HNO}_3])$$

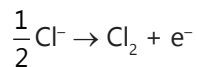
$$0.65 + 0.06 + 0.1 \log [\text{HNO}_3]$$

$$= 0.48 + 0.18 + 0.18 \log [\text{HNO}_3]$$

$$0.08 \log [\text{HNO}_3] = 0.71 - 0.66 = 0.05$$

$$\log [\text{HNO}_3] = \frac{5}{8}$$

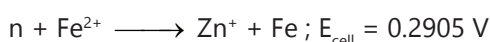
$$[\text{HNO}_3] = 10^{0.625} \approx 10^{0.66}$$

**Match the Columns****Sol 20 (A)**  $\rightarrow$  p, q $\text{Cl}^-$  will not oxidise at low concentration.

$$E = E^\circ - 0.06 \log \frac{P_{\text{Cl}_2}}{[\text{Cl}^-]^{1/2}}$$

(B)  $\rightarrow$  p, qSEP of  $\text{Na}^+ <$  SEP of  $\text{H}_2\text{O}$  $\therefore$  Water will get reduced to  $\text{H}_2$  at cathode(C)  $\rightarrow$  q, r $\text{Cl}^-$  will be oxidised as concentrated solution(D)  $\rightarrow$  p, sSEP of  $\text{Ag}^+ <$  SEP of  $\text{H}_2\text{O}$  $\therefore$   $\text{Ag}^+$  will be reduced to deposit Ag at cathode.**Previous Years' Questions****Sol 1: (C)** In electrolytic cell, electrolysis occur at the cost of electricity :At cathode :  $\text{M}^{n+} + \text{ne}^- \rightarrow \text{M}$  (electron gone in solution)At anode :  $\text{X}^{n-} \rightarrow \text{X} + \text{ne}^-$  (electron supplied to anode)

Therefore, electron is moving from cathode to anode via internal circuit.

**Sol 2: (B)** The cell reaction is :

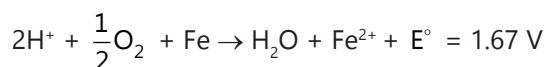
$$\Rightarrow E = E^\circ - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]}$$

$$\Rightarrow E^\circ = 0.2905 + \frac{0.059}{2} \log \frac{0.1}{0.01} = 0.32\text{V}$$

$$\text{Also, } E^\circ = \frac{0.059}{n} \log K$$

$$\Rightarrow \log K = \frac{2E^\circ}{0.059} = \frac{0.32}{0.0295}$$

$$\Rightarrow K = (10)^{0.32/0.0295}$$

**Sol 3: (B)** The net reaction is

$$\Delta G^\circ = -nE^\circ F$$

$$= \frac{2 \times 1.67 \times 96500}{1000} \text{kJ}$$

$$= -322.31 \text{kJ}$$

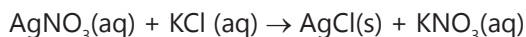
**Sol 4: (B)** 0.01 mol  $\text{H}_2 = 0.02$  g equivalent

$$\Rightarrow \text{Coulombs required} = 0.02 \times 96500 = 1930 \text{ C}$$

$$\Rightarrow Q = It = 1930 \text{ C}$$

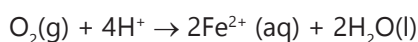
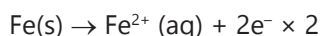
$$\Rightarrow t = \frac{1930}{10 \times 10^{-3}} = 19.3 \times 10^4 \text{ s}$$

**Sol 5: (D)** As  $\text{AgNO}_3$  is added to solution,  $\text{KCl}$  will be displaced according to following reaction



For every mole of  $\text{KCl}$  displaced from solution, one mole of  $\text{KNO}_3$  comes in solution resulting in almost constant conductivity. As the end point is reached, added  $\text{AgNO}_3$  remain in solution increasing ionic concentration, hence conductivity increases.

**Sol 6: (D)** The half reactions are



$$E = E^\circ - \frac{0.059}{4} \log \frac{(10^{-3})^2}{(10^{-3})^4(0.1)} = 1.57 \text{ V}$$

**Sol 7: (A, B, D)** Metals with  $E^\circ$  value less than 0.96 V will able to reduce  $\text{NO}_3^-$  in aqueous solution. Therefore, metals V ( $E^\circ = -1.19 \text{ V}$ ),

$\text{Fe}$  ( $E^\circ = -0.04 \text{ V}$ ),  $\text{Hg}$  ( $E^\circ = 0.86 \text{ V}$ ) will all reduce  $\text{NO}_3^-$  but  $\text{Au}$  ( $E^\circ = 1.40 \text{ V}$ ) cannot reduce  $\text{NO}_3^-$  in aqueous solution.

### Paragraph 1

**Sol 8: (B)**  $E^\circ$  for  $2\text{Ag}^+ + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \longrightarrow 2\text{Ag}(\text{s}) + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+$  is 0.75V

$$\text{Also, } E^\circ = \frac{0.0592}{2} \log K$$

$$\Rightarrow \log K = \frac{2E^\circ}{0.0592} = 25.33$$

$$\Rightarrow \ln K = 2.303 \log K = 58.35$$

**Sol 9: (C)** On increasing concentration of  $\text{NH}_3$ , the concentration of  $\text{H}^+$  ion decreases, therefore,

$$E_{\text{red}} = E^\circ_{\text{red}} - \frac{0.0592}{2} \log [\text{H}^+]^2$$

$$= 0 - \frac{0.0592}{2} \times 2 \log 10^{-11} = 0.65 \text{ V}$$

i.e.  $E_{\text{red}}$  increases by 0.65 V.

**Sol 10: (D)**  $\text{NH}_3$  has no effect on the  $E^\circ$  of glucose/gluconic acid electrode.

### Paragraph 2

**Sol 11: (B)** Moles of  $\text{NaCl}$  electrolysed =  $4 \times \frac{500}{1000} = 2.0$

$$\Rightarrow \text{Moles of } \text{Cl}_2 \text{ produced} = 1.0$$



**Sol 12: (D)** At cathode :  $\text{Na}^+ + \text{e}^- \xrightarrow{\text{Hg}} \text{Na}(\text{Hg})_{\text{amalgam}}$

Two moles of  $\text{Na}$  formed during electrolysis would produce two moles of  $\text{Na}(\text{Hg})$  amalgam.

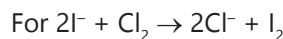
$$\Rightarrow \text{Mass of amalgam} = 2 \times (23 + 200) = 446 \text{ g}$$

**Sol 13: (D)** Two Faraday of electric charge would be required for electrolysis of 2.0 moles of  $\text{NaCl}$ .

$$\Rightarrow \text{total coulombs} = 2 \times 96500 = 193000 \text{ C}$$

### Paragraph 3

**Sol 14: (C)** For spontaneous redox reaction:  $E^\circ_{\text{cell}} > 0$

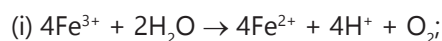


$$E^\circ = 1.36 - 0.54 = 0.82 \text{ V} > 0$$

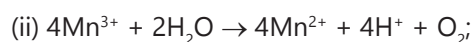
i.e.  $\text{Cl}_2$  will spontaneously oxidize  $\text{I}^-$ .

**Sol 15: (D)** In other cases  $E^\circ_{\text{cell}} < 0$ , they are non-spontaneous.

For the reaction:



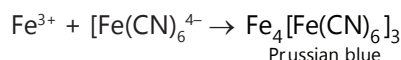
$$E^\circ = -0.46 \text{ V}$$

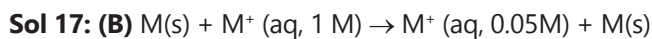


$$E^\circ = +0.27 \text{ V}$$

**Sol 16: (A)** As evidenced above, reaction (i) is non-spontaneous, therefore,  $\text{Fe}^{3+}$  is stable in acid solution. However, reaction (ii) is spontaneous  $\text{Mn}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$  and itself reduced to  $\text{Mn}^{2+}$  in acidic medium.

Sodium fusion extract from aniline produces  $\text{NaCN}$  which reacts with  $\text{Fe}^{2+}$  to form  $[\text{Fe}(\text{CN})_6]^{4-}$ . The complex ion then reacts with  $\text{Fe}^{3+}$  give blue precipitate of Prussian blue.

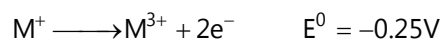


**Paragraph 4**

$$E_{\text{cell}} = 0 - \frac{2.303 RT}{F} \log \frac{0.05}{1} > 0$$

Hence,  $|E_{\text{cell}}| = E_{\text{cell}} = 0.70 \text{ V}$  and  $\Delta G < 0$  for spontaneity of reaction.

**Sol 18: (C)**  $E_{\text{cell}} = E^\circ - \frac{0.0538}{1} \log 0.0025 = 0.139 \text{ V}$   
 $= 139 \text{ V}$



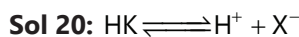
$\Delta G^\circ$  for the this reaction is

$$\Delta G^\circ = -nFE^\circ = -2 \times (-0.25) \times 96500 = 48250 \text{ J/mol}$$

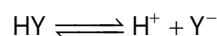
48.25 kJ/mole

So the number of moles of  $M^+$  oxidized using  $X \rightarrow Y$  will be

$$= \frac{193}{48.25} = 4 \text{ moles}$$



$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$



$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

$$\Lambda_m \text{ for HX} = \Lambda_{m_1}$$

$$\Lambda_m \text{ for HX} = \Lambda_{m_2}$$

$$\Lambda_{m_1} = \frac{1}{10} \Lambda_{m_2}$$

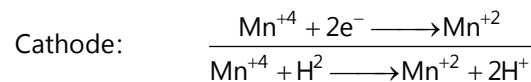
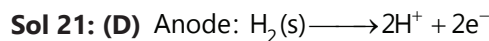
$$K_a = C \alpha^2$$

$$K_{a_1} = C_1 \times \left( \frac{\Lambda_{m_1}}{\Lambda_{m_1}^0} \right)^2$$

$$K_{a_2} = C_2 \times \left( \frac{\Lambda_{m_2}}{\Lambda_{m_2}^0} \right)^2$$

$$\frac{K_{a_1}}{K_{a_2}} = \frac{C_1}{C_2} \times \left( \frac{\Lambda_{m_2}}{\Lambda_{m_2}^0} \right)^2 = \frac{0.01}{0.1} \times \left( \frac{1}{10} \right)^2 = 0.001$$

$$pK_{a_1} - pK_{a_2} = 3$$



$$E = E^\circ - \frac{0.059}{2} \log_{10} \left( \frac{[\text{Mn}^{+2}][\text{H}^+]^2}{[\text{Mn}^{+4}]P_{\text{H}_2}} \right)$$

$$0.092 = 0.151 - \frac{0.059}{2} \log_{10}(10^X)$$

$$0.092 = 0.151 - \frac{0.059}{2} X$$

$$\Rightarrow X = 2$$

**Sol 22: (A)** In a galvanic cell, the salt bridge does not participate chemically in the cell reaction.