SOLVED EXAMPLES

Ex. 1 Stomach acid is a solution of HCl with concentration of 2.2×10^{-3} M. what is the pH of stomach acid :

(A) 3.92   (B) 2.65   (C) 4.92   (D) 1.92

Sol. **(B)**

HCl is 100 % ionised so

$[H_3O^+] = 2.2 \times 10^{-3}$ M

$pH = -\log(2.2 \times 10^{-3}$ M$)$ or pH $= 2.65$

Ex. 2 Calculate the $[H_3O^+]$ of blood, the pH of which is 7.2 (slightly basic).

(A) 5×10^{-8} M   (B) 6.3×10^{-8} M   (C) 5×10^{-9} M   (D) 4×10^{-7} M

Sol. **(B)**

As pH $= 7.2$ so $[H_3O^+] = $ antilog $(-7.2) = 6.3 \times 10^{-8}$ M

Ex. 3 The pH of an aqueous solution at 25°C made up to 0.3 M, with respect to NaOH and 0.5 M, with respect to acetic acid ($pK_a = 4.76$) would be nearly :
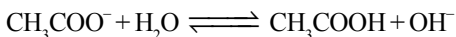
(A) 4.25   (B) 4.93   (C) 4.75   (D) 5.05

Sol. **(B)**

$$pH = pK_a - \log \frac{[\text{acid}]}{[\text{salt}]}$$

0.3 M NaOH will react with acid to form 0.3 M CH_3COONa and therefore CH_3COOH concentration will be reduced to 0.2 M.

$$pH = 4.76 - \log \frac{0.2}{0.3} = 4.93$$

Ex. 4 Calculate the pOH and pH of a 0.1 M CH_3COO^- solution ($K_a = 1.8 \times 10^{-5}$).

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

(A) 6.12, 7.88   (B) 4.12, 9.88   (C) 5.13, 8.87   (D) none of the above

Sol. **(C)**

$$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

$$= 7 + \frac{1}{2} \times 4.74 + \frac{1}{2} \log(0.1)$$

pH $= 8.87$

pOH $= 14 - 8.87 = 5.13$

Ex. 5 The pH of a solution of NH_3 is 5.806. If its concentration is 0.95 M then what is the value of its dissociation constant ?

(A) anti log $[28 + \log(0.95) - 23.242]$ (B) anti log $[11.612 - \log(0.95) - 28]$

(C) anti log $[11.612 - \log(0.95) - 14]$ (D) anti log $[14 + \log(0.95) - 11.612]$

Sol. **(B)**

Since pH $= 14 - $ pOH and pOH $= \frac{1}{2} pK_b - \frac{1}{2} \log C$

or   pH $= 14 - \frac{1}{2} pK_b + \frac{1}{2} \log C$

or $pK_b = 2(14 + \frac{1}{2} \log C - pH)$

or $K_b = $ antilog $[11.612 - \log(0.95) - 28]$

Ex. 6 The solubility product of $BaSO_4$ is 1.5×10^{-9}. The precipitation in a 0.01 M Ba^{2+} ions solution will start on adding H_2SO_4 of concentration :

(A) 10^{-9} M (B) 10^{-8} M (C) 10^{-7} M (D) 10^{-6} M

Sol. (D)

$[Ba^{2+}][SO_4^{2-}] = 1.5 \times 10^{-9} (K_{sp})$ and $[Ba^{2+}] = 0.01$ M

so Required $[SO_4^{2-}] = \dfrac{1.5 \times 10^{-9}}{0.01} = 1.5 \times 10^{-7}$

so $[H_2SO_4] > 1.5 \times 10^{-7}$ for precipitation of $BaSO_4$.

Ex. 7 pH of a saturated solution of $Ca(OH)_2$ is 12. Its solubility product is :

(A) 10^{-6} (B) 4×10^{-6} (C) 5×10^{-7} (D) None of these

Sol. (C)

pH = 12 so $[OH^-] = 10^{-2}$ M

Now $Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+} + 2OH^-$

$\qquad\qquad\qquad\quad 5 \times 10^{-3} M \quad 10^{-2}$ M
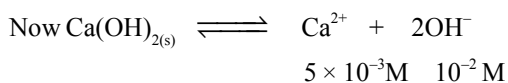
so $K_{sp} = [Ca^{2+}][OH^-]^2$

$\qquad = (5 \times 10^{-3})(10^{-2})^2 = 5 \times 10^{-7}$

Ex. 8 A sample of 100 ml of 0.10 M acid HA ($K_a = 1 \times 10^{-7}$) is titrated with standard 0.10 M KOH. How many mL of KOH will have to be added when the pH in the titration flask will be 7.00 ?

(A) 0 (B) 10 (C) 100 (D) 50

Sol. (D) $pH = pK_a + \log \dfrac{[Salt]}{[Acid]}$

$7 = 7 + \log \dfrac{[N_2V_2]}{[N_1V_1 - N_2V_2]}$

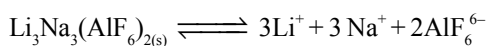$1 = \dfrac{0.1 \times V_2}{0.1 \times 100 - 0.1 \times V_2}$

or $10 - 0.1\, V_2 = 0.1\, V_2$

or $V_2 = 50\, mL$

Ex. 9 If the solubility of lithium sodium hexafluoroaluminate, $Li_3Na_3(AlF_6)_2$ is 's' mol L^{-1}, its solubility product is equal to:

(A) s^8 (B) $12\, s^3$ (C) $18\, s^3$ (D) $2916\, s^8$

Sol. (D)

$Li_3Na_3(AlF_6)_{2(s)} \rightleftharpoons 3Li^+ + 3\, Na^+ + 2AlF_6^{6-}$

Let solubility of salt is 's' mol L^{-1}

so $[Li^+] = 3s = [Na^+]$

$\qquad [AlF_6^{6-}] = 2s$

so $K_{sp} = [Li^+]^3[Na^+]^3[AlF_6^{6-}]^2$

$\qquad\quad = (3s)^3(3s)^3(2s)^2$

$\qquad\quad = 2916\, s^8$

Ex. 10 pH of a buffer containing 6.0 g of CH_3COOH and 8.2 g of CH_3COONa in 1 L of water is ($pK_a = 4.74$) :

    (A) 7.5   **(B)** 4.74   **(C)** 5.5   **(D)** 6.5

Sol. **(B)**

$$[CH_3COOH] = \frac{6.0}{60} \times 1 = 0.1 \text{ M}$$

$$[CH_3COONa] = \frac{8.2}{82} \times 1 = 0.1 \text{ M}$$

so $pH = pK_a + \log \dfrac{[Salt]}{[Acid]}$ or $pH = 4.74 + \log \left(\dfrac{0.1}{0.1} \right) = 4.74$

Ex. 11 For the hydrolytic equilibrium ; $B^+ + H_2O \rightleftharpoons BOH + H^+$

$K_b = 1 \times 10^{-5}$. Calculate the hydrolysis constant :

    (A) 10^{-5} **(B)** 10^{-19} **(C)** 10^{-10} **(D)** 10^{-9}

Sol. **(D)**

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1 \times 10^{-5}} = 10^{-9}$$

Ex. 12 The solution of a salt of a weak acid and weak base will have pH :

($K_b = 10^{-4}$; $K_a = 10^{-6}$)

    (A) 7   **(B)** 8   **(C)** 6   **(D)** 4

Sol. **(B)**

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b = 7 + 3 - 2 = 8$$

Ex. 13 Determine the effect on the concentrations of NH_3, NH_4^+ and OH^- when small amounts of each of the following is added to a solution of NH_3 in water.

    (A) HCl   **(B)** NH_3 **(C)** NaOH   **(D)** NH_4Cl

    (E) KNO_3

Sol. The equilibria of NH_3 in water will be

        $NH_3 + H_2O \rightleftharpoons NH_4^+ (aq.) + OH^- (aq.)$

    (A) If HCl is added it will furnish H^+ and Cl^- ions as it is a strong electrolyte. Now H^+ will form H_2O with OH^- ions (neutralisation) so $[NH_3]$ will decrease, $[NH_4^+]$ and $[OH^-]$ increase since equilibria will shift in forward direction.

    (B) If more NH_3 is added, then $[NH_3]$, $[NH_4^+]$ and $[OH^-]$ will increase.

    (C) If NaOH is added it will furnish $[Na^+]$ and $[OH^-]$ ions since it is a strong electrolyte and $[OH^-]$ will suppress the ionisation of weak base NH_3 so $[NH_3]$ increases, $[NH_4^+]$ decreases and $[OH^-]$ increases.

    (D) NH_4Cl will also apply common ion effect on NH_4OH but now $[NH_3]$ increases, $[NH_4^+]$ increases but $[OH^-]$ decreases.

    (E) NO effect expected.

Ex. 14 The pH of 0.0516 M solution of HCN is 2.34, what is K_a for HCN ?

Sol. For weak acid.

$$pH = \frac{1}{2} pK_a - \frac{1}{2} \log C$$

$$2.34 = \frac{1}{2} pK_a - \frac{1}{2} \log (0.0516)$$

$pK_a = 3.3926$ or $K_a = $ anti log (-3.3926)

$K_a = 4.04 \times 10^{-4}$

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Ex. 15 A buffer with pH 10 is to prepared by mixing NH_4Cl and NH_4OH. Calculate the number of moles of NH_4Cl that should be added to one litre of 1 M NH_4OH. ($K_b = 1.8 \times 10^{-5}$) :

Sol. Handerson equation for base buffer may be given as :

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$$14 - pH = pK_b + \log \frac{[Salt]}{[Base]} \qquad ....(i)$$

Given, pH $= 10$

$[Base] = [NH_4OH] = 1$ M

$pK_b = -\log K_b$

$= -\log[1.8 \times 10^{-5}] = 4.7447$

Hence, from Eq. **(i)**, we get

$$14 - 10 = 4.7447 + \log \frac{[Salt]}{1}$$

$[Salt] = 0.18$ M

No. of moles of $NH_4Cl = 0.18$

Ex. 16 Fluoroacetic acid has a K_a of 3.6×10^{-3}. What concentration of the acid is needed so that $[H^+]$ is 2.0×10^{-3} ?

Sol. $HC_2H_2FO_2 + H_2O \rightleftharpoons C_2H_2FO_2^- + H_3O^+$

$$K_a = \frac{[H_3O^+][C_2H_2FO_2^-]}{[HC_2H_2FO_2]} = \frac{(2.0 \times 10^{-3})^2}{[HC_2H_2FO_2]} = 3.6 \times 10^{-3}$$

Thus $[HC_2H_2FO_2] = \dfrac{(2.0 \times 10^{-3})^2}{(3.6 \times 10^{-3})} = 1.11 \times 10^{-3}$ M remaining in solution.

Total concentration

$= (2.0 \times 10^{-3}) + (1.1 \times 10^{-3}) = 3.1 \times 10^{-3}$ M

Ex. 17 K_b of base imidazole at 25°C is 8.8×10^{-8}.

(A) In what amounts should 0.02 M HCl and 0.02 M imidazole be mixed 100 mL of a buffer at pH = 7?

(B) When the resulting buffer is diluted to one litre, calculate pH of the diluted buffer.

Sol. **(A)** As pH = 7, pOH = 14 – 7 = 7 (at 25°C), $pK_b = -\log K_b = -\log(8.8 \times 10^{-8}) = 7.0555$

Applying

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$$7 = 7.0555 + \log \frac{[Salt]}{[Base]}$$

$$\log \frac{[Salt]}{[Base]} = -0.0555$$

Taking antilog, $\dfrac{[Base]}{[Salt]} = 1.14$

or $\dfrac{\text{millimole of base}}{\text{millimole of salt}} = 1.14 \qquad .....(1)$

Suppose V_1 ml of HCl is mixed with V_2 ml of imidazole (base) to make the buffer.

millimole of HCl $\quad = 0.02\ V_1$

millimole of imidazole $= 0.02\ V_2$

As the buffer is of the base and its salt, 0.02 millimole of HCl will combine with 0.02 millimole of base to give 0.02 millimole of salt.

$\therefore$ millimole of salt $\quad =$ millimole of HCl

$\qquad\qquad\qquad\qquad = 0.02\ V_1$

and   m.m. of base left $\quad = 0.02\ V_2 - 0.02\ V_1$

$\therefore$ From (1), we get, $\dfrac{0.02(V_2 - V_1)}{0.02\ V_1} = 1.14$

or $\qquad \dfrac{V_2 - V_1}{V_1} = 1.14$ .....(2)
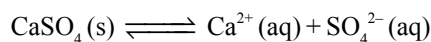
Given that $V_1 + V_2 = 100\ mL$ .....(3)

From (2) and (3) we get, $V_1 = 31.84\ mL$ and $V_2 = 68.15\ mL$

(B)   pH shall remain the same on dilution as both K_b and [salt]/[base] will not change.

Ex. 18 A solution is prepared by mixing 200 mL of 0.025 $CaCl_2$ and 400 mL of 0.15 M Na_2SO_4. Should $CaSO_4$ precipitate from a solution ?

Given $K_{sp} = 2.4 \times 10^{-5}$

Sol. The equation for the equilibrium is

$$CaSO_4\ (s) \rightleftharpoons Ca^{2+}\ (aq) + SO_4^{2-}\ (aq)$$

and the solubility product expression is

$$K_{sp} = [Ca^{2+}]\ [SO_4^{2-}] = 2.4 \times 10^{-5}$$

If we assume that the volumes of the solutions that are mixed are additive, the final solution will have a volume of 600 ml. This total volume contains the equivalent of 200 mL of $CaCl_2$, so the concentration of Ca^{2+} ions is

$$[Ca^{2+}] = \left(\frac{200\ mL\ CaCl_2\ solution}{600\ mL\ total\ volume}\right) \times (0.025\ M) = 8.33 \times 10^{-3}\ M \text{ and the concentration of } SO_4^{2-} \text{ ions is}$$

$$[SO_4^{2-}] = \left(\frac{400\ mL\ Na_2SO_4\ solution}{600\ mL\ total\ volume}\right) \times (0.15\ M) = 0.1\ M$$

The ionic product is

$$[Ca^{2+}]\ [SO_4^{2-}] = (8.33 \times 10^{-3})\,(1.0 \times 10^{-1}) = 8.33 \times 10^{-4}$$

Which is larger than K_{sp}, so $CaSO_4$ should precipitate from the solution.

Ex. 19 Calculate the pH of a solution of 0.10 M acetic acid. Calculate the pH after 100 mL of this solution is treated with 50.0

mL of 0.10 M NaOH. $(K_a CH_3COOH = 1.8 \times 10^{-5})$

Sol. $HC_2H_3O_2 + H_2O \longrightarrow H_3O^+ + C_2H_3O_2^-$

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

Before treatment :

$$[H_3O^+] = [C_2H_3O_2^-] = X$$
$$[HC_2H_3O_2] = 0.10 - X \approx 0.10$$

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5} \text{ thus}$$

$$x = 1.35 \times 10^{-3} = [H_3O^+] \text{ and } pH = 2.87$$

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$
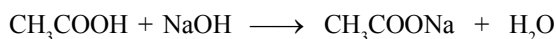
100×0.1	50×0.1		
$= 10$	$= 5$	–	–
5	0	5	–

this is the buffer solution

$$pH = pk_a + \log \frac{[salt]}{[acid]} = 4.74 + \log \frac{[5]}{[5]} = 4.74$$

Ex. 20 Ionic product of water and ionization constant of acetic acid at 25°C are 1×10^{-14} and 1.75×10^{-5} respectively. Calculate the hydrolysis constant of sodium acetate and its degree of hydrolysis in 10^{-3} M solution. Also calculate the pH of the solution ?

Sol. CH_3COONa is salt of weak acid and strong base ; its degree of hydrolysis may be calculated using the formula :

$$h = \sqrt{\left(\frac{K_h}{C}\right)} = \sqrt{\left(\frac{K_w}{CK_a}\right)} \qquad \qquad ......(i)$$

Hence, from Eq. **(i)**

$$h = \sqrt{\frac{10^{-14}}{10^{-3} \times 1.75 \times 10^{-5}}} = 7.55 \times 10^{-4}$$

K_h (hydrolysis constant) $= \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$

pH after salt hydrolysis may be calculated as -

$$pH = \frac{1}{2} [pK_w + pK_a + \log C] \qquad \qquad .....(ii)$$

$pK_w = -\log K_w = -\log 10^{-14} = 14$
$pK_a = -\log K_a = -\log (1.75 \times 10^{-5}) = 4.7569$
$\log C = \log 10^{-3} = -3$
Substituting the values in Eq.**(ii)**, we get

$$pH = \frac{1}{2} [14 + 4.7569 - 3]$$

or $\quad pH = 7.88$

Ex. 21 If $[Cd^{2+}] = [Zn^{2+}] = 0.1$ M initially, what $[H^+]$ must be maintained in a saturated H_2S (0.1 M) to precipitate CdS but not ZnS ?

$$K_{sp}(CdS) = 8 \times 10^{-27}$$
$$K_{sp}(ZnS) = 1 \times 10^{-21}$$
$$K_a(H_2S) = 1.1 \times 10^{-21}$$

Sol. In order to prevent precipitation of ZnS,

$$[Zn^{2+}]\,[S^{2-}] < K_{sp}(ZnS) = 1 \times 10^{-21}$$

(Ionic product)

or $(0.1).[S^{2-}] < 1 \times 10^{-21}$

or $[S^{2-}] < 1 \times 10^{-20}$

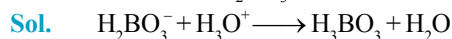This is the maximum value of $[S^{2-}]$ before ZnS will precipitate. Let $[H^+]$ to maintain this $[S^{2-}]$ be x.

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

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{x^2(1\times10^{-20})}{0.1} = 1.1 \times 10^{-21}$$

or $x = [H^+] = 0.1$ M.

∴ No ZnS will precipitate at a concentration of H^+ greater than 0.1 M.

Ex. 22 If 0.10 M KH_2BO_3 is titrated with 0.10 M HCl, what indicator should be used for this titration? $[K_a\,7.3 \times 10^{-10}]$

Sol. $H_2BO_3^- + H_3O^+ \longrightarrow H_3BO_3 + H_2O$

At the equivalence point, 0.050 M H_3BO_3 would be produced. Only the first ionization step of H_3BO_3 is important to the pH.
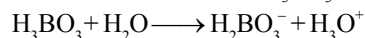
$$H_3BO_3 + H_2O \longrightarrow H_2BO_3^- + H_3O^+$$

$$K_a = \frac{[H_3O^+][H_2BO_3^-]}{[H_3BO_3]} = \frac{x^2}{0.050}$$

$= 7.3 \times 10^{-10}$ thus $x = 6.0 \times 10^{-6}$ and pH = 5.22

pH 5.22 is in the middle of the range of methyl red, which would therefore be suitable.

Ex. 23 In an attempted determination of the solubility product constant of $T\ell_2S$, the solubility of this compound in pure CO_2 free water was determined as 6.3×10^{-6} mol/L. Assume that the dissolved sulphide hydrolysis almost completely to HS^- and that the further hydrolysis to H_2S can be neglected. What is the computed K_{sp}? $(K_2 = 1.0 \times 10^{-14})$

Sol. $T\ell_2S \rightleftharpoons 2T\ell^+ + S^{2-}$, $K_{sp} = [T\ell^+]^2[S^{2-}]$

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$$
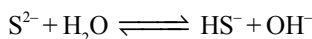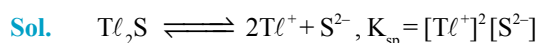
$$K_h = \frac{K_w}{K_2} = \frac{1.0\times10^{-14}}{1.0\times10^{-14}} = 1.0$$

$[T\ell^+] = 2(6.3 \times 10^{-6})$ M, $[S^{-2}] = 6.3 \times 10^{-6}$ M, and since $[HS^-] = [S^{-2}]$

$$K_h = \frac{(6.3\times10^{-6})^2}{[S^{-2}]} = 1.0$$

$$[S^{2-}] = (6.3 \times 10^{-6})^2$$

$$K_{sp} = (6.3 \times 10^{-6})^2[2(6.3 \times 10^{-6})]^2$$

$$= 6.3 \times 10^{-21}$$

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Ex. 24 To reduce $[Cu^{2+}]$ to 10^{-12} how much NH_3 should be added to a solution of 0.0010 M $Cu(NO_3)_2$? Neglect the amount of copper in complexes containing fewer than 4 ammonia molecules per copper atom.

$(K_d\, Cu(NH_3)_4^{2+} = 1 \times 10^{-12})$

Sol. $Cu(NH_3)_4^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$

$$K_d = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]} = 1.0 \times 10^{-12}$$

since the sum of the concentration of copper in the complex and in the free ionic state must equal 0.0010 mol/L, and since the amount of the free ion is very small, the concentration of the complex is taken to be 0.0010 mol/L.

Let $\quad x^4 = [NH_3]$

Then $\quad \dfrac{(10^{-12})(x^4)}{0.0010} = 1.0 \times 10^{-3}$

or $\quad x^4 = 1.0 \times 10^{-2}$

or $\quad x = 0.178$

The concentration of NH_3 at equilibrium is 0.178 mol/L. The amount of NH_3 used up in forming 0.0010 mol/L of complex is 0.0040 mol/L, an amount negligible compared with the amount remaining at equilibrium. Hence the amount of NH_3 to be added is 0.178 mol/L.

Ex. 25 The solubility of $Pb(OH)_2$ in water is 7.6×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in buffer solution of $pH = 8$.

Sol. $\quad\quad K_{sp_{(Pb(OH)_2)}} = 4S^3 = 4 \times (7.6 \times 10^{-6})^3 = 1.755 \times 10^{-15}$

The pH of buffer solution $= 8$, $pOH = 6$

$\therefore \quad [OH^-] = 10^{-6}$

For left solubility of $Pb(OH)_2$

$[Pb^{2+}][OH^-]^2 = K_{sp}$

$\Rightarrow \quad (S)(2S + 10^{-6})^2 = 1.755 \times 10^{-15}$

$\Rightarrow \quad S = \dfrac{1.755 \times 10^{-15}}{10^{-12}} \quad\quad\quad\quad (2S + 10^{-6} \approx 10^{-6})$

$\Rightarrow \quad S = \mathbf{1.755 \times 10^{-3}\ mol/L}$

Ex. 26 Calculate pH of the following mixtures. Given that $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$:

(A) 50 mL of 0.05 M NaOH + 50 mL of 0.10 M CH_3COOH

(B) 50 mL of 0.10 M NaOH + 50 mL of 0.10 M CH_3COOH

Sol. **(A)**

	CH_3COOH	+ NaOH	$\longrightarrow$ CH_3COONa	+ H_2O
Initial	50×0.1	50×0.05	0	0
Millimoles	= 5	2.5		
Millimoles after reaction	2.5	0	2.5	2.5

The solution consists of CH_3COOH and CH_3COONa and thus for buffer

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

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

$\Rightarrow \quad pH = -\log 1.8 \times 10^{-5} + \log \frac{2.5 / 100}{2.5 / 100} \Rightarrow pH = 4.7447$

(B) $\qquad\qquad\qquad\qquad CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Initial millimoles	50×0.1	50×0.1	0	0
	$= 5$	$= 5$	0	0
Final millimoles	0	0	5	5

Finally concentration of $CH_3COONa = \dfrac{5}{100}$, and pH is decided by salt hydrolysis.

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$
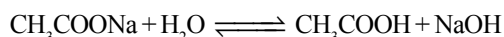
C	0	0
$C(1-h)$	Ch	Ch

$$[OH^-] = Ch = C\sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w \times C}{K_a}} = \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5}} \times \frac{5}{100}} = 5.27 \times 10^{-6}\,M$$

$$[H^+] = \frac{10^{-14}}{5.27 \times 10^{-6}} = \frac{10^{-8}}{5.27} = 0.189 \times 10^{-8}\text{ or pH} = 8.72$$

Ex. 27 Calculate the pH of an aqueous solution of 0.2 M ammonium formate assuming complete dissociation (pK_a of formic acid $= 3.8$ and pK_b of ammonia $= 4.8$)

Sol. $\qquad HCOONH_4 + H_2O \rightleftharpoons HCOOH + NH_4OH$
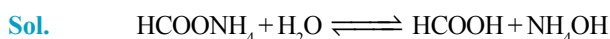
The pH of the salt of weak acid and weak base is given by

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b] \Rightarrow pH = \frac{1}{2}[14 + 3.8 - 4.8] = 6.5$$

Ex. 28 Should $Mg(OH)_2$ precipitate from a solution that is 0.001 M $MgCl_2$ if the solution is also made 0.10 M in $NH_3 [K_{sp[Mg(OH)_2]} = 1.8 \times 10^{-11}, K_{b(NH_4OH)} = 1.8 \times 10^{-5}]$.

Sol. $\qquad [OH^-]$ in 0.10 M $NH_4OH = \sqrt{K_b C}$ $\qquad\qquad\qquad$ (Ostwald's dilution law)
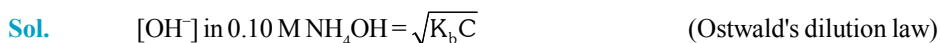
$$= \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3}\,M$$

$\Rightarrow \qquad [Mg^{2+}] \qquad = 0.001\,M$

Ionic product $\qquad = [Mg^{2+}][OH^-]^2 = (0.001) \times (1.34 \times 10^{-3})^2$

$\qquad\qquad\qquad\qquad = 1.8 \times 10^{-9} > Ksp$

As, Ionic product is greater than K_{sp} of Mg $(OH)_2$, hence precipitation should occur.

Ex. 29   Calculate the pH at which an acid indicator with $K_a = 1 \times 10^{-5}$ changes colour when indicator concentration is 1×10^{-3} M. Also report the pH at which coloured ions are 60% present.

Sol.   For indicator dissociation equilibrium

$$HI_n \rightleftharpoons H^+ + I_n^-$$

Colour A   Colour B
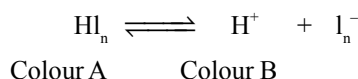
$$K_{In} = \frac{[H^+][I_n^-]}{[HI_n]}$$

The mid - point of the colour change of an indicator HI_n is the point at which

$[In^-] = [HI_n],$ $K_{In} = [H^+] = 1 \times 10^{-5}$

$\therefore$ pH = 5

Thus, at pH = 5 the indicator will change its colour.

$$K_{In} = \frac{[H^+][I_n^-]}{[HI_n]} \Rightarrow 1 \times 10^{-5} = \frac{[H^+] \times 60/100}{20/100}$$

$\therefore [H^+] = 0.666 \times 10^{-5}$

$\therefore$ pH = **5.1760**

Ex. 30   A solution has 0.1 M Mg^{2+} and 0.05 M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in solution. $K_{sp_{[Mg(OH)_2]}} = 18.0 \times 10^{-12}$ and ionisation constant of NH_3 is 1.8×10^{-5}.

Sol.   The minimum $[OH^-]$ at which there will be no precipitation of $Mg(OH)_2$ can be obtained by $K_{sp} = [Mg^{2+}][OH^-]^2$

$\Rightarrow$ $18.0 \times 10^{-12} = (0.1) \times [OH^-]^2$

$\therefore$ $[OH^-] = 1.34 \times 10^{-5}$ M

Thus, solution having $[OH^-] = 1.34 \times 10^{-5}$ M will not show precipitation of $Mg(OH)_2$ in 0.1 M Mg^{2+}. These hydroxyl ions are to be derived by basic buffer of NH_4Cl and NH_4OH.

$$pH = pK_b + \log\frac{[Salt]}{[Base]} \Rightarrow pH = pK_b + \log\frac{[NH_4^+]}{[NH_4OH]}$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
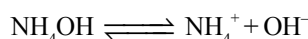
In presence of $[NH_4Cl]$, all the NH_4^+ ions provided by NH_4Cl as due to common ion effect, dissociation of NH_4OH will be suppressed.

$$-\log[OH^-] = -\log 1.8 \times 10^{-5} + \log\frac{[NH_4^+]}{[0.05]}$$

$\therefore$ $[NH_4^+] = 0.067$ M   or $[NH_4Cl] = 0.067$ M

Ex. 31   What is pH of 1 M CH_3COOH solution? To what volume must one litre of this solution be diluted so that the pH of resulting solution will be twice the original value. Given : $K_a = 1.8 \times 10^{-5}$

Sol.

	H_3CCOOH	+	H_2O	$\rightleftharpoons$	H_3CCOO^-	+	H_3O^+
Initial	1 M				0		0
	– x M				x M		x M
Final	(1–x) M				x		x
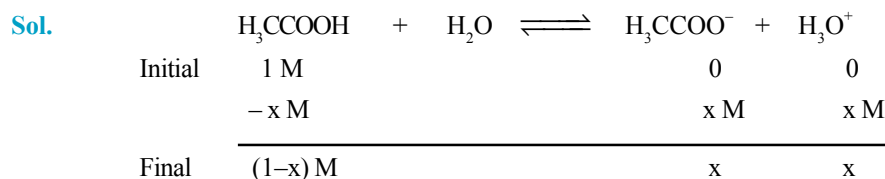
$$K_a = \frac{x^2}{1-x} \approx \frac{x^2}{1} \quad \therefore x = \sqrt{K_a} = 4.2 \times 10^{-3} = [H_3O^+]$$

$pH = -\log[H_3O^+] = -\log\{4.2 \times 10^{-3}\} = 3 - \log 4.2 = 2.37$

Now, let 1 L of 1 M AcOH solution be diluted to V L to double the pH and the conc. of diluted solution be C.

New pH $= 2 \times$ Old pH $= 2 \times 2.37 = 4.74$

pH $= -\log [H_3O^+] = 4.74$

$\therefore [H_3O^+] = 1.8 \times 10^{-5}$

	H_3CCOOH	$+$	H_2O	$\rightleftharpoons$	H_3CCOO^-	$+$	H_3O^+
Initial	C				0		0
	-1.8×10^{-5}				1.8×10^{-5}		1.8×10^{-5}
Final	$C - 1.8 \times 10^{-5}$				1.8×10^{-5}		1.8×10^{-5}
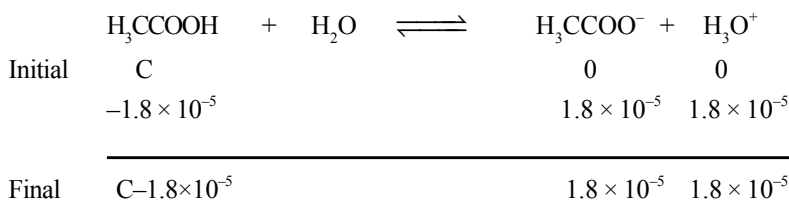
$$K_a = \frac{[CH_3COO^-] \times [H_3O^+]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}{C - 1.8 \times 10^{-5}}$$

$\therefore C = 3.6 \times 10^{-5} M$

On dilution,

$M_1 V_1 = M_2 V_2$

$1 M \times 1 L = 3.6 \times 10^{-5} M \times V_2$

$\therefore V_2 = 2.78 \times 10^4 L$

Ex. 32 A sample of AgCl was treated with 10 mL of 1.7 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate solubility product of AgCl. $K_{sp(Ag2CO3)} = 8.2 \times 10^{-12}$

Sol. $[CO_3^{2-}] = [Na_2CO_3] = 1.7 M$

At eqm., $[Cl^-] = [NaCl] = \dfrac{0.0026}{35.5} = 7.32 \times 10^{-5} M$

	$2AgCl \, (s)$	$+$	Na_2CO_3	$\rightleftharpoons$	$Ag_2CO_3 \, (s)$	$+$	$2NaCl$
Initial			1.7 M				0
At eqm.			$(1.7 - 7.32 \times 10^{-5})$				$7.32 \times 10^{-5} M$
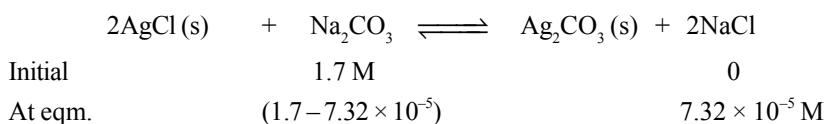
$[Ag^+]^2 [CO_3^{2-}] = K_{sp(Ag2CO3)}$

$$\therefore [Ag^+] = \sqrt{\frac{K_{sp(Ag2CO3)}}{[CO_3^{2-}]}} = \sqrt{\frac{8.2 \times 10^{-12}}{1.7}} = 2.1963 \times 10^{-6} M$$

$\therefore K_{sp(AgCl)} = [Ag^+][Cl^-] = (2.1963 \times 10^{-6}) \times (7.32 \times 10^{-5}) = 1.61 \times 10^{-10}$

Ex. 33 Given $Ag^+(NH_3)_2 \rightleftharpoons Ag^+ + 2NH_3$, $K_c = 8.2 \times 10^{-8}$ and $K_{sp(AgCl)} = 2.378 \times 10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia.

Sol. $[Ag(NH_3)_2]^+ (aq) \rightleftharpoons Ag^+ (aq) + 2NH_3 (aq)$

$\qquad\qquad\qquad\qquad x + y \qquad 2x$

$AgCl \, (s) \rightleftharpoons Ag^+ \, (aq) + Cl^- (aq)$

$\qquad\qquad\qquad x + y \qquad\quad y$
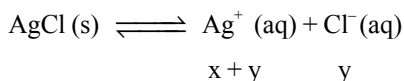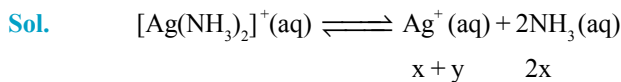
In case of simultaneous solubility, Ag^+ remains same in both the equilibrium

$$K_c = \frac{(x+y) \times (2x)^2}{[Ag(NH_3)_2]^+} \qquad ....(1)$$

$$K_{sp} = (x+y) \times y \qquad ....(2)$$

$$\therefore \quad \frac{K_c}{K_{sp}} = \frac{(2x)^2}{[Ag(NH_3)_2]^+ \times y} \quad \text{Given, } [NH_3] = 2x = 1 \text{ M}$$

$[Ag(NH_3)_2]^+ = [Cl^-] = y$ because Ag^+ obtained from AgCl passes in $[Ag(NH_3)_2]^+$ state.

$$\frac{K_c}{K_{sp}} = \frac{1}{y \times y} \Rightarrow y^2 = \frac{2.378 \times 10^{-10}}{8.2 \times 10^{-8}} = 0.29 \times 10^{-2} \therefore y = 0.539 \times 10^{-1} = 0.0539 \text{ M}$$

That is, $[Ag(NH_3)_2]^+ = 0.539$ M

Ex. 34 How many moles of NH_3 must be added to 1 litre of 0.1 M $AgNO_3$ solution to reduce Ag^+ concentration to 2×10^{-7} M. $K_d[Ag(NH_3)_2]^+ = 7.2 \times 10^{-8}$

Sol. As $K_f[Ag(NH_3)_2]^+ = \dfrac{1}{7.2 \times 10^{-8}}$ = very-very large

Hence, almost all Ag^+ ions will be converted to $[Ag(NH_3)_2]^+$

$$\therefore \quad [Ag(NH_3)_2]^+ \approx 0.1 \text{ M}$$
$$[Ag^+] = 2 \times 10^{-7}$$

$$K = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+} \Rightarrow 7.2 \times 10^{-8} = \frac{2 \times 10^{-7} \times [NH_3]^2}{0.1}$$

$[NH_3] = 0.189$ M

It is the concentration of free NH_3.

$[NH_3]_{total} = [NH_3]_{free} + [NH_3]_{complexed} = 0.189 + 2 \times 0.1 = 0.389$ M

Ex. 35 **(i)** What mass of Pb^{2+} ion is left in solution when 50 mL of 0.2 M $Pb(NO_3)_2$ is added to 50.0 mL of 1.5 M NaCl ? ($K_{sp} PbCl_2 = 1.7 \times 10^{-4}$)

(ii) 0.16 g of N_2H_4 is dissolved in water and the total volume made up to 500 mL. Calculate the percentage of N_2H_4 that has reacted with water at this dilution. The K_b for N_2H_4 is 9.0×10^{-6} M.

Sol. **(i)** Millimoles of Pb^{2+} before precipitation = $50 \times 0.2 = 10$

Millimoles of Cl^- before precipitation = $50 \times 1.5 = 75$

Assuming complete precipitation of $PbCl_2$ followed by establishment of equilibrium.

Millimoles of Cl^- left after precipitation

= $75 - 20 = 55$ in 100 mL.

After precipitation $[Cl^-] = 0.55$ M

That means, we have to find out solubility of $PbCl_2$ in 0.55 M Cl^- ion solution.

$$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-, K_{sp} = [Pb^{2+}][Cl^-]^2$$
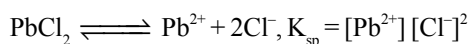
$$[Pb^{2+}] = \frac{K_{sp}}{[Cl^-]^2} = \frac{1.7 \times 10^{-4}}{(0.55)^2} = 5.6 \times 10^{-4} \text{M}$$

$$\text{Mass of Pb}^{2+} \text{ in solution} = \frac{5.6 \times 10^{-4}}{1000} \times 100 \times 208 = 1165 \text{ mg}$$

(ii) $[N_2H_4] = \dfrac{0.16}{32} \times \dfrac{1000}{500} = 0.01 \text{ M}$

$$N_2H_4 \;+\; H_2O \;\rightleftharpoons\; N_2H_5^+ \;+\; OH^-$$

$$\begin{array}{cccc} 1 & & 0 & 0 \\ (1-\alpha) & & \alpha & \alpha \end{array}$$
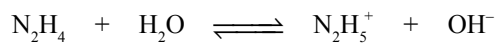
$K_b = C\alpha^2,$

$$\alpha^2 = \frac{K_b}{C} = \frac{9.0 \times 10^{-6}}{0.01} = 9 \times 10^{-4}$$

$\Rightarrow \qquad \alpha = \sqrt{9.0 \times 10^{-4}} = 3 \times 10^{-2} = 3\,\%$

Ex. 36 If very small amount of phenolphthalein is added to 0.15 M solution of sodium benzoate, what fraction of the indicator will exist in the coloured form ?

$K_{a(\text{Benzoic acid})} = 6.2 \times 10^{-5}$

$K_{w(H_2O)} = 1 \times 10^{-14}$

$K_{In(\text{Phenolphthalein})} = 3.16 \times 10^{-10}$

Sol. Formula for pH of solution due to hydrolysis of C_6H_5COONa

$$pH = \frac{1}{2}\,[pK_w + pK_a + \log C] = \frac{1}{2}\,[14 - \log 6.2 \times 10^{-5} + \log 0.15] = 8.6918$$

Formula for pH of indicator

$$pH = pK_{In} + \log \frac{[In^-]}{[H_{In}]} \Rightarrow 8.6918 = -\log(3.16 \times 10^{-10}) + \log \frac{[In^-]}{[H_{In}]}$$

$\therefore \dfrac{[In^-]}{[H_{In}]} = 0.16$ (Fraction of indicator in coloured form $= 0.16$)

Ex. 37 What will be the Ag^+ ion concentration in a solution of 0.2 M solution of $[Ag(NH_3)_2]^+$?

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3 ; \qquad\qquad K_{dis} = 5.8 \times 10^{-8}$$
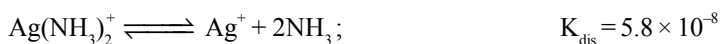
Sol. Let, concentration of Ag^+ at equilibrium be C

$\therefore [NH_3] = 2C$

$$K_{dis} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} \Rightarrow 5.8 \times 10^{-8} = \frac{C \times 4C^2}{0.2}$$

$\therefore C = 0.0014 \text{ M}.$

360

Ex. 38   A solution contains 0.1 M Cl^- and 0.001 M CrO_4^{2-}. If solid $AgNO_3$ is gradually added to this solution which will precipitate first, AgCl or Ag_2CrO_4? Assume that the addition causes no change in volume. Given $K_{sp(AgCl)}= 1.6 \times 10^{-10} M^2$ and $K_{sp(Ag_2CrO_4)}= 1.79 \times 10^{-12} M^3$. What % of Cl^- remains in solution when CrO_4^{2-} starts precipitating ?

Sol. Ag^+ ion concentration required for precipitation

For AgCl, $[Ag^+] = \dfrac{K_{sp(AgCl)}}{[Cl^-]} = \dfrac{1.6 \times 10^{-10}}{0.1} = 1.6 \times 10^{-10}$ M

For Ag_2CrO_4, $[Ag^+]^2 = \dfrac{K_{sp(Ag_2CrO_4)}}{[CrO_4^{2-}]} = \dfrac{1.79 \times 10^{-12}}{(0.001)}$

$\therefore [Ag^+] = [1.79 \times 10^{-9} M^2]^{1/2} = 4.23 \times 10^{-5}$ M

AgCl will precipitate first because it requires low concentration of Ag^+. Remaining concentration of Cl^- when

Ag_2CrO_4 starts precipitating $= \dfrac{K_{sp(AgCl)}}{[Ag^+]} = \dfrac{1.6 \times 10^{-10}}{4.23 \times 10^{-5}} = 3.78 \times 10^{-6}$ M.

% of remaining concentration of $Cl^- = \dfrac{3.78 \times 10^{-6}}{0.1} \times 100 = 3.78 \times 10^{-3}$ %

Ex. 39   Determine the concentration of NH_3 solution whose one litre can dissolve 0.10 mol of AgCl. $K_{sp(AgCl)}$ and $K_{f[Ag(NH_3)_2]^+}$ are $10^{-9} M^2$ and $1.6 \times 10^6 M^{-2}$ respectively.

Sol.

$$AgCl\ (s) \rightleftharpoons Ag^+ + Cl^- \qquad\qquad K_1 = K_{sp}$$

$$Ag^+ + 2NH_3 \rightleftharpoons Ag^+(NH_3)_2 \qquad\qquad K_2 = K_f$$

$$\overline{AgCl\ (s) + 2NH_3 \rightleftharpoons Ag^+ (NH_3)_2 + Cl^- \qquad K = K_{sp} \times K_f}$$
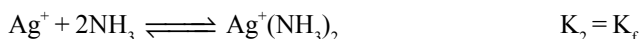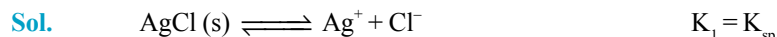
$\therefore K = \dfrac{[Ag(NH_3)_2]^+ [Cl^-]}{[NH_3]^2}$ (Given solubility of AgCl = 0.10)

$\therefore [Ag(NH_3)_2]^+ = 0.10$ M,

Also, $[Cl^-] = 0.1$

$1 \times 10^{-9} \times 1.6 \times 10^6 = \dfrac{0.1 \times 0.1}{[NH_3]^2}$

$\therefore [NH_3]^2 = 6.25 \Rightarrow [NH_3] = 2.5$ M

Thus, $[NH_3]$ at equilibrium = 2.5 M

Also 0.2 M of NH_3 must have been used to dissolve 0.1 M AgCl

$\therefore [NH_3]_{Total} = 2.5 + 0.2 = 2.7$ M

Exercise # 1   [Single Correct Choice Type Questions]

1. In the following reaction $HC_2O_4^-(aq) + PO_4^{3-}(aq) \rightleftharpoons HPO_4^{2-}(aq) + C_2O_4^{2-}(aq)$, which are the two Bronsted bases?
(A) $HC_2O_4^-$ and PO_4^{3-} (B) HPO_4^{2-} and $C_2O_4^{2-}$ (C) $HC_2O_4^-$ and HPO_4^{2-} (D) PO_4^{3-} and $C_2O_4^{2-}$

2. Boric acid H_3BO_3 is a :
(A) Arrhenius acid   (B) Bronsted acid   (C) Lewis acid   (D) All of these

3. The following equilibrium is established when $HClO_4$ is dissolved in weak acid HF.
$$HF + HClO_4 \rightleftharpoons ClO_4^- + H_2F^+$$
Which of the following is correct set of conjugate acid base pair ?
(A) HF and $HClO_4$ (B) HF and ClO_4^- (C) HF and H_2F^+ (D) $HClO_4$ & H_2F^+

4. Identify the amphoteric species from the following :
(I) H_2O (II) NH_3 (III) $H_2PO_4^-$ (IV) HCO_3^-
(A) I, II   (B) III, IV   (C) I, II, III   (D) I, II, III, IV

5. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid
$$HCl(aq) + CH_3COOH(aq) \rightleftharpoons Cl^-(aq) + CH_3COOH_2^+(aq).$$
The set that characterises the conjugate acid-base pairs is
(A) (HCl, CH_3COOH) and $(CH_3COOH_2^+, Cl^-)$ (B) $(HCl, CH_3COOH_2^+)$ and (CH_3COOH, Cl^-)
(C) $(CH_2COOH_2^+, HCl)$ and (Cl^-, CH_3COOH) (D) (HCl, Cl^-) and $(CH_3COOH_2^+, CH_3COOH)$.

6. Which of the following relations is correct ?
(A) $\Delta G° = RT \ln K_{eq}$ (B) $[H_3O^+] = 10^{pH}$

(C) $\log \dfrac{Kw_2}{Kw_1} = \dfrac{\Delta H°}{2.303R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$ (D) $[OH^-] = 10^{-7}$, for pure water at all temperatures.

7. pOH of H_2O is 7.0 at 298 K . If water is heated at 350 K, which of the following statement should be true?
(A) pOH will decrease.
(B) pOH will increase.
(C) pOH will remain 7.0.
(D) concentration of H^+ ions will increase but that of OH^- will decrease.

8. K_w of H_2O at 373 K is 1×10^{-12}. Identify which of the following is incorrect.
(A) pK_w of H_2O is 12   (B) pH of H_2O is 6   (C) H_2O is neutral   (D) H_2O is acidic

9. Which of the following expression is not true ?
(A) $[H^+] = [OH^-] = \sqrt{K_W}$ for a neutral solution at all temperatures.
(B) $[H^+] > \sqrt{K_W}$ & $[OH^-] < \sqrt{K_W}$ for an acidic solution
(C) $[H^+] < \sqrt{K_W}$ & $[OH^-] > \sqrt{K_W}$ for an alkaline solution
(D) $[H^+] = [OH^-] = 10^{-7}$ M for a neutral solution at all temperatures .

10. Which of the following is incorrect ?
(A) K_a (weak acid). K_b (conjugate weak base) = K_w
(B) K_a (strong acid). K_b (conjugate weak base) = K_w
(C) K_a (weak acid). K_b (weak base) = K_w
(D) K_a (weak acid). K_b (conjugate strong base) = K_w

11. In pure liquid of HCOOH, concentration of $HCOO^- = 10^{-3}$ M at 27^0C. What is the self ionisation constant $(K = [HCOOH_2^+][HCOO^-])$

(A) 10^{-3} (B) 10^3 (C) 10^6 (D) 10^{-6}

12. Pure water ionise as
$$2H_2O\,(l) \rightleftharpoons H_3O^+(aq) + OH^-\,(aq)$$
At 25°C the pH of pure water is approximately 7.0 At 37°C its pH is :

(A) More than 7.0   (B) Less than 7.0   (C) Equal to 7.0   (D) None of these

13. K_a for the acid HA is 1×10^{-6}. The value of K for the reaction $A^- + H_3O^+ \rightleftharpoons HA + H_2O$ is

(A) 1×10^{-6} (B) 1×10^{12} (C) 1×10^{-12} (D) 1×10^6

14. The pK_a value of NH_4^+ is 9. The pK_b value of NH_4OH would be :

(A) 9   (B) 5   (C) 7   (D) 8

15. K_{b_1} of N_2H_4 is 4.0×10^{-6}. Then what is the acid dissociation constant of $N_2H_5^+$ and $N_2H_6^{+2}$ respectively.

(A) data insufficient, 4×10^{-6}
(B) data insufficient, 2.5×10^{-8}
(C) 2.5×10^{-9}, data insufficient
(D) 2.5×10^{-9}, 4×10^{-6}

16. Given $HF + H_2O \xrightarrow{K_a} H_3O^+ + F^-$

         $F^- + H_2O \xrightarrow{K_b} HF + OH^-$

Which relation is correct.

(A) $K_b = K_w$ (B) $K_a \cdot K_b = K_w$ (C) $K_b = \dfrac{1}{K_w}$ (D) $\dfrac{K_a}{K_a} = K_w$

17. How many moles of NaOH must be removed from one litre of aqueous solution to change its pH from 12 to 11 ?

(A) 0.009   (B) 0.01   (C) 0.02   (D) 0.1

18. Which of the following solution will have a pH exactly equal to 8 ?

(A) 10^{-8} M HCl solution at 25°C
(B) 10^{-8} M H^+ solution at 25°C
(C) 2×10^{-6} M $Ba(OH)_2$ solution at 25°C
(D) 10^{-5} M NaOH solution at 25°C

19. The $[OH^-]$ in 100.0 ml of 0.016 M-HCl (aq) is :

(A) 5×10^{12} M   (B) 3×10^{-10} M   (C) 6.25×10^{-13} M   (D) 2.0×10^{-9} M.

20. 0.1 mol HCl is dissolved in distilled water of volume V then at $\lim_{V \to \infty} (pH)_{solution}$ is equal to

(A) zero   (B) 1   (C) 7   (D) 14

21. The pH of a solution obtained by mixing 50 ml of 0.4 N HCl and 50 ml of 0.2 N NaOH is :

(A) 13   (B) 12   (C) 1.0   (D) 2.0

22. Which of the following solution will have pH close to 1.0 ?

(A) 100 ml of M/10 HCl + 100 ml of M/10 NaOH
(B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH
(C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH
(D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH.

23. Concentration of the anion will be $3c.\alpha$ for the following weak electrolytes.

(A) AB_2 (B) AB   (C) AB_3 (D) A_3B_4

24. Ostwald's dilution law gives satisfactory results with the solution of which electrolyte ?

(A) HCl   (B) HNO_3 (C) CH_3COOH (D) NaOH

25. Dissociation constant of mono basic acids A, B, C and D are 6 x 10^{-4}, 5 x 10^{-5}, 3.6 x 10^{-6} and 7 x 10^{-10} respectively. The pH values of their 0.1M aqueous solution are in the order.

(A) D> C> B> A   (B) A> B >C > D   (C) D > C > A> B   (D) None

26. Which of the following has the highest degree of ionisation ?

(A) 1 M NH_3 (B) 0.001 M NH_3 (C) 0.1 M NH_3 (D) 0.0001 M NH_3.

27. At infinite dilution the percentage dissociation of both weak acid and weak base is:

(A) 1%   (B) 20%   (C) 50%   (D) 100%

28. One litre of solution contains 10^{-5} moles of H^+ ions at 25°C. Percentage ionisation of water in solution is :

(A) 1.8×10^{-7} %   (B) 1.8×10^{-9} %   (C) 3.6×10^{-9} %   (D) 1.8×10^{-11} %.

29. Which statement/relationship is correct?

(A) pH of 0.1 M HNO_3, 0.1M HCl, 0.1M HI is not equal.

(B) $pH = -\log \dfrac{1}{[H^+]}$

(C) At 25°C the pH of pure water is 7.

(D) The value of pK_w at 25 °C is 7.

30. In a solution of 0.1 M H_3PO_4 acid, (given $K_{a_2} = 10^{-3}$, $K_{a_2} = 10^{-7}$, $K_{a_3} = 10^{-12}$)

(i) Concentration of H_3PO_4 is :

(A) 0.01   (B) 0.09   (C) 0.05   (D) 0.1

(ii) Concentration of $H_2PO_4^-$ is :

(A) 0.01   (B) 0.09   (C) 0.02   (D) 0.04

(iii) Concentration of $H_2PO_4^{2-}$ is :

(A) 10^{-7} (B) 10^{-8} (C) 10^{-3} (D) 10^{-4}

(iv) Concentration of PO_4^{3-} is :

(A) 10^{-20} (B) 10^{-17} (C) 10^{-15} (D) 10^{-12}

(v) pH of solution is :

(A) 1   (B) 2   (C) 4   (D) 5

31. For ortho phosphoric acid,

H_3PO_4 (aq) + H_2O (aq) $\rightleftharpoons$ H_3O^+ (aq) + $H_2PO_4^-$ (aq); K_a

H_2PO_4 (aq) + H_2O (aq) $\rightleftharpoons$ H_3O^+ (aq) + HPO_4^{2-} (aq); K_{a_2}

HPO_4^{2-} (aq) + H_2O (aq) $\rightleftharpoons$ H_3O^+ (aq) + PO_4^{3-} (aq); K_{a_3}

The correct order of K_a values is :

(A) $K_{a_1} > K_{a_2} < K_{a_3}$ (B) $K_{a_1} < K_{a_2} < K_{a_3}$ (C) $K_{a_1} > K_{a_2} > K_{a_3}$ (D) $K_{a_1} < K_{a_2} > K_{a_3}$

32. Approximate pH of 0.1 M aqueous H_2S solution when K_1 and K_2 for H_2S at 25ºC are 1×10^{-7} and 1.3×10^{-13} respectively :

(A) 4   (B) 5   (C) 6   (D) 8

33. Consider an aqueous solution, 0.1 M each in HOCN, HCOOH, $(COOH)_2$ and H_3PO_4, for HOCN, we can write

$K_a(HOCN) = \dfrac{[H^+][OCN^-]}{[HOCN]}$. $[H^+]$ in this expression refers to

(A) H^+ ions released by HOCN

(B) Sum of H^+ ions released by all monoprotic acids

(C) Sum of H^+ ions released only the first dissociation of all the acids.

(D) Overall H^+ ion concentration in the solution.

34. The dissociation constant of acetic acid at a given temperature is 1.69×10^{-5}. The degree of dissociation of 0.01 M acetic acid in the presence of 0.01 M HCl is equal to

(A) 0.41   (B) 0.13   (C) 1.69×10^{-3} (D) 0.013.

35. The pH of a solution obtained by mixing 100 ml of 0.2 M CH_3COOH with 100 ml of 0.2 M NaOH would be : (pK_a for $CH_3COOH = 4.74$)

(A) 4.74   (B) 8.87   (C) 9.10   (D) 8.57

36. pH of 0.1M Na_2HPO_4 and 0.2M NaH_2PO_4 are respectively : pK_a for H_3PO_4 are 2.2, 7.2 and 12.0.

(A) 4.7, 9.6   (B) 9.6, 4.7   (C) 4.7, 5.6   (D) 5.6, 4.7

37. The pH of 0.1 M solution of the following salts increases in the order :   **[JEE-1999]**

(A) $NaCl < NH_4Cl < NaCN < HCl$ (B) $HCl < NH_4Cl < NaCl < NaCN$

(C) $NaCN < NH_4Cl < NaCl < HCl$ (D) $HCl < NaCl < NaCN < NH_4Cl$

38. A pair of salts are given in a solution each in 0.1M concentration. Which solution has a higher pH ?

(A) NaCN and NaOBr   (B) NaF and NaOCl   (C) NaF and NaOBr   (D) NaCN and NaOCl

39. Which of the following salts undergoes anionic hydrolysis?

(A) $CuSO_4$ (B) NH_4Cl (C) $AlCl_3$ (D) K_2CO_3.

40. The sodium salt of a certain weak monobasic organic acid is hydrolysed to an extent of 3% in its 0.1M solution at 25^0C. Given that the ionic product of water is 10^{-14} at this temperature, what is the dissociation constant of the acid?

(A) $\approx 1 \times 10^{-10}$ (B) $\approx 1 \times 10^{-9}$ (C) 3.33×10^{-9} (D) 3.33×10^{-10}

41. Consider following statements :

I : CH_3COOH (a weak acid) behaves as a strong acid in NH_3.

II : HNO_3 (strong acid) behaves as a base in HF (anhydrous).

III : H_2SO_4 dissociates to a very small extent in glacial CH_3COOH.

Select correct alternate for these statements.

(A) I, III   (B) II, III   (C) I, II   (D) I, II, III

42. When 0.1 mole solid NaOH is added in 1lt of 0.1 M NH_3(aq) then which statement is wrong? ($K_b = 2 \times 10^{-5}$, log 2 = 0.3)

(A) degree of dissociation of NH_3 approaches to zero.

(B) change in pH by adding NaOH would be 1.85

(C) In solution, $[Na^+] = 0.1$ M, $[NH_3] = 0.1$ M, $[OH^-] = 0.2$ M.

(D) on addition of OH^-, K_b of NH_3 does not changes.

43. At what molar concentration of HCl will its aqueous solution have an $[H^+]$ to which equal contributions come from HCl and H_2O.

(A) $\sqrt{60} \times 10^{-7}$ M   (B) $\sqrt{50} \times 10^{-8}$ M   (C) $\sqrt{40} \times 10^{-9}$ M   (D) $\sqrt{30} \times 10^{-8}$

44. The correct relationship between the pH of isomolar solutions of Na_2O (pH_1), Na_2S (pH_2) $Na_2Se(pH_3)$ and $Na_2Te(pH_4)$ is:

(A) $pH_1 > pH_2 > pH_3 > pH_4$ (B) $pH_1 < pH_2 < pH_3 < pH_4$

(C) $pH_1 < pH_2 < pH_3 = pH_4$ (D) $pH_1 > pH_2 = pH_3 > pH_4$

45. The pH of which salt is independent of its concentration :

1. $(CH_3COO)C_5H_5NH$ 2. NaH_2PO_4 3. Na_2HPO_4 4. NH_4CN

(A) 1, 2, 3, 4   (B) 1, 4   (C) 2, 3   (D) 1, 2, 3

46. 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 acidic acid remains unreacted ? K_a for acetic acid = 2×10^{-5}.
(A) 1.5   (B) 3   (C) 2   (D) 3.25

47. For a weak electrolyte (HA) dissociation as lim c→0, then:
(A) Electrolyte is assumed to be 100% ionised
(B) Its dissociation constant remains same
(C) The interionic attractions diminishe to zero
(D) All of these

48. An acid with molelcular formula $C_7H_6O_3$ forms three types of sodium salts. i.e., $C_7H_5O_3Na$, $C_7H_4O_3Na_2$ and $C_7H_3O_3Na_3$. The basicity of the acid:
(A) One   (B) Two   (C) Three   (D) Four

49. In water, the acid $HClO_4$. HCl, H_2SO_4 and HNO_3 exhibit the same strength as they are completely ionised in water (a base). This is called.......of the solvent water.
(A) Strength   (B) Capacity   (C) Buffer effect   (D) Levelling effect

50. The conjugate base of $[Al(H_2O)_3(OH)_3]$ is :
(A) $[Al(H_2O)_3(OH)_2]^+$ (B) $[Al(H_2O)_3(OH)_2O]^-$ (C) $[Al(H_2O)_3(OH)_3]^-$ (D) $[Al(H_2O)_2(OH)_4]^-$

51. Which of the following is not correct :
(A) $[H^+] = [OH^-] = \sqrt{K_w}$ for a neutral solution at all temperatures
(B) $[H^+] = [OH^-] = 10^{-7}$ for a neutral solution at all temperatures
(C) $[H^+] > \sqrt{K_w}$ and $[OH^-] < \sqrt{K_w}$ for an acidic solution
(D) $[H^+] < \sqrt{K_w}$ and $[OH^-] > \sqrt{K_w}$ for an alkaline solution

52. Which of the following correctly explains the nature of boric acid in aqueous medium:
(A) $H_3BO_3 \xrightarrow{H_2O} H_3^+O + H_2BO_3^-$ (B) $H_3BO_3 \xrightarrow{2H_2O} 2H_3^+O + HBO_3^{2-}$
(C) $H_3BO_3 \xrightarrow{3H_2O} 3H_3^+O + BO_3^{3-}$ (D) $H_3BO_3 \xrightarrow{H_2O} B(OH)_4^- + H^+$

53. pH for the solution of salt undergoing anionic hydrolysis (say CH_3COONa) is given by:
(A) pH = 1/2 $[pK_w + pK_a + logC]$ (B) pH = 1/2 $[pK_w + pKa - logC]$
(C) pH = 1/2 $[pK_w + pK_b - logC]$ (D) None of these

54. The pH of 0.1 M solution of the following salts increases in the order:
(A) $NaCl < NH_4Cl < NaCN < HCl$ (B) $HCl < NH_4Cl < NaCl < NaCN$
(C) $NaCN < NH_4Cl < NaCl < HCl$ (D) $HCl < NaCl < NaCN < NH_4Cl$

55. The pH of the solution obtanied by mixing 10 mL of 10^{-1} N HCl and 10 mL of 10^{-1} N NaOH is:
(A) 8   (B) 2   (C) 7   (D) None of these

56. pH of water is 7.0 at 25°C. If water is heated to 70°C, the:
(A) pH will decrease and solution becomes acidic
(B) pH will increase
(C) pH will remain constant as 7
(D) pH will decrease but solution will be neutral

57. The ratio of dissociation constant of two weak acids HA and HB is 4. At what moar concentration ratio, the two acids will have same pH in separate solutions:
(A) 2   (B) 0.5   (C) 4   (D) 0.25

58. The reverse process of neutralisation is:
(A) Hydrolysis   (B) Decomposition   (C) Dehydration   (D) Synthesis

59. 10^{-6} M HCI is diluted to 100 times. Its pH is:
(A) 6.0   (B) 8.0   (C) 6.95   (D) 9.5

60. Which solution will have pH closer to 1.0:
(A) 100 mL of (M/10) HCI + 100 mL of (M/10) NaOH
(B) 55 mL of (M/10) HCI + 45 mL of (M/10) NaOH
(C) 10 mL of (M/10) HCI + 90 mL of (M/10) NaOH
(D) 75 mL of (M/5) HCI + 25 mL of (M/5) NaOH

61. $Ca_3(PO_4)_2$ is insoluble in water. On adding a few drops of HCI to solid $Ca_3(PO_4)_2$ in contact with water, the solid dissolves. The reason is:
(A) The solvent becomes more polar on adding HCI
(B) $Ca_3(PO_4)_2$ combines with HCI to form soluble $CaCI_2$ and H_3PO_4
(C) $Ca(H_2PO_4)_2$ is formed, which dissolves
(D) H_3PO_4, a weak acid is formed and the solubility product of $Ca_3(PO_4)_2$ decrease

62. A certain weak acid has a dissociation contant 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is:
(A) 1.0×10^{-4} (B) 1.0×10^{-10} (C) 1×10^{-10} (D) 1.0×10^{-14}

63. K_a for the acid HA is 1×10^{-6}. The value of K for the reaction $A^- + H_3O^+ \rightleftharpoons HA + H_2O$ is
(A) 1×10^{-6} (B) 1×10^{12} (C) 1×10^{-12} (D) 1×10^{6}

64. The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2M, the percentage hydrolysis of the salt should be:
(A) 100 %   (B) 50 %   (C) 25 %   (D) None of these

65. Precentage ionisation of weak acid can be calculated using the formula:
(A) $100\sqrt{\dfrac{K_a}{C}}$ (B) $\dfrac{100}{1+10^{(pK_a-pH)}}$ (C) Both (A) and (B)   (D) None of these

66. pH of 0.01 M HS^- will be:
(A) $pH = 7 + \dfrac{pK_a}{2} + \dfrac{\log C}{2}$ (B) $pH = 7 - \dfrac{pK_a}{2} + \dfrac{\log C}{2}$

(C) $pH = 7 + \dfrac{pK_1 + pK_2}{2}$ (D) $pH = 7 + \left(\dfrac{pK_a + pK_b}{2}\right)$

67. 10 mL of 10^{-6} M HCI solution is mixed with 90 mL H_2O. pH will change approximately:
(A) By one unit   (B) By 0.3 unit   (C) By 0.7 unit   (D) By 0.1 unit

68. Number of H^+ ions present in 10 mL of solution of pH = 3 are:
(A) 10^{13} (B) 6.02×10^{18} (C) 6.02×10^{13} (D) 6.02×10^{10}

69. For pure water :
(A) pH increases and pOH decreases with rise in temperature
(B) pH decreases and pOH increases with rise in temperature
(C) Both pH and pOH increase with rise in temperature
(D) Both pH and pOH decrease with rise in temperature

70. The self ionisation constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$ has been estimated as 10^{-6} at room temperature. The density of formic acid is $1.15 \, g/cm^3$. The percentage of formic acid molecules in pure fomic acid are converted to formate ion:
(A) 0.002%　　　　(B) 0.004%　　　　(C) 0.006%　　　　(D) 0.008%

71. 10 mL, of a strong acid solution of pH = 2.000 are mixed with 990 mL of another strong acid solution of pH = 4.000. The pH of the resulting solution will be:
(A) 4.002　　　　(B) 4.000　　　　(C) 4.200　　　　(D) 3.7

72. At infinite dilution the percentage dissociation of both weak acid and weak base is:
(A) 1%　　　　(B) 20%　　　　(C) 50%　　　　(D) 100%

73. An acid solution with pH = 6 at 25°C is diluted by 10^2 times. The pH of solution will:
(A) Decrease by 2　　　　　　　　　　(B) Increase by 2
(C) Decrease by 0.95 approximately　　　　(D) Increase by 0.95 approximately

74. When 0.1 mole solid NaOH is added in 1lt of 0.1M $NH_3(aq)$ then which statement is going to wrong? $(K_b = 2 \times 10^{-5}, \log 2 = 0.3)$
(A) degree of dissociation of NH_3 approaches to zero.
(B) change in pH would be 1.85
(C) conc of $[Na^+] = 0.1M, [NH_3] = 0.1M, [OH^-] = 0.2M$
(D) on addition of OH^-, K_b of NH_3 does not changes.

75. Match list I (Solutions of salts of ...) with list II (pH of the solution is given by) and select the correct answer using the codes given below the lists:

List I		List II
(A) Weak acid and strong base	1.	$\dfrac{1}{2} pK_w$
(B) Strong acid and weak base	2.	$\dfrac{1}{2}(pK_w - pK_b + pK_a)$
(C) Weak acid and weak base	3.	$\dfrac{1}{2}(pK_w - pK_b - \log C)$
(D) Strong acid and strong base	4.	$\dfrac{1}{2}(pK_w + pK_a + \log C)$

Code :	A	B	C	D		A	B	C	D
(A)	1	2	3	4	(B)	4	3	2	1
(C)	4	3	1	2	(D)	3	4	2	1

76. Which of the following is true
(A) pK_b for OH^- is – 1.74 at 25°C
(B) The equilibrium constant for the reaction between HA ($pK_a = 4$) and NaOH at 25°C will be equal to 10^{10}.
(C) The pH of a solution containing 0.1 M HCOOH ($K_a = 1.8 \times 10^{-4}$) and 0.1 M HOCN.
　　$(K_a = 3.2 \times 10^{-4})$ will be nearly $(3 - \log 7)$.
(D) all the above are correct.

77. K_a for formic acid and acetic acid are 2.1×10^{-4} and 1.1×10^{-5} respectively. The relative strenth of acids is:
(A) $19:1$ (B) $2.3:1$ (C) $1:2.1$ (D) $4.37:1$

78. At 25°C K_b for BOH $= 1.0 \times 10^{-12}$. 0.01 M solution of BOH has $[OH^-]$:
(A) 1.0×10^{-6} M   (B) 1.0×10^{-7} M   (C) 1.0×10^{-5} M   (D) 2.0×10^{-6} M

79. K_a for HCN is 5×10^{-10} at 25°C. For maintaining a constant pH of 9, the volume of 5 M KCN solution required to be added to 10 ml of 2M HCN solution is ($\log 2 = 0.3$)
(A) 4 ml   (B) 8 ml   (C) 2 ml   (D) 10 ml

80. A buffer solution is prepared by mixing 'a' moles of CH_3COONa and 'b' moles of CH_3COOH such that $(a + b) = 1$, into water to make 1L buffer solution. If the instantaneous (differantial) buffer capacity of this buffer solution is plotted against moles of salt CH_3COONa **(A)** then the plot obtained will be (to the scale) approximately. **(As shown in figure in options)**
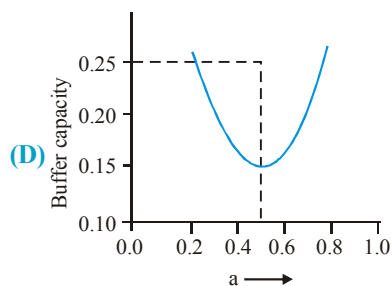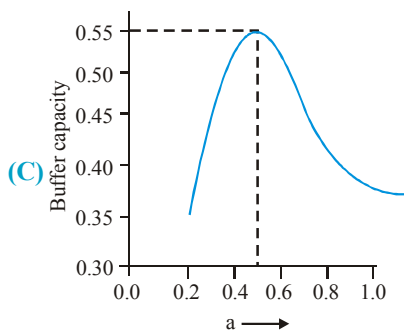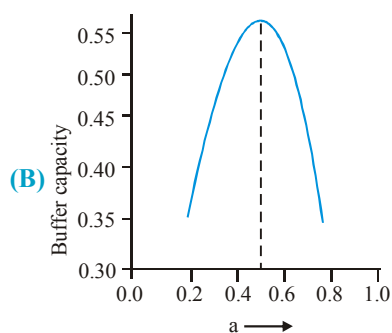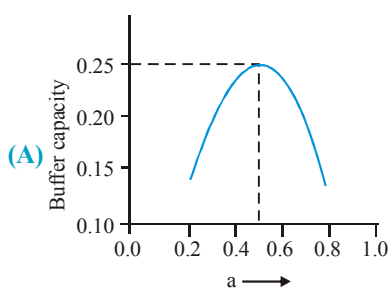
81. What % of the carbon in the $H_2CO_3 - HCO_3^-$ buffer should be in the form of HCO_3^- so as to have a neutral solution? ($K_a = 4 \times 10^{-7}$)
(A) 20 %   (B) 40 %   (C) 60 %   (D) 80%

82. Buffer capacity of a buffer solution is x, the volume of 1 M NaOH added to 100 mL of this solution if change the pH by 1 is
(A) $0.1\,x$ mL   (B) $10\,x$ mL   (C) $100\,x$ mL   (D) x mL

83. A solution is 0.1 M CH_3COOH and 0.1 M CH_3COONa. Which of the following solution will change its pH significantly?
(A) Addition of water
(B) Addition of small amount of CH_3COONa with out change in volume
(C) Addition of small amount of CH_3COOH with out change in volume
(D) None will change the pH significantly.

84. The best indicator for the detection of end point in titration of a weak acid and a strong base is :
(A) Methyl orange (3 to 4)   (B) Methyl red (5 to 6)
(C) Bromothymol blue (6 to 7.5)   (D) Phenolphthalein (8 to 9.6).

85. What fraction of an indicator HIn is in basic form at a pH of 6 if the pK_a of the indicator is 5 ?

(A) $\dfrac{1}{2}$ (B) $\dfrac{1}{11}$ (C) $\dfrac{10}{11}$ (D) $\dfrac{1}{10}$

86. A certain indicator (an organic dye) has $pK_a = 5$. For which of the following titrations may it be suitable.
(A) acetic acid against NaOH   (B) aniline hydrochloride against NaOH
(C) sodium carbonate against HCl   (D) barium hydroxide against oxalic acid

87. Which is/are correct statements :
(i) In any strong acid's solution, the concentration of $[OH^-]$ will be zero.
(ii) If $\Delta G°$ of a reaction is positive, then the reaction will not proceed at all, in the forward direction for any concentrations of reactants and products.
(iii) Titration curves are drawn for (about the figure shown)
  (a) 1M HCl (50 mL) with 1 M NaOH and
  (b) 0.01 M HCl (50 mL) with 0.01 M NaOH on the same graph paper they look like:
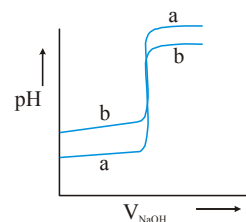
(A) i & ii   (B) iii only   (C) ii only   (D) i & iii

88. Which is/are correct statements :

(a) When 100 ml of 0.1 M NaCN solution is titrated with 0.1 M HCl solution the variation of pH of solution with volume of HCl added will be (as shown in figure):
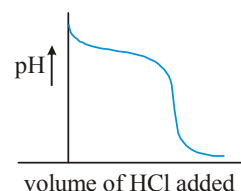
(b) Variation of degree of dissociation α with concentration for a weak electrolyte at a particular temperature is best represented by (as shown in figure) :
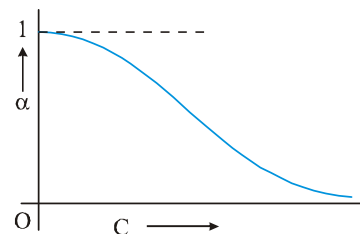
(c) 0.1 M acetic acid solution is titrated against 0.1 M NaOH solution. The difference in pH between 1/4 and 3/4 stages of neutralization of acid will be 2 log 3.

(A) a & c   (B) b & c   (C) a, b & c   (D) b only

89. If 50 ml of 0.2 M KOH is added to 40 ml of 0.5 M HCOOH. the pH of the resulting solution is:
$(K_a = 1.8 \times 10^{-4}, \log 18 = 1.26)$
(A) 3.74   (B) 5.64   (C) 7.57   (D) 3.42

90. When 100 ml of 0.4 M CH_3COOH are mixed with 100 ml of 0.2 M NaOH, the $[H_3O^+]$ in the solution is approximately : $[K_a(CH_3COOH) = 1.8 \times 10^{-5}]$
(A) 1.8×10^{-6} M   (B) 1.8×10^{-5} M   (C) 9×10^{-6} M   (D) 9×10^{-5} M.

91. Which of the following solutions would have same pH?
(A) 100 ml of 0.2 M HCl + 100 ml of 0.4 M NH_3 (B) 50 ml of 0.1 M HCl + 50 ml of 0.2 M NH_3
(C) 100 ml of 0.3 M HCl + 100 ml of 0.6 M NH_3 (D) All will have same pH.

92. To a 200 ml of 0.1 M weak acid HA solution 90 ml of 0.1 M solution of NaOH be added. Now, what volume of 0.1 M NaOH be added into above solution so that pH of resulting solution be 5. $[(K_a(HA) = 10^{-5}]$
(A) 2 ml   (B) 20 ml   (C) 10 ml   (D) 15 ml

93. 50 mL of 0.1 M NaOH is added to 60 mL of 0.15 M H_3PO_4 solution (K_1, K_2 and K_3 for H_3PO_4 are 10^{-3}, 10^{-8} and 10^{-13} respectively). The pH of the mixture would be about ($\log 2 = 0.3$)

(A) 3.1   (B) 5.5   (C) 4.1   (D) 6.5

94. 100 mL of 0.02 M benzoic acid (pKa = 4.2) is titrated using 0.02 M NaOH. pH after 50 mL and 100 mL of NaOH have been added are

(A) 3.50, 7   (B) 4.2, 7   (C) 4.2, 8.1   (D) 4.2, 8.25

95. Aniline behaves as a weak base. When 0.1 M, 50 ml solution of aniline was mixed with 0.1 M, 25 ml solution of HCl the pH of resulting solution was 8. Then the pH of 0.01 M solution of aniliniumchloride will be ($K_w = 10^{-14}$)

(A) 6   (B) 6.5   (C) 5   (D) 5.5

96. 1 M benzoic acid (pK_a = 4.20) and 1M C_6H_5COONa solutions are given separately. What is the volume of benzoic acid required to prepare a 300 ml buffer solution of pH = 4.5 ? [$\log 2 = 0.3$]

(A) 200 ml   (B) 150 ml   (C) 100 ml   (D) 50 ml

97. To prepare a buffer of pH 8.26 amount of $(NH_4)_2SO_4$ to be added to 500 mL of 0.01 M NH_4OH solution [p$K_a(NH_4^+) = 9.26$] is

(A) 0.05 mole   (B) 0.025 mole   (C) 0.10 mole   (D) 0.005 mole

98. Pure water is added into the following solutions causing a 10% increase in volume of each. The greatest % change in pH would be observed in which case (A), (B), (C) or (D) ?

(A) 0.1 M $NaHCO_3$ (B) 0.2 M NaOH

(C) 0.3 M NH_3 – 0.2 M NH_4^+ system   (D) 0.4 M CH_3COONH_4

99. An acid-base indicator which is a weak acid has a pK_{In} value = 5.45. At what cocentration ratio of sodium acetate to acetic acid would the indicator show a colour half-way between those of its acid and conjugate base forms? [pK_a of acetic acid = 4.75, $\log 2 = 0.3$]

(A) 4 : 1   (B) 6 : 1   (C) 5 : 1   (D) 3 : 1

100. What will be the pH at the equivalence point during the titration of a 100 mL 0.2 M solution of CH_3COONa with 0.2 M solution of HCl ? $K_a = 2 \times 10^{-5}$.

(A) $3 - \log \sqrt{2}$ (B) $3 + \log \sqrt{2}$ (C) $3 - \log 2$ (D) $3 + \log 2$

101. 20 mL of a weak monobasic acid (HA) requires 20 mL 0.2 M NaOH for complete titration. If pH of solution upon addition of 10 mL of this alkali to 25 mL of the above solution of HA is 5.8. The pK_a of the weak acid is

(A) 6.1   (B) 5.8   (C) 5.98   (D) 5.58

102. What is the difference in pH for 1/3 and 2/3 stages of neutralisation of 0.1 M CH_3COOH with 0.1 M NaOH.

(A) $2 \log 3$ (B) $2 \log (1/4)$ (C) $2 \log (2/3)$ (D) $2 \log 2$

103. A weak acid (HA) after treatment with 12 mL of 0.1 M strong base (BOH) has a pH of 5. At the end point, the volume of same base required is 27 mL. K_a of acid is ($\log 2 = 0.3$)

(A) 1.8×10^{-5} (B) 8×10^{-6} (C) 1.8×10^{-6} (D) 8×10^{-5}

104. A buffer solution contains 1 mole of $(NH_4)_2SO_4$ and 1 mole of NH_4OH ($K_b = 10^{-5}$). The pH of solution will be :

(A) 5   (B) 9   (C) 5.3   (D) 8.7

105. The total number of different kind of buffers obtained during the titration of H_3PO_4 with NaOH are:

(A) 3   (B) 1   (C) 2   (D) Zero

106. Which may be added to one litre of water to act a buffer:

(A) One mole of CH_3COOH and one mole of HCI   (B) One mole of NH_4OH and one mole of NaOH

(C) One mole of NH_4CI and one mole of HCI   (D) One mole of CH_3COOH and 0.5 mole of NaOH

Exercise # 2 — Part # I — [Multiple Correct Choice Type Questions]

1. If K_{a1} and K_{a2} of H_2SO_4 are 10^{-2} and 10^{-6} respectively then
(A) $K_{a1} > K_{a2}$ because it is easy to abstract H^+ from H_2SO_4 and less easy to abstract H^+ from HSO_4^-.
(B) K_{a1} and K_{a2} may be measured in acetic acid.
(C) K_{a1} and K_{a2} are measured in H_2O.
(D) the H^+ ion conc. of 0.01 M H_2SO_4 will be less than 0.02 M.

2. Which of the following solutions when added to 1L of a 0.01 M CH_3COOH solution will cause no change in the degree of dissociation of CH_3COOH and pH of the solution ? $K_a = 1.6 \times 10^{-5}$ for CH_3COOH?
(A) 0.6 mM HCOOH ($K_a = 8 \times 10^{-4}$)
(B) 0.1 M CH_3COONa
(C) 0.4 mM HCl
(D) 0.01 M CH_3COOH

3. K_a values for HA, HB and HD are 10^{-5}, 10^{-7} and 10^{-9} respectively. Which of the following will be correct for decimolar aqueous solutions of NaA, NaB and NaD at 25^0C?
(A) $(pH)_{NaA} < (pH)_{NaB}$
(B) $(pH)_{NaD} < (pH)_{NaB}$
(C) $(pH)_{NaA} < (pH)_{NaD}$
(D) $(pH)_{NaB} = 7$

4. 0.1 M CH_3COOH is diluted at $25°C$ ($K_a = 1.8 \times 10^{-5}$), then which of the following will be found correct
(A) $[H^+]$ will increase
(B) pH will increase
(C) number of H^+ will increase
(D) all the above are correct

5. Degree of hydrolysis for a salt of strong acid and weak base is
(A) independent of dilution
(B) increases with dilution
(C) increases with decrease in K_b of the bases
(D) decreases with decrease in temperature.

6. Equal volumes of following solutions are mixed, in which case the pH of resulting solution will be average value of pH of two solutions.
(A) Aqeous HCl of pH = 2, aqueous NaOH of pH = 12
(B) Aqeous HCl of pH = 2, aqueous HCl of pH = 4
(C) Aqeous NaOH of pH = 12, aqueous NaOH of pH = 10
(D) Aqeous CH_3COOH of pH = 5, aqueous NH_3 of pH = 9. [$K_a (CH_3COOH) = K_b (NH_3)$]

7. Which statement is/are correct:
(A) All Bronsted bases are also Lewis bases
(B) All Bronsted acids are not Lewis acids
(C) All cations are acids and anions are bases
(D) All of these

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) $\left(\dfrac{\alpha}{1-\alpha}\right) = \dfrac{1.75}{1.3} \times \left(\dfrac{\beta}{1-\beta}\right)$, 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.

9. For two different acids with same concentration

(A) the relative strength is expressed as $\dfrac{\alpha_1}{\alpha_2}$

(B) relative strength is expressed as $\dfrac{K_{\alpha_1}}{K_{\alpha_2}}$

(C) relative strength is expressed as $\sqrt{\dfrac{K_{\alpha_1}}{K_{\alpha_2}}}$

(D) $\dfrac{pH_1}{pH_2}$

10. Which one is the correct graph (figure) for the corresponding acid base titration?

(A)
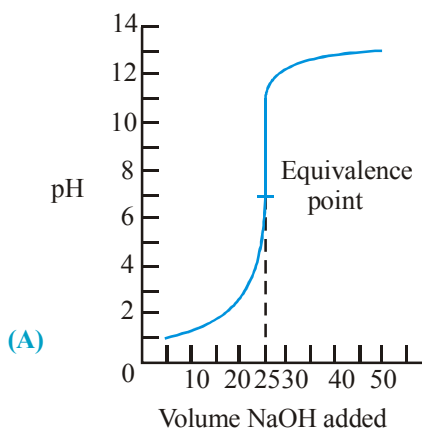
Titration curve of strong acid
(HCl with a strong base (NaOH)

(B)
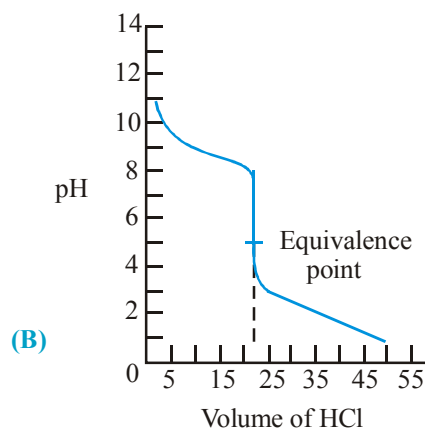
The pH titration curve of waek base
(NH$_4$OH) and strong acid(HCl)

(C)

Volume of strong base
added to a weak dibasic acid

(D)

[diacidic base] = 0.1 M, V = x
[monobasic acid] = 0.1 M

Volume of strong acid
added to a weak diacidic base
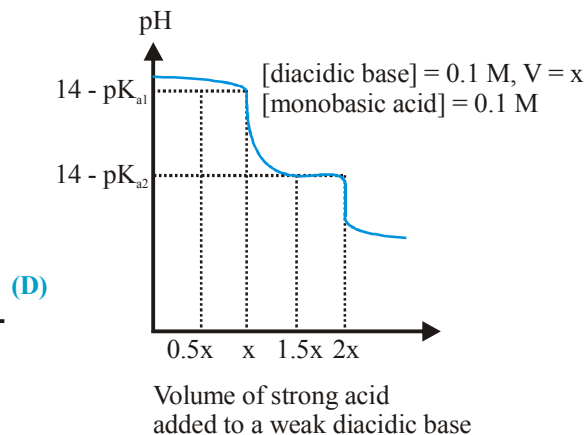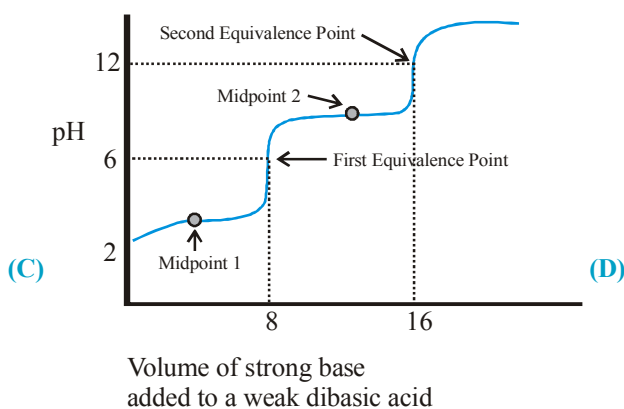
11. Which of the following are true for an acid−base titration ?
(A) Indicators catalyse the acid base reactions by releasing or accepting H^+ ions.
(B) Indicators do not significantly affect the pH of the solution to which they are added.
(C) Acid−base reactions do not occur in absence of indicators.
(D) Indicators have different colours in dissociated and undissociated forms.

12. A buffer solution can be prepared from a mixture of   **[JEE-1999]**
(A) Sodium acetate and acetic acid in water   (B) Sodium acetate and hydrochloric acid in water
(C) Ammonia and ammonium chloride in water   (D) Ammonia and soldium hydroxide in water

13. Which of the following is/are correct regarding buffer solution ?
(A) It contains weak acid and its conjugate base
(B) It contains weak base and its conjugate acid
(C) It shows large change in pH on adding small amount of acid or base.
(D) All of the above.

14. A weak acid (or base) is titrated against a strong base (or acid), volume v of strong base (or acid) is plotted against pH of the solution (as shown in figure). The weak electrolyte (i.e. acid or base) could be

(A) Na_2CO_3 (B) $Na_2C_2O_4$

(C) $H_2C_2O_4$ (D) $CH_2(COOH)_2$

Volume of strong base added to a weak dibasic acid
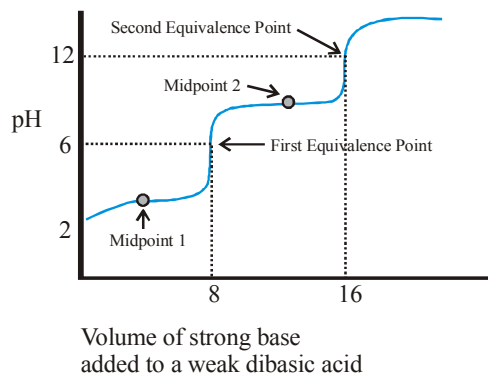
15. When weak base solution (50 ml of 0.1 N NH_4OH) is titrated with strong acid 0.1 N HCl, the pH of solution initially decreases fast and then decreases slowly till near equivalence point (as shown) in the figure. Which of the following is true.

(A) The slow decrease of pH is due to formation of an acidic buffer solution after addition of some HCl

(B) The slope of shown pH graph magnitude only will be minimum when 25 ml of 0.1 N HCl is added

(C) The slow decrease of pH is due to formation of a basic buffer solution

(D) The initial fast decrement in pH is due to fast consumption of free OH^- ions by HCl.
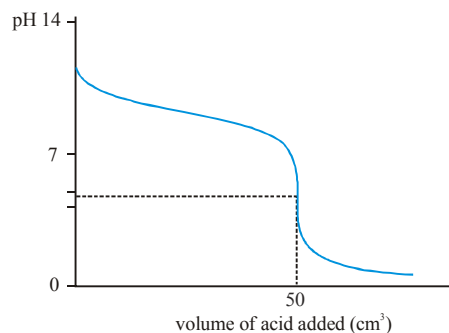
16. Which of the following is incorrect statement.

(A) If K_1 and K_2 for dissociation of H_2A is 10^{-7} and 10^{-14} then A^{2-} concentration in 0.1 M H_2A solution is 10^{-7}.

(B) A solution of pH = 1 has H^+ ion concentration 3 times than that of a solution of pH = 3.

(C) If a salt solution of weak acid & weak base is diluted upto limited extent then its pH will decrease.

(D) pH of acidic buffer solution depends upon pK_a and relative molar amount of weak acid and its conjugate base.

17. Choose the correct statement

(A) pH of acidic buffer solution decrease if more salt is added.

(B) pH of acidic buffer solution increases if more salt is added.

(C) pH of basic buffer decreases if more salt is added.

(D) pH of basic buffer increases if more salt is added.

18. Which of following can act as buffer ?

(A) $NaCl + NaOH$ (B) $NaHCO_3 + H_2CO_3$ (C) $NaH_2PO_4 + Na_2HPO_4$ (D) $NH_4Cl + NH_4OH$.

19. Which of the following will show common ion effect and form a buffer solution ?

(A) CH_3COONH_4 and CH_3COOH (B) $NH_4Cl + NH_4OH$

(C) $H_2SO_4 + NaHSO_4$ (D) $NaCl + NaOH$.

20. Which of the following mixtures will act as buffer ?

(A) $H_2CO_3 + NaOH$ (1.5 : 1 molar ratio)   (B) $H_2CO_3 + NaOH$ (1.5 : 2 molar ratio)

(C) $NH_4OH + HCl$ (5 : 4 molar ratio)   (D) $NH_4OH + HCl$ (4 : 5 molar ratio)

21. Let the colour of the indicator HIn (colourless) will be visible only when its ionised form (pink) is 25% or more in a solution. Suppose HIn (pK_a = 9.0) is added to a solution of pH = 9.6 predict what will happen. (Take log 2 = 0.3)

(A) pink colour will be visible   (B) pink colour will not be visible

(C) % of ionised form will be less than 25%   (D) % of ionised form will be more than 25%

22. Titration curves for 0.1M solutions of three weak acids HA_1, HA_2 and HA_3 with ionization constants K_1, K_2 and K_3 respectively are plotted as shown in the figure. Which of the following is/are true?
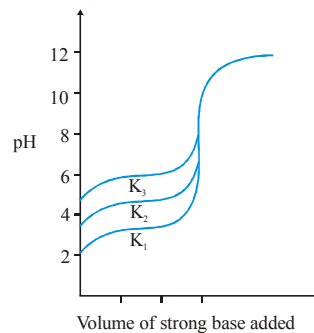
(A) $K_2 = (K_1 + K_3)/2$

(B) $K_1 < K_3$

(C) $K_1 > K_2$

(D) $K_2 > K_3$

23. A 0.1 M sodium acetate solution was prepared. The $K_h = 5.6 \times 10^{-10}$
   (A) The degree of hydrolysis is 7.48×10^{-5}
   (B) The $[OH^-]$ concentration is 7.48×10^{-3} M
   (C) The $[OH^-]$ concentration is 7.48×10^{-6} M
   (D) The pH is approximately 8.88.

24. In which of the following solutions, the solubility of AgCN will be greater than that in pure water :
   Given $K_{sp}(AgCN) = 4 \times 10^{-16}$, $K_a(HCN) = 5 \times 10^{-10}$
   (A) 0.01 M Ag NO_3 solution
   (B) A buffer solution of pH = 12
   (C) 0.2 M NH_3 solution
   (D) A buffer solution of pH = 5

25. The solubility of a sparingly soluble salt $A_x B_y$ in water at 25ºC = 1.4×10^{-4} M. The solubility product is 1.1×10^{-11}. The possibilities are
   (A) $x = 1, y = 2$ (B) $x = 2, y = 1$ (C) $x = 1, y = 3$ (D) $x = 3, y = 1$

26. Select the correct statements :

   (A) pH of $NaHCO_3$ solution can be given by $\dfrac{pK_{H_2CO_3} + pK_{HCO_3^-}}{2}$

   (B) Al^{3+} ion is amphoteric
   (C) K_{SP} values of metal nitrates are very-very high
   (D) Na^+ (aq). is conjugate acid of NaOH (aq).

27. The pH of an acidic buffer mixture is:
   (A) > 7   (B) < 7   (C) = 7   (D) Depends upon K_a of acid

28. From separate solutions of for sodium salts NaW, NaX, NaY and NaZ has pH 7.0, 9.0 10.0 and 11.0 respectively. When each solution was 0.1 M, the strongest acid is:
   (A) HW   (B) HX   (C) HY   (D) HZ

29. pH of a mixture containing 0.10 M X^- and 0.20 M HX is: $[pK_b(X^-) = 4]$
   (A) $4 + \log 2$ (B) $4 - \log 2$ (C) $10 + \log 2$ (D) $10 - \log 2$

30. Solution of aniline hydrochloride is X due to hydrolysis of Y. X and Y are :
   (A) Basic, $C_6H_5NH_3^+$ (B) Acidic, $C_6H_5NH_3^+$ (C) Basic, Cl^- (D) Acidic, Cl^-

31. Strong acids are generally used as standard solution in acid-base titrations because:
   (A) The pH at equivalence point will be 7
   (B) They titrate both strong and weak base
   (C) They form more stable solutions than weak acids
   (D) The salts of strong acids do not hydrolyse

32. The pK_a of acetylasliclic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be:
(A) Unionised in the small intestine and in the stomach
(B) Completely ionised in the small intestine and in the stomach
(C) Ionised in the stomach and almost unisonised in the small intestine
(D) Ionised in the small intestine and almost unionized in the stomach

33. Fear or excitement, generally cause one to breathe rapidly and it results in the decrease of concentration of CO_2 in blood. In what way it will change pH of blood.
(A) pH will increase   (B) pH will decrease   (C) No change   (D) pH will be 7

34. The composition of an acidic buffer mixture made up of HA and NaA of total molarity 0.29 having pH $= 4.4$ and $K_a = 1.8 \times 10^{-5}$ in terms of concentration of salt and acid respectively is :
(A) 0.09 M and 0.20 M   (B) 0.20 M and 0.09   (C) 0.1 M and 0.19 M   (D) 0.19 M and 010 M

35. A weak acid HA after treatment with 12 mL of 0.1 M strong base BOH has a pH of 5. At the end point the volume of same base required is 26.6 mL . Calculate K_a of acid is :
(A) 1.8×10^{-5} (B) 8.22×10^{-6} (C) 1.8×10^{-6} (D) 8.2×10^{-5}

36. In which of the following combinations, is buffer action expected?
1. $NH_3 + NH_4CI$ in 1 : 1 mole ratio
2. $HCI + NaCI$ in 1 : 1 mole ratio
3. $NH_3 + HCI$ in 2 : 1 mole ratio
Select the correct answer using the code given below:
(A) 1 and 2   (B) 1 and 3   (C) 2 and 3   (D) 1, 2 and 3

37. A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. The pH of the buffer is:
(A) 4   (B) 7   (C) 10   (D) 14

38. 50 mL of 2N acetic acid mixed with 10 mL of 1N sodium acetate solution will have an approximate pH of $(K_a = 10^{-5})$
(A) 4   (B) 5   (C) 6   (D) 7

39. The solubility of CaF_2 $(K_{sp} = 3.4 \times 10^{-11})$ in 0.1 M solution of NaF would be
(A) 3.4×10^{-12} M   (B) 3.4×10^{-10} M   (C) 3.4×10^{-9} M   (D) 3.4×10^{-13} M.

40. The solubility of Ag_2CO_3 in water at 25°C is 1×10^{-4} mole/litre. What is its solubility in 0.01 M Na_2CO_3 solution? Assume no hydrolysis of CO_3^{2-} ion.
(A) 6×10^{-6} mole/litre   (B) 4×10^{-5} mole/litre   (C) 10^{-5} mole /litre   (D) 2×10^{-5} mole/litre

41. In a saturated solution of Ag_2CO_3, silver ion concentration is 2×10^{-4} M. Its solubility product is
(A) 4×10^{-12} (B) 3.2×10^{-11} (C) 8×10^{-12} (D) 10^{-12}

42. Let the solubilities of AgCl in pure water, 0.01 M $CaCl_2$, 0.01 M NaCl & 0.05 M $AgNO_3$ be s_1, s_2, s_3 & s_4 respectively what is the correct order of these quantities . Neglect any complexation.
(A) $s_1 > s_2 > s_3 > s_4$ (B) $s_1 > s_2 = s_3 > s_4$
(C) $s_1 > s_3 > s_2 > s_4$ (D) $s_4 > s_2 > s_3 > s_1$

43. If the solubility of lithium sodium hexafluorido aluminate, $Li_3Na_3(AlF_6)_2$ is 's' mol lt^{-1}, its solubility product is equal to
(A) $729\, s^8$ (B) $12\, s^8$ (C) $3900\, s^8$ (D) $2916\, s^8$

44. The solubility product of $BaCrO_4$ is 2.4×10^{-10} M^2. The maximum concentration of $Ba(NO_3)_2$ possible without precipitation in a 6×10^{-4} M K_2CrO_4 solution is
(A) 4×10^{-7} M   (B) 1.2×10^{10} M   (C) 6×10^{-4} M   (D) 3×10^{-4} M.

45. What is the solubility of $Al(OH)_3$, $(K_{sp} = 1 \times 10^{-33})$ in a buffer solution pH = 4 ?
   (A) 10^{-3} M   **(B)** 10^{-6} M   **(C)** 10^{-4} M   **(D)** 10^{-10} M.

46. The solubility of $Fe(OH)_3$ would be maximum in
   (A) 0.1 M NaOH   **(B)** 0.1 M HCl   **(C)** 0.1 M KOH   **(D)** 0.1 M H_2SO_4.

47. The best explanation for the solubility of MnS in dilute HCl is that :
   (A) Solubility product of $MnCl_2$ is less than that of MnS
   (B) Concentration of Mn^{2+} is lowered by the formation of complex ions with chloride ions
   (C) Concentration of sulphide ions is lowered by oxidation to free sulphur
   (D) Concentration of sulphide ions is lowered by formation of weak acid H_2S

48. The solubility product of AgCl is 1.8×10^{-10}. Precipitation of AgCl will occur only when equal volumes of solutions of
   (A) 10^{-4}M Ag^+ and 10^{-4} M Cl^- are mixed.   **(B)** 10^{-7} M Ag^+ and 10^{-7} M Cl^- are mixed.
   (C) 10^{-5} M Ag^+ and 10^{-5} M Cl^- are mixed.   **(D)** 2×10^{-5} M Ag^+ and 2×10^{-5} M Cl^- are mixed.

49. Arrange in increasing order of solubility of AgBr in the given solutions.
   (i) 0.1 M NH_3 (ii) 0.1 M $AgNO_3$ (iii) 0.2 M NaBr   (iv) pure water
   (A) (iii) < (ii) < (iv) < (i)   **(B)** (iii) < (ii) < (i) < (iv)
   (C) (iii) < (ii) = (i) < (iv)   **(D)** (ii) < (iii) < (iv) < (i)

50. A solution containing a mixture of 0.05 M NaCl and 0.05 M NaI is taken (K_{sp} of AgCl = 10^{-10} and K_{sp} of AgI = 4×10^{-16}). When $AgNO_3$ is added to such a solution.
   (A) the concentration of Ag^+ required to precipitate $Cl^- = 4 \times 10^{-9}$ mol/L.
   (B) the concentration of Ag^+ required to precipitate $I^- = 8 \times 10^{-15}$ mol/L.
   (C) AgCl and AgI will be precipitated together.
   (D) None of these

51. Which of the following statements is correct for a solution saturated with AgCl and AgBr if their solubilities in moles per litre in separate solutions are x and y respectively ?
   (A) $[Ag^+] = x + y$ **(B)** $[Ag^+] = [Br^-] + [Cl^-]$
   (C) $[Br^-] = y$ **(D)** $[Cl^-] > x$.

52. At 25ºC, the solubility product values of AgCl and AgCNS are 1.8×10^{-10} and 1.6×10^{-11} respectively. When a solution is saturated with both solids, calculate the ratio $[Cl^-]/[CNS^-]$ and also $[Ag^+]$ in the solution.
   (A) $1.125, 4 \times 10^{-6}$ M   **(B)** $11.25, 1.4 \times 10^{-5}$ M   **(C)** $1.25, 4 \times 10^{-5}$ M   **(D)** $1.25, 4 \times 10^{-6}$ M

53. What is the minimum pH when $Fe(OH)_3$ starts precipitating from a solution containing 0.1M $FeCl_3$? K_{sp} of $Fe(OH)_3$ = 8×10^{-13} M^3
   (A) 3.7   **(B)** 5.7   **(C)** 10.3   **(D)** 8.3

54. A solution prepared by dissolving 2.8 g of lime (CaO) in enough water to make 1.00 L of lime water ($Ca(OH)_2$(aq.)). If solubility of $Ca(OH)_2$ in water is 1.48 gm/lt. The pH of the solution obtained will be:
   [log 2 = 0.3, Ca = 40 , O = 16, H = 1]
   (A) 12.3   **(B)** 12.6   **(C)** 1.3   **(D)** 13

55. The solubility product of AgCl is 10^{-10}. The minimum volume (in L) of water required to dissolve 1.722 mg of AgCl is (molecular weight of AgCl = 143.5).
   (A) 10 lt.   **(B)** 2.2 lt.   **(C)** 1.2 lt.   **(D)** 20 lt.

56. 0.1 millimole of $CdSO_4$ are present in 10 mL acid solution of 0.08 N HCl. Now H_2S is passed to precipitate all the Cd^{2+} ions. The pH of the solution after filtering off precipitate, boiling off H_2S and making the solution 100 mL by adding H_2O is

(A) 2   (B) 4   (C) 6   (D) 8

57. A well is dug in a bed of rock containing fluorspar (CaF_2). If the well contains 20000 L of water, what is the amount of F^- in it ? $K_{sp} = 4 \times 10^{-11} (10^{1/3} = 2.15)$

(A) 4.3 mol   (B) 6.8 mol   (C 8.6 mol   (D) 13.6 mol

58. When different types of salts have nearly same solubility product constant K_{SP} which are less than one. The most soluble salt is that.

(A) Which produces maximum number of ions   (B) Which produces minimum number of ions
(C) Which produces more charge on ion   (D) None of these

59. Solubility of BaF_2 in a solution of $Ba(NO_3)_2$ will be represented by the concentration term:

(A) $[Ba^{2+}]$ (B) $[F^-]$ (C) $1/2[F^-]$ (D) $2[NO_3^-]$

60. Which of the following is most soluble in water:

(A) MnS $(K_{SP} = 8 \times^{-37})$ (B) ZnS $(K_{SP} = 7 \times 10^{-16})$
(C) Bi_2S_3 $(K_{SP} = \times 10^{-70})$ (D) Ag_2S $(K_{SP} = 6 \times 10^{-51})$

61. When pure water is saturated with $CaCO_3$ and CaC_2O_4, the concentration of calcium ion in the solution under equilibrium is 8×10^{-5} M. If the ratio of the solubility product of $CaCO_3$ to that of CaC_2O_4 is 3, what is the solubility product of $CaCO_3$ in pure water?

(A) 4.80 x 10⁻⁸   (B) 9.60 x 10⁻⁹   (C) 9.60 x 10⁻⁸   (D) 4.80 x 10⁻⁹

62. A solution is a mixture of 0.05 M KCI and 0.05 M NaI. The concentration of I^- in the solution when AgCI just starts to precipitate is equal to: $(K_{SP}AgCI = 10^{-10}$ M²; $K_{SP}AgI = 4 \times 10^{-16}$ M²)

(A) 4×10^{-6} M   (B) 2×10^{-8} M   (C) 2×10^{-7} M   (D) 8×10^{-15} M

63. The solubility products of $Al(OH)_3$ and $Zn(OH)_2$ are 8.5×10^{-23} and 1.8×10^{-14} respectively. If NH_4OH is added to a solution containing 0.01 M concentraion of Al^{3+} and Zn^{2+} ions, then substance precipitated first is:

(A) $Al(OH)_3$ (B) $Zn(OH)_2$ (C) Both together   (D) None at all

64. At 30°C the solubility of Ag_2CO_3 $(K_{SP} = 8 \times 10^{-12})$ would be greatest in one litre of:

(A) 0.05M Na_2CO_3 (B) 0.05 M $AgNO_3$ (C) Pure water   (D) 0.05 M K_2CO_3

65. A solution of Na_2CO_3 is added drop by drop to litre of a solution containing 10^{-4} mole of Ba^{2+} and 10^{-5} mole of Ag^+, if K_{SP} for $BaCO_3$ is 8.1×10^{-9} and K_{SP} for Ag_2CO_3 is 6.9×10^{-12} then which is not true:

(A) No precipitate of $BaCO_3$ will appear until [CO_3^{2-}] reaches 8.1×10^{-5} mol per litre

(B) A precipitate of Ag_2CO_3 will appear when [CO_3^{2-}] reaches 6.9×10^{-5} mol litre⁻¹

(C) No precipitate of Ag_2CO_3 will appear until [CO_3^{2-}] reaches 6.9×10^{-2} mole per litre

(D) $BaCO_3$ will be precipitated first

66. The solubility of $PbCI_2$ in water is 0.01 M 25°C. Its maximum concentration in 0.1 M NaCI will be:

(A) 2×10^{-3} M   (B) 1×10^{-4} M   (C) 1.6×10^{-2} M   (D) 4×10^{-4} M

67. The volume of the water needed to dissolve 1 g of $BaSO_4$ ($K_{SP} = 1.1 \times 10^{-10}$) at 25°C is:
(A) 280 litre   (B) 410 litre   (C) 205 litre   (D) None of these

68. $M(OH)_x$ has K_{SP} 4×10^{-12} and solubility 10^{-4} M. The value of x is:
(A) 1   (B) 2   (C) 3   (D) 4

69. Slaked lime, $Ca(OH)_2$ is used extensively in sewage treatment. What is the maximum pH that can be established in $Ca(OH)_2(aq)$:

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq) \quad ; \quad K_{SP} = 5.5 \times 10^{-6}$$

(A) 1.66   (B) 12.35   (C) 7.0   (D) 14.0

70. K_{SP} if $Mg(OH)_2$ is 1×10^{-12}. 0.01M $MgCI_2$ will show precipitation in a solution of pH greater than:
(A) 3   (B) 9   (C) 12   (D) 8

71. Silver nitrate solution is gradually added to an aqueous solution containing 0.01 M each of chloride, bromide and iodide ions. The correct sequence in which the halides will be precipitated is:
(A) Bromide, chloride iodide
(B) Iodide, chloride, bromide
(C) Iodide, bromide, chloride
(D) Brodide chloride

72. Which set is not correct for the solubility product (K_{SP}), solubility (sg/litre) of sparingly soluble salt A_3B_2 (mol. wt. M) in water:

1. $K_{SP} = 108s^5$ **2.** $K_{SP} = \left[\dfrac{3s}{M}\right]^2 \left[\dfrac{2s}{M}\right]^2$ **3.** $K_{SP} = [1A^{2+}]^3 [2B^{3-}]^2$

4. $[B^{3-}] = \dfrac{2s}{M}$ **5.** $\dfrac{[B^{3-}]}{K_{SP}} = \dfrac{1}{54}\dfrac{M^4}{s^4}$

(A) 1, 3   (B) 1, 3 , 5   (C) 2, 3, 4   (D) 2, 4, 5

73. The solubility products of MA, MB, MB and MD are 1.8×10^{-10}, 4×10^{-3}, 4×10^{-8} and 6×10^{-5} respectively. If a solution of MX is added dropwise to a mixture containing 0.01 M each of A^-, B^-, C^- and D^- ions, then the one which precipitated first will be:
(A) MA   (B) MB   (C) MC   (D) MD

74. Which of the following statements are true for a solution saturated with AgCI and AgBr if their solubilities in mol per litre in separate solution are x and y mole respectively:
(A) $[Ag^+] = [Br^-] \times [CI^-]$ (B) $[CI^-] > [Br]$
(C) $[Br^-] > y$ (D) $[Ag^+] = x + y$

75. Which of the following species is more soluble in water:
(A) $M(OH)_3$ ($K_{SP} = 1 \times 10^{-35}$)   (B) $M(OH)_2$ ($K_{SP} = 1 \times 10^{-30}$)
(C) MOH   ($K_{SP} = 1 \times 10^{-28}$)   (D) MOH   ($K_{SP} = 1 \times 10^{-26}$)

76. The concentration of hydroxyl ion in a solution left after mixing 100 mL of 0.1 M $MgCI_2$ and 100 mL of 0.2 M NaOH (K_{SP} of $Mg(OH)_2 = 1.2 \times 10^{-11}$):
(A) 2.88×10^{-3} (B) 2.88×10^{-2} (C) 2.88×10^{-4} (D) 2.88×10^{-5}

Each question has 5 choices (A), (B), (C), (D) and (E) out of which only one is correct.

(A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1.

(B) Statement-1 is true, Statement-2 is true and Statement-2 is not correct explanation for Statement-1.

(C) Statement-1 is true, Statement-2 is false

(D) Statement-1 is false, Statement-2 is true

(E) Both Statements are false

1. **Statement-1 :** Aqueous solutions of all strong acids contain only the same acid, the hydronium ion.

   Statement-2 : Hydronium ion is the strongest acid that can exist in any significant concentration in dilute aqueous solution.

2. **Statement-1 :** Acids that have more than one proton that can be donated to base are called polyprotic acids.

   Statement-2 : For all diprotic acids, the equilibrium constant K_{a2}, for the second stage of ionisation is smaller than the equilibrium constant, K_{a1}, for the first stage of ionisation.

3. **Statement-1 :** 0.20 M solution of NaCN is more basic than 0.20 M solution of NaF.

   Statement-2 : K_a of HCN is very much less than that of HF.

4. **Statement-1 :** A substance that can either act as an acid as well as a base is called ampholyte.

   Statement-2 : Bisulphide ion (HS^-) and biscarbonate ion (HCO_3^-) are ampholytes.

5. **Statement-1 :** The H_3O^+ has additional water molecules closely associated with it.

   Statement-2 : In solid state the species $H_5O_2^+$ and $H_9O_4^+$ have been found to exist.

6. **Statement-1 :** The proton transfer reaction between NH_3 and H_2O proceeds only to a slight extent.

   Statement-2 : Proton transfer reaction is virtually complete in the case of HCl in dilute solution.

7. **Statement-1 :** Addition of HCl(aq) to HCOOH(aq), decrease the ionization of HCOOH(aq)

   Statement-2 : Due to common ion effect of H^+, ionization of HCOOH decreased.

8. **Statement-1 :** pH of 10^{-7} M HCl is less than 7 at 25ºC.

   Statement-2 : At very low concentration of HCl, contribution of H^+ from water is considerable.

9. **Statement-1 :** In a titration of weak monoprotic acid with strong base, the pH at the half equivalent point is pK_a.

   Statement-2 : At half equivalence point, it will form acidic buffer at it's maximum capacity where [acid] = [salt].

10. **Statement-1 :** Solubility of AgCl in NH_3(aq) is greater than in pure water.

    Statement-2 : When AgCl dissolve in NH_3(aq), complex ion $[Ag(NH_3)_2^+]$ formation takes place and solubility equilibrium of AgCl shifted in forward direction.

11. **Statement-I :** On dilution of a concentrated solution of CH_3COOH, the concentration of $[H^+]$ decreases

    Statement-II : Because increase in the volume is more than the increase in degree of ionisation

12.   **Statement-I :** pH of boiling water is less than the water at 4 °C

        Statement-II : Because density of water is maximum at 4 °C

13.   **Statement-I :** Solubility of $BaSO_4$ in 0.1 M Na_2SO_4 is 10^{-9} M hence its K_{sp} is 10^{-18}

        Statement-II : Because for $BaSO_4 K_{sp} = (s)^2$

14.   **Statement-I :** Aqueous solution of CH_3COONH_4 is found to be neutral

        Statement-II : because this salt does not undergo hydrolysis

15.   **Statement-I :** An aqueous solution of HCl is a much better conductor of electricity than an aqueous solution of CH_3COOH of the same concentration.

        Statement-II : The freezing point depression and the boiling point elevation of weak electrolytes are significantly less than for strong electrolytes of the same concentration.

16.   **Statement-I :** $CH_3NH_3^+ CH_3NH_2$ is acid base conjugate pair.

        Statement-II : H_3O^+, OH^- is acid base conjugate pair.

17.   **Statement-I :** The equilibrium constant for the reaction,

        $$HONO(aq.) + CN^-(aq) \rightleftharpoons HCN (aq.) + ONO^-(aq.) \text{ is } 1.1 \times 10^6$$

        Statement-II : This shows that CN^- is stronger base than ONO^-

Exercise # 3 — Part # I — [Matrix Match Type Questions]

1. (Use $\log 1.8 = 0.26$, Ka of formic acid $= 1.8 \times 10^{-4}$, Ka of acetic acid $= 1.8 \times 10^{-5}$, K_b of ammonia$=1.8\times10^{-5}$, Ka_1 of $H_2S = 10^{-7}$ and Ka_2 of $H_2S = 10^{-14}$, for the following matchings)

Match the entries of column II for which the equality or inequality given in the column I are satisfied.

Column I	Column II
(A) 10^{-5} M HCl solution > 0.1 M H_2S solution	**(p)** α_{water} (degree of dissociation of water)
(B) CH_3COOH solution at pH equal to 4.74 $= NH_4OH$ solution at pH equal to 9.26	**(q)** $[OH^-]$
(C) 0.1 M CH_3COOH solution $= 1.0$ M HCOOH solution	**(r)** α (degree of dissociation)
(D) 0.1 M of a weak acid HA_1 (Ka $= 10^{-5}$) solution < 0.01 M of a weak acid HA_2 (Ka $= 10^{-6}$) solution	**(s)** pH

2. Match the effect of addition of 1 M NaOH to 50 ml of 1 M $H_2C_2O_4$ (diprotic acid) in column I with column II (Given: $Ka_1 = 10^{-4}$, $Ka_2 = 10^{-9}$)

Column I	Column II
(A) 25 mL of NaOH	**(p)** Buffer solution
(B) 50 mL of NaOH	**(q)** pH is independent of concentration of species present in the solution.
(C) 75 mL of NaOH	**(r)** anionic hydrolyisis
(D) 100 mL of NaOH	**(s)** pH > 7

3. Match the correct value of Ksp expression in term of solubility (s)

Column-I	Column-II
(A) Al_2O_3	**(p)** $4s^3$
(B) CaO	**(q)** $27s^4$
(C) $Al(OH)_3$	**(r)** $108s^5$
(D) CaF_2	**(s)** s^2

4. Match the effect of addition of 1 M NaOH to 100 mL 1 M CH_3COOH (in Column I) with pH (in Column II) :

Column-I	Column-II
(A) 25 mL of NaOH	**(p)** pK_a
(B) 50 mL of NaOH	**(q)** $pK_a + \log 3$
(C) 75 mL of NaOH	**(r)** $pK_a - \log 3$
(D) 100 mL of NaOH	**(s)** $\dfrac{1}{2}[pK_w + pK_a - \log 2]$

5. When we titrate sodium carbonate solution (in beaker) with hydrochloric acid.

Column-I	Column-II
(A) At the start of titration	**(p)** Buffer solution of HCO_3^- and CO_3^{2-}
(B) Before the first equivalent point	**(q)** Buffer solution of H_2CO_3 and HCO_3^-
(C) At the first equivalent point	**(r)** Amphiprotic anion, $pH = 1/2(pK_{a_1} + pK_{a_2})$
(D) Between the first and second equivalent points	**(s)** Hydrolysis of CO_3^{2-}

Comprehension # 1

Consider a solution of CH_3COONH_4 which is a salt of weak acid & weak base.

The equilibrium involved in the solutions are :

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \qquad ....(1)$$
$$NH_4^- + H_2O \rightleftharpoons NH_4OH + H^+ \qquad ....(2)$$
$$H^+ + OH^- \rightleftharpoons H_2O \qquad ....(3)$$

If we add these three reactions, then the net reaction is

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH \qquad ....(4)$$

Both CH_3COO^- and NH_4^+ get hydrolysed independently and their hydrolysis depends on

(i) their initial concentration

(ii) the value of K_h which is $\dfrac{K_w}{K_a}$ for CH_3COO^- and $\dfrac{K_w}{K_b}$ for NH_4^+.

Since both of the ions were produced from the same salt, their initial concentrations are same. Therefore unless &

untial the value of $\dfrac{K_w}{K_a}$ and $\dfrac{K_w}{K_b}$ or K_a and K_b is same, the degree of hydrolysis of ion can't be same.

To explain why we assume that degree of hydrolysis of cation and anion is same, we need to now look at the third reaction i.e., combination of H^+ and OH^- ions. It is obvious that this reaction happens only because one reaction produced H^+ ion and the other produced OH^- ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. Keep this thing in mind that the equilibrium which has smaller value of equilibrium conxtant is affected more by the common ion effect. For the same reason if for any reason a reaction is made to occur to a greater extent by the comsumption of any one of the product ion, the reaction with the smaller value of equilibrium constant tends to get affected more.

Therefore we conclude that firstly the hydrolysis of both the ions ocurs more in the presence of each other (due to consumption of the product ions) than in each other is absence. Secondly the hydrolysis of the ion which occurs to a lesser extent (due to smaller value of K_h) is affected more than the one whose K_h is greater. Hence we can see that the degree of hydrolysis of both the ions would be close to each other when they are getting hydrolysed in the presence of each other.

1. In the hydrolysis of salt of weak acid & weak base :
   (A) degree of hydrolysis of cation and anion is different
   (B) degree of hydrolysis of cation and anion is same
   (C) degree of hydrolysis of cation and anion is different and they can never be assumed same.
   (D) degree of hydrolysis of cation and anion is different but they are very close to each other when they are getting hydrolysed in the presence of each other.

2. For 0.1 M CH_3COONH_4 salt solution given, $K_a(CH_3COOH) = K_b(NH_4OH) = 2 \times 10^{-5}$.
   In this case : degree of hydrolysis of cation and anion are
   (A) exactly same
   (B) slightly different
   (C) can't say
   (D) different but can be take approximatly same

Comprehension # 2

The pH basic buffer mixtures is given by : $pH = pK_a + \log \dfrac{[Base]}{[Salt]}$, whereas pH of acidic buffer mixtures is given by

: $pH = pK_a + \log \dfrac{[Salt]}{[Acid]}$. Addition of little acid or base although shows no appreciable change in pH for all practical

purposes, but since the ratio $\dfrac{[Base]}{[Salt]}$ for $\dfrac{[Salt]}{[Acid]}$ changes, a slight decrease or increase in pH results.

1. The amount of $(NH_4)_2SO_4$ to be added to 500 mL of 0.01 M NH_4OH solution (pK_a for NH_4^+ is 9.26) prepare a buffer of pH 8.26 is:

    (A) 0.05 mole   (B) 0.025 mole   (C) 0.10 mole   (D) 0.005 mole

2. A solution containing 0.2 mole of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) and 0.1 mole sodium dichloroacetate in one litre solution has $[H^+]$:

    (A) 0.05 M   (B) 0.025 M   (C) 0.10 M   (D) 0.005 M

3. The volume of 0.2 M NaOH needed to prepare a buffer of pH 4.74 with 50 mL of 0.2 M acetic acid (pK_b of $CH_3COO^- = 9.26$) is:

    (A) 50 mL   (B) 25 mL   (C) 20 mL   (D) 10 mL

4. The ratio of pH of solution(I) containing 1 mole of CH_3COONa and 1 mole of HCI and solution(II) containing 1 mole of CH_3COONa and 1 mole of acetic acid in one litre is:

    (A) 1 : 2   (B) 2 : 1   (C) 1 : 3   (D) 3 : 1

Comprehension # 3

Strontium fluoride (SrF_2) is a sparingly soluble salt. Let s_1 be its solubility (in mol/lt.) in pure water at 25°C, assuming no hydrolysis of F^- ions. Also, let s_2 be its solubility (in mol/lt.) in 0.1 M NaF solution at 25°C, assuming no hydrolysis of F^- ions and no complex formation.
However, it is known that $s_1 : s_2 = 10^6 : 256$. Now, answer the following questions.

1. The K_{sp} value of SrF_2 at 25°C is :
    (A) 2.048×10^{-9} (B) 1.372×10^{-9} (C) 1.864×10^{-9} (D) 2.916×10^{-9}

2. The mass of NaF to be added to 100 ml solution of 0.0011 M Sr^{+2} ions to reduce its concentration to 2×10^{-4} M is : [Assume no hydrolysis of F^- ions]
    (A) 0.42 g   (B) 0.063 g   (C) 0.021 g   (D) 0.084 g

3. The solubility of SrF_2(in mol/L) in a buffer solution of pH =5 at 25°C is : [Given : K_a for HF = $\dfrac{1}{7} \times 10^{-5}$]
    (A) 1.6×10^{-3} (B) 3.2×10^{-3} (C) 4.8×10^{-3} (D) 6.4×10^{-3}
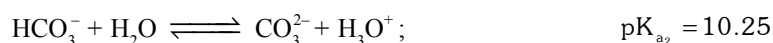
Comprehension # 4

The importance of pH maintenance in Blood

Maintenance of the pH in blood and in intracellular fluids is absolutely crucial to the processes that occur in living organisms. This primarily because the functioning of enzymes-catalysts for these processes - is sharply pH dependent. The normal pH value of blood plasma is 7.4. Severe illness or death can result from sustained variations of a few tenths of pH unit.

Among the factors that lead to a condition of acidosis, in which there is decreases in the pH of blood are heart failure, kidney failure diabetes mellitus, persistent diarrhoea or a long term high protein diet. A temporary condition acidosis may result from prolonged, intensive exercise. Alkalosis, which causes increase in pH of blood, may occur as a result of severe vomiting overbreathing or exposure to high altitudes.

Several factors are involved in the control of the pH of blood. A particularly important one is the ratio of dissolved HCO_3^- to H_2CO_3. $CO_2(g)$ is moderately soluble in water and in aqueous solution reacts only to a limited extent to produce H_2CO_3.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \text{ (aq)}$$

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+, \qquad\qquad pK_{a_1} = 6.11$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ ; \qquad\qquad pK_{a_2} = 10.25$$
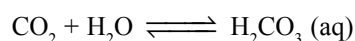
In the H_2CO_3, HCO_3^- buffer system we deal only with the first ionisation step (K_{a_1}) : H_2CO_3 is weak acid and HCO_3^- is the conjugate base (salt). CO_2 enters the blood from tissues as the by - product of metabolic reaction. In lungs, CO_2 (g) is exchanged for O_2 (g), which is transported throughout the body by the blood.

1. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentration. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3 in order to maintain its pH? :

    (A) 40 mL   **(B)** 38 mL   **(C)** 50 mL   **(D)** 78 mL

2. Important diagnostic analysis in the blood is :

    (A) $[H_2PO_4^-]/[HPO_4^-]$ **(B)** $[HCO_3^-]/[CO_2]$

    (C) $[CO_3^{2-}]/[HCO_3^{2-}]$ **(D)** $[PO_4^{3-}]/[HPO_4^{2-}]$

3. Following reaction occurs in the body :

    $$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

    If CO_2 escapes from the system :

    (A) pH will decreases

    (B) pH will increases

    (C) $[H_2CO_3]$ remains unchanged

    (D) forward reaction is promoted

Comprehension # 5

Phosphoric acid is of great importance in fertilizer production. Besides, phosphoric acid and its various salts have a number of application in metal treatment, food, detergent and toothpaste industries.

$$pK_{a_1} = 2.12, pK_{a_2} = 7.21, pK_{a_3} = 12.32$$

Small quantities of phosphoric acid are extensively used to impart the sour or tart taste to many soft drinks such as colas and roots beers, in which a density of 1.00 g mL^{-1} contains 0.05% by weight of phosphoric acid.

Phosphoric acid is used as a fertiliser for agriculture and an aqueous soil digesting. 1.00×10^{-3} M phosphoric acid is found to have pH = 7. Zinc is an essential micronutrient for plant growth. Plants can absorb zinc in water soluble from only. In the given soil, zinc phosphate is only the source of zinc and phosphate ions, K_{sp} (zinc phosphate) = 9.1×10^{-33}.

1.   Phosphoric acid is a tribasic acid with three-step ionisation constants. Thus, its structure is :

(A) $H-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-O-H$ (B) $H-\underset{\underset{O}{\|}}{\overset{\overset{O-H}{|}}{P}}-O-H$ (C) $H-O-\underset{\underset{O}{\|}}{\overset{\overset{O-H}{|}}{P}}-O-H$ (D) $H-O-\underset{O \quad O}{\overset{\overset{H}{|}}{P}}-H$
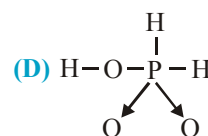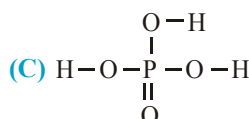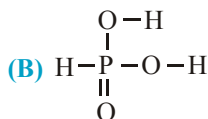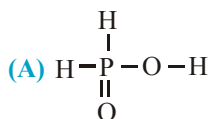
2.   What is the pH of the cola assuming that the acidity of the cola arises only from phosphoric acid and second and third ionisation constants are of no importance ?

(A) 2.2   (B) 3.3   (C) 4.4   (D) 1.8

3.   Molar concentration of phosphate ion in the soil with pH 7 is :

(A) 1.2×10^{-4} M   (B) 2.2×10^{-4} M

(C) 1×10^{-3} M   (D) 1.1×10^{-10} M

4.   Concentration of $[Zn^{2+}]$ in the soil is :

(A) 9.1×10^{-5} M   (B) 5.7×10^{-9} M

(C) 4.0×10^{-10} M   (D) 3.0×10^{-6} M

Exercise # 4 — [Subjective Type Questions]

1. Calculate the change in pH when 4 gm of solid NaOH & 10 mmol of H_2SO_4 are added to a solution of volume 5 litre, which was prepared by mixing 20 mmol of HCl, 40 mmol of H_2SO_4 and 2 gm of NaOH and sufficient water. Ignore the volume change. (log 2 = 0.3, log 3 = 0.48)

2. If both the functional groups of salicylic acid, HOC_6H_4COOH, ionise in water, with $K_a = 1 \times 10^{-3}$ for the –COOH group and 4.2×10^{-13} for the –OH group, calculate pH of the saturated solution of the acid. (Solubility of salicylic acid in water = 1.725 g/L, log 2 = 0.3).

3. A solution is prepared by mixing of acetic acid ($K_a = 2 \times 10^{-5}$) and HCl. In the mixture acetic acid is 0.2 M and HCl is 0.1 M. Calculate
(i) pH of 0.2 M acetic acid and its degree of dissociation.
(ii) pH of final solution.
(iii) CH_3COO^- ion concentration in final solution.
(iv) % decrease of α of acetic acid due to common ion effect.

4. If the acid-base reaction $HA(aq) + B^-(aq) \rightleftharpoons HB(aq) + A^-(aq)$ has a $K_{eq.} = 10^{-4}$, which of the following statements are true ?
(i) HB is stronger acid than HA
(ii) HA is stronger acid than HB
(iii) HA and HB have the same acidity
(iv) B^- is stronger base than A^-
(v) A^- is stronger base than B^-
(vi) B^- and HB are conjugate acid-base pair
(vii) the acid and base strengths connot be compared

5. A 1 litre solution of pH = 6 (solution of a strong acid) is added to the 7/3 litre of water. What is the pH of resulting solution. (log 2 = 0.3) (Neglect the common ion effect on H_2O).

6. If the equilibrium constant for the reaction of weak acid HA with strong base is 10^9, then pH of 0.1 M Na A is

7. K_a for ascorbic acid (HAsc) is 5×10^{-5}. Calculate the hydrogen ion concentration and percentage hydrolysis in an aqueous solution in which concentration of Asc^- ions is 0.02 M .

8. The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodiums nitrite solution and also its degree of hydrolysis.

9. Consider a solution of monoprotic weak acid having dissociation constant K_a. What is the minimum concentration C in terms of K_a, such that the concentration of the undissociated acid can be equated to C within a 10% limit of error. Assume that activity coefficient corrections are negligigible.

10. How many mole of $Ca(OH)_2$ must be dissolved to produce 250 mL of an aqueous solution of pH 10.65, assuming complete dissociation ?

11. A typical aspirin tablet contains 324 mg of aspirin (acetyl salicylic acid $C_9H_8O_4$) a monoprotic acid having $K_a = 3.0 \times 10^{-4}$. What is the degree of dissociation and pH of the solution if two aspirin tables are dissolved to prepare 300 mL solution in water.

12. The ionization constant of dimethyl amine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethyl amine is ionized if the solution is also 0.1 M in NaOH ?

13. Calculate the degree of ionization of 0.05 M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution is also **(a)** 0.01 M and **(b)** 0.1 M in hydrochloric acid ?

14. Phenol (C_6H_5OH, $K_a = 1.3 \times 10^{-10}$) is a weak acid used in mouth washes and pyridine (C_5H_5N, $K_b = 1.8 \times 10^{-9}$) is a weak base used as a solvent. Calculate the value of K_n for neutralizatin of phenol by pyridine. Does the neutralisation reaction proceed veryfar towards completion ?

15. A 50 mL solution of 0.125 M HCOONa (aq.) is mixed with 10 mL of 0.025 M HCl (aq.). Calculate the pH and the molarity of HCOOH in the mixture. pK_a for HCOOH = 3.75.

16. Calculate $[H^+]$ in a 0.20 M solution of dichloroacetic acid $[K_a = 5 \times 10^{-2}]$ that also contains 0.1 M sodium dichloroacetate. Neglect hydrolysis of sodium salt.

17. An aqueous solution contains 10% ammonia by mass and has a density of 0.952 g cm^{-3}. Calculate hydroxyl and hydrogen ion concentration in this solution. K_a for $NH_4^+ = 5.0 \times 10^{-10}$ M. **[Roorkee-95]**

18. A solution contains 0.10 M H_2S and 0.2 M HCl. Calculate the concentration of $[S^{2-}]$ and $[HS^-]$ ions in the solution For H_2S, $K_{a1} = 1.0 \times 10^{-7}$, $K_{a2} = 1.3 \times 10^{-13}$ **[Roorkee-92]**

19. Prove that degree of dissociation of a weak acid is given by :

$$\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$$

where K_a is its dissociation constant.

20. Calculate the concentration of fluoroacetic acid which is required to get $[H^+] = 1.50 \times 10^{-3}$ M. K_a of acid = 2.5×10^{-3}

21. Diborane, B_2H_6 reacts with water to form boric acid and hydrogen. What is the pH of solution which results when 1.0 g B_2H_6 reacts with 100 mL water. Assume that final volume be 100 mL water. K_a for $H_3BO_3 = 7.3 \times 10^{-10}$. (B = 10.8)

22. Calculate the pH of solution obtained by mixing 10 mL of 0.1 M HCl and 40 mL of 0.2 M H_2SO_4.

23. Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.

24. 100 mL of HCl gas at 25°C and 740 mm pressure were dissolved in one litre of water. Calculate the pH of solution. Given, V.P. of H_2O at 25°C is 23.7 mm.

25. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M ?
$[K_a$ for $C_6H_5NH_3^+ = 2.4 \times 10^{-5}$ M] **[Roorkee-96]**

26. What volume of concentrated HCl(aq) that is 36.5% HCl by mass, and has a density 1.25 g cm^{-3} is required to produce 2.5 L of a solution of pH = 1.

27. Calculate the concentrations of all species present in 0.1 M H_3PO_4 solution. $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, $K_3 = 3.6 \times 10^{-13}$.

28. For an organic monoprotic acid solution of concentration C_0 mole litre^{-1}, if K_a has a value comparable to K_w, show that the hydronium ion concentration is given by :

$$[H^+] = \left[\frac{K_w}{[H^+]} + \frac{K_a.C_0}{[K_a + H^+]} \right]$$

If $[H^+] = 10^{-3}$ M and $C_0 = 10^{-1}$ M in a solution of some organic monoprotic acid, what, according to the above equation, must be the order of magnitude of K_a ?

29. Calculate $[H^+]$ and $[CHCl_2COO^-]$ in a solution that is 0.01 M in HCl and 0.01 M in CCl_2COOH.
Take $(K_a = 2.0 \times 10^{-2})$.

30. K_1 and K_2 for oxalic acid, $H_2C_2O_4$, are 5.6×10^{-2} and 5.0×10^{-6}. What is $[OH^-]$ in a 0.5 mM solution of $Na_2C_2O_4$?

31. Calculate the pH of a 0.15 M aquesous solution of $AlCl_3$. Given : $\log 2 = 0.3$, $\log 3 = 0.48$
$[Al(H_2O)_6]^{3+} + H_2O\,(\ell) \rightleftharpoons [Al(H_2O)_5\,OH]^{2+}\,(aq) + H_3O^+\,(aq), K_a = 1.5 \times 10^{-5}$

32. The dissociation constant for hydrogen sulphide (dissociated into $2H^+$ and S^{2-}) is 1.1×10^{-22} at 18°C. What is the concentration of sulphide ion in a 0.1 N hydrochloric acid solution which is saturated with hydrogen sulphide at 18°C, assuming that the concentration of H_2S is 0.1 M?

33. The artificial sweetener saccharin is a weak organic acid that can be represented by HSac. On adding in a drink, it ionizes to give H^+ ions & Sac^- ions. Calculate $[Sac^-]$ ions if 0.002 mole of saccharin is added in a 250 mL glass of black tea containing lemon juice having an initial pH of 2.0. $K_a\,(HSac) = 2 \times 10^{-12}$

34. The ionization constant of phenol is 1.0×10^{-10} . What is the concentration of phenolate ion in 0.05 M solution of phenol ? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate ?

35. Phosphoric acid ionizes according to the equations
$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)\,; \qquad K_1 = 7 \times 10^{-3}$$
$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)\,; \qquad K_2 = 6 \times 10^{-8}$$
$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)\,; \qquad K_3 = 4.5 \times 10^{-13}$$
(a) If you are asked to prepare a buffer with a pH = 7.00, identify the species that should be used in the solution and calculate their molar ratio.
(b) Assume 50 mL of the buffer prepared in part **(a)** is available in which more abundant species has a concentration of 0.10 M. If to this solution 20 mL 0.1 M NaOH is added further, what will be the new pH ?
$(\log 2 = 0.3, \log 3 = 0.48)$

36. 0.98 gm of H_3PO_4 is dissolved in 100 ml of buffer solution (pH = 5). Calculate the equilibrium concentrations of $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and H_3PO_4 in the solution. $Ka_1 = 10^{-3}$, $Ka_2 = 10^{-8}$, $Ka_3 = 0^{-12}$.

37. A 0.252 g sample of unknown organic base is dissolved in water and titrated with a 0.14 M HCl solution. After the addition of 20 mL of acid, a pH of 10.7 is recorded. The equivalence point is reached when a total of 40 mL of HCl is added. The base and acid combine in a 1 : 1 ratio.
(a) What is the molar mass of the organic base ?
(b) What is the K_b value for the base ?

38. An NH_4^+ - NH_3 buffer is supposed to keep the pH of the solution constant within 0.3 pH unit during the reaction.
$$CH_3COOCH_3(aq) + 2H_2O\,(aq) \longrightarrow CH_3COO^-(aq) + H_3O^+(aq) + CH_3OH(aq)$$
If this solution had initial concentrations : $[NH_4^+]_0 = 0.1$ M, $[NH_3]_0 = 0.06$ M, $[CH_3COOCH_3]_0 = 0.02$ M.
What would be the initial and final pH of the solution ? Is this a satisfactory buffer ? $[K_b(NH_3) = 1.8 \times 10^{-5}$, $\log 2 = 0.3, \log 3 = 0.48]$.

39. A certain solution has a hydrogen ion concentration 4×10^{-3} M. At pH = 2, half of the indicator, thymol blue is in unionised form. Find the % of indicator in unionised form in the solution with $[H^+] = 4 \times 10^{-3}$ M.

40. How much of 0.3 M ammonium hydroxide should be mixed with 30 mL of 0.2 M solution of ammonium chloride to give buffer solutions of pH 8.65 and 10. (Given pK_b of $NH_4OH = 4.75$, $\log 2 = 0.3$, $\log 0.18 = -0.75$)

41. Calculate the change in pH of one litre of buffer solution containing 0.10 mole each of NH_3 & NH_4Cl upon addition of, **(i)** 0.02 mole of dissolved gaseous HCl **(ii)** 0.02 mole of dissolved NaOH .
Assume no change in solution volume . (K_b for $NH_3 = 1.8 \times 10^{-5}$) **[Roorkee-92]**

42. What volume of 0.10 M sodium formate solution should be added to 50 ml of 0.05 M formic acid to produce a buffer solution of pH 4. [pK_a for formicacid is 3.7] **[Roorkee-90]**

43. Calculate the amount of NH_3 and NH_4CI required to prepare a buffer solution of pH 9.0 when total concentration of buffering reagents is 0.6 mol L^{-1}. (pK_b for $NH_3 = 4.7$, $\log 2 = 0.30$). **[Roorkee-97]**

44. Calculate the pH of a buffer solution prepared by dissolving 31.8 g of Na_2CO_3 in 500 mL of an aqueous solution containing 150 mL of 1 M HCl. K_a for $HCO_3^- = 5 \times 10^{-11}$.

45. A 0.1 M solution of weak acid HA is 1% dissociated at 25ºC. What is its K_a ? If this solution is dissociated with respect to NaA 0.2 M, what will be the new degree of dissociation of HA and pH ?

46. 0.1 M CH_3COOH solution is titrated against 0.05 M NaOH solution. Calculate pH at 1/4th and 3/4 stages of neutralization of acid. The pH for 0.1 M CH_3COOH is 3.

47. How many mole of HCI will be required to prepare one litre of buffer solution (containing NaCN+ HCN) of pH 8.5 using 0.01 g formula weight of NaCN ? $K_{HCN} = 4 \times 10^{-10}$ **[IIT-98]**

48. A 40.0 ml solution of a weak base BOH is titrated with 0.1 N HCl solution . The pH of the solution is found to be 10.04 and 9.14 after adding 5.0 ml and 20.0 ml of the acid respectively . Find out the dissociation constant of the base.

[IIT-91]

49. 25 ml of a dilute aqueous solution of p-hydroxy benzoic acid is titrated with NaOH (aq), the solution has pH = 4.7 when 8.12 ml of 0.02M NaOH had been added, and pH = 7.5 after 16.24 ml had been added (the equivalence point). Use these data to determine K_{a1} and K_{a2} for p-hydroxy benzoic acid. (log 2 = 0.3)

50. How many mmole HCI should be added to 100 ml of a 0.1 M solution of an ampholyte ($pK_a = 9.7$ and $pK_b = 11.7$) to make a solution of pH = 2.6 ? The volume change is neglected. $pK_w = 14.0$.

51. All enviremental chemist needs a carbonate buffer of pH 10.00 to study the effects of the acidification of limestone– rich soils. How many grams of Na_2CO_3 must be added to 1.5 L of freshly prepared 0.20 M $NaHCO_3$ to make the buffer? K_a of $HCO_3^- = 4.7 \times 10^{-11}$.(log 4.7 = 0.672)

52. To a solution of acetic acid, solid sodium acetate is added gradually. When x mole of salt is added, the pH has a certain value. If y mole of salt is added, the pH at this time changes by 0.6 units to previous pH. What is the ratio of x and y. Given that y > x.

53. Calculate the pH at the equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M of NaOH. [K_a for acetic acid is 1.9×10^{-5}]   **[Roorkee-90]**

54. A 0.50 gram mixture containing $NaHCO_3$, Na_2CO_3 and KCl was dissolved in 50.00 mL water and titrated with 0.15 M HCl resulting in the following titration curve.

Determine weight percentage of $NaHCO_3$, Na_2CO_3 and KCl in the mixture.

55. 0.2 moles of $MgCl_2(s)$ is mixed with 0.2 moles of NaOH(s) in a total volume of 1.0 litre.
(log2 = 0.3, log3 = 0.48)
(a) Calculate pH of this solution. K_{sp} of $Mg(OH)_2$ is 1.6×10^{-12} .
(b) Also determine pH when 0.04 moles of NaOH(s) is added in the solution **(a)**.
(c) Also determine pH of solution obtained after adding 0.04 mole of HCl(g) to solution **(a)**.

56. The solubility product $Mg(OH)_2$ in water at 25˚C is 2.56×10^{-13}(mol/lt)³ while that of $Al(OH)_3$ is 4.32×10^{-34}(mol/lt)⁴. If s_1 and s_2 are the solubilities of $Mg(OH)_2$ and $Al(OH)_3$ in water in mol/lt at 25⁰C, what is the approximate ratio, s_1/s_2 ?

57. Silver ion forms $Ag(CN)_2^-$ in the presence of excess CN^-. How much solid KCN should be added to 1 litre of a 0.0009 M Ag^+ solution in order to reduce $[Ag^+]$ to 1×10^{-19}. [K_{diss} of $Ag(CN)_2^- = 1 \times 10^{-21}$]

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58. A buffer solution is 0.25 M CH_3COOH and 0.15 M CH_3COONa, saturated with H_2S (0.1 M) and has $[Mn^{2+}] = 0.015$ M. Given : $K_a\,(CH_3COOH) = 1.8 \times 10^{-5}$, $K_a(H_2S) = 9 \times 10^{-21}$, $K_{sp}(MnS) = 2.4 \times 10^{-13}$.
(a) Will MnS precipitate
(b) Which buffer component should be increased in concentration and to which minimium value to just start precipition of MnS ?

59. Calculate the solubility of CaC_2O_4 in a solution with a fixed H_3O^+ concentration of 10^{-4} M. The oxalate containing species ($C_2O_4^{2-}$, $HC_2O_4^-$, $H_2C_2O_4$) exist in solution & the relevant equilibria are,
$$CaC_2O_4\,(s) \rightleftharpoons Ca^{2+} + C_2O_4^{2-} \qquad K_{sp} = 2.7 \times 10^{-9}$$
$$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^-\ K_1 = 5 \times 10^{-2}$$
$$HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-}\ K_2 = 5 \times 10^{-5}$$

60. 0.01 mole of $AgNO_3$ is added to 1 litre of a solution which is 0.1 M in Na_2CrO_4 and 0.005 M in $NaIO_3$. Calculate the mole of precipiate formed at equilibrium and the concentrations of Ag^+, IO_3^- and CrO_4^{2-} (K_{SP} values of Ag_2CrO_4 and $AgIO_3$ are 10^{-8} and 10^{-13} respectively)

61. The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the saturated solution.

62. A solution made up to be 0.0100 M $Co(NO_3)_2$ and 0.0200 M N_2H_4 was found to have an equilibrium concentration of $[Co^{2+}]$ is 6×10^{-3} M. Assuming that the only complex formed was $Co(N_2H_4)^{2+}$, what is the apparent K_f for complex formation ?

63. In an excess of $NH_{3(aq.)}$, Cu^{2+} ion forms a deep blue complex ion $[Cu(NH_3)_4]^{2+}$ having formation constant $K_f = 5.6 \times 10^{11}$. Calculate the concentration of Cu^{2+} ion a solution prepared by adding 5.0×10^{-3} mol of $CuSO_4$ to 0.50 litre of 0.40 M NH_3.

64. K_{SP} of $BaSO_4$ is 1.6×10^{-9}. Calculate its solubility in :
(i) pure water ; (ii) 0.10 M $BaCl_2$.

65. K_{SP} for $PbCl_2$ is 10^{-13}. What will be $[Pb^{2+}]$ in a solution prepared by mixing 100 mL of 0.1 M $Pb(NO_3)_2$ and 1 mL of 1 M HCl ?

66. $BaSO_4$ and $BaCrO_4$ have solubility product values in the ratio 1 : 2.5 at 25ºC. When pure water is saturated with both solids simultaneously, the total concentration of Ba^{2+} ion in the solution is 1.4×10^{-5} M. Calculate the solubility product of $BaCrO_4$. Calculate also the solubility of $BaSO_4$ in 0.01 M Na_2SO_4 solution.

67. A particular water sample has 136 ppm $CaSO_4$. What fraction of the water must be evaporated in a container before solid $CaSO_4$ begins to deposit K_{SP} of $CaSO_4 = 9.0 \times 10^{-6}$?

68. To a solution of 0.1 M Mg^{2+} and 0.8 M NH_4Cl, an equal volume of NH_3 is added which just gives precipitate. Calculate $[NH_3]$ in solution. K_{SP} of $Mg(OH)_2 = 1.25 \times 10^{-11}$ and K_b of $NH_4OH = 2 \times 10^{-5}$.

69. 10 mL of 0.3 M Na_2SO_4 are mixed with 20 mL solution having initially 0.1 M Ca^{2+} and 0.1 M Sr^{2+} in it. What are the final concentration of Ca^{2+}, Sr^{2+} and SO_4^{2-} in solution ? Given K_{SP} of $SrSO_4 = 7.6 \times 10^{-7}$ and K_{SP} of $CaSO_4 = 2.4 \times 10^{-5}$.

70. 100.0 mL of a clear saturated solution of Ag_2SO_4 is added to 250.0 mL of a clear saturated solution of $PbCrO_4$. Will any precipitate form and if so what ? Given K_{SP} values for Ag_2SO_4, Ag_2CrO_4, $PbCrO_4$ and $PbSO_4$ are 1.4×10^{-5}, 2.4×10^{-12}, 2.8×10^{-13} and 1.6×10^{-8} respectively.

71. What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K. For calcium sulphate, K_{SP} is 9×10^{-6}.

72. 50 mL of a sample of clear saturated solutions of Ag_2CrO_4 requires 20 mL of a X M $Pb(NO_3)_2$ for its titration. What is the value of X. K_{SP} for Ag_2CrO_4 is 3.2×10^{-12}.

73. Calculate pH of a saturated solution of $Mg(OH)_2$. K_{SP} for $Mg(OH)_2$ is 8.9×10^{-12}.

74. 0.00050 mole of $NaHCO_3$ is added to a large volume of a solution buffered at pH = 8.00. How much material will exist in each of the three forms, H_2CO_3, HCO_3^- and CO_3^{2-} K_1 and K_2 for H_2CO_3 are 4.9×10^{-7} and 10^{-12} respectively.

75. K_{SP} of $PbBr_2$ is 2.56×10^{-7}. If the salt is 80% dissociated in solution, calculate the solubility of salt in g per litre.

76. 25.0 mL clear saturated solution of PbI_2 (aq) requires 13.3 mL of $AgNO_3$(aq) solution for complete precipitation. What is molarity of $AgNO_3$ solution ? K_{SP} of PbI_2 is 7.1×10^{-9}.

77. K_{SP} for $SrF_2 = 2.8 \times 10^{-9}$ at 25°C. How much NaF should be added to 100 mL of solution having 0.016 M in Sr^{2+} ions to reduce its concentration to 2.5×10^{-3} M ?

78. 0.10 mole of AgCl(s) is added to 1 litre of H_2O. Next crystal of NaBr are added until 75% of the AgCl is converted to AgBr(s), the less soluble silver halide. What is Br⁻ at this point ? K_{SP} of AgCl is 1.75×10^{-10} and K_{SP} of AgBr is 5.25×10^{-13}.

79. The K_{SP} of $Ca(OH)_2$ is 4.42×10^{-5} at 25°C. A 500 mL of saturated solution $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in mg is precipitated ? **[IIT-92]**

80. A sample of hard water contains 0.005 moles of $CaCl_2$ per litre. What is the minimum concentration of Na_2SO_4 which must be added for removing Ca^{2+} ions from the water sample. K_{sp} for $CaSO_4$ is 2.4×10^{-5} at 25°C.

81. The solubility of $CaCO_3$ is 7 mg / litre. Calculate the solubility product of $BaCO_3$ from this information and from the fact that when Na_2CO_3 is added slowly to a solution containing equimolar concentration of Ca^{+2} and Ba^{+2}, no precipitate of $CaCO_3$ is formed until 90% of Ba^{+2} has been precipitated as $BaCO_3$

82. Determine solubility of $CaF_2(K_{sp} = 4 \times 10^{-11})$
    (a) at pH = 7,   **(b)** at pH = 5. $K_a = 3.45 \times 10^{-4}$

83. Equal volumes of 0.02 M $AgNO_3$ and 0.02 M HCN were mixed. Calculate [Ag⁺] at equilibrium. Take $K_a (HCN) = 4 \times 10^{-10}$, $K_{sp} (AgCN) = 4 \times 10^{-16}$

84. An aqueous solution of a metal bromide MBr_2 (0.05 M) is saturated with H_2S. What is the minimum pH at which MS will precipitate ? K_{sp} for MS = 6.0×10^{-21}, concentration of saturated $H_2S = 0.1$ M , $K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$ for H_2S.

[IIT-93]

85. Calculate pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.10 M Mg^{2+} ions. K_{SP} of $Mg(OH)_2 = 1 \times 10^{-11}$. **[Roorkee-92]**

86. A solution has 0.05 M Mg^{2+} & 0.05 M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in this solution. K_{sp} of $Mg(OH)_2 = 9.0 \times 10^{-12}$ & ionization constant of $NH_3 = 1.8 \times 10^{-5}$. **[Roorkee-93]**

87. Determine the number of moles of AgI which may be dissolved in 1.0 litres of 1.0 M CN⁻ solution . K_{sp} for AgI & K_f for $[Ag(CN)_2]^-$ are 1.2×10^{-17} M² & 7.1×10^{19} M⁻² respectively. **[Roorkee-98]**

88. Calculate the Simultaneous solubility of AgCl and AgI.
$K_{sp} (AgCl) = 1 \times 10^{-10}$, $K_{sp} (AgI) = 8.5 \times 10^{-17}$

89. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8. **[JEE-1999]**

90. **(a)** At what minimum pH will 1.0×10^{-3} mol of $Al(OH)_3$ go into 1L solution as $[Al(OH)_4^-]$.
    (b) At what maximum pH will 5.0×10^{-3} mol of $Al(OH)_3$ go into 1L solution at Al^{3+}?
    Given $K_{sp} [Al(OH)_3] = 5.0 \times 10^{-33}$ and for $[Al(OH)_4^-] \rightleftharpoons Al^{3+} + 4OH^-$. K = 1.0×10^{-34}.

91. At what concentration of OH⁻ , is the solubility of $Zn(OH)_2$ minimum ? What is the minimum solubility ? Given K_{sp} $[Zn(OH)_2]$ and $K_f [Zn(OH)_4^{2-}]$ are 1.2×10^{-17} and 10^{16} respectively.

Exercise # 5 | Part # I | [Previous Year Questions] [AIEEE/JEE-MAIN]

1. The conjugate base of $H_2PO_4^-$ is **[AIEEE-2004]**

   (1) PO_4^{3-} (2) P_2O_5 (3) H_3PO_4 (4) HPO_4^{2-}

2. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is s. The corresponding solubility product is K_{sp}. s is given in terms of K_{sp} by the relation **[AIEEE-2004]**

   (1) $s = (K_{sp}/128)^{1/4}$ (2) $s = (128K_{sp})^{1/4}$ (3) $s = (256K_{sp})^{1/5}$ (4) $s = (K_{sp}/256)^{1/5}$

3. The solubility product of a salt having general formula MX_2, in water is : 4×10^{-12}. The concentration of M^{2+} ions in the saturated aqueous solution of the salt is : **[AIEEE-2005]**

   (1) 2.0×10^{-6} M (2) 1.0×10^{-4} M (3) 1.6×10^{-4} M (4) 4.0×10^{-10} M

4. What is the conjugate base of OH^- ? **[AIEEE-2005]**

   (1) O_2 (2) H_2O (3) O^- (4) O^{2-}

5. Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be **[AIEEE-2005]**

   (1) 3.98×10^8 (2) 3.88×10^6 (3) 3.68×10^{-6} (4) 3.98×10^{-6}

6. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be **[AIEEE-2007]**

   (1) 5.0×10^{-15} (2) 0.2×10^5 (3) 5.0×10^{-5} (4) 5.0×10^{15}

7. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA, in which 50% of the acid is ionized, is : **[AIEEE-2007]**

   (1) 9.5 (2) 7.0 (3) 4.5 (4) 2.5

8. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (Molecular mass = 283) the equilibrium which sets in is

   $$AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$$

   If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 ml of its saturated solution? **[AIEEE-2007]**

   (1) 1.0×10^{-7} g (2) 1.0×10^{-4} g (3) 28.3×10^{-2} g (4) 2.83×10^{-3} g

9. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be **[AIEEE-2008]**

   (1) 4.79 (2) 7.01 (3) 9.22 (4) 9.58

10. Solid $Ba(NO_3)_2$ is gradually dissolved in 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form ? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$) : **[AIEEE-2009]**

   (1) 5.1×10^{-5} M (2) 8.1×10^{-8} M (3) 8.1×10^{-7} M (4) 4.1×10^{-5} M

11. Solubility product of silver bromide is 5.0×10^{-13} . This quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is : **[AIEEE-2010]**

    (1) 1.2×10^{-10} g (2) 1.2×10^{-9} g (3) 6.2×10^{-5} g (4) 5.0×10^{-8} g

12. At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At Which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions ? **[AIEEE-2010]**

(1) 9   (2) 10   (3) 11   (4) 8

13. Three reactions involving $H_2PO_4^-$ are given below : **[AIEEE-2010]**

(i) $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$

(ii) $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$

(iii) $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid ?

(1) (ii) only   (2) (i) and (ii)   (3) (iii) only   (4) (i) only

14. In aqueous solution the ionization constants for carbonic acid are **[AIEEE-2010]**

$K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid.

(1) The concentration of CO_3^{2-} is 0.034 M.

(2) The concentration of CO_3^{2-} is greater than that of HCO_3^-.

(3) The concentration of H^+ and HCO_3^- are approximately equal.

(4) The concentration of H^+ is double that of CO_3^{2-}.

15. How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? **[JEE(Main) 2013]**

(1) 0.1 L   (2) 0.9 L   (3) 2.0 L   (4) 9.0 L

16. Which of the following salts is the most basic in aqueous solution ? **[JEE(Main) 2018]**

(1) CH_3COOK (2) $FeCl_3$ (3) $Pb(CH_3COO)_2$ (4) $Al(CN)_3$

17. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is: **[JEE(Main) 2018]**

(1) 3×10^{-20} (2) 6×10^{-21} (3) 5×10^{-19} (4) 5×10^{-8}

Part # II ▷▷ **[Previous Year Questions][IIT-JEE ADVANCED]**

1. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 0.1 M solution of NaX is : **[JEE-2004]**

(A) 0.0001%   (B) 0.01 %   (C) 0.1 %   (D) 0.15 %

2. 0.1 M NaOH is titrated with 0.1 M HA till the end point; K_a for HA is 5.6×10^{-6} and degree of hydrolysis is less compared to 1. Calculate pH of the resulting solution at the end point. **[JEE-2004]**

3. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution? What will be the H^+ concentration in the solution? **[JEE-2005]**

(A) 8×10^{-2} M   (B) 8×10^{-11} M   (C) 1.6×10^{-11} M   (D) 8×10^{-5} M

4. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base (K_b = 1 x 10^{-12} at 25° C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C. The

concentration of H⁺ at equivalence point is (K_w = 1 x 10^{-14} at 25°C) **[JEE-2008]**

(A) 3.7 x 10^{-14} M (B) 3.2 x 10^{-7}M (C) 3.2 x 10^{-2} M (D) 2.7 x 10^{-2} M

5. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm⁻³) of the salts at temperature T are in the order: **[JEE-2008]**

(A) $MX > MX_2 > M_3X$ (B) $M_3X > MX_2 > MX$

(C) $MX_2 > M_3X > MX$ (D) $MX > M_3X > MX_2$

6. The dissociation constant of a substituted benzoic acid at 25ºC is 1.0×10^{-4}. The pH of 0.01 M solution of its sodium salt is **[JEE-2009]**

7. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is : **[JEE-2010]**

KCN K_2SO_4 $(NH_4)_2C_2O_4$ NaCl $Zn(NO_3)_2$

$FeCl_3$ K_2CO_3 NH_4NO_3 LiCN

8. Aqueous solutions of HNO_3, KOH, CH_3COOH, and CH_3COONa of identical concentrations are provided. The pair (s) of solutions which form a buffer upon mixing is (are) : **[JEE-2010]**

(A) HNO_3 and CH_3COOH (B) KOH and CH_3COONa

(C) HNO_3 and CH_3COONa (D) CH_3COOH and CH_3COONa

9. In 1 L saturated solution of AgCl [K_{sp}(AgCl) = 1.6×10^{-10}], 0.1 mol of CuCl [K_{sp}(CuCl) = 1.0×10^{-6}] is added. The resultant concentration of Ag⁺ in the solution is 1.6×10^{-x}. The value of "x" is : **[JEE-2011]**

10. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is $1/100^{th}$ of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is : **[JEE(Advanced)-2013]**

(A) 1×10^{-4} (B) 1×10^{-5} (C) 1×10^{-6} (D) 1×10^{-3}

11. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation **(A)** of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is **[JEE(Advanced)-2014]**

12. The correct statement(s) about the oxoacids, $HClO_4$ and HClO, is(are) **[JEE(Advanced)-2017]**

(A) The central atom in both $HClO_4$ and HClO is sp^3 hybridized

(B) $HClO_4$ is formed in the reaction between Cl_2 and H_2O

(C) The conjugate base of $HClO_4$ is weaker base than H_2O

(D) $HClO_4$ is more acidic than HClO because of the resonance stabilization of its anion

13. The solubility of a salt of weak acid (AB) at pH 3 is Y × 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]**

14. Dilution processes of different aqueous solutions, with water, are given in LIST-I. The effects of dilution of the solution on [H$^+$] are given in LIST-II.

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

LIST - I

(P) (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL

(Q) (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic dilution acid) diluted to 80 mL

(R) (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL

(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).

LIST-II

(1) The value of [H$^+$] does not change on dilution

(2) The value of [H$^+$] changes to held of its initial value on dilution

(3) The value of [H$^+$] changes to two times of its initial value on dilution

(4) The value of [H]$^+$ changes to $\dfrac{1}{\sqrt{2}}$ 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 $\rightarrow$ 4, 5 ; Q $\rightarrow$ 2 ; R $\rightarrow$ 3 ; S $\rightarrow$ 1

(B) P $\rightarrow$ 4, 4 ; Q $\rightarrow$ 3 ; R $\rightarrow$ 2 ; S $\rightarrow$ 3

(C) P $\rightarrow$ 1 ; Q $\rightarrow$ 4 ; R $\rightarrow$ 5 ; S $\rightarrow$ 3

(D) P $\rightarrow$ 1, 5 ; Q $\rightarrow$ 5 ; R $\rightarrow$ 4 ; S $\rightarrow$ 1

MOCK TEST

SECTION - I : STRAIGHT OBJECTIVE TYPE

1. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid
    $$HCl\,(aq) + CH_3COOH\,(aq) \rightleftharpoons Cl^-\,(aq) + CH_3\,COOH_2{}^+(aq).$$
    The set that characterises the conjugate acid-base pairs is
    (A) (HCl, CH_3COOH) and $(CH_3COOH_2{}^+, Cl^-)$ (B) $(HCl, CH_3COOH_2{}^+)$ and (CH_3COOH, Cl^-)
    (C) $(CH_2COOH_2{}^+, HCl)$ and (Cl^-, CH_3COOH) (D) (HCl, Cl^-) and $(CH_3COOH_2{}^+, CH_3COOH)$.

2. The following equilibrium is established when $HClO_4$ is dissolved in weak acid HF.
    $$HF + HClO_4 \rightleftharpoons ClO_4{}^- + H_2F^+$$
    Which of the following is correct set of conjugate acid base pair ?
    (A) HF and $HClO_4$ (B) HF and $ClO_4{}^-$ (C) HF and H_2F^+ (D) $HClO_4$ & H_2F^+

3. Identify the amphoteric species from the following :
    (I) H_2O (II) NH_3 (III) $H_2PO_4{}^-$ (IV) $HCO_3{}^-$
    (A) I, II   (B) III, IV   (C) I, II, III   (D) I, II, III, I

4. Which of the following relations is correct ?
    (A) $\Delta G^\circ = RT \ln K_{eq}$ (B) $[H_3O^+] = 10^{pH}$

    (C) $\log \dfrac{Kw_2}{Kw_1} = \dfrac{\Delta H^\circ}{2.303R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$ (D) $[OH^-] = 10^{-7}$, for pure water at all temperatures.

5. Which of the following is incorrect ?
    (A) K_a (weak acid). K_b (conjugate weak base) $= K_w$
    (B) K_a (strong acid). K_b (conjugate weak base) $= K_w$
    (C) K_a (weak acid). K_b (weak base) $= K_w$
    (D) K_a (weak acid). K_b (conjugate strong base) $= K_w$

6. K_a for the acid HA is 1×10^{-6}. The value of K for the reaction $A^- + H_3O^+ \rightleftharpoons HA + H_2O$ is
    (A) 1×10^{-6} (B) 1×10^{12} (C) 1×10^{-12} (D) 1×10^6

7. The pK_a value of NH_4^+ is 9. The pK_b value of NH_4OH would be :
    (A) 9   (B) 5   (C) 7   (D) 8

8. Which of the following solution will have a pH exactly equal to 8 ?
    (A) 10^{-8} M HCl solution at 25ºC   (B) 10^{-8} M H$^+$ solution at 25ºC
    (C) 2×10^{-6} M $Ba(OH)_2$ solution at 25ºC   (D) 10^{-5} M NaOH solution at 25ºC

9. Which of the following solution will have pH close to 1.0 ?
    (A) 100 ml of M/10 HCl + 100 ml of M/10 NaOH   (B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH
    (C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH   (D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH.

10. 0.1mol HCl is dissolved in distilled water of volume V then at $\lim_{V \to \infty}$ $(pH)_{solution}$ is equal to
    (A) zero   (B) 1   (C) 7   (D) 14

11.   Dissociation constant of mono basic acids A, B, C and D are 6 x 10^{-4}, 5 x 10^{-5}, 3.6 x 10^{-6} and 7 x 10^{-10}respectively. The pH values of their 0.1M aqueous solution are in the order.
        (A) D> C> B > A   (B) A> B >C > D   (C) D > C > A> B   (D) None

12.   Which statement/relationship is correct?

        (A) pH of 0.1 M HNO_3, 0.1M HCl, 0.1M HI is not equal. (B) $pH = -\log \dfrac{1}{[H^+]}$

        (C) At 25°C the pH of pure water is 7.   (D) The value of pK_w at 25 °C is 7.

13.   Approximate pH of 0.1 M aqueous H_2S solution when K_1 and K_2 for H_2S at 25°C are 1×10^{-7} and 1.3×10^{-13} respectively :
        (A) 4   (B) 5   (C) 6   (D) 8

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

14.   Which of the following solutions when added to 1L of a 0.01 M CH_3COOH solution will cause no change in the degree of dissociation of CH_3COOH and pH of the solution ? $K_a = 1.6 \times 10^{-5}$ for CH_3COOH?
        (A) 0.6 mM HCOOH ($K_a = 8 \times 10^{-4}$)   (B) 0.1 M CH_3COONa
        (C) 0.4 mM HCl   (D) 0.01 M CH_3COOH

15.   Equal volumes of following solutions are mixed, in which case the pH of resulting solution will be average value of pH of two solutions.
        (A) Aqeous HCl of pH = 2, aqueous NaOH of pH = 12
        (B) Aqeous HCl of pH = 2, aqueous HCl of pH = 4
        (C) Aqeous NaOH of pH = 12, aqueous NaOH of pH = 10
        (D) Aqeous CH_3COOH of pH = 5, aqueous NH_3 of pH = 9. [$K_a (CH_3COOH) = K_b (NH_3)$]

16. K_a values for HA, HB and HD are 10^{-5}, 10^{-7} and 10^{-9} respectively. Which of the following will be correct for decimolar aqueous solutions of NaA, NaB and NaD at 25°C?
        (A) $(pH)_{NaA} < (pH)_{NaB}$ (B) $(pH)_{NaD} < (pH)_{NaB}$ (C) $(pH)_{NaA} < (pH)_{NaD}$ (D) $(pH)_{NaB} = 7$

17.   0.1 M CH_3COOH is diluted at 25°C ($K_a = 1.8 \times 10^{-5}$), then which of the following will be found correct
        (A) $[H^+]$ will increase   (B) pH will increase
        (C) number of H^+ will increase   (D) all the above are correct

SECTION - III : ASSERTION AND REASON TYPE

Each question has 5 choices (A), (B), (C), (D) and (E) out of which only one is correct.
(A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1.
(B) Statement-1 is true, Statement-2 is true and Statement-2 is not correct explanation for Statement-1.
(C) Statement-1 is true, Statement-2 is false
(D) Statement-1 is false, Statement-2 is true
(E) Both Statements are false

18.   **Statement-1 :** Aqueous solutions of all strong acids contain only the same acid, the hydronium ion.
        Statement-2 : For all diprotic acids, the equilibrium constant K_{a2}, for the second stage of ionisation is smaller than the equilibrium constant, K_{a1} , for the first stage of ionisation.

19.   **Statement-1 :** 0.20 M solution of NaCN is more basic than 0.20 M solution of NaF.
        Statement-2 : K_a of HCN is very much less than that of HF.

20. **Statement-1 :** A substance that can either act as an acid as well as a base is called ampholyte.
Statement-2 : Bisulphide ion (HS^-) and biscarbonate ion (HCO_3^-) are ampholytes.

21. **Statement-1 :** Addition of HCl(aq) to HCOOH(aq), decrease the ionization of HCOOH(aq)
Statement-2 : Due to common ion effect of H^+, ionization of HCOOH decreased.
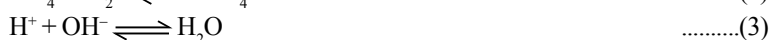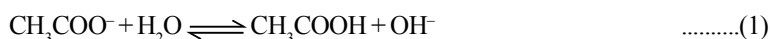
SECTION - IV : COMPREHENSION TYPE

Read the following comprehensions carefully and answer the questions.

Comprehension # 1

Consider a solution of CH_3COONH_4 which is a salt of weak acid & weak base.
The equilibrium involved in the solutions are :

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \qquad \qquad ....(1)$$
$$NH_4^- + H_2O \rightleftharpoons NH_4OH + H^+ \qquad \qquad ....(2)$$
$$H^+ + OH^- \rightleftharpoons H_2O \qquad \qquad ....(3)$$

If we add these three reactions, then the net reaction is

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH \qquad ....(4)$$

Both CH_3COO^- and NH_4^+ get hydrolysed independently and their hydrolysis depends on
(i) their initial concentration

(ii) the value of K_h which is $\dfrac{K_w}{K_a}$ for CH_3COO^- and $\dfrac{K_w}{K_b}$ for NH_4^+.

Since both of the ions were produced from the same salt, their initial concentrations are same. Therefore unless &

untial the value of $\dfrac{K_w}{K_a}$ and $\dfrac{K_w}{K_b}$ or K_a and K_b is same, the degree of hydrolysis of ion can't be same.

To explain why we assume that degree of hydrolysis of cation and anion is same, we need to now look at the third reaction i.e., combination of H^+ and OH^- ions. It is obvious that this reaction happens only because one reaction produced H^+ ion and the other produced OH^- ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. Keep this thing in mind that the equilibrium which has smaller value of equilibrium conxtant is affected more by the common ion effect. For the same reason if for any reason a reaction is made to occur to a greater extent by the comsumption of any one of the product ion, the reaction with the smaller value of equilibrium constant tends to get affected more.

Therefore we conclude that firstly the hydrolysis of both the ions ocurs more in the presence of each other (due to consumption of the product ions) than in each other is absence. Secondly the hydrolysis of the ion which occurs to a lesser extent (due to smaller value of K_h) is affected more than the one whose K_h is greater. Hence we can see that the degree of hydrolysis of both the ions would be close to each other when they are getting hydrolysed in the presence of each other.

22. In the hydrolysis of salt of weak acid & weak base :
(A) degree of hydrolysis of cation and anion is different
(B) degree of hydrolysis of cation and anion is same
(C) degree of hydrolysis of cation and anion is different and they can never be assumed same.
(D) degree of hydrolysis of cation and anion is different but they are very close to each other when they are getting hydrolysed in the presence of each other.

23. For 0.1 M CH_3COONH_4 salt solution given, K_a (CH_3COOH) = K_b (NH_4OH) = 2×10^{-5}.
In this case : degree of hydrolysis of cation and anion are
(A) exactly same **(B)** slightly different
(C) can't say **(D)** different but can be take approximatly same

SECTION - V : MATRIX - MATCH TYPE

24. (Use log 1.8 = 0.26, Ka of formic acid = 1.8×10^{-4}, Ka of acetic acid = 1.8×10^{-5}, K_b of ammonia=1.8×10^{-5}, Ka_1 of H_2S = 10^{-7} and Ka_2 of H_2S = 10^{-14}, for the following matchings)

   Match the entries of column II for which the equality or inequality given in the column I are satisfied.

Column I	Column II
(A) 10^{-5} M HCl solution > 0.1 M H_2S solution	(p) α_{water} (degree of dissociation of water)
(B) CH_3COOH solution at pH equal to 4.74 = NH_4OH solution at pH equal to 9.26	(q) $[OH^-]$
(C) 0.1 M CH_3COOH solution = 1.0 M HCOOH solution	(r) α (degree of dissociation)
(D) 0.1 M of a weak acid HA_1(Ka = 10^{-5}) solution < 0.01 M of a weak acid HA_2(Ka = 10^{-6}) solution	(s) pH

SECTION - VI : SUBJECTIVE TYPE

25. If both the functional groups of salicylic acid, HOC_6H_4COOH, ionise in water, with $K_a = 1 \times 10^{-3}$ for the –COOH group and 4.2×10^{-13} for the –OH group, calculate pH of the saturated solution of the acid. (Solubility of salicylic acid in water = 1.725 g/L, log 2 = 0.3).

26. A solution is prepared by mixing of acetic acid ($K_a = 2 \times 10^{-5}$) and HCl. In the mixture acetic acid is 0.2 M and HCl is 0.1 M. Calculate

   (i) pH of 0.2 M acetic acid and its degree of dissociation.

   (ii) pH of final solution.

   (iii) CH_3COO^- ion concentration in final solution.

   (iv) % decrease of α of acetic acid due to common ion effect.

27. If the equilibrium constant for the reaction of weak acid HA with strong base is 10^9, then pH of 0.1 M Na A is

28. The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodiums nitrite solution and also its degree of hydrolysis.

29. K_a for ascorbic acid (HAsc) is 5×10^{-5}. Calculate the hydrogen ion concentration and percentage hydrolysis in an aqueous solution in which concentration of Asc^- ions is 0.02 M .

ANSWER KEY

EXERCISE - 1

1. D	**2.** C	**3.** C	**4.** D	**5.** D	**6.** C	**7.** A	**8.** D	**9.** D	**10.** C	**11.** D	**12.** B	**13.** D
14. B	**15.** C	**16.** B	**17.** A	**18.** B	**19.** C	**20.** C	**21.** C	**22.** D	**23.** C	**24.** C	**25.** A	**26.** D
27. D	**28.** B	**29.** C	**30. (i)** B **(ii)** A **(iii)** C **(iv)** B **(vi)** B						**31.** C	**32.** A	**33.** D	**34.** C
35. B	**36.** B	**37.** B	**38.** A	**39.** D	**40.** A	**41.** D	**42.** C	**43.** B	**44.** A	**45.** A	**46.** C	**47.** D
48. C	**49.** D	**50.** D	**51.** B	**52.** D	**53.** A	**54.** B	**55.** C	**56.** D	**57.** D	**58.** A	**59.** C	**60.** D
61. B	**62.** C	**63.** D	**64.** B	**65.** C	**66.** A	**67.** C	**68.** B	**69.** D	**70.** B	**71.** D	**72.** D	**73.** D
74. C	**75.** B	**76.** D	**77.** D	**78.** B	**79.** C	**80.** B	**81.** D	**82.** C	**83.** D	**84.** D	**85.** C	**86.** C
87. B	**88.** C	**89.** A	**90.** B	**91.** D	**92.** C	**93.** A	**94.** C	**95.** C	**96.** C	**97.** B	**98.** B	**99.** C
100. A	**101.** C	**102.** D	**103.** B	**104.** D	**105.** A	**106.** D						

EXERCISE - 2 : PART # I

1. A, B, D	**2.** A, C, D	**3** A, C	**4** B, C	**5** B, C, D	**6** A, D	**7** D	**8** A, C, D
9 A, C	**10** A, B, C, D	**11** B, D	**12** A, B, C	**13** A, B	**14** C, D	**15** B, C, D	**16** A, B, C
17 B, C	**18** B, C, D	**19** A, B	**20** A, B, C	**21** A, D	**22** C, D	**23** A, C, D	**24** C, D
25 A, B	**26** A, C, D	**27.** D	**28.** A	**29.** D	**30.** B	**31.** B	**32.** D	**33.** A	**34.** A	**35.** B	**36.** B
37. A	**38.** A	**39.** C	**40.** C	**41.** A	**42.** C	**43.** D	**44.** A	**45.** A	**46.** D	**47.** D	**48.** A	**49.** A
50. B	**51.** B	**52.** B	**53.** C	**54.** B	**55.** C	**56.** A	**57.** C	**58.** A	**59.** C	**60.** B	**61.** D	**62.** C
63. A	**64.** C	**65.** B	**66.** D	**67.** B	**68.** B	**69.** B	**70.** B	**71.** C	**72.** A	**73.** A	**74.** B	**75.** A
76. C							

PART # II

1. A	**2.** B	**3.** A	**4.** B	**5.** B	**6.** B	**7.** A	**8.** A	**9.** A	**10.** A	**11.** A	**12.** B	**13.** D
14. C	**15.** B	**16.** C	**17.** A									

EXERCISE - 3 : PART # I

1. A → (p, q, r, s), B → (p, r), C → (r), D → (p, q, s)   2. A → (p, q), B → (q, r), C → (p, q, s), D → (r, s)
3. A → (r), B → (s), C → (q), D → (p)   4. A → (r), B → (p), C → (q), D → (s)
5. A → (s), B → (p), C → (r), D → (q)

PART # II

Comprehension # 1 :   **1.** D **2.** A

Comprehension # 2 :   **1.** B **2.** A **3.** B **4.** A

Comprehension # 3 :   **1.** A **2.** C **3.** B

Comprehension # 4 :   **1.** D **2.** B **3.** B

Comprehension # 5 :   **1.** C **2.** A **3.** B **4.** B

EXERCISE - 5 : PART # I

1. 4 **2.** 4 **9.** 3 **4.** 4 **5.** 4 **6.** 1 **7.** 1 **8.** 4 **9.** 2
10. 1 **11.** 2 **12.** 2 **13.** 1 **14.** 3 **15.** 4 **16.** 1 **17.** 1

PART # II

1. B **2.** $8.98 \approx 9$ **3.** B **4.** D **5.** D **6.** 8 **7.** 3 **8.** C, D **9.** 7 **10.** A **11.** 2
12. A, C, D **13.** 4.47×10^{-3} **14.** D

MOCK TEST

1. D **2.** C **3.** D **4.** C **5.** C **6.** D **7.** B
8. B **9.** D **10.** C **11.** A **12.** C **13.** A **14.** (A,C,D)
15. (A,D) **16.** (A,C) **17.** (B,C) **18.** A **19.** A **20.** B **21.** A
22. D **23.** A
24. A → (p, q, r, s) ; B → (p, r) ; C → (r) ; D → (p, q, s)