

Topic : Electro Chemistry

Type of Questions

Type of Questions	M.M., Min.
Single choice Objective ('-1' negative marking) Q.1 to Q.5	[15, 15]
Subjective Questions ('-1' negative marking) Q.6 to Q.8	[12, 15]
Match the Following (no negative marking) Q. 9	[8, 10]
True or False (no negative marking) Q.10 & Q.11	[4, 4]

- $E_{\text{Al}^{3+}/\text{Al}}^{\circ} = -1.66 \text{ V}$  and  $K_{\text{sp}}$  of  $\text{Al}(\text{OH})_3 = 1.0 \times 10^{-33}$ . Reduction potential of the above couple at  $\text{pH} = 14$  is :

(A)  $-2.31 \text{ V}$  (B)  $+2.31$  (C)  $-1.01 \text{ V}$  (D)  $+1.01 \text{ V}$ .
- At  $298 \text{ K}$  the standard free energy of formation of  $\text{H}_2\text{O}(\ell)$  is  $-257.20 \text{ kJ/mole}$  while that of its ionisation into  $\text{H}^+$  ion and hydroxyl ions is  $80.35 \text{ kJ/mole}$ , then the emf of the following cell at  $298 \text{ K}$  will be : (take  $F = 96500 \text{ C}$ ) :

$\text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(1 \text{ M}) \parallel \text{OH}^-(1 \text{ M}) \mid \text{O}_2(\text{g}, 1 \text{ bar})$

(A)  $0.40 \text{ V}$  (B)  $0.50 \text{ V}$  (C)  $1.23 \text{ V}$  (D)  $-0.40 \text{ V}$
- $\text{pH}$  of the solution in the anode compartment of the following cell at  $25^\circ\text{C}$  is  $x$  when  $E_{\text{cell}} - E_{\text{cell}}^{\circ} = 0.0591 \text{ V}$ ,  $\text{Pt}(\text{H}_2)$  ( $1 \text{ atm}$ )  $\mid \text{pH} = x \parallel \text{Ni}^{2+}(1 \text{ M}) \mid \text{Ni}$  is :

(A) 4 (B) 3 (C) 2 (D) 1
- The emf of the cell,  $\text{Ag} \mid \text{Ag}^+(1 \text{ M}) \parallel \text{I}^-(1 \text{ M}) \mid \text{AgI} \mid \text{Ag}$  is  $E$ . The solubility product of  $\text{AgI}$  can be expressed as :

(A)  $K_s = \frac{nF}{2.303 RT} \log E$  (B)  $\ln K = nF \left[ \frac{\partial E}{\partial T} - E \right]$  (C)  $\ln K_s = \frac{nF}{E}$  (D)  $\log K_s = \frac{nFE}{2.303 RT}$
- The emf of the cell  $\text{Zn} \mid \text{ZnCl}_2(0.05 \text{ M}) \mid \text{AgCl}(\text{s}) \mid \text{Ag}$  is  $1.015 \text{ V}$  at  $298 \text{ K}$  and the temperature coefficient of its emf is  $-4.92 \times 10^{-4} \text{ V/K}$ . How many of the reaction thermodynamic parameters  $\Delta G$ ,  $\Delta S$  and  $\Delta H$  are negative at  $298 \text{ K}$ ?

(A) None of them (B) One of them (C) Two of them (D) All of them
- If  $E_{\text{Ag}^+/\text{Ag}}^{\circ} = 0.80 \text{ V}$  at  $298 \text{ K}$  and  $K_{\text{sp}}$  ( $\text{AgCl}$ ) is  $1.56 \times 10^{-10}$ , calculate  $E^{\circ}$  for  $\text{Cl}^- \mid \text{AgCl} \mid \text{Ag}$  half-cell.
- Calculate solubility of  $\text{AgBr}$  in  $0.1 \text{ M AgNO}_3$  solution.

Given  $\text{Ag}^+ + e^- \longrightarrow \text{Ag}(\text{s}), E^{\circ} = 0.80 \text{ V}$ .

$\text{AgBr}(\text{s}) + e^- \longrightarrow \text{Ag}(\text{s}) + \text{Br}^-, E^{\circ} = 0.073 \text{ V}$ .
- At  $25^\circ\text{C}$ ,  $\left( \frac{dE^{\circ}}{dT} \right)_p = -1.25 \times 10^{-3} \text{ V K}^{-1}$  and  $E^{\circ} = 1.36 \text{ V}$  for the cell,  $\text{Pt} \mid \text{H}_2(\text{g}) \mid \text{HCl}(\text{aq}) \mid \text{Cl}_2(\text{g}) \mid \text{Pt}$ .

Calculate the enthalpy and entropy change for cell reaction.
- | Column - I                        | Column - II                     |
|-----------------------------------|---------------------------------|
| (A) $\text{H}^+(\text{aq})$       | (p) $\Delta H_f^{\circ} = 0$    |
| (B) $\text{H}(\text{gas})$        | (q) $\Delta H_f^{\circ} \neq 0$ |
| (C) $\text{H}_2(\text{gas})$      | (r) $\Delta G_f^{\circ} = 0$    |
| (D) $\text{C}(\text{s, diamond})$ | (s) $\Delta H_f^{\circ} > 0$    |
- $S_1$  : 1 mole  $\text{O}_2$  gas at STP has more entropy than 1 mole  $\text{O}_2$  gas at  $273 \text{ K}$  in a volume of  $11.2 \text{ litre}$ .

$S_2$  : Expansion of a sample of ideal gas always represents an increase in entropy of the system.

$S_3$  : On keeping a heated metal block into open atmosphere, there occurs an increase in entropy of universe.

$S_4$  : 1 mole  $\text{O}_2$  gas at STP has more entropy than 1 mole  $\text{O}_2$  gas at  $273 \text{ K}$  and  $0.25 \text{ atm}$ .

(A) T T T F (B) T F T F (C) F F F T (D) F T F T
- $S_1$  : For an irreversible adiabatic compression process, entropy change of surrounding will be equal to zero.

$S_2$  : Molar entropy of a substance follows the order  $(S_m)_{\text{Solid}} < (S_m)_{\text{liquid}} < (S_m)_{\text{gas}}$

$S_3$  : Entropy change for the reaction  $\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g})$  is +ve.

$S_4$  : Molar entropy of a non-crystalline solid will be zero at absolute zero temperature.

(A) F T T F (B) T T T F (C) T T F T (D) F F T T

# Answer Key

## DPP No. # 30

1. (A)      2. (B)      3. (D)      4. (D)      5. (D)  
6. 0.2204 V      7.  $5 \times 10^{-12}$       8.  $\Delta S^\circ = -241.45 \text{ JK}^{-1}$ ,  $\Delta H^\circ = -3.3437 \times 10^2 \text{ kJ}$ .  
9. (A) - p,r; (B) - q,s; (C) - p,r; (D) - q,s      10. (B)      11. (B)

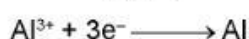
# Hints & Solutions

## PHYSICAL / INORGANIC CHEMISTRY

### DPP No. # 30

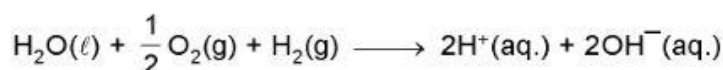
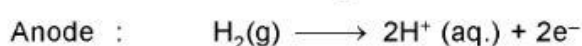
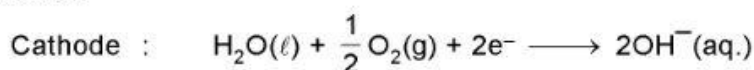
1.  $\text{pH} = 14 \Rightarrow [\text{OH}^-] = 1 \text{ M}$

$$[\text{Al}^{3+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^3} = 10^{-33}$$

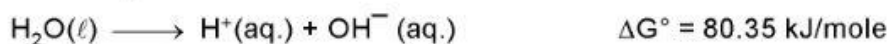


$$E_{\text{cell}} = E_{\text{Al}^{3+}/\text{Al}}^\circ - \frac{0.0591}{3} \log \frac{1}{[\text{Al}^{3+}]}$$

2. Cell reaction



Also we have



Hence for cell reaction

$$\Delta G^\circ = -96.50 \text{ kJ/mole}$$

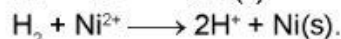
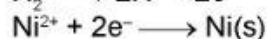
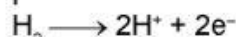
$$\text{So, } E^\circ = -\frac{\Delta G^\circ}{nF} = \frac{96500}{2 \times 96500} = 0.50 \text{ V}$$



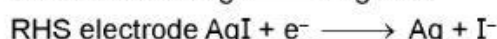
$$3. \quad E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{-0.0591}{2} \log \frac{[\text{H}^+]^2}{[\text{Ni}^{2+}][\text{H}_2]}$$

$$\Rightarrow E_{\text{cell}} - E_{\text{cell}}^{\circ} = \frac{-0.0591}{1} \log [\text{H}^+] = 0.0591 \times \text{pH}$$

$$\Rightarrow \text{pH} = 1$$



4. For the cell  $\text{Ag} | \text{Ag}^+ || \text{I}^-, \text{AgI} ; \text{Ag}$



Cell reaction,  $\text{AgI} \rightleftharpoons \text{Ag}^+ + \text{I}^-$

The equilibrium constant (K) = The solubility product  $K_{\text{s}}$

$$\Delta G = -nFE$$

$$\Delta G^{\circ} = -2.303 RT \log K$$

$$\log K = \frac{nFE}{2.303 RT}$$

5.  $\text{Zn} | \text{ZnCl}_2 (0.05\text{M}) | \text{AgCl(s)} | \text{Ag} \quad E_{\text{cell}} = 1.015\text{V}$

$$\left( \frac{dE_{\text{cell}}}{dT} \right) = -4.92 \times 10^{-4} \frac{\text{V}}{\text{K}}$$

$$\begin{aligned} \Delta G &= -nFE_{\text{cell}} = -ve \quad (\text{as } E_{\text{cell}} = +ve) \\ &= -2 \times 96500 \times 1.015 \\ &= -195.895 \text{ kJ.} \end{aligned}$$

$$\begin{aligned} \Delta S &= nF \left( \frac{dE_{\text{cell}}}{dT} \right) \\ &= 2 \times 96500 \times -4.92 \times 10^{-4} \\ &= -94.956 \text{ J/K.} \end{aligned}$$

$$\begin{aligned} \Rightarrow \Delta G &= \Delta H - T\Delta S \\ &= -195.895 + \frac{298}{1000} \times (-94.956) \\ &= -224.19 \text{ kJ.} \end{aligned}$$

So, all are negative.

$$\begin{aligned} 6. \quad E_{\text{Cl}^- / \text{AgCl}, \text{Ag}}^{\circ} &= E_{\text{Ag}^+ / \text{Ag}}^{\circ} + 0.0591 \log k_{\text{sp}} (\text{AgCl}) \\ &= 0.8 + 0.0591 \log 1.56 \times 10^{-10} \\ &= 0.8 + 0.0591 (-10 + \log 1.56) = 0.2204 \text{ V} \end{aligned}$$

$$\begin{aligned} 7. \quad \text{Ag} &\longrightarrow \text{Ag}^+ + \text{e}^- & E^{\circ} &= -0.8 \text{ V} \\ \text{AgBr} + \text{e}^- &\longrightarrow \text{Ag} + \text{Br}^- & E^{\circ} &= 0.073 \\ \text{AgBr} &\rightleftharpoons \text{Ag}^+ + \text{Br}^- \\ E_{\text{cell}}^{\circ} &= 0.073 - 0.8 - 0.0591 \log [\text{Ag}^+][\text{Br}^-] \\ 0.8 - 0.073 &= -0.0591 \log K_{\text{sp}} (\text{AgBr}) \\ K_{\text{sp}} &= 4.998 \approx 5 \times 10^{-13} \\ [\text{Ag}^+][\text{Br}^-] &= 5 \times 10^{-13} \end{aligned}$$

$$[\text{Br}^-] = \frac{5 \times 10^{-13}}{0.1} = 5 \times 10^{-12}$$

Solubility of  $\text{AgBr} = [\text{Br}^-] = 5 \times 10^{-12}\text{M}$

$$8. \quad \Delta S^\circ = nF \left( \frac{dE^\circ}{dt} \right)_p$$

$$= 2 \times 96500 \times [-1.25 \times 10^{-3}] = 241.45 \text{ Jk}^{-1}$$

$$\Delta H^\circ = -nF E_{\text{cell}}^\circ + n F T \frac{dE_{\text{cell}}^\circ}{dT}$$

$$= -2 \times 96500 \times 1.36 + 2 \times 96500 \times 298 \times (-1.25 \times 10^{-3})$$

$$= -3.3437 \times 10^2 \text{ KJ.}$$

10. For same amount of gas at constant temperature, lesser is the volume, lower will be the entropy.
11.  $S_2$  : Molar entropy of gas is much greater than that of solid and liquid.  
 $S_3$  : Entropy change is positive if  $\Delta n_g$  is positive.  
 $S_4$  : Molar entropy of a crystalline solid will be zero at absolute zero temperature.

