VARUN

ADVANCE 2026

PHYSICAL CHEMISTRY

Lecture - 01

Ionic Equilibrium

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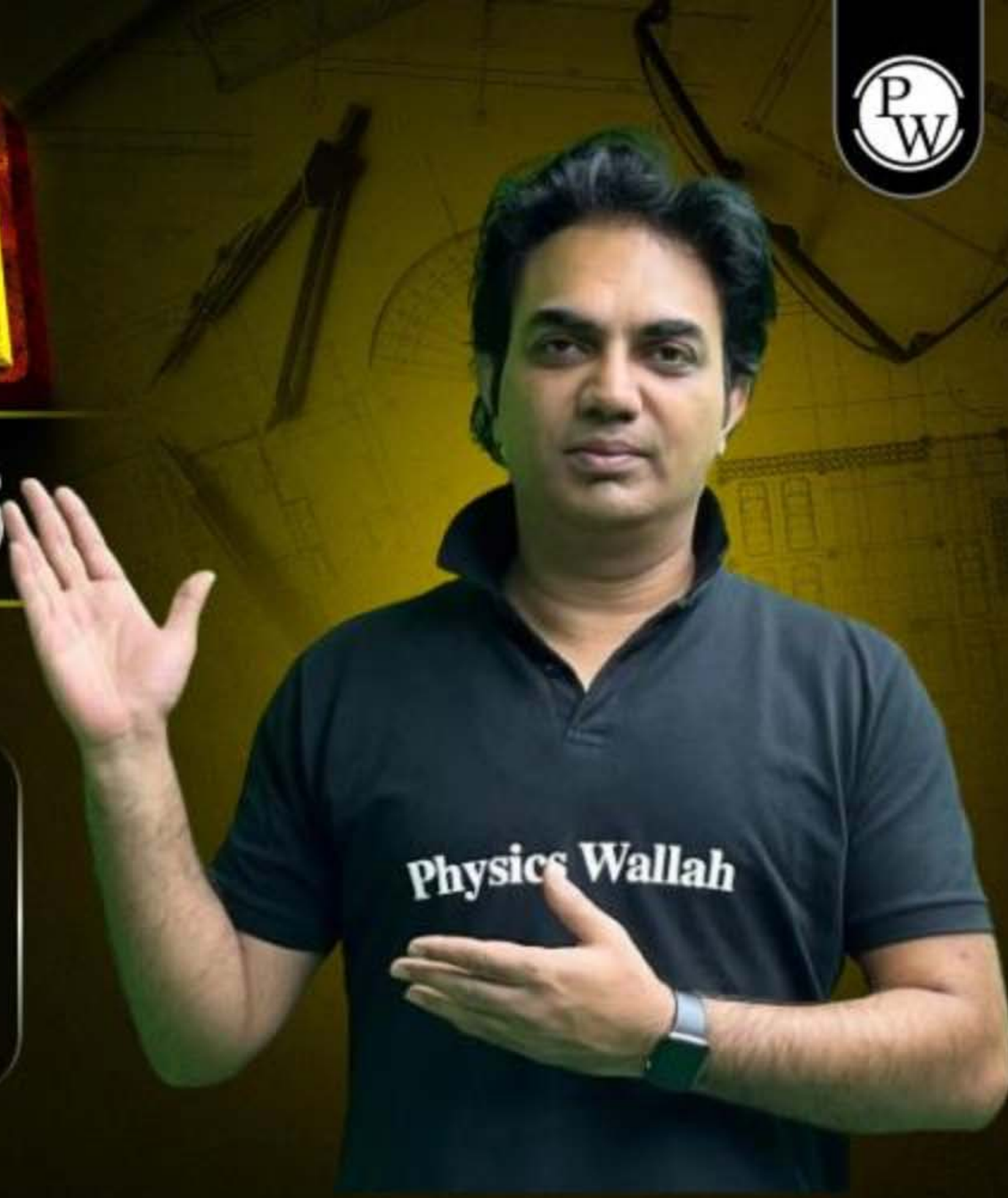


Topics to be covered

1. Questions

QUESTION

$[N_2O_5]_{initial} = \frac{4}{2} = 2\ M$

$x + y = 2.5$

When $N_2O_5(g)$ is heated to 600 K, it dissociates as $N_2O_5(g) \rightleftharpoons N_2O_3(g) + O_2(g)$; $K_C = 2.5$ M. Simultaneously, $N_2O_3(g)$ decomposes as $N_2O_3(g) \rightleftharpoons N_2O(g) + O_2(g)$. When initially 4.0 moles of $N_2O_5(g)$ is taken in a 2.0 L flask and allowed to attain equilibrium, the equilibrium concentration of $O_2(g)$ is found to be 2.5 M. The equilibrium concentration of $N_2O(g)$ (in M) is

$$K_C = \frac{[N_2O_3][O_2]}{[N_2O_5]}$$

$$2.5 = \frac{(x-y)(2.5)}{2-x}$$

$$2 - x = x - y$$

$$2 = 2x - y = 2(2.5 - y) - y = 5 - 3y$$

$y = 1$ M Ans

$$N_2O_5 \rightleftharpoons N_2O_3 + O_2$$

$2-x$ $\quad x-y$ $\quad x+y$

$$N_2O_3 \rightleftharpoons N_2O + O_2$$

$x-y$ $\quad y$ $\quad x+y$

Ans : 1

QUESTION

$x = 2$, $z = 1$

$xA + yB \rightleftharpoons zC$

A reaction at 300 K with $\Delta G^\circ = -1743$ J consists of 3 moles of A(g), 6 moles of B(g) and 3 moles of C(g). If A, B and C are in equilibrium in 1 L container, then the reaction may be (In 2 = 0.7, R = 8.3 J/K-mol)

(A) ~~A + B ⇋ C~~

(B) ~~A ⇋ B + 2C~~

(C) ✓ 2A ⇋ B + C

(D) ~~A + B ⇋ 2C~$

$\Delta G^\circ = -RT(2.303)\log K$

$-1743 = -8.3 \times 300 \times 2.303 \log K$

$\log K = 0.3$

$K = 2$

$K = 3^0 2^1$

$K = \frac{[C]^z}{[A]^x[B]^y}$

$K = \frac{3^z}{3^x 6^y} = 3^{z-x-y} \cdot 2^{-y}$

Comparing K values —

$y = -1$

$z - x - y = 0$

$z - x = -1$

Ans : C

QUESTION

$\frac{\lambda}{2} = 10.5 \Rightarrow \lambda = 21$

If for the equilibria $NH_2COONH_4(s) \leftrightharpoons N_2 + H_2 + CO + O_2$, the value of K_p at 800 K is $27 \times 2^{\lambda/2}$ and the equilibrium pressure is 22 atm. The value of λ is

A 21

B 22

C 11

D 12

$$NH_2COONH_4(s) \rightleftharpoons N_2 + 3H_2 + CO + \frac{1}{2}O_2$$

$$P \quad 3P \quad P \quad \frac{P}{2}$$

$$P + 3P + P + \frac{P}{2} = 22$$

$$\frac{11P}{2} = 22$$

$$P = 4$$

$$K_p = P_{N_2} \cdot P_{H_2}^3 \cdot P_{CO} \cdot P_{O_2}^{\frac{1}{2}}$$

$$= 4 \times 12^3 \times 4 \times 2^{\frac{1}{2}}$$

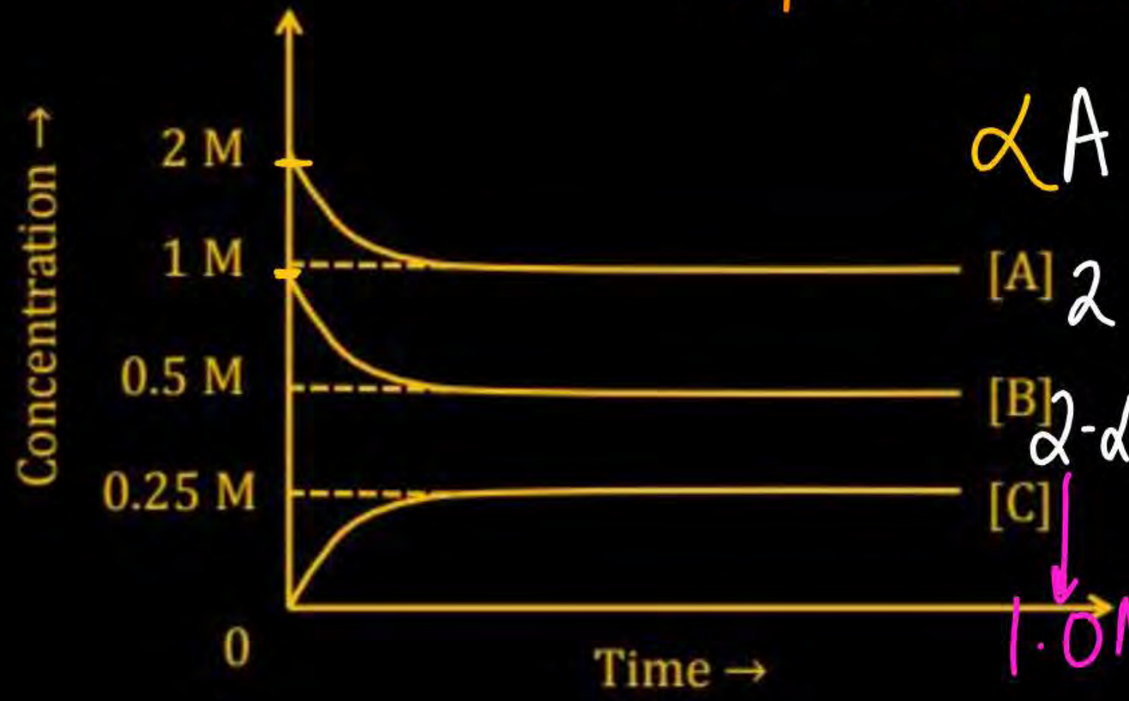
$$= 2^2 \times 3^3 \times 4^3 \times 4 \times 2^{\frac{1}{2}}$$

$$= 27 \times 2^{10.5}$$

Ans : A

QUESTION

From the following graphical representation, what is the value of $(\alpha + \beta + \gamma)$ in following equilibrium reaction?



$\alpha = 4$
$\beta = 2$
$\gamma = 1$

$\alpha + \beta + \gamma = 7$

$1 - \beta \quad \frac{0.25}{2} = 0.5$

$p = \frac{0.5 \times 2}{0.25} = 4$

α, β and γ are coeff of A, B and C.

$$\alpha A + \beta B \rightleftharpoons \gamma C$$

	A	B	C
	2	1	0
	$2-\alpha x$	$1-\beta x$	γx
	1.0 M	0.5 M	0.25 M

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QUESTION

Dissociation constants of acids HA and HB are 2.0×10^{-4} and 5×10^{-5}, respectively. The $[H^+]$ in the resulting solution obtained by mixing 20 ml of 0.5 M-HA solution and 30 ml of 0.2 M-HB solution is

Ka_1 Ka_2

$$\alpha_i = \frac{Ka_i}{\sqrt{\sum Ka_i C_i}}$$

$$[H^+] = \sqrt{\sum Ka_i C_i} \quad \{\text{when } \sqrt{\sum Ka_i C_i} \geq 10^{-6}\ M\}$$

$$[H^+] = \sqrt{\sum Ka_i C_i + K_w} \quad \{\sqrt{\sum Ka_i C_i} < 10^{-6}\ M\}$$

A. 1.05×10^{-2} M

B. 6.78×10^{-3} M

C. 1.05×10^{-3} M

D. 6.78×10^{-2} M

For two weak acids

$$[H^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2}$$

For three weak acids

$$[H^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2 + K_{a_3}C_3}$$

$$H_2O \rightleftharpoons H^+ + \bar{O}H$$

$$K_a = \frac{[H^+][\bar{O}H]}{[H_2O]}$$

$$K_a[H_2O] = [H^+][\bar{O}H] = K_w$$

$K_a \times C$

$$[HA]_{new} = \frac{20 \times 0.5}{(20+30)} M = 0.2\,M$$

$$[HB]_{new} = \frac{30 \times 0.2}{(20+30)} M = \frac{3}{25} M = 0.12\,M$$

$$[H^+] = \sqrt{(2 \times 10^{-4} \times 0.2) + (5 \times 10^{-5} \times 0.12)}$$

$$= \sqrt{4 \times 10^{-5} + 0.6 \times 10^{-5}} = \sqrt{46 \times 10^{-6}}$$

$$= \sqrt{46} \times 10^{-3}\,M$$

$$= 6.8 \times 10^{-3}\,M$$

Ans: (B)

QUESTION

$[H^+] = \sqrt{K_{a_1} \times C} = \sqrt{2 \times 10^{-5} \times 0.2}$

$= 2 \times 10^{-3}$ M

$2 \times 10^{-5} \times 5 \times 10^{-9} \times 4 \times 10^{-12}$

For a tribasic acid, H3A. $K_{a1} = 2 \times 10^{-5}$, $K_{a2} = 5 \times 10^{-9}$ and $K_{a3} = 4 \times 10^{-12}$. The value of $\frac{[A^{3-}]}{[H_3A]}$ at equilibrium in an aqueous solution originally having 0.2 M – H_3A is

A. 5×10^{-17}

B. 5×10^{-9}

C. 1×10^{-17}

D. 2×10^{-22}

$H_3A \rightleftharpoons H_2A^- + H^+$ K_{a_1}

$H_2A^- \not\rightleftharpoons HA^{2-} + H^+$ K_{a_2}

$HA^{2-} \not\rightleftharpoons A^{3-} + H^+$ K_{a_3}

$H_3A \rightleftharpoons 3H^+ + A^{3-}$ $K_{eq} = K_{a_1} \times K_{a_2} \times K_{a_3}$

$K_{eq} = \frac{[H^+]^3 [A^{3-}]}{[H_3A]}$

$\frac{[A^{3-}]}{[H_3A]} = \frac{K_{eq}}{[H^+]^3} = \frac{4 \times 10^{-25}}{[H^+]^3}$

$= \frac{4 \times 10^{-25}}{(2 \times 10^{-3})^3}$

$= 0.5 \times 10^{-16}$

Ans

Ans : (A)

QUESTION

$$pH = pK_a + \log \frac{[\text{conj Base}]}{[\text{Acid}]}$$

$$pH = pK_a$$

The buffer capacity (β) for a weak acid (A) – conjugated base (B) buffer is defined as the number of moles of strong acid or base needed to change the pH of strong acid or base needed to change the pH of 1 L of solution by 1pH unit, where $\beta = \frac{2.303\,(C_A + C_B)K_a[H^+]}{([H^+]+K_a)^2}$. Under what condition will be buffer best resist a change in pH?

A. $pH = 3\,pK_a$

B. $2\,pH = pK_a$

C. $pH = pK_a$ ✓

D. $pH = 2\,pK_a$

$$\frac{d\beta}{dH^+} = 0$$

For Acidic Buffer

$$[\text{Acid}] = [\text{conj Base}]$$

For Basic Buffer

$$[\text{Base}] = [\text{conj Acid}]$$

Ans: (C)

QUESTION

$K_2CrO_4(s) \rightarrow K_2CrO_4(aq) \rightarrow 2K^+(aq) + CrO_4^{2-}(aq)$

Calculate the degree of hydrolysis of 0.005 M-K_2CrO_4. For H_2CrO_4, K_{a1} = infinite, $K_{a2} = 5 \times 10^{-7}$.

A 0.002

B 0.02

C 0.2

D 0.005

$CrO_4^{2-}(aq) + H_2O \rightleftharpoons HCrO_4^-(aq) + OH^-$ (ch)

$c(1-h)$

$K_{h_1} = \frac{K_w}{K_{a_2}}$

$HCrO_4^-(aq) + H_2O \not\rightleftharpoons H_2CrO_4(aq) + OH^-$ (ch)

$K_{h_2} = \frac{K_w}{K_{a_1}}$

$K_{h_2} = \frac{[H_2CrO_4][OH^-][H^+]}{[HCrO_4^-][H^+]} = \frac{K_w}{K_{a_1}}$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ ; Ka_1 = \frac{[HCrO_4^-][H^+]}{[H_2CrO_4]}$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ ; K_{a_2} = \frac{[CrO_4^{2-}][H^+]}{[HCrO_4^-]}$$

$$K_{h_1} = \frac{K_w}{Ka_2} = \frac{ch \times ch}{c(1-h)} \simeq ch^2$$

$$h = \sqrt{\frac{K_w}{CKa_2}} = \sqrt{\frac{10^{-14}}{0.005 \times 5 \times 10^{-7}}}$$

$$= \frac{1}{5} \times 10^{-2} = 0.002$$

$$[H^+] = \sqrt{\frac{K_w K_{a_2}}{C}}$$

$$pH = -\log \sqrt{\frac{K_w K_{a_2}}{C}}$$

Ans: (A)

QUESTION

What is the solubility of MnS in pure water, assuming hydrolysis of S^{2-} ions? K_{sp} of MnS $= 2.5 \times 10^{-10}$, $K_{a1} = 1 \times 10^{-7}$ and $K_{a2} = 1 \times 10^{-14}$ for H_2S. $(0.63^3 = 0.25)$

A. 6.3×10^{-4} M

B. 2.5×10^{-4} M

C. 6.3×10^{-3} M

D. 1.58×10^{-5} M

$\frac{10^{-14}}{10^{-14}} = 1$

$MnS_{(s)} \rightleftharpoons \underset{S}{Mn^{2+}_{(aq)}} + \underset{S-x}{S^{2-}_{(aq)}}$; $K_{sp} = S(S-x)$ — (1)

$\underset{S-x}{S^{2-}_{(aq)}} + H_2O \rightleftharpoons \underset{x}{HS^-} + \underset{x}{OH^-}$; $K_h = \frac{K_w}{K_{a_2}}$

$HS^-_{(aq)} + H_2O \rightleftharpoons H_2S + OH^-$

$1 = \frac{x^2}{S-x}$ — (2)

$S = ?$

Ans: (A)

Comprehension

The first and second dissociation constants of H_2CO_3 are 4.0×10^{-6} and 2.5×10^{-11}, respectively. In a particular titration, 50 ml of 1.0 M-Na_2CO_3 is taken in a flask and 1.0 M-HCl solution is added drop by drop. Determine the pH of the resulting solution on adding the following volume of HCl solution. Assume that volume is additive. (log 2 = 0.3, log 3 = 0.48).

QUESTION

25 ml ?

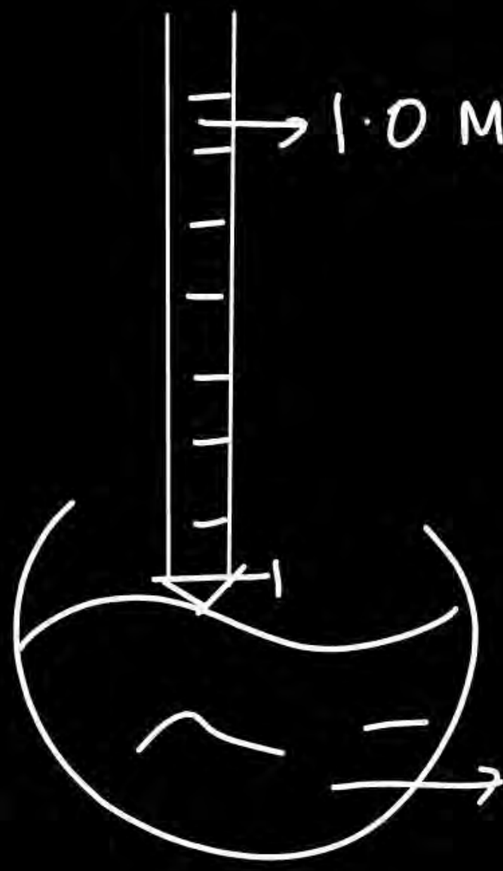
A 10.6

B 10.3

C 10.9

D 3.4

1) 0 ml HCl



$$pH = -\log\sqrt{\frac{K_w K_{a_2}}{C}}$$

$$= -\log\sqrt{\frac{10^{-14}\times 2.5\times 10^{-11}}{}}$$

H_2CO_3 → K_{a_1}, K_{a_2}

Na^{+} (×) + CO_3^{2-} (✓) (Polyanion)

$$= -\log 5\times 10^{-13}$$

$$= 13 - \log 5 = 13 - 0.7 = 12.3$$

b) 25 mL HCl

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

50 // 25 // 0

25 // 0 // 25

WA – CB

$HCO_3^- - CO_3^{2-}$

Buffer

$\times \; NaHCO_3 + HCl \longrightarrow H_2CO_3 + NaCl$

$H_2CO_3 \rightarrow HCO_3^- + H^+$ K_{a_1}

$HCO_3^- \rightarrow CO_3^{2-} + H^+$ K_{a_2}

$pH = pK_a + \log \frac{[C.B]}{[Acid]}$

$= pK_{a_2} + \log \frac{25 \rightarrow 0}{25}$

$pH = pK_{a_2} = -\log 2.5 \times 10^{-11} = 11 - \log 2.5$

$11 - 0.4 = 10.6$

Ans.

Ans: (A)

Comprehension

The first and second dissociation constants of H_2CO_3 are 4.0×10^{-6} and 2.5×10^{-11}, respectively. In a particular titration, 50 ml of 1.0 M-Na_2CO_3 is taken in a flask and 1.0 M-HCl solution is added drop by drop. Determine the pH of the resulting solution on adding the following volume of HCl solution. Assume that volume is additive. (log 2 = 0.3, log 3 = 0.48).

QUESTION

50 ml ?

A 10.6

B 5.4

C 8.0

D 6.0

✓ $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

50 50 0 0

0 0 50

× $NaHCO_3 + HCl \longrightarrow H_2CO_3 + NaCl$

$NaHCO_3 \longrightarrow \underset{\times}{Na^+} + \underset{\checkmark}{HCO_3^-}$ (amphiprotic)

$[H^+] = \sqrt{Ka_1 \times Ka_2}$ | $pH = \frac{pKa_1 + pKa_2}{2}$

$= \sqrt{4 \times 10^{-6} \times 2.5 \times 10^{-11}} = 10^{-8}\ M$

$$H_2CO_3 \xleftarrow{Ka_1} HCO_3^- \xrightarrow{Ka_2} CO_3^{2-}$$

$$[H^+] = \sqrt{Ka_1 \times Ka_2} \Rightarrow pH = \frac{pKa_1 + pKa_2}{2}$$

Q

C M Na_2HPO_4

$Na^+ + HPO_4^{2-}$

× ✓

K_{a_1}, K_{a_2} & K_{a_3} of H_3PO_4 are given.

$$H_2PO_4^- \xleftarrow{K_{a_2}} HPO_4^{2-} \xrightarrow{K_{a_3}} PO_4^{3-}$$

$$[H^+] = \sqrt{K_{a_2} * K_{a_3}} \Rightarrow pH = \frac{pK_{a_2} + pK_{a_3}}{2}$$

Ans : (C)

Comprehension

The first and second dissociation constants of H_2CO_3 are 4.0×10^{-6} and 2.5×10^{-11}, respectively. In a particular titration, 50 ml of 1.0 M-Na_2CO_3 is taken in a flask and 1.0 M-HCl solution is added drop by drop. Determine the pH of the resulting solution on adding the following volume of HCl solution. Assume that volume is additive. (log 2 = 0.3, log 3 = 0.48).

QUESTION

75 ml ?

A 10.6

B 8.6

C 8.0

D 5.4

$Na_2CO_3 + HCl \longrightarrow NaHCO_3$

50 75 0

0 25 50

$NaHCO_3 + HCl \longrightarrow H_2CO_3$

50 25 0

25 0 25

WA C.B

$H_2CO_3 - HCO_3^-$

Buffer.

$pH = pK_{a_1} + \log \frac{25}{25}$

$\log \frac{25}{25} \to 0$

$pH = -\log 4 \times 10^{-6} = 6 - 0.6$

5.4

Ans: (D)

Comprehension

The first and second dissociation constants of H_2CO_3 are 4.0×10^{-6} and 2.5×10^{-11}, respectively. In a particular titration, 50 ml of 1.0 M-Na_2CO_3 is taken in a flask and 1.0 M-HCl solution is added drop by drop. Determine the pH of the resulting solution on adding the following volume of HCl solution. Assume that volume is additive. (log 2 = 0.3, log 3 = 0.48).

QUESTION

100 ml ?

A 2.94

B 11.06

C 5.4

D 5.88

Ans : (A)

JEE Adv.2013

The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is

A 1.1×10^{-11}

B 1.1×10^{-10}

C 1.1×10^{-12}

D 1.1×10^{-9}

[Ans : B]

JEE Adv. 2022

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_{a_1} and pK_{a_2} of H_2CO_3 are 6.37 and 10.32, respectively; log 2 = 0.30]

[Ans : 10.02]

JEE Adv. 2020

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, $K_{net} = K_1K_2 = 1 \times 10^{-21}$.

Ans : 0·2 M

JEE Adv. 2022

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_{a_1} is very larger and $K_{a_2} = 1.2 \times 10^{-2}$]

QUESTION

Calculate the pH of the following solutions.

H_3PO_4 ; $K_{a_1} = 7.5 \times 10^{-3}, K_{a_2} = 6.2 \times 10^{-8}, K_{a_3} = 10^{-12}$

(A) 50 mL of 0.12 M H_3PO_4 + 20 mL of 0.15 M NaOH;

(B) 50 mL of 0.12 M H_3PO_4 + 40 mL of 0.15 M NaOH;

(C) 40 mL of 0.12 M H_3PO_4 + 40 mL of 0.18 M NaOH;

(D) 40 mL of 0.10 M H_3PO_4 + 40 mL of 0.25 M NaOH;

Comprehension

The solubility product of AgCN is 1.0×10^{-16} and the formation constant of $Ag(CN)_2^-$ is 1.5×10^{17}.

QUESTION

The solubility of AgCN in 0.02 M-KCN solution, assuming no complex formation, is

A 1.0×10^{-8} M

B 5.0×10^{-15} M

C 0.02 M

D 5.0×10^{-14} M

[Ans : B]

QUESTION

The solubility of AgCN in 0.02 M-KCN solution, assuming complex formation, is

A $0.3\ M$

B $0.02\ M$

C $1.33 \times 10^{-19}\ M$

D $1.87 \times 10^{-2}\ M$

[Ans : D]

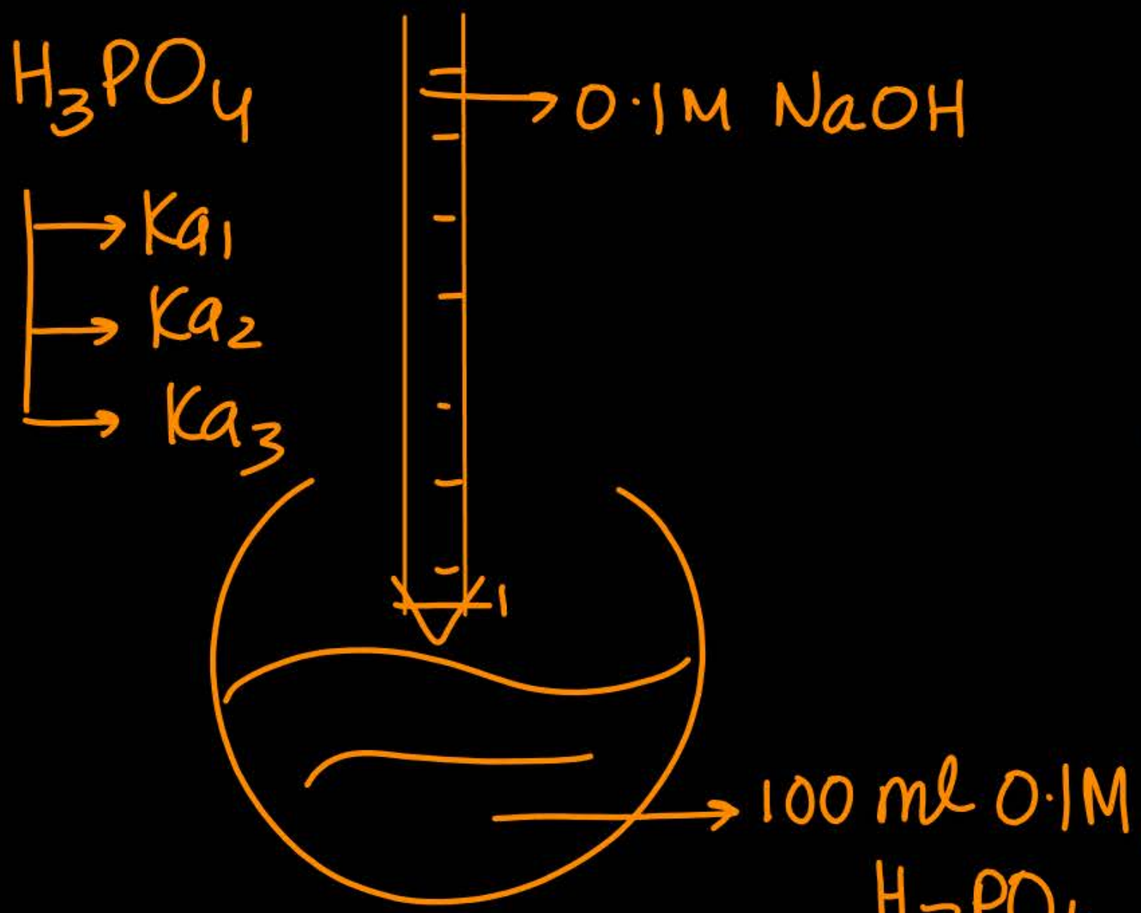
QUESTION

The solubility product (K_{sp}) of $Ca(OH)_2$ at 25°C is 3.2×10^{-5}. A 500 ml of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 1.6 M-NaOH. How much $Ca(OH)_2$ (in milligrams) is precipitated?

Ans: 740 mg

Question

Calculate the pH of a soln when –



i) 0 ml NaOH

ii) 50 ml NaOH

iii) 100 ml NaOH

iv) 150 ml NaOH

v) 200 ml NaOH

vii) 300 ml NaOH

THANK YOU