

Topic : Electro Chemistry

Type of Questions

| 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] |

- When 0.1 mole HCl gas is added in 1lt of 0.1 M $\text{CH}_3\text{COOH}(\text{aq})$ 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 $[\text{Cl}^-] = 0.1 \text{ M}$, $[\text{CH}_3\text{COOH}] = 0.1 \text{ M}$, $[\text{H}^+] = 0.2 \text{ M}$ in final solution
(D) on addition of HCl, K_a of CH_3COOH does not change.
- Calculate E° and E for the cell $\text{Sn} | \text{Sn}^{2+} (1\text{M}) || \text{Pb}^{2+} (10^{-3} \text{ M}) | \text{Pb}$, $E^\circ (\text{Sn}^{2+} / \text{Sn}) = -0.14\text{V}$.
 $E^\circ (\text{Pb}^{2+} / \text{Pb}) = -0.13\text{V}$. What do you infer from cell EMF?
- Calculate the equilibrium constant for the reaction $\text{Fe} + \text{CuSO}_4 \rightleftharpoons \text{FeSO}_4 + \text{Cu}$ at 25°C . Given
 $E^\circ (\text{Fe}/\text{Fe}^{2+}) = 0.44\text{V}$, $E^\circ (\text{Cu}/\text{Cu}^{2+}) = -0.337 \text{ V}$.
- For a cell $\text{Mg}(\text{s}) | \text{Mg}^{2+} (\text{aq}) || \text{Ag}^+ (\text{aq}) | \text{Ag}$, Calculate the equilibrium constant at 25°C . Also find the maximum work that can be obtained by operating the cell. $E^\circ (\text{Mg}^{2+} / \text{Mg}) = -2.37\text{V}$, $E^\circ (\text{Ag}^+/\text{Ag}) = 0.8 \text{ V}$.
- At 25°C the value of K for the equilibrium $\text{Fe}^{3+} + \text{Ag} \rightleftharpoons \text{Fe}^{2+} + \text{Ag}^+$ is 0.531 mol/litre. The standard electrode potential for $\text{Ag}^+ + e \rightleftharpoons \text{Ag}$ is 0.799V. What is the standard potential for $\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$?

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. $E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76\text{V}$, hence for the reaction $\text{Zn} + 2\text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2$, ΔG° 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 : $E_{\text{Ag}^+/\text{Ag}}^\circ = 0.80 \text{ V}$ | ; | $E_{\text{N}_2/\text{N}_3^-}^\circ = -3.09 \text{ V}$ |
| $E_{\text{ClO}_4^-/\text{ClO}_3^-}^\circ = 1.23 \text{ V}$ | ; | $E_{\text{Na}^+/\text{Na}}^\circ = -2.71 \text{ V}$ |
| $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = 0.77 \text{ V}$ | ; | $E_{\text{O}_2/\text{H}_2\text{O}_2}^\circ = -1.03 \text{ V}$ |
| $E_{\text{H}_2\text{O}_2/\text{H}_2\text{O}}^\circ = 1.76 \text{ V}$ | ; | $E_{\text{O}_3/\text{O}_2}^\circ = 2.07 \text{ V}$ |
| $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ = 1.54 \text{ V}$ | ; | $E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^\circ = 1.33 \text{ V}$ |

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 4×10^{-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) $\text{CH}_3\text{COONH}_4$ (9) A 4 : 3 molar ratio mixture of NH_4OH and HCl .

Answer Key

DPP No. # 29

1. (C)
 2. $E^\circ_{\text{cell}} = + 0.01 \text{ V}$, $E_{\text{cell}} = - 0.0785 \text{ V}$, correct representation is $\text{Pb} | \text{Pb}^{2+} (10^{-3} \text{ M}) || \text{Sn}^{2+} (1\text{M}) | \text{Sn}$.
 3. $\log K_{\text{eq.}} = \frac{2 \times 0.777}{0.0591}$, $K_{\text{eq.}} = 2.18 \times 10^{26}$ 4. $K_c = 1.864 \times 10^{107}$, $\Delta G^\circ = -611.8 \text{ kJ}$
 5. $E^\circ = 0.7826 \text{ V}$ 6. (C) 7. (C) 8. (B) 9. 8 10. 5

Hints & Solutions

PHYSICAL / INORGANIC CHEMISTRY

DPP No. # 29



$$E_{(\text{Sn}^{2+}/\text{Sn})}^0 = -0.14 \text{ V.} \quad \text{and} \quad E_{(\text{Pb}^{2+}/\text{Pb})}^0 = -0.13 \text{ V.}$$

$$E_{\text{cell}}^0 = -0.13 + 0.14 = 0.01 \text{ V.}$$

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

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

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

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

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

$$\Delta G^0 = -2.303 RT \log 1.864 \times 10^{107} = -2.303 \times 8.314 \times 298 \log 1.86 \times 10^{107}$$

5. $0 = E_{\text{cell}}^0 - \frac{0.0591}{1} \log 0.531$

$$E_{\text{cell}}^0 = 0.0591 \log 0.531 = 0.0591 \log 5.31 \times 10^{-1}$$

$$E_{\text{C}}^0 - E_{\text{A}}^0 = -0.01624$$

$$E_{\text{C}}^0 = -0.01624 + 0.799 = 0.7826 \text{ V.}$$

6. For the given options

(A) Sodium ion and azide ion



$$E^0 = -2.71 + 3.09 < 1.7 \text{ V}$$

(B) Silver ion and perchlorate ion



$$E^0 = 1.23 - 0.80 < 1.7 \text{ V}$$

(C) Silver ion and azide ion

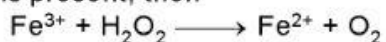


$$E^0 = 0.80 + 3.09 \\ = 3.89 > 1.7 \text{ V}$$



So will lead to explosion

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



$$E^\circ = 0.77 + 1.03 = 1.8 \text{ V} > 0$$

so spontaneous



$$E^\circ = 1.76 + 0.77 = 0.99 > 0$$

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. $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$

$$c(1-h)$$

$$ch$$

$$ch$$

where h is degree of hydrolysis

$$[\text{OH}^-] = ch;$$

$$\text{Also; } h = \sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w}{K_a \cdot c}} = \sqrt{\frac{10^{-14}}{4 \times 10^{-4} \times 0.04}} = 2.5 \times 10^{-5}$$

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

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

10. (1) $\text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log C)$; (2) $\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_{a_2} + \log C)$



$$\therefore \text{pH}_{\text{WA}} = \frac{1}{2} (\text{p}K_{a_1} - \log C)$$



i

5

2

f

3

0

2

2



i

3

2

f

1

0

2

2



i

1

2

f

0

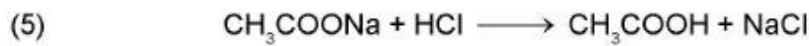
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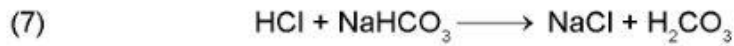
$$\therefore \text{Buffer solution} \quad \therefore \quad \text{pH} = \text{pK}_{a_3} + \log_{10} \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$



$$\begin{array}{l} \text{i} \quad \quad \quad 5 \quad \quad \quad 4 \\ \text{f} \quad \quad \quad 1 \quad \quad \quad 0 \quad \quad 4 \quad \quad 4 \end{array}$$

$$\therefore \text{Acidic buffer} \quad \therefore \quad \text{pH} = \text{pK}_a + \log_{10} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

(6) $\text{pH} = \frac{\text{pK}_{a_2} + \text{pK}_{a_1}}{2}$

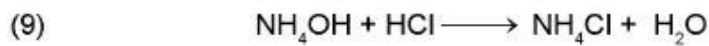


$$\begin{array}{l} \text{i} \quad \quad \quad 2 \quad \quad \quad 1 \\ \text{f} \quad \quad \quad 1 \quad \quad \quad 0 \quad \quad \quad 1 \quad \quad 1 \end{array}$$

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

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

(8) $\text{pH} = \frac{1}{2} (\text{pK}_w + \text{pK}_a - \text{pK}_b)$



$$\begin{array}{l} \text{i} \quad \quad \quad 4 \quad \quad \quad 3 \\ \text{f} \quad \quad \quad 1 \quad \quad \quad 0 \quad \quad \quad 3 \quad \quad 3 \end{array}$$

$$\therefore \text{Basic buffer} \quad \therefore \quad \text{pOH} = \text{pK}_b + \log_{10} \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

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

