PHYSICAL / INORGANIC CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

DPP No. 28

Total Marks : 43

Max. Time : 45 min.

Topic : Electro Chemistry

Type of Questions		M.M., Min.
Single choice Objective ('–1' negative marking) Q.1 to Q.7	(3 marks, 3 min.)	[21, 21]
Multiple choice objective ('–1' negative marking) Q.8	(4 marks, 4 min.)	[4, 4]
Subjective Questions ('–1' negative marking) Q.9 to Q.10	(4 marks, 5 min.)	[8, 10]

1. Which of the following concentration cells will produce maximum E_{cell} at 298 K.

[Take p_{H_2} = 1.0 atm in each case.]

(A) Pt | H_2(g) | H^+ (0.01 M) || H^+ (0.1 M) | H_2(g) | Pt
(B) Pt | H_2(g) | NH_4Cl (0.01 M) || HCl (0.1 M) | H_2(g) | Pt
(C) Pt | H_2(g) | H^+ (0.1 M) || H^+ (0.2 M) | H_2(g) | Pt
(D) Pt | H_2(g) | H^+ (pH = 0.0) || H^+ (pH = 0.0) | H_2(g) | Pt.

2. Given that (at T = 298 K)

Cu(s) | Cu^{2+} (1.0 M) || Ag^+ (1.0 M) | Ag(s) $\quad E^o_{cell}$ = 0.46 V
Zn(s) | Zn^{2+} (1.0 M) || Cu^{2+} (1.0 M) | Cu(s) $\quad E^o_{cell}$ = 1.10 V

Then E_{cell} for

Zn | Zn^{2+} (0.1 M) || Ag^+ (1.0 M) | Ag at 298 K will be

(A) 1.59 V (B) 1.53 V
(C) 2.53 V (D) cannot be calculated due to insufficient data

3. What is the value of the reaction quotient, Q, for the cell -

Ni(s) | $Ni(NO_3)_2$ (0.190M) | | KCl(0.40M)| Cl_2(g, 0.10 atm) |Pt(s)

(A) 3 x 10^{-1} (B) 1.3 x 10^{-1} (C) 8.0 x 10^{-2} (D) 3.0 x 10^{-2}

4. A hydrogen electrode placed in a buffer solution of CH_3COONa and CH_3COOH in the molar ratios x : y and y : x has oxidation potentials E_1 and E_2 volts respectively at 298 K. $(p_{H_2} = 1atm)$.The pK_a value of acetic acid will be given by .

(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) None of these

5. For the cell Pt | H_2(g) | solution X || KCl (saturated) | Hg_2Cl_2 | Hg | Pt
the observed EMF at 25°C was 600 mV. When solution X was replaced by a standard phosphate buffer with pH = 7.00, the EMF was 718 mV. Find the pH of solution X.

(A) 3 (B) 4 (C) 5 (D) 6

6. The dissociation constant for $[Ag(NH_3)_2]^+$ into Ag^+ and NH_3 is 10^{-13} at 298 K. If $E^0_{Ag^+/Ag}$ = 0.8 V, then E^0 for the half cell $[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2NH_3$ will be

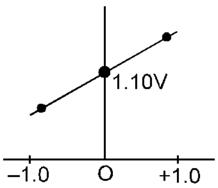
(A) 0.33 V (B) – 0.33 V (C) – 0.033 V (D) 0.033 V

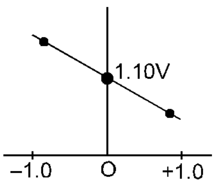
7. You are given the following cell at 298 K with $E^o_{cell} = 1.10$ V

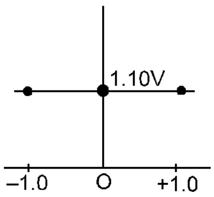
$$Zn(s) \mid Zn^{2+}(C_1) \parallel Cu^{++}(C_2) \mid Cu(s)$$

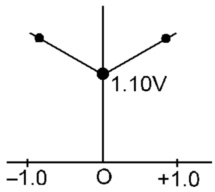
where C_1 and C_2 are the concentration in mol/lit then which of the following figures correctly correlates E_{cell} as a function of concentrations..

x-axis : $\log \frac{C_1}{C_2}$ and y-axis : E_{cell}

(A)


(B)


(C)


(D)


8. Make out the right combination of cell and condition for the spontaneity :

(A) $Pt(H_2) \mid HCl \mid Pt(H_2)$; $P_1 > P_2$
P_1 1M P_2

(B) $Zn \mid Zn^{2+}(C_1) \parallel Zn^{2+}(C_2) \mid Zn$; $C_2 > C_1$

(C) $Pt(Cl_2) \mid Cl^-(C_1) \parallel Cl^-(C_2) \mid Pt(Cl_2)$; $C_2 > C_1$
1 atm 1 atm

(D) $Pt(H_2) \mid HCl(C_1) \parallel HCl(C_2) \mid Pt(H_2)$; $C_2 > C_1$
1 atm 1 atm

Single Integer

9. Depression of freezing point of 0.01 molal aqueous CH_3COOH solution is 0.02046°. 1 molal aqueous urea solution freezes at – 1.86°C. Assuming molality to be equal to molarity, calculate pH of CH_3COOH solution.

10. The active ingredient in aspirin is acetyl salicylic acid,

$$HC_9H_7O_4 + H_2O \rightleftharpoons H_3O^+ + C_9H_7O_4^-, \; K_a = 6.25 \times 10^{-9}$$

What is the pH of the solution obtained by dissolving two aspirin tablets in 250mL of water ? Assume that each tablet contains 0.36 g of acetyl salicylic acid.

Answer Key

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1.	(B)	**2.**	(A)	**3.**	(A)	**4.**	(C)	**5.**	(C)
6.	(D)	**7.**	(B)	**8.**	(A,B,D)	**9.**	3	**10.**	5

Hints & Solutions

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1. $E_{cell} = -0.0591 \log \frac{[H^+]anode}{[H^+]cathode}$

For (A) $E_{cell} = 0.0591$ V

(B) $E_{cell} = 0.273$ V

$$[H^+]_{Anode} = \sqrt{\frac{K_W}{K_b}.C} = \sqrt{\frac{10^{-14}}{18 \times 10^{-5}} \times 10^{-2}} = \sqrt{\frac{10}{1.8}} \times 10^{-6}$$

(C) $E_{cell} = -0.0591 \log \frac{1}{2} = 0.0591 \log 2 = 0.0178$ V

(D) $E_{cell} = -0.0591 \log \frac{1}{1} = 0.$

2. $E^o_{Ag^+/Ag} - E^o_{Cu^{2+}/Cu} = 0.46V$

(+) $E^o_{Cu^{2+}/Cu} - E^o_{Zn^{2+}/Zn} = 1.1V$

$E^o_{Ag^+/Ag} - E^o_{Zn^{2+}/Zn} = 1.56$ V

Zn/Zn^{2+} (0.1M) || Ag^+ (1.0M) | Ag $E^o_{cell} = 1.56$

$E_{cell} = E^o_{cell} - \frac{0.059}{n} \log Q.$

Cell reaction :

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

+ $(Ag^+ + e^- \longrightarrow Ag) \times 2$

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

$$Q = \frac{[Zn^{2+}]}{[Ag^+]^2} = \frac{(0.1)}{(1)^2} = 0.1$$

$\Rightarrow \quad E_{cell} = E^o_{cell} - \frac{0.059}{2} \log 0.1$

$= 1.56 - \frac{0.059}{2} \times -1$

$= 1.59V$ **Ans.**

3. $Ni(s) + Cl_2 \longrightarrow Ni^{2+}(aq) + 2Cl^-$.

$Q = \frac{[Ni^{2+}][Cl^-]^2}{P_{Cl_2}} = \frac{(0.19)(0.4)^2}{0.1} = \mathbf{0.304}$.

4. $pH_1 = pK_a + \log \frac{x}{y}$ ——(1)

$pH_2 = pK_a + \log \frac{y}{x}$ ——(2)

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

$E_1 = E^\circ_{H_2/H^+} - \frac{0.0529}{2} \log [H^+]^2{}_1 = 0.0529\, pH_1$

$E_2 = 0.0529\, pH_2$

$\Rightarrow \quad E_1 + E_2 = 00529\,(2pK_a)$

$\Rightarrow \quad pK_a = \frac{E_1 + E_2}{0.118}$.

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

$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$

$H_2 + Hg_2Cl_2 \longrightarrow 2H^+ + 2Cl^- + 2Hg$

$E^{initial} = E^\circ + \frac{0.059}{2} \log \frac{1}{[H^+]^2[Cl^-]^2} = 0.6$ $\quad E^{final} = E^\circ + \frac{0.059}{2} \log \frac{1}{(10^{-7})^2[Cl^-]^2} = 0.718$

subtracting we get $\quad 0.118 = 0.059 \log \frac{[H^+]}{10^{-7}} \Rightarrow \frac{[H^+]}{10^{-7}} = 100 \Rightarrow [H^+] = 10^{-5} \quad \Rightarrow pH = 5.$

6. $[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag^+ + 2NH_3 \quad K_d = 10^{-13}$

$\Delta G^\circ_1 = RT \ln K_d$

$Ag^+ + e^- \longrightarrow Ag \quad \Delta G^\circ_3 = -1 \times F \times 0.8$

$[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2NH_3 \quad \Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2$

$-1 \times F \times E^{\circ} = -RT \ln k_d - 1 \times F \times 0.8$

$$E^{\circ} = -\frac{RT}{F} \ln k_d + 0.8 \quad \Rightarrow \quad \frac{8.314 \times 298}{96500} \times 2.303 \times (-13) + 0.8$$

$E^{\circ} = 0.0313$ V.

7.

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

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

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{2} \log \frac{C_1}{C_2}$$

Since slope is –ve i.e. $-\frac{0.0591}{2}$

$\therefore$ Ans is (B).

8. For spontaneity, $E_{cell} > 0$

$E^{o}_{cell} = 0$ for concentration cell.

(A) Anode : $H_2 \longrightarrow Zn^{+} + 2e^-$

Cathode : $Zn^{+} + 2e^- \longrightarrow H_2$

$$H_2 / \text{anode} \longrightarrow H_2 / \text{cathode}$$

$$E_{cell} = -\frac{0.0591}{2} \log \frac{H_2/\text{cathode}}{H_2/\text{anode}} = -\frac{0.0591}{2} \log \frac{P_2}{P_1}$$

= +ve

(B) Anode : $Zn\ (s) \longrightarrow Zn^{2+} + 2e^-$

Cathode : $Zn^{2+} + 2e^- \longrightarrow Zn\ (s)$

$$Zn^{2+} / \text{cathode} \longrightarrow Zn^{2+} / \text{anode}$$

$$E_{cell} = -\frac{0.0591}{2} \log \frac{Zn^{2+}/\text{anode}}{Zn^{2+}/\text{cathode}} = -\frac{0.0591}{2} \log \frac{C_1}{C_2}$$

= +ve.

9. For urea

$\Delta T_f = k_f \times m$

or $k_f = \frac{\Delta T_f}{m} = \frac{1.86}{1} = 1.86$

Now for CH_3COOH

$\Delta T_f = i\, k_f\, m$

so $i = \frac{0.02046}{1.86 \times 0.01} = 1.1$

Now $i = 1 + \alpha$

so $\alpha = 1.1 - 1 = 0.1$

Now

CH_3COOH	$\rightleftharpoons$ CH_3COO^-	+	H^+
C	0		0
$C - C\alpha$	$C\alpha$		$C\alpha$

$[H^+] = C\alpha = 0.01 \times 0.1 = 0.001$

so $pH = 3.$

10. [Acetyl saliclic acid] $= \frac{0.36}{250} \times 2 \times 1000 \text{ g L}^{-1}$

$= \frac{0.36 \times 8}{180} = 0.016 \text{ M}$

By Ostwald's dilution law $[H_3O^+]$

$$= \sqrt{K_aC} = \sqrt{6.25 \times 10^{-9} \times 0.016} = 10^{-5} \text{ M}$$

$pH = -\log [H_3O^+] = 5$