PHYSICAL / INORGANIC CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

DPP No. 30

Total Marks : 39

Max. Time : 44 min.

Topic : Electro Chemistry

Type of Questions		**M.M., Min.**
Single choice Objective ('–1' negative marking) Q.1 to Q.5	**(3 marks, 3 min.)**	**[15, 15]**
Subjective Questions ('–1' negative marking) Q.6 to Q.8	**(4 marks, 5 min.)**	**[12, 15]**
Match the Following (no negative marking) Q. 9	**(8 marks, 10 min.)**	**[8, 10]**
True or False (no negative marking) Q.10 & Q.11	**(2 marks, 2 min.)**	**[4, 4]**

1. $E^{o}_{Al^{3+}/Al}$ = – 1.66 V and K_{SP} of $Al(OH)_3$ = 1.0 × 10^{-33}. Reduction potential of the above couple at pH = 14 is :

(A) – 2.31 V (B) + 2.31 (C) – 1.01 V (D) + 1.01 V.

2. At 298K the standard free energy of formation of $H_2O(\ell)$ is –257.20 kJ/mole while that of its ionisation into H^+ ion and hydroxyl ions is 80.35 kJ/mole, then the emf of the following cell at 298 K will be : (take F = 96500 C] : H_2(g,1 bar) | H^+ (1M) || OH^- (1M) | O_2 (g, 1bar)

(A) 0.40 V (B) 0.50 V (C) 1.23 V (D) – 0.40 V

3. pH of the solution in the anode compartment of the following cell at 25ºC is x when $E_{cell} - E^o_{cell}$ = 0.0591 V, Pt(H_2) (1 atm) | pH = x | | Ni^{2+} (1 M) | Ni x is :

(A) 4 (B) 3 (C) 2 (D) 1

4. The emf of the cell, Ag | Ag^+ (1 M) || I^- (1 M) | AgI | Ag is E

The solubility product of 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) $\log K_s = \frac{nFE}{2.303\,RT}$

5. The emf of the cell Zn | $ZnCl_2$ (0.05 M) | AgCl(s) | Ag is 1.015 V at 298 K and the temperature coefficient of its emf is – 4.92 × 10^{-4} V/K. How many of the reaction thermodynamic parameters ΔG, ΔS and ΔH are negative at 298 K?

(A) None of them (B) One of them (C) Two of them (D) All of them

6. If $E^{o}_{Ag^+/Ag}$ = 0.80 V at 298 K and K_{SP} (AgCl) is 1.56 × 10^{-10} , calculate Eº for Cl^- | AgCl | Ag half-cell.

7. Calculate solubility of AgBr in 0.1 M $AgNO_3$ solution.

Given $Ag^+ + e^- \longrightarrow Ag(s)$, Eº = 0.80 V.

$AgBr(s) + e^- \longrightarrow Ag(s) + Br^-$, Eº = 0.073 V.

8. At 25ºC, $\left(\frac{dE^o}{dT}\right)_P$ = – 1.25 × 10^{-3} V K^{-1} and Eº = 1.36 V for the cell, Pt |H_2 (g)| HCl (aq) | Cl_2 (g) | Pt.

Calculate the enthalpy and entropy change for cell reaction.

9.

	Column – I		**Column – II**
(A)	H^+ (aq)	(p)	$\Delta H_f^0 = 0$
(B)	H (gas)	(q)	$\Delta H_f^0 \neq 0$
(C)	H_2 (gas)	(r)	$\Delta G_f^0 = 0$
(D)	C (s, diamond)	(s)	$\Delta H_f^0 > 0$

10. **S_1** : 1 mole O_2 gas at STP has more entropy than 1 mole O_2 gas at 273 K in a volume of 11.2 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 O_2 gas at STP has more entropy than 1 mole O_2 gas at 273 K and 0.25 atm.

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

11. **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 $(S_m)_{Solid} < (S_m)_{liquid} < (S_m)_{gas}$

S_3 : Entropy change for the reaction $H_2(g) \longrightarrow 2H(g)$ 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

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

Hints & Solutions

PHYSICAL / INORGANIC CHEMISTRY

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1. pH = 14 $\Rightarrow$ $[CH^-] = 1$ M

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

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

$$E_{cell} = E^o_{Al^{3+}/Al} - \frac{0.0591}{3} \log \frac{1}{[Al^{3+}]}.$$

2. Cell reaction

Cathode : $H_2O(\ell) + \frac{1}{2}O_2(g) + 2e^- \longrightarrow 2OH^-(aq.)$

Anode : $H_2(g) \longrightarrow 2H^+(aq.) + 2e^-$

$$H_2O(\ell) + \frac{1}{2}O_2(g) + H_2(g) \longrightarrow 2H^+(aq.) + 2OH^-(aq.)$$

Also we have

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$ $\qquad \Delta G^\circ_f = -257.2$ kJ/mole

$H_2O(\ell) \longrightarrow H^+(aq.) + OH^-(aq.)$ $\qquad \Delta G^\circ = 80.35$ kJ/mole

Hence for cell reaction

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

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

3. $E_{cell} = E^{\circ}_{cell} \frac{-0.0591}{2} \log \frac{[H^+]^2}{[Ni^{2+}][H_2]}$

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

$\Rightarrow \quad pH = 1$

$H_2 \longrightarrow 2H^+ + 2e^-$

$Ni^{2+} + 2e^- \longrightarrow Ni(s)$

$H_2 + Ni^{2+} \longrightarrow 2H^+ + Ni(s).$

4. For the cell Ag | Ag^+ || I^- , AgI ; Ag

LHS electrode $Ag \longrightarrow Ag^+ + e^-$

RHS electrode $AgI + e^- \longrightarrow Ag + I^-$

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

The equilibrium constant (K) = The solubility product K_s

$\Delta G = -nFE$

$\Delta G^o = -2.303 \, RT \log K$

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

5. Zn | $ZnCl_2$ (0.05M) | AgCl(s) | Ag $E_{cell} = 1.015V$

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

$\Delta G = -nFE_{cell} = -ve \qquad (\text{as } E_{cell} = +ve)$

$= -2 \times 96500 \times 1.015$

$= -195.895$ kJ.

$\Delta S = nF\left(\frac{dE_{cell}}{dT}\right)$

$= 2 \times 96500 \times -4.92 \times 10^{-4}$

$= -94.956$ J/K.

$\Rightarrow \quad \Delta G = \Delta H - T\Delta S.$

$= -198.895 + \frac{298}{1000} \times (-94.956)$

$= -224.19$ KJ.

So, all are negative.

6. $E^{\circ}_{Cl^- / AgCl, Ag} = E^{\circ}_{Ag^+ / Ag} + 0.0591 \log k_{sp}\,(AgCl)$

$= 0.8 + 0.0591 \log 1.56 \times 10^{-10}$

$= 0.8 + 0.0591 (-10 + \log 1.56) = 0.2204$ V

7. $Ag \longrightarrow Ag^+ + e^- \qquad E^o = -0.8$ V

$AgBr + e^- \longrightarrow Ag + Br^- \qquad E^o = 0.073$

$AgBr \rightleftharpoons Ag^+ + Br^-$

$E^o_{cell} = 0.073 - 0.8 - 0.0591 \log [Ag^+][Br^-]$

$0.8 - 0.073 = -0.0591 \log K_{sp}\,(AgBr^-)$

$K_{sp} = 4.998 \approx 5 \times 10^{-13}$

$[Ag^+][Br^-] = 5 \times 10^{-13}$

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

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

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

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

$\Delta H^o = -nF\ E^{\circ}_{cell} + n\ F\ T\ \frac{dE^{\circ}_{cell}}{dT}$

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

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

10. For same amount of gas at constant temperature, lesser is the volume, lower will be the entropy.

11. $\mathbf{S_2}$: Molar entropy of gas is much greater than that of solid and liquid.

$\mathbf{S_3}$: Entropy change is positive if Δn_g is positive.

$\mathbf{S_4}$: Molar entropy of a crystalline solid will be zero at absolute zero temperature.