PHYSICAL / INORGANIC **CHEMISTRY**



DPP No. 23

Total Marks: 46

Max. Time: 51 min.

[8, 10]

Topic: Ionic Equilibrium

Type of Questions		M.M., Min.
Single choice Objective ('-1' negative marking) Q.1 to Q.6	(3 marks, 3 min.)	[18, 18]
Multiple choice objective ('-1' negative marking) Q.7 to Q.8	(4 marks, 4 min.)	[8, 8]
Subjective Questions ('-1' negative marking) Q.9 to Q.11	(4 marks, 5 min.)	[12, 15]

1. In which of the following cases the resulting solution is acidic.

I. BeCl,

II. KCN

III. Na₂CO₃

IV. C₅H₆NBr

(8 marks, 10 min.)

(A) I & IV

(B) I & III

(C) I, III and IV

(D) Only IV

2. We know that NH₂ is a stronger base than CH₄. Which of the following is correct?

(A) NH₃ is a stronger acid than CH₄.

Match the Following (no negative marking) Q. 12

(B) NH₃ is a weaker acid than CH₄.

(C) NH,+ is a weaker acid than CH,.

(D) All of these

3. In terms of K_1 , K_2 and K_3 of a weak triprotic acid H_3B , the value of K_b for BH^{2-} will be :

(A) K_{w}/K_{1}

(B) K_u/K_o

(C) K₂/K₁₁

(D) K₁/K₂

If a solution contains 10⁻⁶ M each of X⁻, Y²⁻ and Z³⁻ ions, then upon addition of AgNO₃(s) slowly to the 4. above solution with stirring : (Given : K_{sp} (AgX) = 9×10^{-14} , K_{sp} (Ag₂Y) = 4.9×10^{-21} , K_{sp} (Ag₃Z) = 5.12×10^{-14}

(A) Ag₃Z will be the first one to precipitate out.

(B) Ag₂Y will be the first one to precipitate out.

(C) AgX will be the first one to precipitate out.

(D) Nothing can be said with certainity.

5. The freezing point depression of a 0.1 M aq. solution of weak acid (HX) is -0.20°C.

What is the value of equilibrium constant for the reaction?

$$HX (aq) \implies H^+(aq) + X^-(aq)$$

[Given: K_r for water = 1.8 kg mol⁻¹ K. & Molality = Molarity]

(A) 1.46×10⁻⁴

(B) 1.35×10^{-3}

(C) 1.21×10^{-2}

(D) 1.35×10^{-4}

Azhar wants to prepare a saturated solution of Ag⁺ ion. He has got only three samples of AgCI (K_{sp}= 6. 1.8×10^{-10}), AgBr (K_{sp} = 5 × 10^{-13}) and Ag₂ CrO₄ (K_{sp} = 2.4×10^{-12}), which compound he should use to have maximum [Ag+]?

(A) AgCI

(B) AgBr

 $(C) Ag_2CrO_4$

(D) Either of them



7. In which of the following solutions, the solubility of AgCN will be greater than that in pure water :

Given
$$K_{sp}(AgCN) = 4 \times 10^{-16}$$
, $K_{sp}(HCN) = 5 \times 10^{-10}$

(A) 0.01 M Ag NO₃ solution

(B) A buffer solution of pH = 12

(C) 0.2 M NH, solution

(D) A buffer solution of pH = 5

8. Acetic acid and propionic acid have K_a values 1.75×10^{-5} and 1.3×10^{-5} respectively at a certain temperature. An equimolar solution of a mixture, of the two acids is partially neutralised by NaOH. How is the ratio of the contents of acetate and propionate ions related to the K_a values and the molarity:

(A)
$$\left(\frac{\alpha}{1-\alpha}\right) = \frac{1.75}{1.3} \times \left(\frac{\beta}{1-\beta}\right)$$
, where α and β are ionised fractions of their acids

- (B) The ratio is unrelated to the K_a values.
- (C) The ratio is unrelated to the molarity of acid.
- (D) The ratio is unrelated to the pH of the solution.
- A certain mixture of HCl and CH_3 –COOH is 0.1 M in each of the acids. 20 ml of this solution is titrated against 0.1M NaOH. By how many units does the pH change from the start to the stage when the HCl is almost completely neutralised and acetic acid remains unreacted? K_a for acetic acid = 2 x 10⁻⁵.
- 10. CH₃COOH (60 ml, 0.1M) is titrated against 0.1M NaOH solution. Calculate the pH at the addition of 10 ml of NaOH. K_a of CH₃COOH is 2×10^{-5} . [log 2 = 0.3]
- 11. How many salts will turn blue litmus to red when dissolved in water?

$$K_2SO_4$$
, LiCN, $C_6H_5NH_3^+CI^-$, $C_6H_5COO^-Na^+$, $FeCI_3$, $(NH_4)_2C_2O_4$, $AI(NO_3)_3$, CH_3COONa

12. Column-II Column-II

(A)	NaHCO₃ (aq.)	(p) Significant cationic hydrolysis
(B)	CH ₃ COONH ₄ (aq.)	(q) Significant anionic hydrolysis

(C)
$$K_2SO_4$$
. $AI_2(SO_4)_3$ (aq.) (r) Acidic (pH < 7)
(D) NaCN (aq) (s) Basic (pH > 7)

(t) pH is independent of concentration

Given : $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-11}$ for H_2CO_3 $K(CH_3COOH) = 1.8 \times 10^{-5}$ $K(NH_4OH) = 1.8 \times 10^{-5}$





Answer Key

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1. (A)

2. (A)

3.

4.

(B)

5. (B)

6. (C)

7.

(C, D)

8.

(B) (A,C,D)

9.

(3)

10. 4

11. 03

12.

(A - q, s, t); (B - p, q, t); (C - p, r); (D - q, s).

Hints & Solutions

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- 1. Hydrolysis of cartion can form H⁺. So Be⁺², C₅H₆N⁺ forms acidic solution.
- BH²⁻ + H₂O ⇒ BH₂⁻ + OH⁻

$$K_b = \frac{K_w}{K_a (\text{of BH}_2^-)}$$

i.e.
$$K_b = \frac{K_w}{K_2}$$

4. [Ag⁺] req for pptation of AgX= $\frac{K_{sp}}{[X^-]} = \frac{9 \times 10^{-14}}{10^{-6}} = 9 \times 10^{-8} \text{ M}$

[Ag*] req for pptation of Ag₂Y =
$$\sqrt{\frac{K_{sp}}{[y^-]}} = \sqrt{\frac{4.9 \times 10^{-21}}{10^{-6}}} = 7 \times 10^{-8} \text{ M}$$

[Ag*] req for pptation of Ag₃Z =
$$3\sqrt{\frac{K_{sp}}{[z^-]}} = 3\sqrt{\frac{5.12 \times 10^{-28}}{10^{-6}}} = 8 \times 10^{-8} \text{ M}$$

clearly, [Ag+] req for pptation of Ag, Y is minimum.



.. Ag, Y will be the first one to pricipitate out.

5.
$$\Delta T_r = i \times k_r \times m$$

$$0.2 = i \times 1.8 \times 0.1$$

$$\Rightarrow i = 1.11$$

$$\Rightarrow \alpha = 0.11$$

$$= \frac{c\alpha^2}{2} = \frac{0.1 \times (0.11)}{2}$$

$$k_a$$
 = $\frac{c\alpha^2}{1-\alpha}$ = $\frac{0.1 \times (0.11)^2}{(1-0.11)}$
= 1.35 × 10⁻³ Ans.

Let the solubility of AgCI, AgBr and $Ag_2 CrO_4$ be xM, yM and zM, then we get 6.

$$K_{sp(AgCI)} = x^2$$
 \Rightarrow $x = \sqrt{1.8 \times 10^{-10}}$ \Rightarrow $x = 10^{-5} \sqrt{1.8}$

Similarly,
$$y = 10^{-7} \sqrt{50}$$

$$K_{sp} Ag_2 CrO_4 = 4z^3 = 2.4 \times 10^{12}$$

 $\Rightarrow z = (60)^{1/3} \times 10^{-4}$

More (Ag+) is needed to precipitate it.

7. In AgNO, solution, the solubility of AgCN will decrease as compared to pure water because of common ion effect of Ag+ ion.

In NH, solution and buffer of pH = 5, the solubility of AgCN will increase due to complex formation in case of NH₃ solution and hydrolysis of CN⁻ ions in case of buffer of pH = 5.

8. In a given mixture, the ionisation of two acids can be written as: Let α , β be degree of ionisation at same

$$\begin{array}{c} \text{CH}_3\text{COOH} & \Longleftrightarrow \\ \text{1--}\alpha & & \beta \end{array} \begin{array}{c} \text{CH}_3\text{COO}^- + \text{H}^+ \\ \beta & \alpha + \beta - \mathbf{x} \end{array}$$

$$C_2H_5COOH \rightleftharpoons C_2H_5COO^- + H^+ \atop 1-\beta \qquad \alpha+\beta-x$$

$$\therefore \qquad \mathsf{K}_{\mathsf{A}\mathsf{A}} = \frac{[\alpha][\alpha + \beta - \mathsf{x}].\mathsf{c}}{[1 - \alpha]}$$

$$\mathsf{K}_{\mathsf{PA}} = \frac{[\beta][\alpha + \beta - \mathsf{x}].\mathsf{c}}{[1 - \beta]}$$

(where 'x' is equivalents of NaOH droped)

$$\therefore \frac{K_{A.A}}{K_{P.A}} = \frac{\alpha}{1-\alpha} \times \frac{1-\beta}{\beta}$$

$$\frac{\mathsf{K}_{\mathsf{A},\mathsf{A}}}{\mathsf{K}_{\mathsf{P},\mathsf{A}}} = \frac{\alpha}{1-\alpha} \times \frac{1-\beta}{\beta} \qquad \qquad \mathsf{or} \qquad \frac{\alpha}{1-\alpha} = \frac{1.75}{1.3} \times \left[\frac{\beta}{1-\beta}\right]$$

Hence, A,C,D

m. moles of HCI = $0.1 \times 20 = 2$ 9.

m. moles of CH₂COOH = $0.1 \times 20 = 2$

After titration of HCI by NaOH

$$[CH_3COOH] = \frac{2}{40} = \frac{1}{20}M$$

∴ pH =
$$\frac{1}{2}$$
 (pK_a - log C) = $\frac{1}{2}$ [5 - log 2 - log ($\frac{1}{20}$)] = 3.

When 10 ml of NaOH is added, it reacts with CH₃COOH to produce salt and water. The solution is 10. then an acidic buffer. So, for acidic buffer,

pH = pK_a + log [Conjugate base]
[Acid]
= 4.7 + log
$$\frac{10 \times 0.1}{60 \times 0.1 - 10 \times 0.1}$$

= 4.7 + log $\frac{1}{5}$ = 4

C.H.NH,+CI-, FeCI,, AI(NO,),. 11.



A -ti