PHYSICAL / INORGANIC CHEMISTRY

DPP
DAILY PRACTICE PROBLEMS

# DPP No. 29

**Total Marks : 34**

**Max. Time : 38 min.**

**Topic : Electro Chemistry**

| Type of Questions | | M.M., Min. |
|---|---|---|
| Single choice Objective ('–1' negative marking) Q.1 | (3 marks, 3 min.) | [3, 3] |
| Subjective Questions ('–1' negative marking) Q.2 to Q.5 | (4 marks, 5 min.) | [16, 20] |
| Comprehension ('–1' negative marking) Q.6 to Q.8 | (3 marks, 3 min.) | [9, 9] |
| Short Subjective Questions ('–1' negative marking) Q.9 to Q.10 | (3 marks, 3 min.) | [6, 6] |

**1.** When 0.1 mole HCl gas is added in 1lt of 0.1 M $CH_3COOH(aq)$ then which statement is wrong? ($K_a = 2 \times 10^{-5}$, log 2 = 0.3)

(A) degree of dissociation of $CH_3COOH$ decreases sharply.

(B) change in pH would be 1.85

(C) conc of $[Cl^-]$ = 0.1 M, $[CH_3COOH]$ = 0.1 M, $[H^+]$ = 0.2 M in final solution

(D) on addition of HCl, $K_a$ of $CH_3COOH$ does not change.

**2.** Calculate E° and E for the cell Sn | $Sn^{2+}$ (1M) || $Pb^{2+}$ ($10^{-3}$ M) | Pb , E° ($Sn^{2+}$ / Sn) = – 0.14V. Eº ($Pb^{2+}$ / Pb) – 0.13V. What do you infer from cell EMF?

**3.** Calculate the equilibrium constant for the reaction $Fe + CuSO_4 \rightleftharpoons FeSO_4 + Cu$ at 25°C. Given Eº ($Fe/Fe^{2+}$) = 0.44V, Eº ($Cu/Cu^{2+}$) = – 0.337 V.

**4.** For a cell Mg(s) |$Mg^{2+}$ (aq) || $Ag^+$ (aq)| Ag, Calculate the equilibrium constant at 25°C. Also find the maximum work that can be obtained by operating the cell. E°($Mg^{2+}$ / Mg) = – 2.37V, E° ($Ag^+/Ag$) = 0.8 V.

**5.** At 25°C the value of K for the equilibrium $Fe^{3+} + Ag \rightleftharpoons Fe^{2+} + Ag^+$ is 0.531 mol/litre. The standard electrode potential for $Ag^+ + e \rightleftharpoons Ag$ is 0.799V. What is the standard potential for $Fe^{3+} + e \Leftrightarrow Fe^{2+}$ ?

**Comprehension # (Q.6 to Q.8)**

**(Read the following passage and answer the questions numbered 5 to 7. They have only one correct option)**

Standard reduction potentials (SRP) for different systems can be used to decide the spontaneity of a reaction e.g. $E^\circ_{Zn^{2+}/Zn}$ = – 0.76V, hence for the reaction $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$, $\Delta G^\circ$ is negative. It has been found experimentally that if (SRP of an oxidant – SRP of a reductant) is more than 1.7V, then their combination may lead to explosion (though it may be prevented by kinetic factors).

Now go through the following data and answer the questions.

Data : $E^\circ_{Ag^+/Ag}$ = 0.80 V ; $E^\circ_{N_2/N_3^-}$ = – 3.09 V

$E^\circ_{ClO_4^-/ClO_3^-}$ = 1.23 V ; $E^\circ_{Na^+/Na}$ = – 2.71 V

$E^\circ_{Fe^{3+}/Fe^{2+}}$ = 0.77 V ; $E^\circ_{O_2/H_2O_2}$ = – 1.03 V

$E^\circ_{H_2O_2/H_2O}$ = 1.76 V ; $E^\circ_{O_3/O_2}$ = 2.07 V

$E^\circ_{MnO_4^-/Mn^{2+}}$ = 1.54 V ; $E^\circ_{Cr_2O_7^{2-}/Cr^{3+}}$ = 1.33 V

**6.** Which of the following ionic combinations may lead to the formation of explosive substance.

(A) Sodium ion and azide ion (B) Silver ion and perchlorate ion

(C) Silver ion and azide ion (D) All the above

**7.** Which of the following ions will be capable of causing catalytic decomposition of $H_2O_2$.

(A) $Fe^{3+}$ (B) $Fe^{2+}$ (C) both (D) None of these

**8.** Which is correct about the reaction between $H_2O_2$ and $O_3$

(A) It is a case of mutual reduction

(B) $O_3$ will oxidise $H_2O_2$ into $O_2$

(C) It is not a redox reaction

(D) $H_2O_2$ being a stronger oxidising agent will decompose ozone into oxygen

## ***SINGLE INTEGER***

**9.** The ionization constant of nitrous acid is $4 \times 10^{-4}$. Calculate the pH of 0.04 M sodium nitrite solution.

**10.** For aqueous solution of how many of the following compounds / mixtures, does the pH remains constant even upon dilution :

(1) $NH_4Cl$ (2) $Na_2CO_3$ (3) A 1 : 2 molar ratio mixture of $Na_2S$ and HCl.

(4) A 5 : 2 molar ratio mixture of NaOH and $H_3PO_4$. (5) A 5 : 4 molar ratio mixture of $CH_3COONa$ and HCl.

(6) $NaH_2PO_4$ (7) A 2 : 1 molar ratio mixture of HCl and $NaHCO_3$.

(8) $CH_3COONH_4$ (9) A 4 : 3 molar ratio mixture of $NH_4OH$ and HCl.

# Answer Key

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**1.** (C)

**2.** $E^\circ_{cell} = +0.01$ V, $E_{cell} = -0.0785$ V, correct representation is $Pb \mid Pb^{2+}(10^{-3}\ M) \mid\mid Sn^{2+}(1M) \mid Sn$.

**3.** $\log K_{eq.} = \frac{2 \times 0.777}{0.0591}$, $K_{eq.} = 2.18 \times 10^{26}$ **4.** $K_c = 1.864 \times 10^{107}$, $\Delta G^\circ = -611.8$ kJ

**5.** $E^\circ = 0.7826$ V **6.** (C) **7.** (C) **8.** (B) **9.** 8 **10.** 5

# Hints & Solutions

## PHYSICAL / INORGANIC CHEMISTRY

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**2.** $Sn \mid Sn^{2+}\ (1\ M) \mid\mid Pb^{2+}\ (10^{-3}\ M) \mid Pb.$

$E^0_{(Sn^{2+}/Sn)} = -0.14$ V. and $E^0_{(Pb^{2+}/Pb)} = -0.13$ V.

$E^\circ_{cell} = -0.13 + 0.14 = 0.01$ V.

$$E_{cell} = 0.01 - \frac{0.0591}{2} \log \frac{1}{10^{-3}} = \mathbf{-0.0785\ V.}$$

**3.** $$\log K_{eq.} = \frac{2 \times 0.777}{0.0591},\ K_{eq.} = 2.18 \times 10^{26}$$

**4.** $$E_{cell} = 3.11 - \frac{0.0591}{2} \log K_{eq.} \qquad E_{cell} = 0.$$

$$\log K_{eq.} = \frac{3.11 \times 2}{0.0591}$$

$K_{eq.} = 1.864 \times 10^{107}$

$\Delta G^\circ = -2.303\ RT \log 1.864 \times 10^{107} = -2.303 \times 8.314 \times 298 \log 1.86 \times 10^{107}$

**5.** $$0 = E^\circ_{cell} - \frac{0.0591}{1} \log 0.531$$

$E^\circ_{cell} = 0.0591 \log 0.531 = 0.0591 \log 5.31 \times 10^{-1}$

$E^\circ_C - E^\circ_A = -0.01624$

$E^\circ_C = -0.01624 + 0.799 = 0.7826$ V.

**6.** For the given options

(A) Sodium ion and azide ion

$Na^+ + N_3^{-1} \longrightarrow Na + N_2$ $\qquad E^\circ = -2.71 + 3.09 < 1.7$ V

(B) Silver ion and perchlorate ion

$ClO_4^- + Ag \longrightarrow Ag^+ + ClO_3^-$ $\qquad E^\circ = 1.23 - 0.80 < 1.7$ V

(C) Silver ion and azide ion

$Ag^+ + N_3^- \longrightarrow Ag + N_2$ $\qquad E^\circ = 0.80 + 3.09 = 3.89 > 1.7$ V

So will lead to explosion

**7.** If $Fe^{3+}$ is present, then

$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + O_2$ $\quad E° = 0.77 + 1.03 = 1.8\ V > 0$ so spontaneous

$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + H_2O$ $\quad E° = 1.76 + 0.77 = 0.99 > 0$

Hence $Fe^{2+}$ and $Fe^{3+}$ both are capable of decomposing $H_2O_2$.

**8.** From SRP values it is clear that $O_3$ will oxidise $H_2O_2$ into $O_2$.

**9.** $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

$c(1-h)$ $\quad ch \quad ch$ $\quad$ where h is degree of hydrolysis

$[OH^-] = ch$ ;

Also; $h = \sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w}{K_a.c}} = \sqrt{\frac{10^{-14}}{4\times10^{-4}\times0.04}} = \mathbf{2.5 \times 10^{-5}}$

$\therefore$ $[OH^-] = 0.04 \times 2.5 \times 10^{-5}$ or $pOH = 6$

$\therefore$ $pH = 14 - pOH = \mathbf{8}$

**10.** (1) $pH = \frac{1}{2}(pK_w - pK_b - \log C)$ ; (2) $pH = \frac{1}{2}(pK_w + pK_{a_2} + \log C)$

(3) $Na_2S + 2HCl \longrightarrow 2NaCl + H_2S$

$\therefore$ $pH_{WA} = \frac{1}{2}(pK_{a_1} - \log C)$

(4)

| | | | | |
|---|---|---|---|---|
| | $NaOH + H_3PO_4 \longrightarrow$ | $NaH_2PO_4$ | + | $H_2O$ |
| i | 5 | 2 | | |
| f | 3 | 0 | 2 | 2 |
| | $NaOH + NaH_2PO_4 \longrightarrow$ | $Na_2HPO_4$ | + | $H_2O$ |
| i | 3 | 2 | | |
| f | 1 | 0 | 2 | 2 |
| | $NaOH + Na_2HPO_4 \longrightarrow$ | $Na_3PO_4$ | + | $H_2O$ |
| i | 1 | 2 | | |
| f | 0 | 1 | 1 | 1 |

$\therefore$ Buffer solution $\therefore$ $pH = pK_{a_3} + \log_{10} \frac{[PO_4^{3-}]}{[HPO_4^{2-}]}$

(5) $CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$

| | | | | |
|---|---|---|---|---|
| i | 5 | 4 | | |
| f | 1 | 0 | 4 | 4 |

$\therefore$ Acidic buffer $\therefore$ $pH = pK_a + \log_{10} \frac{[CH_3COO^-]}{[CH_3COOH]}$

(6) $pH = \frac{pK_{a_2} + pK_{a_1}}{2}$

(7) $HCl + NaHCO_3 \longrightarrow NaCl + H_2CO_3$

| | | | | |
|---|---|---|---|---|
| i | 2 | 1 | | |
| f | 1 | 0 | 1 | 1 |

For a mixture of WA + SA, major $H^+$ ions will come from HCl.

$\therefore$ $pH = -\log_{10}[H^+]_{HCl}$

(8) $pH = \frac{1}{2}(pK_w + pK_a - pK_b)$

(9) $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

| | | | | |
|---|---|---|---|---|
| i | 4 | 3 | | |
| f | 1 | 0 | 3 | 3 |

$\therefore$ Basic buffer $\therefore$ $pOH = pK_b + \log_{10} \frac{[NH_4^+]}{[NH_4OH]}$

Clearly, pH of solutions 4, 5, 6, 8 and 9 is not affected by dilution.