PHYSICAL CHEMISTRY

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 1.8×10^{-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 _________.

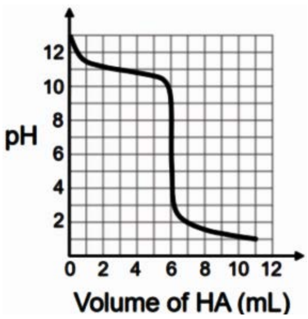
[Given: Solubility product of $PbSO_4$ (K_{sp}) = 1.6×10^{-8}. For H_2SO_4, K_{a1} is very large and $K_{a2} = 1.2 \times 10^{-2}$]

[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) = 1.25×10^{-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 $Y \times 10^{-3}$ mol L^{-1}. The value of Y is_______.

(Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB(K_a) = 1×10^{-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 (α) 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 ºC 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 = 2.0×10^{-5}) was mixed with 100 mL of 1.0M NaOH (under identical conditions to **(Expt-1))** where a temperature rise of 5.6 ºC 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

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

s   s–x

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

s–x 10^{-2} $x \simeq s$

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

$\Rightarrow s \simeq x$

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

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

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

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

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

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

2. Ans. (10.00 - 10.04)

Sol.

	H_2CO_3 +	$NaOH \longrightarrow$	$NaHCO_3 + H_2O$
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

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

$pH = pKa_2 + \log \left(\frac{10}{20}\right)$ [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

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

1.8×10^{-2} M - -

3.6×10^{-2} M 1.8×10^{-2} M

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

1M 1M 1.8×10^{-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 - 1.2×10^{-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, $[Zn^{+2}]\ [S^{-2}] = K_{sp}$

$[S^{-2}] = \frac{1.25\times10^{-22}}{0.05} = 2.5 \times 10^{-21}\ M$

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

$K_{Net} = 10^{-21} = \frac{[H^+]^2 \times 2.5\times10^{-21}}{0.1}$

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

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

7. Ans. (4.47)

Sol. $S = \sqrt{K_{sp}\left(\frac{[H^+]}{K_a}+1\right)} = \sqrt{2\times10^{-10}\left(\frac{10^{-3}}{10^{-8}}+1\right)} \simeq \sqrt{2\times10^{-5}} = 4.47 \times 10^{-3}\ M$

8. **Ans. (D)**

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

pH = pKa ⇒ $[H^+]$ 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.

HCl	+	NaOH	$\longrightarrow$	NaCl	+	H_2O
100 m.mol		100 m.mol		–		–
–		–		100 m.mol		100 m.mol

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

CH_3COOH	+	NaOH	$\rightarrow$	CH_3COONa	+	H_2O
200		100		–		–
100		–		100		–

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

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

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

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