# IONIC EQUILIBRIUM

**1.** On decreasing the $pH$ from 7 to 2, the solubility of a sparingly soluble salt (MX) of a weak acid (HX) increased from $10^{-4}$ mol $L^{-1}$ to $10^{-3}$ mol $L^{-1}$. The $pK_a$ of HX is:

**[JEE(Advanced) 2023]**

(A) 3 (B) 4 (C) 5 (D) 2

**2.** A solution is prepared by mixing 0.01 mol each of $H_2CO_3$, $NaHCO_3$, $Na_2CO_3$, and NaOH in 100 mL of water. pH of the resulting solution is ______.

[Given : $pK_{a1}$ and $pK_{a2}$ of $H_2CO_3$ are 6.37 and 10.32, respectively ; log 2 = 0.30]

**[JEE(Advanced) 2022]**

**3.** Concentration of $H_2SO_4$ and $Na_2SO_4$ in a solution is 1 M and $1.8 \times 10^{-2}$ M, respectively. Molar solubility of $PbSO_4$ in the same solution is $X \times 10^{-Y}$ M (expressed in scientific notation). The value of Y is _________.

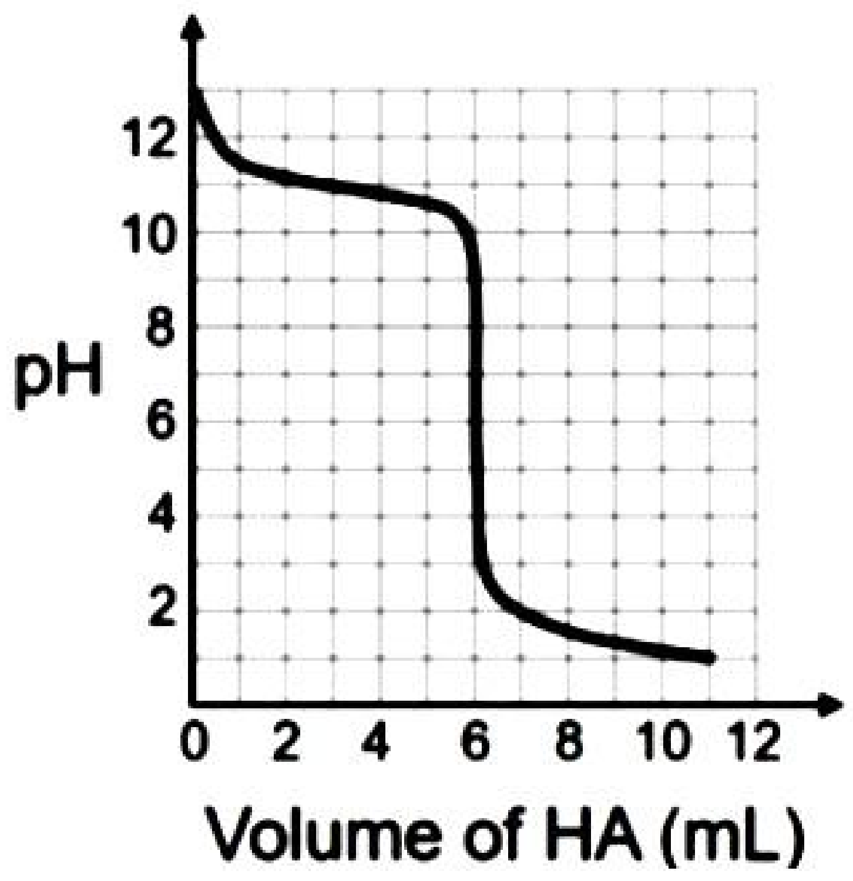
[Given: Solubility product of $PbSO_4$ ($K_{sp}$) $= 1.6 \times 10^{-8}$. For $H_2SO_4$, $K_{a1}$ is very large and $K_{a2} = 1.2 \times 10^{-2}$]

**[JEE(Advanced) 2022]**

**4.** 5.00 mL of 0.10 M oxalic acid solution taken in a conical flask is titrated against NaOH from a burette using phenolphthalein indicator. The volume of NaOH required for the appearance of permanent faint pink color is tabulated below for five experiments. What is the concentration, in molarity, of the NaOH solution ? **[JEE(Advanced) 2020]**

| Exp. No. | Vol. of NaOH (mL) |
|---|---|
| 1 | 12.5 |
| 2 | 10.5 |
| 3 | 9.0 |
| 4 | 9.0 |
| 5 | 9.0 |

**5.** A solution of 0.1 M weak base (B) is titrated with 0.1 M of a strong acid (HA). The variation of pH of the solution with the volume of HA added is shown in the figure below. What is the $pK_b$ of the base? The neutralization reaction is given by $B + HA \rightarrow BH^+ + A^-$. **[JEE(Advanced) 2020]**



**6.** An acidified solution of 0.05 M $Zn^{2+}$ is saturated with 0.1 M $H_2S$. What is the minimum molar concentration (M) of $H^+$ required to prevent the precipitation of ZnS ?

[Use $K_{sp}$ (ZnS) $= 1.25 \times 10^{-22}$ and Overall dissociation constant of $H_2S$, $K_{NET} = K_1K_2 = 1 \times 10^{-21}$]

**[JEE(Advanced) 2020]**

**7.** The solubility of a salt of weak acid(AB) at pH 3 is $Y \times 10$ mol L . The value of Y is_______.

(Given that the value of solubility product of AB ($K_{sp}$) $= 2 \times 10^{-10}$ and the value of ionization constant of HB($K_a$) $= 1 \times 10^{-8}$) **[JEE(Advanced) 2018]**

**8.** Dilution process of different aqueous solutions; with water, are given in List-I. The effects of dilution of the solutions on $[H^+]$ are given in List-II.

(Note : Degree of dissociation ($\alpha$) of weak acid and weak base is << 1; degree of hydrolysis of salt <<1; $[H^+]$ represents the concentration of $H^+$ ions) **[JEE(Advanced) 2018]**

| **List-I** | **List-II** |
|---|---|
| P. (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL | 1. the vale of $[H^+]$ does not change on dilution |
| Q. (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL | 2. the value of $[H^+]$ change to half of its initial value on dilution |
| R. (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL | 3. the value of $[H^+]$ changes to two times of its initial value on dilution |
| S. 10 mL saturated solution of $Ni(OH)_2$ in equilibrium with excess solid $Ni(OH)_2$ is diluted to 20 mL (solid $Ni(OH)_2$ is still present after dilution). | 4. the value of $[H^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution |
| | 5. the value of $[H^+]$ changes to $\sqrt{2}$ times of its initial value on dilution |

Match each process given in LIST-I with one or more effect(s) in LIST-II. The correct option is

(A) P → 4; Q → 2; R → 3; S → 1
(B) P → 4; Q → 3; R → 2; S → 3
(C) P → 1; Q → 4; R → 5; S → 3
(D) P → 1; Q → 5; R → 4; S → 1

### Paragraph For Questions No. 9 and 10

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents. **(Expt-1).** Because the enthalpy of neutralisation of a strong acid with a strong base is a constant (–57.0 kJmol$^{-1}$), this experiment could be used to measure the calorimeter constant. In a second experiment **(Expt-2)**, 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0M NaOH (under identical conditions to **(Expt-1))** where a temperature rise of 5.6 °C was measured.

(Consider heat capacity of all solutions as 4.2 Jg$^{-1}$K$^{-1}$ and density of all solutions as 1.0 g mL$^{-1}$)

**9.** Enthalpy of dissociation (in kJ mol$^{-1}$) of acetic acid obtained from the **Expt-2** is **[JEE(Advanced) 2015]**

(A) 1.0 (B) 10.0 (C) 24.5 (D) 51.4

**10.** The pH of the solution after **Expt-2** **[JEE(Advanced) 2015]**

(A) 2.8 (B) 4.7 (C) 5.0 (D) 7.0

# SOLUTIONS

**1. Ans. (B)**

**Sol.** At pH = 7 $\Rightarrow$ pure water

solubility $= S_1 = \sqrt{K_{sp}}$

At pH = 2

$$\Rightarrow \quad MX(s) + aq \xrightleftharpoons{K_{sp}} M^{+}(aq) + X^{-}(aq)$$

$$s \qquad s - x$$

$$X^{-}(aq) + H^{+}(aq) \xrightleftharpoons{1/K_a} HX(aq)$$

$$s - x \qquad 10^{-2} \qquad\qquad x \simeq s$$

Approximation : $s - x \simeq 0$ [$X^{-}$ is limiting reagent]

$\Rightarrow s \simeq x$

$\Rightarrow \quad s(s - x) = K_{sp}$ ....(1)

$$\frac{s}{(s - x)\,(10^{-2})} = \frac{1}{K_a} \quad ....(2)$$

Multiply (1) × (2) $\Rightarrow \dfrac{s^2}{10^{-2}} = \dfrac{K_{sp}}{K_a}$

$$\Rightarrow s = \frac{\sqrt{K_{sp}}}{10\sqrt{K_a}}$$

Now given : $\dfrac{s}{s_1} = \dfrac{10^{-3}}{10^{-4}}$

$$\Rightarrow \frac{\dfrac{\sqrt{K_{sp}}}{10\sqrt{K_a}}}{\sqrt{K_{sp}}} = 10 \qquad \Rightarrow \frac{1}{10\sqrt{K_a}} = 10 \Rightarrow \sqrt{K_a} = 10^{-2} \Rightarrow K_a = 10^{-4} \Rightarrow pK_a = 4$$

**2. Ans. (10.00 - 10.04)**

**Sol.** $H_2CO_3 + NaOH \longrightarrow NaHCO_3 + H_2O$

| | $H_2CO_3$ | NaOH | $NaHCO_3$ |
|---|---|---|---|
| Milli moles | 10 | 10 | – |
| At end | 0 | 0 | 10 + 10 = 20 |

Final mixture has 20 milli moles $NaHCO_3$ and 10 milli moles $Na_2CO_3$

$$pH = pKa_2 + \log\frac{Salt}{Acid}$$

$$pH = pKa_2 + \log\left(\frac{10}{20}\right) \qquad [\text{Buffer} : Na_2CO_3 + NaHCO_3]$$

$= 10.32 - \log 2 = 10.02$

**3.** **Ans. (6)**

**Sol.** $H_2SO_4 \rightleftharpoons HSO_4^- + H^+$

1M - -

- 1M 1M

$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$

$1.8 \times 10^{-2}$ M - -

$3.6\times10^{-2}$ M $1.8\times10^{-2}$ M

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ ; $K_{a_2} = 1.2 \times 10^{-2}$ M

1M 1M $1.8\times10^{-2}$ M

Since $Q_C > K_C$ it will move in backward direction.

$1 + x$ $1 - x$ $1.8 \times 10^{-2} - x$

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{(1-x)(1.8\times10^{-2}-x)}{(1+x)}$$

Since x is very small $(1 + x) \simeq$ **1 and (1 – x)** $\simeq 1$

$$x = (1.8\times10^{-2} - 1.2\times10^{-2})M$$

$$[SO_4^{2-}] = (1.8\times10^{-2} - 0.6\times10^{-2})M$$

$$= 1.2 \times 10^{-2} M$$

$PbSO_4 \longrightarrow Pb^{2+} + SO_4^{2-}$

s - $1.2\times10^{-2}$ M

- s $(s + 1.2 \times 10^{-2})$

$K_{sp} = s\,(s + 1.2 \times 10^{-2}) = 1.6 \times 10^{-8}$

$(PbSO_4)$

Here, $(s + 1.2 \times 10^{-2}) \simeq 1.2 \times 10^{-2}$ (since 's' is very small)

$s(1.2\times10^{-2}) = 1.6 \times 10^{-8}$

$$\Rightarrow s = \frac{1.6}{1.2}\times10^{-6} M = X\times10^{-Y} M \qquad \Rightarrow Y = 6$$

**4.** **Ans. (0.11)**

**Sol.** No. of eq. of oxalic acid = No. of eq. of NaOH

or $$\frac{5.00\times0.10}{1000}\times2 = \frac{9.0\times M}{1000}\times1$$

$\therefore$ Molarity of NaOH solution $= \frac{1}{9} = 0.11M$

**5. Ans. (2.80 TO 3.20)**

**Sol.** $B + HA \longrightarrow BH^+ + A^-$

0.1 M, V ml

0.1 V m mol   0.1V m mol   0.1 V 0.1 V

$$[BH^+] = \frac{0.1\,V}{2\,V} = 0.05\,M$$

pH at eq. pt = 6 to 6.28

$pH = 7 - \frac{1}{2}\,[pK_b + \log 0.05]$

So $pK_b = 2.30 - 2.80$

Possible

**Solution-2**

at V = 6 ml rxn is complete

So V = 3 ml is half of eq. pt

at which   pH = 11

$pOH = (14 - 11) = pK_b + \log 1$

$pK_b = 3$

**6. Ans. (0.20)**

**Sol.** For ppt, $[Zn^{+2}]\,[S^{-2}] = K_{sp}$

$[S^{-2}] = \frac{1.25 \times 10^{-22}}{0.05} = 2.5 \times 10^{-21}\,M$

$H_2S \rightleftharpoons 2H^+ + S^{-2}$

$K_{Net} = 10^{-21} = \frac{[H^+]^2 \times 2.5 \times 10^{-21}}{0.1}$

$[H^+]^2 = \frac{1}{25}$

$[H^+] = \frac{1}{5}\,M = 0.2\,M$

**7. Ans. (4.47)**

**Sol.** $S = \sqrt{K_{sp}\left(\frac{[H^+]}{K_a} + 1\right)} = \sqrt{2 \times 10^{-10}\left(\frac{10^{-3}}{10^{-8}} + 1\right)} \simeq \sqrt{2 \times 10^{-5}} = 4.47 \times 10^{-3}\,M$

**8.** **Ans. (D)**

**Sol.** **P.** $\underset{0.1M,\,20ml}{CH_3COOH} + \underset{0.1M,10ml}{NaOH} \rightarrow CH_3COONa + H_2O$

$pH = pKa \Rightarrow [H^+]$ will not change on dilution

correct match : P-1

**Q.** $\underset{0.1M,\,20ml}{CH_3COOH} + \underset{0.1M,20ml}{NaOH} \rightarrow CH_3COONa + H_2O$

— — 0.05 M

$$[OH^-] = \sqrt{K_H C} = \sqrt{\left(\frac{k_w}{k_a}C\right)}$$

$$[H^+]_1 = \sqrt{\frac{k_w k_a}{C}}$$

$$\frac{[H^+]_2}{[H^+]_1} = \sqrt{\frac{C_1}{C_2}} = \sqrt{\frac{0.05}{0.025}} = \sqrt{2}$$

correct match : Q-5

**R.** $\underset{0.1M,20ml}{NH_4OH} + \underset{0.1M,20ml}{HCl} \rightarrow \underset{0.05M}{NH_4Cl}$

$$[H^+] = \sqrt{K_H C}$$

$$\frac{[H^+]_2}{[H^+]_1} = \sqrt{\frac{C_2}{C_1}} = \frac{1}{\sqrt{2}}$$

correct match : R-4

**S.** Because of dilution solubility does not change so $[H^+]$ = constant

**9.** **Ans. (A)**

**Sol.**
$$\begin{array}{lllll} HCl & + \; NaOH & \longrightarrow NaCl & + & H_2O \\ 100 \text{ m.mol} & 100 \text{ m.mol} & - & & - \\ - & - & 100 \text{ m.mol} & & 100 \text{ m.mol} \end{array}$$

$$Q = +57 \times 1000 \times \frac{100}{1000} = [200 \times 4.2 + C] \times 5.7 \qquad ....(1)$$

$$\begin{array}{lllll} CH_3COOH & + \; NaOH & \rightarrow CH_3COONa & + & H_2O \\ 200 & 100 & - & & - \\ 100 & - & 100 & & - \end{array}$$

$$\Rightarrow |\Delta H| \times 1000 \times \frac{100}{1000} = [200 \times 4.2 + C] \times 5.6 \qquad ....(2)$$

By eq. (1) / eq. (2)

$\Rightarrow |\Delta H| = 56$

$\Rightarrow \Delta H_{nuetralisation} = -56$ kJ/mol

$\Rightarrow -56 = -57 + \Delta H_{IE}$

$\Rightarrow \Delta H_{IE} = 1$ kJ/mol

**10.** **Ans.(B)**

**Sol.** Solution is buffer

$$pH = pK_a + \log \frac{CH_3COONa}{CH_3COOH}$$

$$= -\log(2 \times 10^{-5}) + \log \frac{0.1}{0.1} = 5 - \log 2 = 4.7$$