HINTS & SOLUTIONS

EXERCISE - 1
Single Choice

1. $HC_2O_4^-(aq) + PO_4^{3-}(aq) \rightleftharpoons HPO_4^{2-}(aq) + C_2O_4^{2-}(aq)$
Acid-1   base-2   base-1   acid-2

2. $H_3BO_3 = $ HO $-$ B $\overset{\text{OH}}{\underset{\overset{\uparrow}{\text{OH}}}{}}$

electron deficient species
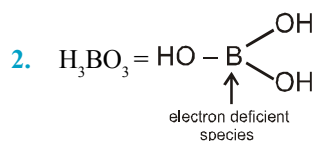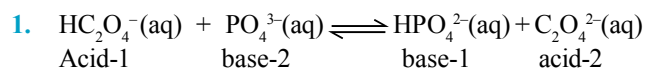
So it will behave as Lewis acid.

3. Conjugate acid base pair are differ by an proton (H^+).

$HF^+ \xrightarrow{\ -H^+\ } HF$
(acid)   (base)
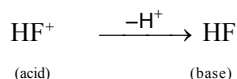
7. $[OH^-] = \sqrt{K_w}$ in pure water.

So as temperature increases K_w decreases
$\Rightarrow [OH^-]$ decreases.

8. $pK_w = -\log K_w = -\log 1 \times 10^{-12} = 12$.
$\quad K_w = [H^+][OH^-] = 10^{-12}$.
$\quad [H^+] = [OH^-]$
$\Rightarrow \quad [H^+]^2 = 10^{-12}$; $[H^+] = 10^{-6}$; $pH = -\log[H^+]$
$\quad = -\log 10^{-6} = 6$.
$\quad H_2O$ is neutral because $[H^+] = [OH^-]$ at 373 K even when pH = 6.
(D) is not correct at 373 K. Water cannot become acidic.

11. $K = [HCOOH_2^+][HCOO^-] = 10^{-3} \times 10^{-3} = 10^{-6}$

13. $K_a = 10^{-6}$ for $HA + H_2O \rightleftharpoons H_3O^+ + A^-$
Thus K for reverse reaction is $\dfrac{1}{10^{-6}} = 10^6$

15. $K_{a_1} = \dfrac{K_w}{K_{b_1}} = \dfrac{10^{-14}}{4 \times 10^{-6}} = 2.5 \times 10^{-9}$

17.
Inital	Final
pH = 12	pH = 11
$[H^+] = 10^{-12}$ M	$[H^+] = 10^{-11}$ M
$[OH^-] = 10^{-2}$ M	$[OH^-] = 10^{-3}$ M
Inital No. of mole of $OH^- = 10^{-2}$	Final No. of mole of $OH^- = 10^{-3}$

So no. of mole of OH^- removed = [.01 – 0.001] = **0.009**

18. **(A)** At 25ºC, $[H^+]$ in a solution of 10^{-8} M HCl $> 10^{-7}$ M.
(B) $[H^+] = 10^{-8}$ M.
(C) $[OH^-] = 4 \times 10^{-6}$ M $\quad\Rightarrow\quad [H^+] = 2.5 \times 10^{-9}$ M.
(D) $[H^+] = 10^{-9}$ M.

21.
	HCl	NaOH
	N = 0.4	N = 0.2
	V = 50 ml	V = 50 ml
No. of milieq =	$0.4 \times 50 = 20$	$0.2 \times 50 = 10$
	$[H^+] = 0.1$ M, pH = 1	

22. **(a)**
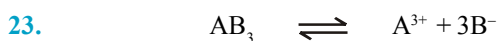|	HCl	NaOH
No. of mili eq. =	$\dfrac{1}{10} \times 100 = 10$	$\dfrac{1}{10} \times 100 = 10$

So solution is Neutral

(b) $\dfrac{1}{10} \times 55 = 5.5$ $\dfrac{1}{10} \times 45 = 4.5$

$[H^+] = \dfrac{1}{100} = 10^{-2}$ M, pH = 2

(c) $\dfrac{1}{10} \times 10 = 1$ $\dfrac{1}{10} \times 90 = 9$ Basic

(d) $\dfrac{1}{5} \times 75 = 15$ $\dfrac{1}{5} \times 25 = 5$

$[H^+] = 0.1$ M, pH = 1

23.
	AB_3	$\rightleftharpoons$	A^{3+}	$+ 3B^-$
Initial mole	1		0	0
Mole at. Eq.	$1 - \alpha$		α	3α

If volume is v, $\dfrac{1-\alpha}{v}$ $\dfrac{\alpha}{v}$ $\dfrac{3\alpha}{v}$

Therefore, $3c.\alpha$

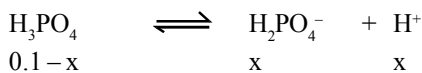**25.** Concentration of Solutions are same therefore $[H^+]$ depends only on Dissociation constant.

28. In this solution, source of OH^- is water
$\therefore \quad C\alpha = [OH^-]$

$\alpha = \dfrac{10^{-9}}{1000/18} = 1.8 \times 10^{-11}$ M

% ionisation = **1.8×10^{-9} M**

30. Sol (i) to (v)

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$$
$$0.1-x \qquad\qquad x \qquad\quad x$$

$$K_{a1} = \frac{x^2}{0.1-x} = 10^{-3}$$

$$x = 0.01 = [H^+] = [H_2PO_4^-]$$

and $[HPO_4^{2-}] = 10^{-7}\,M$

$$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \Rightarrow \qquad 10^{-12} \qquad =$$

$$\frac{(0.01)\,[PO_4^{3-}]}{10^{-7}}$$

$$[PO_4^{3-}] = 10^{-17}\,M$$
$$[OH^-] = 10^{-12}\,M$$

32. pH of 0.1 M H_2S solution can be derived by :

$$H_2S \rightleftharpoons H^+ + HS^-\,;\, K_1 = 1\times10^{-7}$$
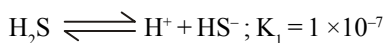
$$\therefore\quad [H^+] = C\alpha = C\sqrt{\frac{K_1}{C}} = \sqrt{K_1\times C} = \sqrt{1\times10^{-7}\times0.1}$$

$$= \sqrt{10^{-8}} = 10^{-4} \quad\therefore\quad pH = 4$$

34.
$$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq)$$
$$t=0 \qquad 0.01$$
$$t=eq \qquad 0.01-x \qquad\qquad x \qquad\qquad x$$
$$[H^+] = x + 0.01 \approx 0.01\,M$$

$$\therefore\quad K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$\Rightarrow\quad 1.69\times10^{-5} = \frac{0.01\times[CH_3COO^-]}{0.01}$$

$$\therefore\quad [CH_3COO^-] = 1.69\times10^{-5}\,M$$

So, degree of dissociation of $CH_3COOH = \dfrac{1.69\times10^{-5}}{0.01}$

$$= 1.69\times10^{-3}$$

35.
$$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$$

$$t=0 \qquad 20 \qquad\quad 20$$
$$t=eq \qquad - \qquad\quad - \qquad\qquad 20$$

So, $[CH_3COO^-] = \dfrac{20}{200} = 0.1\,M$

$$pH = 7 + \frac{1}{2}\,pK_a + \frac{1}{2}\,\log C = 7 + 2.37 + \frac{1}{2}\,\log 10^{-1}$$

$$= 7 + 2.37 - 0.5 = 8.87$$

36. For Na_2HPO_4, $pH = \dfrac{pK_{a_2} + pK_{a_3}}{2} = \dfrac{7.28+12}{2} = 9.6.$

For Na_2HPO_4, $pH = \dfrac{pK_{a_1} + pK_{a_2}}{2} = \dfrac{2.2+7.2}{2} = 4.7.$

37. Solution of HCl & NH_4Cl will be acidic, solution of NaCl neutral whereas solution of NaCN will be basic.

40. $h = 0.03$ \qquad\qquad $C = 0.1\,M$
$$K_h = Ch^2 = 9\times10^{-5}$$

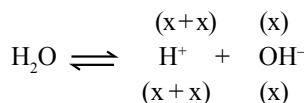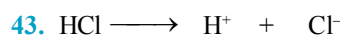$$K_h = \frac{K_w}{K_a} = 9\times10^{-5}$$

$$\Rightarrow\quad K_a = \frac{10^{-14}}{9\times10^{-5}} \quad = 1.11\times10^{-10} \approx 1\times10^{-10}$$

42. Initial pH $= \dfrac{1}{2}\,(pK_b - \log C) = \dfrac{1}{2}\,(5 - \log 2 - \log 0.1)$

$$= 2.85$$
After adding NaOH, pOH of solution $= 1$
Change in pOH $= 1.85$

43.
$$HCl \longrightarrow H^+ + Cl^-$$
$$\qquad\qquad (x+x) \quad (x)$$
$$H_2O \rightleftharpoons H^+ + OH^-$$
$$\qquad\qquad (x+x) \quad (x)$$

Ionic product $= K_w = (2x)\,(x) = 10^{-14}$

$$\Rightarrow\quad 2x^2 = 10^{-14} \quad\Rightarrow\quad x = \sqrt{50}\times10^{-8}$$

46. m. moles of HCl $= 0.1\times20 = 2$
m. moles of $CH_3COOH = 0.1\times20 = 2$
After titration of HCl by NaOH

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

$$\therefore\, pH = \frac{1}{2}\,(pK_a - \log C) = \frac{1}{2}\,[5 - \log 2 - \log\left(\frac{1}{20}\right)] = \textbf{3.}$$

47. This is ostwald dilution law.

48. The molecule shows three H atoms are replaceable, i.e., basicity of acid.
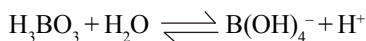
49. It is definition of Levelling effect,

50. Acid $\xrightarrow{-H^+}$ Conjugate base,

Base $\xrightarrow{+H^+}$ Conjugate acid

51. K_w changes with temperature.

52. H_3BO_3 is weak, Lewis monobasic acid and shows the given equilibrium.

$$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$

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

$$\therefore [OH^-] = C.h \;\; = C\sqrt{\frac{K_H}{C}} \;=\; \sqrt{K_H.C} \;=\; \sqrt{\frac{K_w}{K_a}C}$$

or $-\log OH = -\dfrac{1}{2}[\log K_w + \log C - \log K_a]$ or

$pOH = \dfrac{1}{2}[pK_w - \log C - pK_a]$

Now $pH + pOH = pK_w$

$\therefore \;\; pH = \dfrac{1}{2}[pK_w + \log C + pK_a]$

54. Higher is pH, lesser is acidic nature. Also $NH_4Cl(aq)$ is acidic and $NaCN(aq)$ is basic.

55. Meq. of HCl $= 10 \times 10^{-1} = 1$
Meq. of NaOH $= = 10 \times 10^{-1} = 1$
Thus both are neutralised and 1 Meq. of NaCl (a salt of strong acid and strong base) which does not hydrolyse and thus pH = 7.

56. On heating water K_w increases and thus pH scale for neutrality changes from 7 to some lower value, i.e., 6.8 or 6.9 depending upon K_w values.

57. $K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{[H^+]^2}{[HA]}$ ($\because [H^+] = [A^-]$) and

$K_b = \dfrac{[H^+][B^-]}{[HB]} = \dfrac{[H^+]^2}{[HB]}$ ($\because [H^+] = [B^-]$)

Also H^+ are same $\therefore \dfrac{K_a}{K_b} = \dfrac{[HB]}{[HA]} = \dfrac{4}{1} \quad \dfrac{[HA]}{[HB]} = \dfrac{1}{4}$

58. $H^+ + OH^- \longrightarrow H_2O$.

59. New concentration of HCl $= \dfrac{10^{-6}}{100} = 10^{-8}$ M

$[H^+] = 10^{-7} + 10^{-8}$ (approximately)
(Little less than 10^{-7} from water).

60. Meq. of HCl $= 75 \times \dfrac{1}{5} = 15$

Meq. of NaOH $= 25 \times \dfrac{1}{5} = 5$

$\therefore$ Meq. of HCl left $= 15 - 5 = 10$

Now [HCl] left $= \dfrac{10}{100} = 10^{-1}$

$\therefore$ pH = 1

61. $Ca_3(PO_4)_2 + 6HCl \rightarrow CaCl_2 + 2H_3PO_4$
$\qquad\qquad\qquad$ soluble

62. $HA \rightleftharpoons H^+ + A^- \qquad K_a = \dfrac{[H^+][A^-]}{[HA]}$ .....(i)

Also $HA + B^+ + OH^- \rightarrow B^+ + A^- + H_2O$

$Keq. = \dfrac{[H_2O][A^-]}{[HA][OH]}$ ......(ii)

By **(i)** and **(ii)**, $\dfrac{K_{eq}}{K_a} = \dfrac{1}{[H^+][OH^-]} = \dfrac{1}{K_w}$

$\therefore \;\; K_{eq'} = \dfrac{K_a}{K_w} = \dfrac{10^{-4}}{10^{-14}} = 10^{10}$

63. $K_a = 10^{-6}$ for $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

Thus K for reverse reaction is $\dfrac{1}{10^{-6}} = 10^6$

64. The degree of hydrolysis of a salt of weak acid and weak base is independent of concentration of salt.

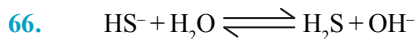**65.** $\alpha = \sqrt{\dfrac{K_a}{C}} \quad \therefore \%\alpha = 100\sqrt{\dfrac{K_a}{C}}$

Also $K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{[H^+].C\alpha}{C(1-\alpha)} = \dfrac{[H^+].\alpha}{(1-\alpha)}$

$\log K_a = \log H^+ + \log \dfrac{\alpha}{(1-\alpha)}$ or $pK_a = pH + \log\dfrac{1-\alpha}{\alpha}$

or $pK_a - pH = \log\dfrac{1-\alpha}{\alpha} \qquad \therefore \dfrac{1-\alpha}{\alpha} = 10^{pK_a-pH}$

or $\dfrac{1}{\alpha} = 10^{pK_a-pH} + 1$ or $\alpha = \dfrac{1}{[1+10^{pK_a-pH}]}$

66. $HS^- + H_2O \rightleftharpoons H_2S + OH^-$

$\therefore$ $[OH^-] = Ch = \sqrt{\dfrac{K_w C}{K_a}}$

$\therefore$ $[H^+] = \dfrac{K_w}{\sqrt{\dfrac{K_w \cdot C}{K_a}}} = \sqrt{\dfrac{K_w K_a}{C}}$

or $pH = 1/2[pK_w + pK_a + \log C]$

67. pH of 10^{-6} M HCI = 6; on dilution

$[HCI] = \dfrac{10^{-6} \times 10}{100} = 10^{-7}$

Thus new pH of HCI is not 7 because it is acid. For new solution pH:
$[H^+] = 10^{-7} + 10^{-7} \text{ (from } H_2O) = 2 \times 10^{-7}$ $\therefore$ pH = 6.7
    (approximately)

68.   Meq. of $H^+ = 10^{-3} \times 10 = 10^{-2}$

$\therefore$ Number of H^+ ions $= \dfrac{10^{-2} \times 6.02 \times 20^{23}}{1000}$

$= 6.02 \times 10^{18}$

69. On heating pure water the value of ionic product of water increases i.e., $K_w = 10^{-14}$ at 25°C and at 100°C $K_w = 10^{-12}$. Thus pH and pOH both becomes 6 at 100°C (pH and pOH = 7 at 25°C).

70.   Given density of formic acid = 1.15 g/cm^3
    $\therefore$ Weight of formic acid in 1 litre solution = 1.15×10^3 g

Thus, $[HCOOH] = \dfrac{1.15 \times 10^3}{46} = 25$ M

Since in case of auto ionisation

$[HCOOH_2^+] = [HCOO^-]$ and

$[HCOO^-][HCOOH_2^+] = 10^{-6} \Rightarrow [HCOO^-] = 10^{-3}$

Now % dissociation of HCOOH $= \dfrac{[HCOO^-] \times 100}{[HCOOH]}$

$= \dfrac{10^{-3}}{25} \times 100 = 0.004\%$.

71. $[H^+]$ after mixing $= \dfrac{10^{-2} \times 10 + 10^{-4} \times 990}{1000}$

$= \dfrac{0.1 + 0.0990}{1000} = \dfrac{0.1990}{1000} = 1.99 \times 10^{-4}$.

$\therefore$ pH = 4 − 0.3 = 3.7

72. At infinite weak electrolytes are 100% dissociated.

73. $[H^+] = 10^{-6}$ at pH = 6
If $[H^+]$ are diluted to 10^2 times, the new $[H^+] > 10^{-7}$ as we get $[H^+]$ from water. Thus pH of solution will be in between 6 to 7 or approximately 6.95.

74. Initial pOH $= \dfrac{1}{2}(pK_b - \log C) = \dfrac{1}{2}(4.7 - \log 0.1) = 2.85$

Final pOH = 1
Change in pOH = Change in pH = 1.85

75. Follow text.

76. (C) $[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2} = \sqrt{5 \times 10^{-5}}$

$pH = \dfrac{5 - \log 5}{2} \approx 3 - \log 7$.

77. Relative strengths of weak acids $= \sqrt{\left(\dfrac{K_{a_1}}{K_{a_2}}\right)}$

Assume C_1 and C_2 are same (Although not given).

$\therefore$ Relative strength $= \sqrt{\left(\dfrac{K_{a_1}}{K_{a_2}}\right)} = \sqrt{\left(\dfrac{2.1 \times 10^{-4}}{1.1 \times 10^{-5}}\right)}$

Relative strength for HCOOH to $CH_3COOH = 4.37 : 1$.

78. $[OH^-] = Ca = C\sqrt{\dfrac{K_b}{C}}$

$= \sqrt{K_b \cdot C} = \sqrt{1.0 \times 10^{-12} \times 0.01} = 1.0 \times 10^{-7}$ M.

79. $K_a = 5 \times 10^{-10}$ $pK_a = 10 \log 5 = 9.3$

$pH = pK_b + \log\left[\dfrac{CN^-}{HCN}\right]$

$9 = 9.3 + \log\left[\dfrac{5 \times V_{ml}}{10 \times 2}\right] \Rightarrow -0.3 = \log\left[\dfrac{V_{ml}}{4}\right]$

$0.3 = \log\left[\dfrac{4}{V_{ml}}\right]$

$\Rightarrow \dfrac{4}{V_{ml}} = 2 \Rightarrow V_{ml} = 2$ ml

81. $pH = pK_a + \log \dfrac{[HCO_3^-]}{[H_2CO_3]}$

$\Rightarrow \quad 7 = 7 - \log 4 + \log \dfrac{[HCO_3^-]}{[H_2CO_3]}$

$\Rightarrow \quad \dfrac{[HCO_3^-]}{[H_2CO_3]} = 4$

% of Carbon in the form of $HCO_3^- = \dfrac{[HCO_3^-]}{[HCO_3^-] + [H_2CO_3]} \times 100$

$= \dfrac{4}{1+4} \times 100 = 80\%$

82. Mole of NaOH is required for 1 lit solution = x
$\therefore$ Mole of NaOH is required for 100 ml of solution = 0.1 x
Now, $\quad 0.1x = 1 \times V \quad \Rightarrow \quad V = 0.1x$ lt = 100x ml.

85. $pH = pK_a + \log \dfrac{[\text{Ionised}]}{[\text{un Ionised}]}$

$\Rightarrow \quad 6 = 5 + \log \dfrac{[\text{Ionised}]}{[\text{un Ionised}]}$

$\Rightarrow \quad 1 = \log \dfrac{[\text{Ionised}]}{[\text{un Ionised}]}$

$\Rightarrow \quad \dfrac{[\text{Ionised}]}{[\text{un Ionised}]} = 10$

$\Rightarrow \quad \dfrac{[\text{Ionised}]}{[\text{Ionised}] + [\text{un Ionised}]} = \left[\dfrac{10}{11}\right]$

86. $pK_{HIn} = 5$
(a) $CH_3COOH + NaOH$, end point $pH > 7$
(b) Auillne hydrochloride $+ NaOH$, end point $pH > 7$
(c) $NaHCO_3 + HCl$, end point $pH < 7$
(d) $Ba(OH)_2 + H_2C_2O_4$, end point $pH > 7$

88. (a) Initially pH will decrease fast, then slowly due to buffer formation and then will decrease fast as buffer action diminishes.
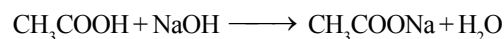**(b)** For a weak electrolyte

$K_a = \dfrac{C\alpha^2}{(1-\alpha)}$

when $\quad \alpha \ll 1$ then $\alpha = \sqrt{\dfrac{K_a}{C}}$

as C increases $\quad \Rightarrow \quad \alpha$ decreases
as C is tending to zero $\Rightarrow \quad \alpha$ will be unity

(c) At 1/4th neutralisation

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$
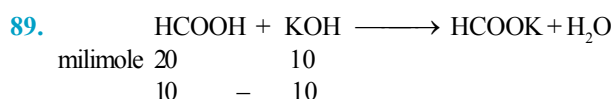
$\left(0.1 \times \dfrac{3}{4}\right) \qquad\qquad \left(0.1 \times \dfrac{1}{4}\right)$

$pH = pK_a + \log \dfrac{[CH_3COO^-]}{[CH_3COOH]} = pK_a + \log\left(\dfrac{1}{3}\right)$

At 3/4th neutralisation
$pH = pK_a + \log 3$

so difference in $pH = \Delta(pH) = \log 3 - \log \dfrac{1}{3} = 2 \log 3$

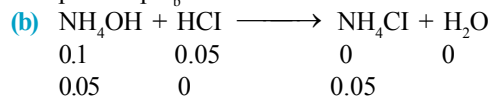**89.** $\qquad HCOOH + KOH \longrightarrow HCOOK + H_2O$
milimole $\quad 20 \qquad\quad 10$
$\qquad\qquad 10 \qquad - \qquad 10$

$pH = pK_a + \log \dfrac{[HCOO^-]}{[HCOOH]} = 3.74 + \log\left(\dfrac{10}{10}\right)$

$\Rightarrow \quad pH = 3.74$

91. (a) $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$
$\quad\quad 0.2\,M \qquad 0.1 \qquad\qquad 0 \qquad\quad 0$
$\quad\quad 0.1 \qquad\quad 0 \qquad\qquad 0.1 \qquad 0.1$
$pOH = pK_b$
(b) $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$
$\quad\quad 0.1 \qquad\quad 0.05 \qquad\quad 0 \qquad\quad 0$
$\quad\quad 0.05 \qquad\quad 0 \qquad\qquad 0.05$
$pOH = pK_b + \log\left(\dfrac{0.05}{0.05}\right) = pK_b$
(c) $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$
$\quad\quad 0.3 \qquad\quad 0.15$
$\quad\quad 0.15 \qquad\quad 0 \qquad\qquad 0.15$
$pOH = pK_b \qquad\qquad$ So all solution have same
$\qquad\qquad\qquad\qquad\qquad$ pH
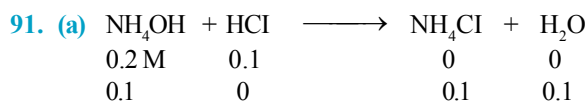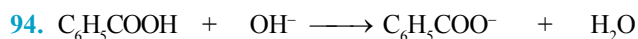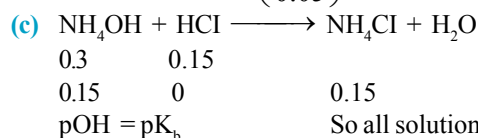
94. $C_6H_5COOH + OH^- \longrightarrow C_6H_5COO^- + H_2O$
$t=0 \qquad\quad 2 \qquad\qquad 1$
$t_{eq} \qquad\quad 1 \qquad\qquad - \qquad\qquad 1$
$pH = pK_a = 4.2$
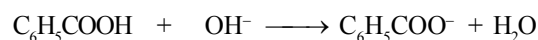
$C_6H_5COOH + OH^- \longrightarrow C_6H_5COO^- + H_2O$
$t=0 \qquad\quad 2 \qquad\qquad 2$
$t_{eq} \qquad\quad - \qquad\qquad - \qquad\qquad 2$

$[C_6H_5COO^-] = \dfrac{2}{200} = 0.01\,M$

$\therefore pH = 7 + pK_a + \dfrac{1}{2}\log C = 7 + \dfrac{4.2}{2} + \dfrac{1}{2}\log(0.01) = \mathbf{8.1}$

95.

$$C_6H_5NH_2 \ + \ H^+ \longrightarrow C_6H_5NH_3{}^+$$

t=0	5	2.5	
t_{eq}	2.5	–	2.5

$$pOH = pK_a = 14 - 8 = 6$$
$$\therefore \quad pK_a = 6$$

Now for the solution of $[C_6H_5NH_3{}^+] = 0.01$ M

$$pH = 7 - \frac{1}{2}\,pK_a - \frac{1}{2}\log C = 7 - \frac{6}{2} - \frac{1}{2}\log(0.01) = \mathbf{5}$$
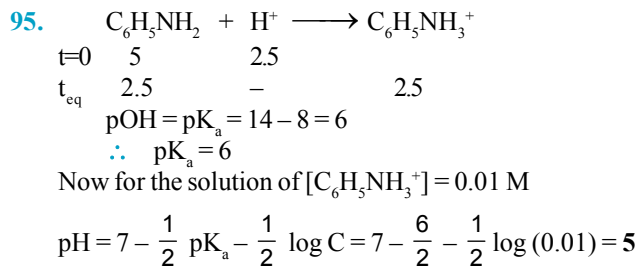
97. For the buffer solution of NH_3 & $NH_4{}^+$

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4{}^+]}$$

$$\Rightarrow \quad 8.26 = 9.26 + \log\frac{(500 \times 0.01)}{\text{m.moles of } NH_4{}^+}$$

$$\Rightarrow \quad \text{m. moles of } NH_4{}^+ = 50$$
$$\therefore \quad \text{moles of } (NH_4)_2SO_4 \text{ required} = \mathbf{0.025.}$$

99. $pK_a = 5.45$

$$pH = pK_{HIn} + \log\frac{[\text{Base form}]}{[\text{Acid form}]} \quad \Rightarrow \quad pH = pK_{HIn} = 5.45$$

For a Buffer solution

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

$$\Rightarrow \quad 5.45 = 4.75 + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$0.7 = \log\frac{[CH_3COONa]}{[CH_3COOH]} \quad \Rightarrow \quad \frac{5}{1} = \frac{[CH_3COONa]}{[CH_3COOH]}$$

100.

$$CH_3COONa \ + \ HCl \longrightarrow NaCl \ + \ CH_3COOH$$

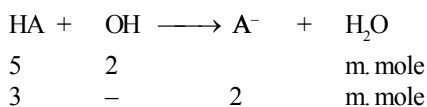|				
t=0	20 m eq.	20 meq.		
$t_{eq.}$	–	–		20 meq.
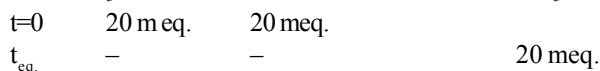
$$[CH_3COOH] = \frac{20}{200} = 0.1 \text{ M}$$

$$pH = \frac{1}{2}\,[pK_a - \log C] = \frac{1}{2}\,[5 - \log 2 + 1]$$

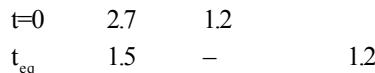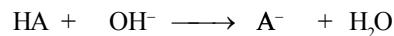$$= \frac{1}{2}\,[6 - \log 2] = 3 - \log\sqrt{2}$$

101. meq. of acid = meq of base $\Rightarrow 20 \times M = 20 \times 0.2 = 4$

Molarity of HA = 0.2 M

$$HA \ + \ OH \longrightarrow A^- \ + \ H_2O$$

5	2		m. mole
3	–	2	m. mole

$$\therefore \quad pH = pK_a + \log\frac{[A^-]}{[HA]} \quad \Rightarrow \quad 5.8 = pK_a + \log\left(\frac{2}{3}\right)$$

$$\Rightarrow \quad pK_a = \mathbf{5.98}$$

103. m. moles of HA taken $= 27 \times 0.1 = 2.7$

$$HA \ + \ OH^- \longrightarrow A^- \ + \ H_2O$$

t=0	2.7	1.2	
t_{eq}	1.5	–	1.2

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$\Rightarrow \quad 5 = pK_a + \log\left(\frac{1.2}{1.5}\right) = pK_a + \log\frac{4}{5}$$

$$\therefore \quad pK_a = 5.1 \quad \Rightarrow \quad K_a = \mathbf{8 \times 10^{-6}.}$$

104. $$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]} = pK_b + \log\frac{[\text{Cation}]}{[\text{Base}]}$$
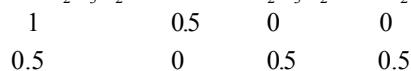
$$[NH_4^+] = 2 \times \text{mole of } (NH_4)_2SO_4$$

$$\therefore \quad pOH = 5 + \log 2 = 5.3$$
$$\text{or} \quad pH = 8.7$$

105. $NaH_2PO_4 + H_3PO_4$; $NaH_2PO_4 + NaHPO_4{}^-$;
$Na_2HPO_4 + Na_3PO_4$.

106.

$$HC_2H_3O_2 \ + \ NaOH \rightarrow C_2H_3O_2Na \ + \ H_2O$$

1	0.5	0	0
0.5	0	0.5	0.5

This solution contains weak acid + its salt with strong base. and thus acts as buffer.

<div align="center">

EXERCISE - 2
Part # I : Multiple Choice

</div>

2. (A) In 0.6 m M HCOOH solution

$$K_a = \frac{[H^+]^2}{C - [H^+]} \quad \Rightarrow \quad 8 \times 10^{-4} = \frac{[H^+]^2}{6 \times 10^{-4} - [H^+]}$$

$$\therefore \quad [H^+] = \mathbf{4 \times 10^{-4}\,M.}$$

So solution in **(A), (C)** & **(D)** are ISOHYDRIC.

4. On the basis of ostwald dilution law, number of H^+ ions will increase but increase in volume will be more.

Therefore, $[H^+]$ decreases, pH increases.

5. Let BA be this salt $\quad BA \rightarrow B^+ + A^-$

A^- does not undergo hydrolysis because HA is strong acid. B^+ undergoes hydroysis

$$h = \sqrt{\frac{K_h}{c}} \quad h = \text{degree of hydrolysis where}$$

K_h = Hydrolysis constant = $\dfrac{K_w}{K_b}$.

$h \propto \sqrt{K_h}$ greater the hydrolysis constant greater the h(degree of hydrolysis).

$h \propto \dfrac{1}{\sqrt{K_b}}$ greater the K_b lesser the h.

Hydrolysis is endothermic, K_h increases with temperature and h also increase with temperature.

$h \propto \sqrt{V}$ V = volume of salt solution hence h increases with dilution. $K_h = \dfrac{K_w}{K_b}$

Both K_w and K_b change with temperature, hence K_h changes with temperature.

Hence, statement **(B)** is correct. h increases if K_b decreases, statement **(C)** correct.

It is found that as temperature increase, K_w and K_b increase but increase in K_w is greater than increase in K_b. Hence, h increases with increase in temperature. or h decrease in temperature., hence statement.

(D) is correct.

(D) is not correct from explanation of **(B)**.

6. **(A)** $[H^+] = 10^{-2}$ and $[OH^-] = 10^{-2}$
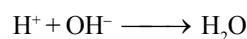
$H^+ + OH^- \longrightarrow H_2O$

This leads complete neutralisation

so, $pH = 7 = \dfrac{2+12}{2}$

(D) $[H^+] = 10^{-5}$ and $[OH^-] = 10^{-5}$

$[H^+] + [OH^-] \longrightarrow H_2O$
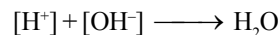
This leads complete neutralisation

so, $pH = 7 = \dfrac{5+9}{2}$

7. Bronsted bases are proton acceptor and each Lewis base contain one or more electron pair and thus accept proton. On the other hand Bronsted acids are proton donor and may or may not be capable of accepting lone pair of electron, e.g., H_2SO_4 is Bronsted acid but not Lewis acid BF_3 is Lewis acid but not Bronsted acid. Also each cation is acid an each anion is base.

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

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$\quad 1-\alpha \qquad\qquad \beta \qquad\qquad \alpha+\beta\!\!-\!\!x$$

$$C_2H_5COOH \rightleftharpoons C_2H_5COO^- + H^+$$
$$\quad 1-\beta \qquad\qquad\qquad \beta \qquad\qquad \alpha+\beta-x$$
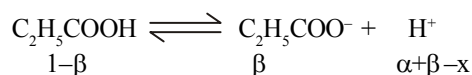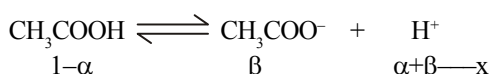
$\therefore$ $K_{A.A} = \dfrac{[\alpha][\alpha+\beta-x].c}{[1-\alpha]}$ $K_{P.A} = \dfrac{[\beta][\alpha+\beta-x].c}{[1-\beta]}$

(where 'x' is equivalents of NaOH droped).

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

$\dfrac{\alpha}{1-\alpha} = \dfrac{1.75}{1.3} \times \left[\dfrac{\beta}{1-\beta}\right]$

Hence,   A,C,D.

9. Let α_1 and α_2 be the degree of dissociation of two acids and α_1 , α_2 are very small when compared to unity.

$$\dfrac{c\alpha_1^2}{1-\alpha_1} = K_{a_1} \qquad\qquad \dfrac{c\alpha_2^2}{1-\alpha_2} = K_{a_2}$$

$$\sqrt{\dfrac{K_{a_1}}{K_{a_2}}} = \dfrac{\alpha_1}{\alpha_2} = \text{relative strength.}$$

Hence choices **(A)** and **(C)** are correct while **(B)** and **(D)** are incorrect.

13. **(A)** A buffer solution is a solution which contains weak acid and its conjugate base. it is acidic buffer.

     (B) Basic buffer contains weak base and its conjugate acid.

     (C) is wrong because it does not show change in pH on adding small amount of acid or base.

     (D) is wrong ; all the above statements are not correct.

16. $[A^{2-}] = K_{a_2} = 10^{-5}$

$pH = 1 \qquad\quad pH = 3$

$[H^+]_1 = 10^{-1} \quad [H^+]_2 = 10^{-3}$

$\dfrac{[H^+]_1}{[H^+]_2} = 100$

$pH = \dfrac{1}{2} (pK_w + pK_a - pK_b)$

pH is independent of dilution with in a limit since no concentration term in pH expression.

17. **(B)** is correct because $pH = pK_a + \log\dfrac{[Salt]}{[Base]}$ for acidic buffer.

If [Salt] increases, pH of acidic buffer will increase.

$$pOH = pK_b + \log\dfrac{[Salt]}{[Acid]} \text{ for basic buffer.}$$

If [Salt] increases, pOH will increase, pH will decrease as pH = 14 – pOH.

Therefore **(C)** is correct but **(D)** is wrong.

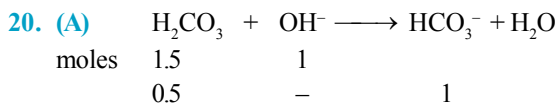**(A)** is not correct $pH = pK_a + \log \dfrac{[Salt]}{[Acid]}$

If [Salt] increase, pH will increase.

19. **(A)** is buffer because it contains weak acid and its salt and they will also show common ion effect.
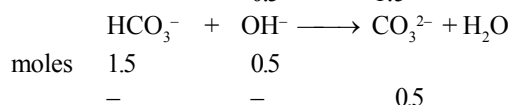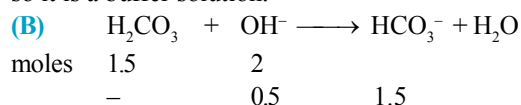
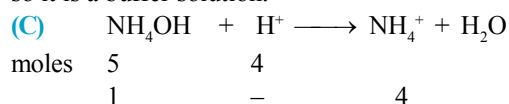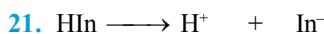**(B)** is also a buffer because it contains a weak acid and its salt. They will not show common ion effect.

(C) is not buffer solution because they contains strong acids and its salt. They will not show common ion effect.

(D) is not a buffer solution because it contains strong acids and its salt. They will not show common ion effect.

20. **(A)** $\quad H_2CO_3 \;+\; OH^- \longrightarrow HCO_3^- + H_2O$

moles $\quad$ 1.5 $\qquad$ 1

$\qquad$ 0.5 $\qquad$ – $\qquad\qquad$ 1

so it is a buffer solution.

(B) $\quad H_2CO_3 \;+\; OH^- \longrightarrow HCO_3^- + H_2O$

moles $\quad$ 1.5 $\qquad$ 2

$\qquad$ – $\qquad$ 0.5 $\qquad$ 1.5

$\qquad HCO_3^- \;+\; OH^- \longrightarrow CO_3^{2-} + H_2O$

moles $\quad$ 1.5 $\qquad$ 0.5

$\qquad$ – $\qquad$ – $\qquad\qquad$ 0.5

so it is a buffer solution.

(C) $\quad NH_4OH \;+\; H^+ \longrightarrow NH_4^+ + H_2O$

moles $\quad$ 5 $\qquad$ 4

$\qquad$ 1 $\qquad$ – $\qquad\qquad$ 4

so it is a buffer solution.

21. $HIn \longrightarrow H^+ \;+\; In^-$

$K_{In} = \dfrac{[H^+][In^-]}{[HIn]} \;\Rightarrow\; \dfrac{[In^-]}{[HIn]} = \dfrac{K_{In}}{[H^+]} = \dfrac{10^{-9}}{10^{-9.6}} = 10^{0.6} = 4$

$\therefore$ % of $[In^-]$ in solution $= \dfrac{4}{5} \times 100 = 80\%$

so pink colour will be visible.

23. $\quad CH_3COO^- + H_2O \rightleftharpoons CH_3COOH \;+\; OH^-.$
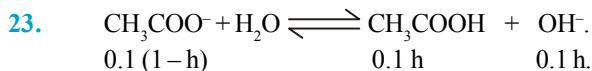
$\quad 0.1\,(1-h) \qquad\qquad 0.1\,h \qquad\quad 0.1\,h.$

$K_h = \dfrac{(0.1\,h)(0.1h)}{0.1(1-h)} = 0.1\,h^2 \;\Rightarrow\; 5.6 \times 10^{-10} = 0.1\,h^2$

$\Rightarrow\; h = 7.48 \times 10^{-5} \qquad\qquad [\therefore h <<<< 1]$

$[OH^-] = ch = 7.48 \times 10^{-5} \times 10^{-1} = 7.48 \times 10^{-6}.$

$[H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{10^{-14}}{7.48 \times 10^{-6}} = 1.33 \times 10^{-9}.$

$\Rightarrow\; pH = 8.8$ approx.

25. $K_{sp} = 1.1 \times 10^{-11} = (1.4 \times 10^{-4})^{x+y}\, x^x . y^y$

so we have x + y = 3 (by comparing values)

so, $\quad x^x . y^y = \dfrac{1.1 \times 10^{-11}}{1.4 \times 1.4 \times 1.4 \times 10^{-12}} = \dfrac{110}{1.96 \times 1.4} = 4$
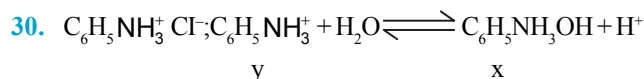
Hence $\quad x = 1, y = 2 \qquad$ or

$\qquad\qquad y = 1 , x = 2$

26. It is factual.

27. $pH = pK_a + \log \dfrac{[Salt]}{[Acid]}$

28. The salt hydrolysis in each case occurs execpt NaW because its. pH = 7. Thus HW is strongest acid.

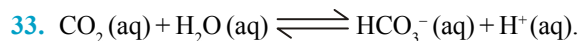**29.** $pOH = pK_b + \log \dfrac{[Salt]}{[Base]} = 4 + \log \dfrac{0.2}{0.1}$

$\therefore pOH = 4 + \log 2$ and $pH = 10 - \log 2$

30. $C_6H_5NH_3^+ Cl^-; C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_3OH + H^+$

$\qquad\qquad\qquad\qquad\quad y \qquad\qquad\qquad\qquad x$

Thus y is $C_6H_5NH_3^+$ and x is acidic.

32. Aspirin a weak acid is unionised in acid medium due to common ion effect and completely ionised in alkaline medium.

33. $CO_2\,(aq) + H_2O\,(aq) \rightleftharpoons HCO_3^-\,(aq) + H^+\,(aq).$

34. $pH = -\log K_a + \log \dfrac{[Salt]}{[Acid]}$

Let a mol litre^{-1} be concentration of salt, then concentration of acid = (0.29 – a).

$4.4 = -\log 1.8 \times 10^{-5} + \log \dfrac{a}{(0.29 - a)}.$
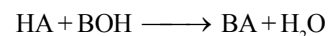
$\therefore \quad a = 0.09.$

$[Salt] = 0.09\,M$

$[Acid] = 0.29 - 0.09 = 0.20\,M.$

35. For neutralisation :

Total Meq. of acid = Meq. of base = $26.6 \times 0.1 = 2.66$.

Now for partial neutralisation of acid.

$\qquad\qquad\qquad\qquad HA + BOH \longrightarrow BA + H_2O$

Meq. before reaction $\quad$ 2.66 $\quad$ 1.2 $\qquad\quad$ 0 $\quad$ 0

Meq. after reaction $\quad$ 1.46 $\quad$ 0 $\qquad\quad$ 1.2 $\quad$ 1.2

The resultant mixture acts as a buffer and [HA] and [BA] may be placed in terms of Meq. sincen volume of mixture is constant.

$pH = -\log K_a + \log \dfrac{[Salt]}{[Acid]}$ or $\quad 5 = -\log K_a + \log \dfrac{1.2}{1.46}$

$K_a = 8.22 \times 10^{-6}.$

36. $NH_3 + HCl$ in 2 : 1 will give $NH_3 + NH_4Cl$ in 1 : 1 ratio.

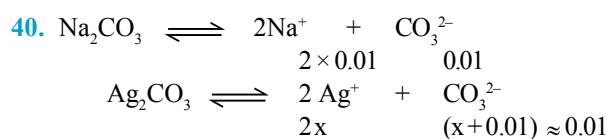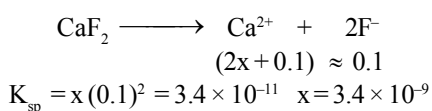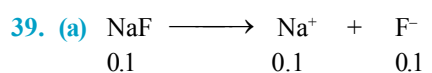**37.** $pH = -\log K_a + \log \dfrac{[Salt]}{[Acid]} = -\log 10^{-4} + \log \dfrac{1}{1} = 4$

[Since $K_a \times K_b = 10^{-14}$ Given $K_b = 10^{-10}$ $\therefore K_a = 10^{-4}$]

38. Meq. of acetic acid $= 50 \times 2 = 100$
Meq. of $CH_3COONa = 10 \times 1 = 10$

$pH = -\log K_a + \log \dfrac{[Salt]}{[Acid]}$ or $pH = -\log$

$10^{-5} + \log \dfrac{10}{100} = 4$

39. (a) $NaF \longrightarrow Na^+ + F^-$
         0.1   0.1   0.1
        $CaF_2 \longrightarrow Ca^{2+} + 2F^-$
                    $(2x + 0.1) \approx 0.1$
     $K_{sp} = x(0.1)^2 = 3.4 \times 10^{-11}$ $x = 3.4 \times 10^{-9}$

40. $Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$
                  2×0.01 0.01
        $Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$
                  $2x$ $(x + 0.01) \approx 0.01$
     $K_{sp} = 4x^2(0.01)$
     $K_{sp} = 4s^3 = 4 \times 10^{-12} = 4x^2(0.01)$ $\Rightarrow x = 10^{-5}$

42. Let K_{sp} of $AgCl = x$

(a) solubility of AgCl in pure water $= s_1 = \sqrt{x}$

(b) solubility of AgCl in 0.01 M $CaCl_2 = s_2 = \dfrac{x}{0.02}$

(c) solubility of AgCl in 0.01 M NaCl $= s_3 = \dfrac{x}{0.01}$

(d) solubility of AgCl in 0.05 M $AgNO_3 = s_4 = \dfrac{x}{0.05}$

So $s_1 > s_3 > s_2 > s_4$

45. $pH = 4$ $\Rightarrow [H^+] = 10^{-4} M \Rightarrow [OH^-] = 10^{-10} M$
$Al(OH)_3 \rightleftharpoons Al^{+3} + 3OH^-$
$K_{sp}(Al(OH)_3) = [Al^{+3}][OH^-]^3$
$[Al^{3+}][OH^-]^3 = 1 \times 10^{-33}$
$[Al^{3+}](10^{-10})^3 = 1 \times 10^{-33}$ $\Rightarrow [Al^{+3}] = 10^{-3} M$
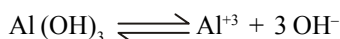
48. $K_{sp} = 1.8 \times 10^{-10}$
Precipitation of AgCl will occuir only where
$K_{IP}(AgCl) > K_{sp}$

$K_{IP} = \dfrac{10^{-4}}{2} \times \dfrac{10^{-4}}{2} = 2.5 \times 10^{-9}$
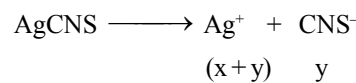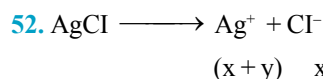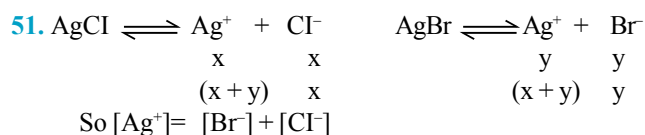
$K_{IP} > K_{SP}$ precipitate is formed.

50. $[Ag^+]$ ion required to precipitate Cl^- ion $= \dfrac{K_{sp}}{[Cl^-]}$

$= \dfrac{10^{-10}}{0.05} = 2 \times 10^{-9} \, mol/L.$

$[Ag^+]$ ion required to precipitate I^- ion $= \dfrac{K_{sp}}{[I^-]}$

$= \dfrac{4 \times 10^{-16}}{0.05} = 8 \times 10^{-15} \, mol/L.$

Since $[Ag^+]$ ion conc. required to precipitate AgI is less than the $[Ag^+]$ ion conc. required to precipitate AgCl, AgI precipitates first.
Hence choices **(A)**,**(B)** and **(D)** are correct while **(C)** is incorrect.

51. $AgCl \rightleftharpoons Ag^+ + Cl^-$ $AgBr \rightleftharpoons Ag^+ + Br^-$
          x   x   y   y
      $(x + y)$ x $(x + y)$ y
So $[Ag^+] = [Br^-] + [Cl^-]$

52. $AgCl \longrightarrow Ag^+ + Cl^-$
           $(x + y)$ x
   $AgCNS \longrightarrow Ag^+ + CNS^-$
             $(x + y)$ y

$\dfrac{K_{SP}(AgCl)}{K_{SP}(AgCNS)} = \dfrac{x}{y} = \dfrac{[Cl^-]}{[CNS^-]}$

So $\dfrac{[Cl^-]}{[CNS^-]} = \dfrac{x}{y} = \dfrac{1.8 \times 10^{-10}}{1.6 \times 10^{-11}}$

$= 1.125 \times 10 = 11.25$

$\Rightarrow \dfrac{x}{y} = 11.25$ $x = 11.25$

$K_{SP}(AgCl) = [Ag^+][Cl^-] = (x + y)x = 1.8 \times 10^{-10}$
$12.25 \, y \times 11.25 \, y = 1.8 \times 10^{-10}$

$y^2 = \dfrac{1.8 \times 10^{-10}}{12.25 \times 11.25}$

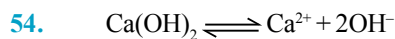$y^2 = \dfrac{180 \times 10^{-12}}{12.25 \times 11.25}$

$y^2 = 1.3 \times 10^{-12}$
$y = 1.14 \times 10^{-6}$
$x = 11.25 \times 1.14 \times 10^{-6} = 12.83 \times 10^{-6}$
$[Ag^+] = [x + y]$
$= 12.83 \times 10^{-6} + 1.14 \times 10^{-6} = 13.97 \times 10^{-6} = 1.4 \times 10^{-5} M$

54. $Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$

$t=0 \quad \dfrac{1.48}{74} = 0.02 \quad 0 \quad 0$

$t_{eq} \qquad 0 \qquad\qquad 0.02 \quad 0.04$

so, $\quad pOH = 2 - \log 4 = 1.4$

so $\quad pH = 12.6$

56. $Cd^{2+} \quad + \quad H_2S \longrightarrow CdS \downarrow \quad + \quad 2H^+$

m.moles 0.1 $\hspace{5cm}$ 0.2

Total m.moles of H^+ in solution after the reaction $= 0.2 + 0.8 = 1$

$\therefore \quad [H^+] = \dfrac{1}{100} = 0.01\,M \qquad \Rightarrow \quad pH = \mathbf{2.}$

57. $CaF_2(s) \rightleftharpoons Ca^{2+} \quad + \quad 2F^-$

$\hspace{4cm} s \hspace{2.5cm} 2s$
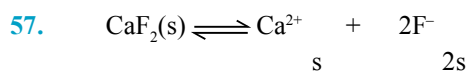
$4s^3 = K_{sp} = 4 \times 10^{-11} \quad \Rightarrow \quad s = 2.15 \times 10^{-4}\,M$

So, amount of F^- in 20000 lt of water $= 2s \times 20000 = \mathbf{8.6\ mol.}$

58. For different salts such as AB, AB_2, AB_3, ...etc. $K_{SP} = s^2, 4s^3, 27s^4 ....$ respectively. If K_{sp} is same for different salts, then s is more for the salt in which more number of ions.

59. Let S is the solubility of BaF_2 in a solution of $BaNO_3$

Then $\quad K_{SP} = [Ba^{2+}]\,[F^-]^2$.

Then $\quad [F^-] = 2S$;

Then $\quad \dfrac{1}{2}\,[F^-] = S$

60. Find solubility for each separately by $S^2 = K_{SP}$ for MnS and ZnS. $108S^5 = K_{SP}$ for Bi_2S_3 and $4S^3 = K_{SP}$ for Ag_2S.

61. $CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2}$

$\hspace{3.5cm} x \hspace{1.3cm} x$

$\hspace{3.3cm} (x+y) \hspace{0.7cm} x$

$CaC_2O_4 \rightleftharpoons Ca^{+2} + C_2O_4^{-2}$

$\hspace{3.5cm} y \hspace{1.3cm} y$
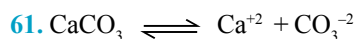
$\hspace{3.3cm} (x+y) \hspace{0.7cm} y$

$\dfrac{K_{SP}(CaCO_3)}{K_{SP}(CaC_2O_4)} = \dfrac{x}{y} = 3 \Rightarrow x = 3y$

$(x + y) = 8 \times 10^{-5}$

$(3y + y) = 8 \times 10^{-5} \Rightarrow y = 2 \times 10^{-5} \quad x = 6 \times 10^{-5}$

$K_{SP}(CaCO_3) \quad = \quad [Ca^{+2}]\,[CO_3^{-2}]$

$\hspace{2.9cm} = \quad 8 \times 10^{-5} \times 6 \times 10^{-5}$

$\hspace{2.9cm} = \quad 48 \times 10^{-10}$

$K_{SP}(CaCO_3) \quad = \quad 4.8 \times 10^{-9}$

62. For AgCl precipitation

$[Ag^+] = \dfrac{K_{SP}AgCl}{[Cl^-]} = \dfrac{10^{-10}}{0.05} = 2 \times 10^{-9}$

For AgI precipitation

$[Ag^+] = \dfrac{K_{SP}AgI}{[I]} = \dfrac{4 \times 10^{-16}}{0.05} = 8 \times 10^{-15}$

Thus AgI will precipitate first. AgCl will precipitate only when,

$[Ag^+] = 2 \times 10^{-9}$; Thus

$[I^-]_{Left} = \dfrac{4 \times 10^{-16}}{2 \times 10^{-9}} = 2 \times 10^{-7}\,M$

63. Solubility of $Al(OH)_3$ is lesser than $Zn(OH)_2$.

64. Presence of common ion decreases the solubility of salt.

65. For precipitation of Ag_2CO_3.

$[CO_3^{2-}] = \dfrac{K_{SP}}{[Ag^+]^2} = \dfrac{6.9 \times 10^{-12}}{[10^{-5}]^2} = 6.9 \times 10^{-2}$

and for precipitation of $BaCO_3$.

$[CO_3^{2-}] = \dfrac{K_{SP}}{[Ba^{2+}]} = \dfrac{8.1 \times 10^{-9}}{10^{-4}} = 8.1 \times 10^{-5}$

66. K_{SP} of $PbCl_2 = 4s^3 = 4 \times (0.01)^3 = 4 \times 10^{-6}$

In NaCl solution for $PbCl_2$; $\hspace{1cm} K_{SP} = [Pb^{2+}]\,[Cl^-]^2$

or $\quad 4 \times 10^{-6} = [Pb^{2+}]\,[0.1]^2 \quad \therefore \quad [Pb^{2+}] = 4 \times 10^{-4}\,M$

67. Solubility of $BaSO_4 = \sqrt{K_{SP}} \quad = \sqrt{1.1 \times 10^{-10}}$

$\hspace{3cm} = 1.05 \times 10^{-5}\,M$

$\therefore$ wt. of $BaSO_4 = 1.05 \times 10^{-5} \times 233 = 244.37 \times 10^{-5}$ g/litre.

$\therefore$ Volume of water needed to dissolve 1g $BaSO_4$ is equal to

$\dfrac{1}{244.37 \times 10^{-5}} = 410$ litre

68. $K_{SP} = 4 \times 10^{-12} = [M^+]\,[OH^-]^x \quad = [10^{-4}]\,[x.10^{-4}]^x$

$\hspace{2.3cm} = x^x.\,(10^{-4})^{1+x}$

$\therefore \quad$ Thus shows that $x = 2$

69. $\hspace{1cm} K_{SP}$ of $Ca(OH)_2 = 4s^3 = 5.5 \times 10^{-6}$

$\therefore \quad s = 3\sqrt{\dfrac{5.5 \times 10^{-6}}{4}} = 1.11 \times 10^{-2}$

$\therefore \quad [OH^-] = 2s = 2 \times 1.11 \times 10^{-2}$

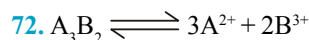$\therefore \quad pOH = 1.65 \hspace{1.5cm} \therefore \quad pH = 12.35$

70. $[Mg^{2+}] [OH^-]^2 = 1 \times 10^{-12}$;

$$\therefore \quad [OH^-] = \sqrt{\frac{10^{-12}}{0.01}} = 10^{-5}$$
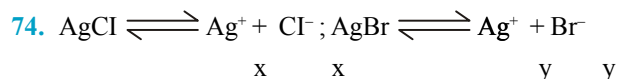
or   pOH = 5.

and thus pH = 9.

71. The K_{SP} values are in the order :

$$AgCl > AgBr > AgI.$$

72. $A_3B_2 \rightleftharpoons 3A^{2+} + 2B^{3+}$

$$K_{SP} = [A^{2+}]^3 [B^{3+}]^2.$$
$$K_{SP} = (3s)^3 (2s)^2 = 108s^2$$

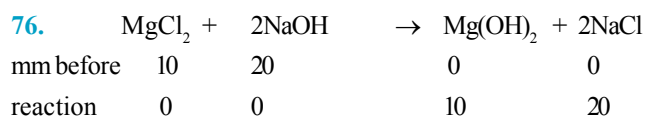**73.** $K_{SP} = [M^+]$ [anion] ; $[M^+]$ required to precipitate MA is less and MA precipitate first.

74. $AgCl \rightleftharpoons Ag^+ + Cl^-$; $AgBr \rightleftharpoons Ag^+ + Br^-$
        x   x   y   y

In simultaneous solubility solution contains $[Ag^+] = [Cl^-] + [Br^-]$

75. Solubility of $M(OH)_3 = \sqrt[4]{\dfrac{K_{SP}}{27}} = \sqrt[4]{\dfrac{10^{-35}}{27}} = 7.8 \times 10^{-10}$

Solubility of $M(OH)_2 = \sqrt[3]{\dfrac{K_{SP}}{4}} = 6.3 \times 10^{-11}$

Solubility of $MOH = \sqrt{K_{SP}} = 10^{-14}$

76. $MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$
mm before   10   20   0   0
reaction   0   0   10   20

Thus, 10 m mole of $Mg(OH)_2$ are formed. The product

of $[Mg^{2+}][OH^-]^2$ is therefore $\left[\dfrac{10}{200}\right] \times \left[\dfrac{20}{200}\right]^2$

$= 5 \times 10^{-4}$ which is more than K_{SP} of $Mg(OH)_2$. Now solubility(s) of $Mg(OH)_2$ can be derived by

$$K_{SP} = 4s^3$$

$$\therefore \quad s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\left[\frac{1.2 \times 10^{-11}}{4}\right]} = 1.4 \times 10^{-4} M$$

$$\therefore \quad [OH^-] = 2s = 2.88 \times 10^{-4} M$$

---

1. Due to very strong extent of hydration of H^+ ion.

3. Since K_a of HCN is less than that of HF, so CN^- is stronger base than F^-

6. NH_3 acts as weak base in aqueous solution. HCl acts as strong acid in aqueous solution.

7. Due to common ion effect, $[H^+]$ increases therefore ionization of HCOOH decreased.

8. At 25ºC, pH of any acidic solution can not be 7.

9. $HA \quad + \quad OH^- \quad \longrightarrow \quad A^- \quad + \quad H_2O$

At the half equivalent point, $[HA] = [A^-] \Rightarrow pH = pK_a$

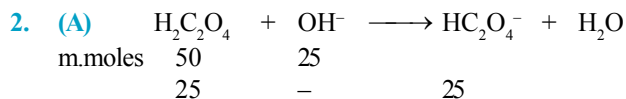**10.** Due to complex formation solubility of sparingly soluble salt increases.

EXERCISE - 3

1. **(A)** $[H^+]$ in HCl solution $= 10^{-5}$ M

$[H^+]$ in H_2S solution $= \sqrt{K_a \times C} = 10^{-4}$ M

so $[H^+]$ in HCl solution $< [H^+]$ in H_2S solution
& $[OH^-]$ in HCl solution $> [OH^-]$ in H_2S solution
&   degree of dissociation of water in HCl solution $>$ degree of dissociation of water in H_2S solution
   pH of HCl solution $>$ pH of H_2S solution.

(B) At pH = 4.74 in CH_3COOH solution, $[CH_3COO^-] = [CH_3COOH]$

$\therefore$ degree of dissociation of $CH_3COOH = \dfrac{1}{2}$

At pH = 9.26 i.e. pOH = 4.74 in NH_4OH solution, $[NH_4^+] = [NH_4OH]$

$\therefore$ degree of dissociation of CH_3COOH = degree of dissociation of NH_4OH

degree of dissociation of water in CH_3COOH solution $>$ degree of dissociation of water in NH_4OH solution.

(C) $[H^+]$ in CH_3COOH solution $= \sqrt{1.8 \times 10^{-5} \times 0.1}$

$= \sqrt{1.8} \times 10^{-3}$ M

$[H^+]$ in HCOOH solution $= \sqrt{1.8 \times 10^{-4} \times 1}$

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

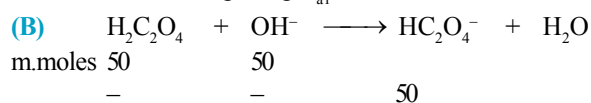so, degree of dissociation of CH_3COOH = degree dissociation of HCOOH.

(D) $[H^+]$ in HA_1 solution = $\sqrt{10^{-5} \times 0.1}$ = 10^{-3} M

$[H^+]$ in HA_2 solution = $\sqrt{10^{-6} \times 0.01}$ = 10^{-4} M
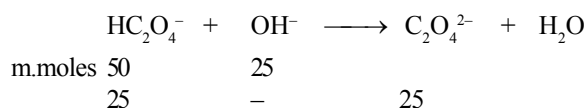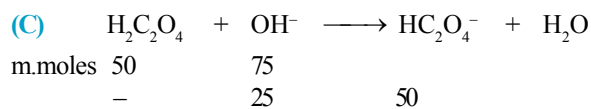
so $[OH^-]$ in solution of $HA_1 < [OH^-]$ in solution of HA_2
pH in solution of $HA_1 <$ pH in solution of HA_2

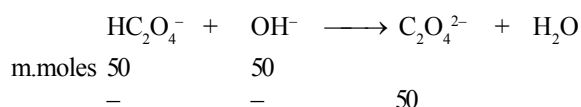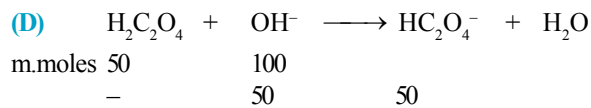& degree of dissociation of water $HA_1 <$ degree of dissociation of water HA_2.

2. (A)
$$H_2C_2O_4 \;+\; OH^- \longrightarrow HC_2O_4^- \;+\; H_2O$$
m.moles 50   25

        25   –   25

Buffer solution pH = pK_{a1}

(B)
$$H_2C_2O_4 \;+\; OH^- \longrightarrow HC_2O_4^- \;+\; H_2O$$
m.moles 50   50

     –   –   50

Amphiprotic, pH = $\dfrac{pK_{a1} + pK_{a2}}{2}$ = $\dfrac{13}{2}$ = 6.5.

(C)
$$H_2C_2O_4 \;+\; OH^- \longrightarrow HC_2O_4^- \;+\; H_2O$$
m.moles 50   75

     –   25   50

$$HC_2O_4^- \;+\; OH^- \longrightarrow C_2O_4^{2-} \;+\; H_2O$$
m.moles 50   25

     25   –   25

Buffer solution pH = pK_{a2}.

(D)
$$H_2C_2O_4 \;+\; OH^- \longrightarrow HC_2O_4^- \;+\; H_2O$$
m.moles 50   100

     –   50   50

$$HC_2O_4^- \;+\; OH^- \longrightarrow C_2O_4^{2-} \;+\; H_2O$$
m.moles 50   50

     –   –   50

Salt hydrolysis, pH > 7.

Part # II : Comprehension

Comprehension # 1 :

2. Since K_a of CH_3COOH & K_b of NH_4OH are same so degree of hydrolysis of CH_3COO^- & NH_4^+ are exactly same.

Comprehension # 2 :

1. pH = $pK_a + \log \dfrac{[Base]}{[Salt]}$

$[Base] = \dfrac{0.01 \times 500}{500} = 0.01$.

$[NH_4^+] = \dfrac{a \times 2}{500}$; Let a millimole of $(NH_4)_2SO_4$ are added.

$\therefore$ $[Salt] = [NH_4^+]$.

pH = $9.26 + \log\left[\dfrac{0.01}{2a/500}\right]$

$8.26 = 9.26 + \log\dfrac{0.01 \times 500}{2a}$.

$\therefore$ a = 25.

$\therefore$ Mole of $(NH_4)_2SO_4$ added = 0.025.

3. Let V mL of NaOH be needed to give CH_3COONa.
$$NaOH \;+\; CH_3COOH \longrightarrow CH_3COONa \;+\; H_2O$$
$0.2 \times V$ 50×0.2 0   0
—   [10–0.2V]   0.2V   0.2V
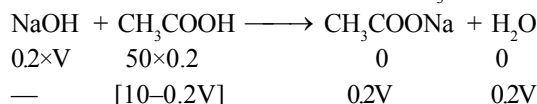
$\therefore$ pH = $pK_a + \log\dfrac{[Salt]}{[Acid]}$ = $pK_w - pK_b + \log\dfrac{[Salt]}{[Acid]}$

$= 14 - 9.26 + \log\dfrac{[Salt]}{[Acid]}$

$= 14 - 9.26 + \log\dfrac{\left[\dfrac{0.2V}{50+V}\right]}{\left[\dfrac{10-0.2V}{50+V}\right]}$

$4.74 = 4.74 + \log\left[\dfrac{0.2\,V}{10-0.2V}\right]$ $\therefore$ V = $\dfrac{10}{0.4} = 25$ mL.

4.
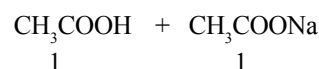$$CH_3COONa \;+\; HCl \rightarrow CH_3COOH \;+\; NaCl$$
   1   1   0   0
   0   0   1   1

$\therefore$ $[CH_3COOH] = \dfrac{1}{1} = 1$.

$\therefore$ $[H^+] = C\alpha = C\sqrt{\dfrac{K_a}{C}} = \sqrt{K_a.C} = \sqrt{K_a}$ or

$pH_1 = -\dfrac{1}{2}\log K_a = \dfrac{1}{2}pK_a$.

$$CH_3COOH \;+\; CH_3COONa$$
    1   1

$\therefore$ pH = $pK_a + \log\dfrac{1}{1}$.

$pH_2 = pK_a$.

$\therefore$ $\dfrac{pH_1}{pH_2} = \dfrac{1}{2}$.

Comprehension # 3 :

1. For SrF_2 in pure water

$$4s_1^3 = K_{sp}$$

For SrF_2 in 0.1 M NaF solution

$$s_2(0.1)^2 = K_{sp}$$

$$\Rightarrow 4s_1^3 = s_2(0.01)$$

$$\Rightarrow 4s_1^3 = s_1 \times \frac{256}{10^6}(0.01)$$

$$\Rightarrow s_1 = 8 \times 10^{-4}\,M$$

$$\therefore K_{sp} = 4s_1^3 = 2.048 \times 10^{-9}$$

2. $[Sr^{2+}]_i = 0.0011 = 11 \times 10^{-4}\,M$

$[Sr^{2+}]_f = 2 \times 10^{-4}\,M$

$\therefore [Sr^{2+}]$ precipitated $= (11-2) \times 10^{-4}\,M$

$$= 9 \times 10^{-4}\,M$$

$[F^-]$ needed for this precipitation $= 2 \times 9 \times 10^{-4} = 18 \times 10^{-4}\,M$

Also, $[Sr^{2+}]_f [F^-]_f^2 = K_{sp} = 2.048 \times 10^{-9}$

But, $[Sr^{2+}]_f = 2 \times 10^{-4}\,M$

$\therefore [F^-]_f = 3.2 \times 10^{-3}\,M$

$\therefore$ Total $[F^-]$ needed $= 3.2 \times 10^{-3} + 18 \times 10^{-4} = 5 \times 10^{-3}\,M$

$\therefore$ NaF needed for 100 ml solution $= \dfrac{5 \times 10^{-3} \times 42}{10} = 0.021\,g$

3. $SrF_2 \longrightarrow Sr^{2+} + 2F^-$

$\qquad\qquad s \qquad 2s$
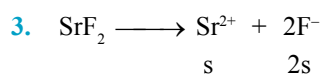
F^- will react with H^+ to produce HF

$F^- + H^+ \rightleftharpoons HF$
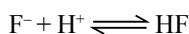
$$K = \frac{1}{K_a} = \frac{[HF]}{[H^+][F^-]} = \frac{7}{10^{-5}}$$

$\therefore [HF] = 7 \times 10^5 [F^-][H^+] \qquad (\because [H^+] = 10^{-5}\,;\,pH=5)$

$\qquad = 7 \times 10^5 [F^-] \times 10^{-5} = 7[F^-]$

Here, $[F^-] + [HF] = 2s$

$$\therefore [F^-] = \frac{s}{4}$$

$$K_{sp} = s\left(\frac{s}{4}\right)^2 = 2.048 \times 10^{-9}$$

$$\therefore s = 3.2 \times 10^{-3}\,mol/L$$

Comprehension # 4 :

1. Suppose volume of $HCO_3^- = V\,mL$

millimoles of $HCO_3^- = 5V$

millimoles of $H_2CO_3 = 20$

$$pH = pK_a + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$7.40 = 6.11 + \log\frac{V}{4}, \qquad \textbf{V = 78 mL}$$

3. If CO_2 escapes, $[H^+]$ decreases, hence pH increases.

Comprehension # 5 :

1. Phosphoric acid with three ionisable hydrogens ions is a tribasic acid. H-atoms are attached to O-atoms,

2. If first step is only taken

$$pH = \frac{1}{2}[pK_{a_1} - \log c] \quad c = [H_3PO_4] = 0.05\,\%$$

$$= \frac{0.05 \times 10}{98}\,mol\,L^{-1}(M) = 5.1 \times 10^{-3}\,M$$

$-\log c = 2.3, \quad pK_{a_1} = 2.12 \quad pH = 2.21$

3. $\dfrac{[H^+]^3[PO_4^{3-}]}{[H_3PO_4]} = K_{a_1} K_{a_2} K_{a_3}$

$3\log[H^+] + \log[PO_4^{3-}]$

$= \log K_{a_1} + \log K_{a_2} + \log K_{a_3} - \log[H_3PO_4]$

$3pH - \log[PO_4^{3-}] = \log[H_3PO_4] = pK_{a_1} + pK_{a_2} + pK_{a_3}$

$21 - \log[PO_4^{3-}] - 3 = 2.12 + 7.21 + 12.32$

$\log[PO_4^{3-}] = -3.65$

$[PO_4^{3-}] = 2.24 \times 10^{-4}\,M$

4. $Zn_3(PO_4)_2 \rightleftharpoons 3Zn^{2+} + 2PO_4^{3-}$
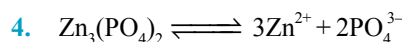
$\therefore K_{sp} = [Zn^{2+}]^3 [PO_4^{3-}]^2$

$9.1 \times 10^{-33} = [Zn^{2+}]^3 (2.2 \times 10^{-4})^2$

$[Zn^{2+}]^3 = 1.88 \times 10^{-25} \quad [Zn^{2+}] = 5.73 \times 10^{-9}\,M$

EXERCISE - 4

Subjective Type

1.

	HCl	H_2SO_4	NaOH
mili mole	20	40	$\dfrac{2}{40} \times 1000 = 50$
milieq.	20	80	50

remain milieq. of Acid $= 50$

$$[H^+] = \frac{50 \times 10^{-3}}{5} = 10^{-2}\,M \Rightarrow pH_1 = 2$$

Now Total milieq. of Acid $= (50 + 10 \times 2) = 70$

$$milieq.\ of\ NaOH = \frac{4 \times 10^3}{40} = 100$$

As milieq of Base is greater than milieq. of Acid so resulting solution is Basic

Remaining milieq. of Base $= 30$

$$[OH^-] = \frac{30 \times 10^3}{5} = 6 \times 10^{-3}\,M$$

$pOH = 3 - \log 6 = 2.22 \implies pH_2 = 11.78$

So change in pH $= 11.78 - 2 = \textbf{9.78}$

3. (i) $CH_3COOH = 0.2\,M$

$[H^+] = \sqrt{K_a \times C} = \sqrt{2 \times 10^{-5} \times 0.2} = \sqrt{4 \times 10^{-6}}$

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

$pH = 3 - \log 2 = \textbf{2.7}$

$C\alpha = [H^+] \implies \alpha = \dfrac{2 \times 10^{-3}}{2 \times 10^{-1}} \implies \alpha = \textbf{0.01}$

(ii) $HCl \longrightarrow H^+ + Cl^-$

$\quad 0.1 \qquad\qquad 0.1 \quad 0.1$

$[H^+] = 0.1 \qquad pH = 1$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$0.2 \qquad\qquad\quad O \qquad\qquad 0.1$

$0.2\,(1-\alpha) \qquad 0.2\,\alpha \qquad 0.1 + 0.2\,\alpha = 0.1$

$K_a = \dfrac{0.2\alpha \times 0.1}{0.2} = 2 \times 10^{-5} \qquad \alpha = 2 \times 10^{-4}$

(iii) $[CH_3COO^-] = 0.2 \times 2 \times 10^{-4} = \textbf{4} \times \textbf{10}^{-5}$

(iv) % change in $\alpha = \dfrac{1 \times 10^{-2} - 2 \times 10^{-4}}{1 \times 10^{-2}} \times 100$

$= \left[1 - \dfrac{2}{100}\right] \times 100 = \textbf{98 \%}$

5. $pH = 6$

$[H^+] = 10^{-6}$

$N_1V_1 = N_1V_2$

$\implies 10^{-6} \times 1 = N_2\left[1 + \dfrac{7}{3}\right] \qquad \implies 10^{-6} = N_2 \times \dfrac{10}{3}$

$N_2 = \dfrac{3}{10} \times 10^{-6} \qquad\qquad \implies N_2 = 3 \times 10^{-7}$

$[H^+] < 10^{-6}$

So $[H^+]$ of water is also added. as common ion effect on H_2O is neglected so

$[H^+] = 3 \times 10^{-7} + 10^{-7} = 4 \times 10^{-7}\,M$

$\implies pH = 7 - \log 4 = 7 - 0.60 = \textbf{6.4}$

6. $HA + NaOH \rightarrow NaA + H_2O; \qquad$ or

$HA + OH^- \rightarrow A^- + H_2O$

$K_{eq.} = 10^9 = \dfrac{[A^-][H_2O]}{[HA][OH^-]}$

Also $\quad HA \rightleftharpoons H^+ + A^- \qquad K_a = \dfrac{[H^+][A^-]}{[HA]}$

$\therefore \dfrac{K_{eq}}{K_a} = \dfrac{1}{K_w}$ or $K_a = 10^9 \times 10^{-14} = 10^{-5} \qquad$ Thus for

$A^- + H_2O \rightleftharpoons HA + OH$
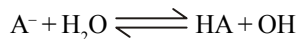
$[OH^-] = Ch = C\sqrt{\dfrac{K_H}{C}} = \sqrt{\dfrac{K_wC}{K_a}} = \sqrt{\dfrac{10^{-14} \times 0.1}{10^{-5}}} = 10^{-5}M$

$\therefore [H^+] = 10^-$ and $pH = 9$

7. $Asc^- + H_2O \rightleftharpoons HAsc + OH^-$

$\therefore [OH^-] = C.h = C\sqrt{\dfrac{K_h}{C}} = \sqrt{K_h.C} = \sqrt{\dfrac{K_w}{K_a} \cdot C}$

$= \sqrt{\dfrac{10^{-14} \times 0.02}{5 \times 10^{-5}}} = 2 \times 10^{-6}$

$\therefore [H^+] = \dfrac{1 \times 10^{-14}}{2 \times 10^{-6}} = 5 \times 10^{-9}\,M$

Also $\quad h = \sqrt{\left[\dfrac{K_h}{C}\right]} = \sqrt{\dfrac{K_w}{K_a \times C}} = \sqrt{\dfrac{10^{-14}}{5 \times 10^{-5} \times 0.02}}$

$= 10^{-4}$ or **0.01 %**

9. $HA + H_2O \rightleftharpoons H_3^+O + A^-$
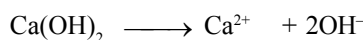
$K_a = \dfrac{[H_3O^+][A^-]}{[HA]} = \dfrac{C^2\alpha^2}{C(1-\alpha)}$

with in an error of 10% $\quad C(1-\alpha)$ or $C - C\alpha = 0.90\,C.$

or $\qquad\qquad\qquad C\alpha = 0.10\,C.$

$K_a = \dfrac{(0.10C)^2}{0.90C} = \dfrac{C}{90} \qquad$ or $\quad C = \textbf{90 } \textbf{K}_\textbf{a}.$

10. Let a mole of $Ca(OH)_2$ be dissoved in 250 mL solution to have $pH = 10.65$.

$[Ca(OH)_2] = \dfrac{a \times 1000}{250} = 4a\,M$

$Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-$

$\qquad\qquad\qquad\qquad\qquad$ Complete ionization

Initial moles 4a $\qquad\qquad 0 \qquad\qquad 0$

Final moles 0 $\qquad\qquad 4a \qquad 2 \times 4a\,M$

$\therefore [OH^-] = 8a\,M$

$[H^+] = \dfrac{10^{-14}}{8a} \qquad\qquad \implies pH = -\log[H^+]$

$\therefore 10.65 = -\log \dfrac{10^{-14}}{8a} \implies \dfrac{10^{-14}}{8a} = 2.238 \times 10^{-11}.$

$\therefore a = \textbf{5.58} \times \textbf{10}^{-5}\textbf{ mole.}$

416

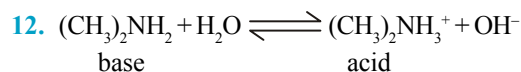**11.** $K_a = \dfrac{C\alpha^2}{1-\alpha}$

$40\,\alpha^2 + \alpha - 1 = 0$

$\alpha = 0.146$

$[H^+] = C\alpha = 1.75 \times 10^{-3}\,M$

$pH = \mathbf{2.76}$

12. $(CH_3)_2NH_2 + H_2O \rightleftharpoons (CH_3)_2NH_3^+ + OH^-$
$\quad\quad$ base $\quad\quad\quad\quad\quad\quad\quad$ acid

$K_b = \dfrac{[(CH_3)_2NH_3^+][OH^-]}{[(CH_3)_2NH_2]} = \dfrac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \dfrac{c\alpha^2}{(1-\alpha)}$

$5.4 \times 10^{-4} = 0.02 \times \alpha^2$.

$\therefore \quad \alpha = 0.164$.

Since $\quad \alpha > 0.1$, we will use $K_b = \dfrac{c\alpha^2}{(1-\alpha)} \quad\quad$ or

$5.4 \times 10^{-4} = \dfrac{0.02 \times \alpha^2}{(1-\alpha)}$

Now $\quad \alpha = 0.151$

In presence of NaOH, the dissociation of diethylamine will decrease due to common ion effect. Thus $0.1 + ca = 0.1 + c\alpha \simeq$ and $0.1 \,\&\, (1-\alpha) \simeq 1$

Thus $\quad K_b = 5.4 \times 10^{-4} = \dfrac{c\alpha \times (0.1 + c\alpha)}{c(1-\alpha)} = \alpha \times 0.1$.

or $\quad\quad \alpha = 5.4 \times 10^{-3} = \mathbf{0.0054}$.

13. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
$\quad\quad 1 \quad\quad\quad\quad\quad 0 \quad\quad\quad 0$
$\quad 1-\alpha \quad\quad\quad\quad\quad \alpha \quad\quad\quad \alpha$
$(pK_a = -\log K_a = 4.74, \quad\quad \therefore \quad K_a = 1.82 \times 10^{-5})$
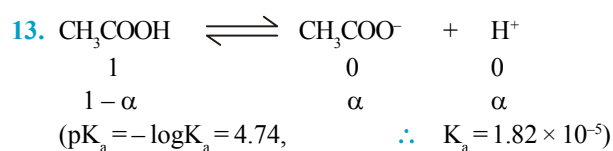
$K_a = \dfrac{c\alpha^2}{(1-\alpha)} = c\alpha^2 \quad\quad\quad\quad (1-\alpha \approx 1)$.

$\therefore \quad \alpha = \sqrt{\dfrac{K_a}{c}} = \sqrt{\dfrac{1.82 \times 10^{-5}}{0.05}} = \mathbf{0.019\ or\ 1.9\%}$.

Always calculate a first by $K_b = c\alpha^2$, if $\alpha > 10\%$ then use again.

$K = \dfrac{c\alpha^2}{(1-\alpha)}$

(a) If H^+ are already present (due to HCl)

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
$\quad\quad 1 \quad\quad\quad\quad\quad 0 \quad\quad\quad 0.01$
$\quad c(1-\alpha) \quad\quad\quad\quad c\alpha \quad\quad [0.01 + c\alpha]$.
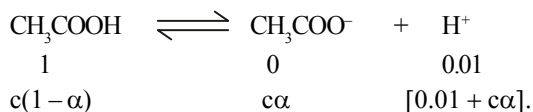
$K_b = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \dfrac{c\alpha \times (0.01 + c\alpha)}{c(1-\alpha)}$

Since presence of H^+ will favour the reverse reaction or α will decrease.

i.e., $\quad 0.01 + c\alpha = 0.01 \quad$ and $\quad 1 - \alpha = 1$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (due to common ion effect).

$\therefore \quad\quad 1.82 \times 10^{-5} = \dfrac{0.05 \times \alpha \times 0.01}{0.05}$.

$\therefore \quad\quad \alpha = 1.82 \times 10^{-3} = \mathbf{0.0018}$.

(b) Similarly solve for 0.1 M HCl

$\quad\quad \alpha = \mathbf{0.00018}$.

14. $C_6H_5OH + C_5H_5N \rightleftharpoons C_6H_5O^- + C_5H_5NH^+$
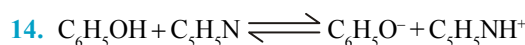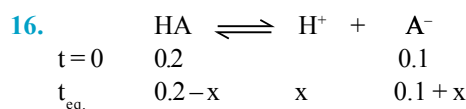
$K_n = \dfrac{K_a K_b}{K_w} = \mathbf{2.34 \times 10^{-5}}$

K_n being small and thus neutralisation does not proceed very far towards completion.

15.
	HCOONa	+ HCl	$\rightleftharpoons$ HCOOH	+ NaCl
Initially mM	6.25	0.25	0	0
Finally mM	6	0	0.25	0.25
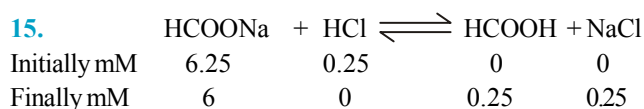
$\therefore \quad pH = 3.75 + \log \dfrac{6}{0.25} = 3.75 + \log 24 = 5.13$

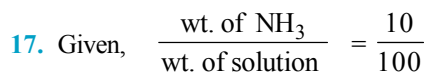Also $\quad [HCOOH] = \dfrac{0.25}{60} = \mathbf{4.17 \times 10^{-3}\ M}$

16.
	HA	$\rightleftharpoons$ H$^+$	+ A$^-$
$t = 0$	0.2		0.1
$t_{eq.}$	$0.2 - x$	x	$0.1 + x$

$K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{x(0.1+x)}{(0.2-x)}$

$\Rightarrow \quad 0.05 = \dfrac{x^2 + 0.1x}{0.2 - x}$

$\Rightarrow \quad 0.01 - 0.05\,x = x^2 + 0.1\,x$

$\quad\quad x^2 + 0.15\,x - 0.01 = 0$

$\quad\quad x = \mathbf{0.05\ M}$

17. Given, $\quad \dfrac{\text{wt. of } NH_3}{\text{wt. of solution}} = \dfrac{10}{100}$

$\therefore \quad$ 100 g dsolution contains 10 g NH_3

$\therefore \quad M_{NH_3} = (10 \times 1000)/[17 \times (100/0.99)]$
$\quad\quad (\because V = \text{mass / density})$

Now $\quad NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

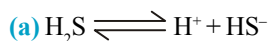$\therefore$ $\quad\quad\quad [OH^-] = C.\alpha = C\sqrt{(K_b/C)} = \sqrt{(K_b.C)}$

$[\therefore C = 5.82\ M$ and $K_b = k_w/K_a = 10^{-14}/(5\times10^{-10})$
$= 2\times10^{-5}]$

$\therefore$ $\quad [OH^-] = \sqrt{[2\times10^{-5}\times5.82]} = \mathbf{1.07\times10^{-2}\ M}$

$\therefore$ $\quad [H^+] = 10^{-14}/1.07\times10^{-2}$
$\quad\quad\quad = \mathbf{0.9268\times10^{-12}\ M}$

$\therefore$ $\quad pH = -\log[H^+] = -\log0.9268\times10^{-12} = \mathbf{12.0330}$

18. Dissociation of H_2S can be represented as

(a) $H_2S \rightleftharpoons H^+ + HS^-$

(b) $HS^- \rightleftharpoons H^+ + S^{2-}$

From the first ionisation of $H_2S = \dfrac{[H^+][HS^{-1}]}{[H_2S]} = K_{a_1}$

Since H_2S is weakly ionised and its ionisation is further decreased in presence of highly ionised HCl, concentration of H^+ in solution will be mainly due to HCl. Thus $[H^+] = 0.2\ M.$
Substituting the value in the above reaction

$\dfrac{0.2[HS^-]}{0.1} = 1\times10^{-7}$

$[HS^-] = 5\times10^{-8}\ M$

From the second ionisation of H_2S,

$\dfrac{[H^+][S^{2-}]}{[HS^-]} = Ka_2$ or $\dfrac{0.2\times[S^{2-}]}{5\times10^{-8}} = 1.3\times10^{-13}$

$[S^{2-}] = 3.25\times10^{-20}\ M$

19. $HA \rightleftharpoons H^+ + A^-$
$\quad c(1-\alpha) \quad\quad c\alpha \quad c\alpha$
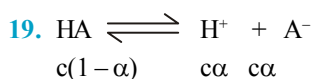
$pH = pK_a + \log\dfrac{[A^-]}{[HA]} = pK_a + \log\dfrac{c\alpha}{c(1-\alpha)}$

$\Rightarrow$ $pH = pK_a + \log\left(\dfrac{\alpha}{1-\alpha}\right) = pK_a - \log\left(\dfrac{1-\alpha}{\alpha}\right)$

$\Rightarrow$ $\log\left(\dfrac{1-\alpha}{\alpha}\right) = pK_a - pH.$

$\Rightarrow$ $\left(\dfrac{1-\alpha}{\alpha}\right) = 10^{(pK_a-pH)}$

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

20. $HA \rightleftharpoons H^+ + A^-$
$\quad c-x \quad\quad x \quad\quad x$
$[H^+] = x = 1.5\times10^{-3}\ M$
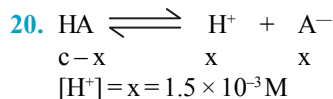
$K_a = \dfrac{x^2}{c-x}$

$2.5\times10^{-3} = \dfrac{(1.5\times10^{-3})^2}{c-1.5\times10^{-3}}$.

$c = \mathbf{2.4\times10^{-3}\ M.}$

21. $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$.
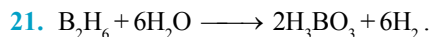
concentration $H_3BO_3 = c = 2\times\dfrac{1}{27.6}\times\dfrac{1000}{100} = 0.725$

$HA \rightleftharpoons H^+ + A^-$
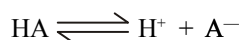
$[H^+] = \sqrt{K_a c} = \sqrt{7.3\times10^{-10}\times0.725} = 2.3\times10^{-5}$.

$pH = -\log[H^+] = \mathbf{4.64.}$

22. meq. of $H^+ = 10\times0.1 + 40\times0.2\times2 = 17$.

$[H^+] = \dfrac{17}{50} = 0.34.$

$pH = \mathbf{0.47}$

23. $[H^+] = \dfrac{10-9.9}{109.9} = \dfrac{0.1}{109.9} = 9.1\times10^{-4}$

$pH = 4.0 - \log9.1 = \mathbf{3.04}$

24. $pV = nRT$

$n = \dfrac{(740-23.7)}{760}\times100\times\dfrac{1}{0.0821\times298}\times10^{-3}$
$= 3.85\times10^{-3}\ M$
$[HCl] = 3.85\times10^{-3}\ M = [H^+]$.
$pH = 3 - \log3.85 = \mathbf{2.41}$

25. $\quad\quad C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$
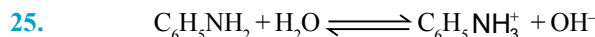
Thus, $\quad K_b = \dfrac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$

$\dfrac{10^{-14}}{2.4\times10^{-5}} = \dfrac{10^{-8}\times[OH^-]}{0.24}$

$\therefore$ $\quad [OH^-] = 10^{-2}\ M$

26. pH of Final Solution $= 1$
$\quad pH = 1$
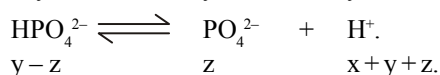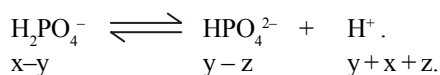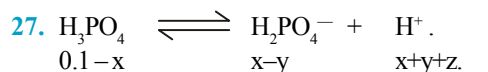$\quad [H^+] = 10^{-1}$

Initial $\to M = \dfrac{P\times d\times10}{M.W.} = \dfrac{36.5\times10\times1.25}{36.5}$ $\quad M = 12.5$

$N_1V_1 = N_2V_2 \quad\Rightarrow 12.5\times V_1 = 10^{-1}\times2.5$

$V_1 = \dfrac{2.5}{125} \quad\quad V_1 = .02\ lit \quad\quad = 20\ ml$

27. $H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+.$
$0.1-x \qquad\quad x-y \qquad x+y+z.$

$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+.$
$x-y \qquad\quad y-z \qquad y+x+z.$

$HPO_4^{2-} \rightleftharpoons PO_4^{2-} + H^+.$
$y-z \qquad\quad z \qquad\quad x+y+z.$

$$K_{a1} = \frac{(x-y)(x+y+z)}{0.1-x} = \frac{x^2}{0.1-x}$$

$(y+z$ are very small compared to $x)$

$$7.5 \times 10^{-3} = \frac{x^2}{0.1-x} \quad \Rightarrow \quad x = 0.024\,M$$

$$K_{a2} = \frac{(y-z)(x+y+z)}{x-y} = \frac{y.x}{x} = y.$$

$y = 6.2 \times 10^{-8}$ \qquad\qquad (here $z \ll y$)

$$K_{a3} = \frac{z(x+y+z)}{y-z} = \frac{z.x}{y}.$$

$$z = K_{a3}.\frac{y}{x}. = 9.3 \times 10^{-19}\,M$$

$\therefore$ $[H_3PO_4] = 0.1 - x = 0.076\,M$
$[H^+] = [H_2PO_4^-] = x = 0.024\,M$
$[HPO_4^{2-}] = 6.2 \times 10^{-8}\,M$
$[PO_4^{3-}] = z = 9.3 \times 10^{-19}\,M$

$$[OH^-] = \frac{K_w}{[H^+]} = 4.17 \times 10^{-13}\,M$$

28. $HA \rightleftharpoons H^+ + A^-$
$C_0-x \qquad x+y \qquad x$

$H_2O \rightleftharpoons H^+ + OH^-$
$\qquad\qquad x+y \quad y$
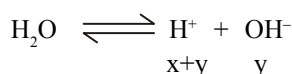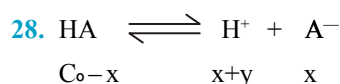
$$K_a = \frac{[H^+]x}{c_0-x}, \qquad [H^+]\,y = 10^{-14} = K_w$$

Where $[H^+] = x + y.$

$$y = \frac{K_W}{[H^+]}, x = \frac{K_a c_0}{K_a + [H^+]}.$$

$$[H^+] = x + y = \frac{K_W}{[H^+]} + \frac{K_a c_0}{K_a + [H^+]}.$$

$$10^{-3} = 10^{-11} + \frac{0.1\,K_a}{K_a + 10^{-3}}$$

$K_a + 10^{-3} = 100\,K_a$

$$K_a = \frac{10^{-3}}{99} \approx 10^{-5}.24$$

29. $HCl \longrightarrow H^+ + Cl^-$
$0.01 \qquad\qquad 0.01 \quad 0.01$

$CHCl_2COOH \rightleftharpoons CHCl_2COO^- + H^+$
$0.01 \qquad\qquad\qquad 0 \qquad\qquad 0.01$
$0.01(1-\alpha) \qquad\quad 0.01\,\alpha \qquad 0.01+0.01\,\alpha$
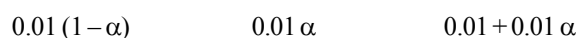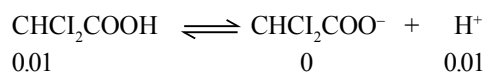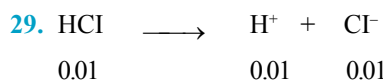
$$K_a = \frac{0.01\alpha\,[0.01+0.01\alpha]}{0.01(1-\alpha)} = 2 \times 10^{-2}$$

$0.01\,\alpha^2 + 0.01\,\alpha = 2 \times 10^{-2}$
$10^{-2}\,\alpha^2 + 10^{-2}\,\alpha = 2 \times 10^{-2}$
$\alpha^2 + \alpha - 2 = 0$

$$\alpha = \frac{-2 \pm \sqrt{1+8}}{2} = \frac{-2+3}{2} \Rightarrow \alpha = 0.56$$

$[H^+] = 10^{-2} + 10^{-2} \times 0.56 = \mathbf{1.56 \times 10^{-2}\,M}$
$[CHCl_2COO^-] = 0.01\,\alpha = \mathbf{5.6 \times 10^{-3}\,M}$

30. pH of $(Na_2C_2O_4)$ $\quad C = 0.5 \times 10^{-3}$
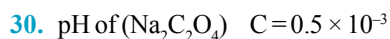
$$pH = 7 + \frac{1}{2}\,pK_{a2} + \frac{1}{2}\,\log C$$

Here $\quad pK_{a2} = [6 - \log 5]$

$$pH = 7 + \frac{1}{2}\,[6 - \log 5] + \frac{1}{2}\,[\log 5 \times 10^{-4}]$$

$$= 7 + \frac{1}{2}\,[6 - \log 5] + \frac{1}{2}\,[\log 5 - 4] = 8$$

$[H^+] = 10^{-8} \quad$ So $\quad [OH^-] = \mathbf{10^{-6}\,M}$

31. $\qquad AlCl_3 \qquad\quad C = 0.15\,M \quad$ ($AlCl_3$ is SAWB)

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H_3O^+$$

At $t = 0 \qquad 0.15 \qquad\qquad - \qquad\qquad O \qquad\qquad O$
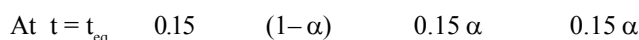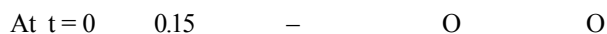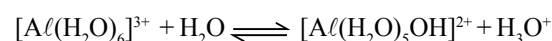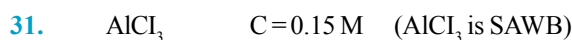
At $t = t_{eq} \quad 0.15 \qquad (1-\alpha) \qquad 0.15\,\alpha \qquad 0.15\,\alpha$
$\qquad\qquad K_a = 1.5 \times 10^{-5}$

$$K_a = \frac{0.15\alpha \times 0.15\alpha}{0.15[1-\alpha]} = 1.5 \times 10^{-5}$$
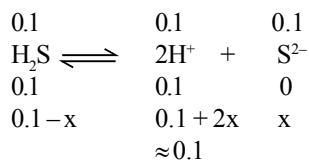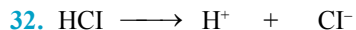
$\Rightarrow$ $1.5 \times 10^{-1}\,\alpha^2 = 1.5 \times 10^{-5}$

$\Rightarrow$ $\alpha^2 = 10^{-4}$
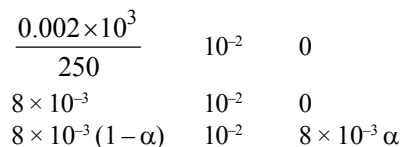
$\Rightarrow$ $\alpha = 10^{-2}$

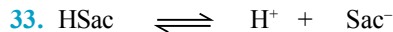$[H_3O^+] = 0.15 \times 10^{-2} = 1.5 \times 10^{-3}\,M$

$\Rightarrow$ $pH = 3 - \log 1.5 = 3 - 0.18 = 2.82$

32. $HCl \longrightarrow H^+ + Cl^-$
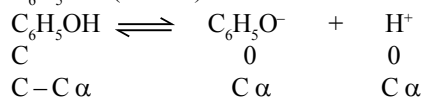
$\qquad$ 0.1 $\qquad$ 0.1 $\qquad$ 0.1

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

$\qquad$ 0.1 $\qquad$ 0.1 $\qquad$ 0

$\qquad$ 0.1 – x $\qquad$ 0.1 + 2x $\qquad$ x

$\qquad\qquad\qquad \approx 0.1$

$K_a = 1.1 \times 10^{-22} = \dfrac{[H^+]^2 [S^{2-}]}{[H_2S]}$

$[S^{2-}] = 1.1 \times 10^{-21} M$

33. $HSac \rightleftharpoons H^+ + Sac^-$

$\dfrac{0.002 \times 10^3}{250} \qquad 10^{-2} \qquad 0$

$8 \times 10^{-3} \qquad\qquad 10^{-2} \qquad 0$

$8 \times 10^{-3}(1-\alpha) \qquad 10^{-2} \qquad 8 \times 10^{-3}\alpha$

$K_a = \dfrac{10^{-2}[8 \times 10^{-3}\alpha]}{8 \times 10^{-3}(1-\alpha)} = 2 \times 10^{-12} \qquad \Rightarrow \quad \alpha = 2 \times 10^{-10}$

$[Sac^-] = 8 \times 10^{-3} \times 2 \times 10^{-10} = 16 \times 10^{-13} = 1.6 \times 10^{-12} M$

34. C_6H_5OH (Phenol) $\longrightarrow$ Weak acid $K_a = 1 \times 10^{-10}$

$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$

$\qquad$ C $\qquad\qquad\qquad$ 0 $\qquad\quad$ 0

$\qquad$ C – C α $\qquad\qquad$ C α $\qquad$ C α
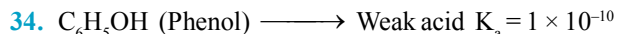
$K_a = C\alpha^2 = 1 \times 10^{-10}$

$\alpha = \sqrt{\dfrac{1 \times 10^{-10}}{0.05}} = \sqrt{20 \times 10^{-10}} \qquad \alpha = 4.47 \times 10^{-5}$

$[C_6H_5O^-] = 4.47 \times 10^{-5} \times 0.05 \qquad = 2.42 \times 10^{-6}$

$[C_6H_5ONa] = 0.01 M$

$C_6H_5ONa \longrightarrow C_6H_5O^- + Na^+$

$\qquad$ 0.01 $\qquad\qquad\qquad$ 0.01 $\qquad$ 0.01

$C_6H_5OH \longrightarrow C_6H_5O^- + H^+$

$\qquad$ 0.05 $\qquad\qquad\qquad$ 0.01 $\qquad$ O

$\qquad$ 0.05 (1 – α) $\qquad\qquad$ 0.01 $\qquad$ 0.05 α
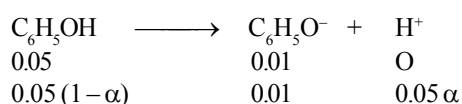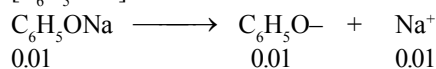
$\dfrac{[0.05\alpha]\, 0.01}{0.05} = 1 \times 10^{-10} \qquad \alpha = 10^{-8}$

36. $H_3PO_4 = \dfrac{0.98}{98} = 10^{-2}\, Mole$
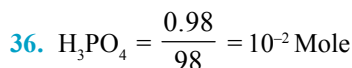
$\Rightarrow [H_3PO_4] = \dfrac{10^{-2}}{100} \times 10^3 = 0.1\, M$

$pH = 5 \quad [H^+] = 10^{-5}$
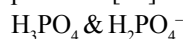
$H_3PO_4 \, \& \, H_2PO_4^-$

$pH = pK_{a1} + \log \dfrac{[H_2PO_4^-]}{[H_3PO_4]}$

$\Rightarrow \quad 5 = 3 + \log \dfrac{[H_2PO_4^-]}{[H_3PO_4]} \qquad \Rightarrow 10^2 = \dfrac{[H_2PO_4^-]}{[H_3PO_4]}$

$[H_2PO_4^-] = 10^2\,[H_3PO_4] \Rightarrow$ But $[H_3PO_4] + [H_2PO_4^-] = 0.1$

$H_3PO_4 + 10^2\,[H_3PO_4] = 0.1 \Rightarrow [1 + 10^2]\,[H_3PO_4] = 0.1$

$[H_3PO_4] = \mathbf{10^{-3}\, M} \qquad\qquad \Rightarrow \quad [H_2PO_4^-] = 0.1\, M$

For $H_2PO_4^- \, \& \, HPO_4^{2-} \Rightarrow \quad pH = pK_{a2} + \log \dfrac{[HPO_4^{2-}]}{[H_2PO_4^1]}$

$5 = 8 + \log \dfrac{[HPO_4^{2-}]}{[H_2PO_4^{-1}]} \qquad \Rightarrow \quad -3 = \log \dfrac{[HPO_4^{2-}]}{[H_2PO_4^1]}$

$\dfrac{[HPO_4^{2-}]}{[H_2PO_4^1]} = 10^{-3} \qquad \Rightarrow [HPO_4^{2-}] = 10^{-3}\,[H_2PO_2^-]$

$[H_2PO_4^-] + [HPO_4^{2-}] = 0.1 \Rightarrow [H_2PO_4^-] + 10^{-3}\,[H_2PO_4^-] = 0.1$

$[1 + 10^{-3}]\,[H_2PO_4^-] = 0.1 \qquad \Rightarrow \quad [H_2PO_4^-] = \mathbf{0.1\, M} \Rightarrow$

$[HPO_4^{2-}] = \mathbf{10^{-4}\, M}$

Again

$pH = pK_{a3} + \log \dfrac{[PO_4^{-3}]}{[HPO_4^{-2}]} \Rightarrow 5 = 12 + \log \dfrac{[PO_4^{-3}]}{[HPO_4^{-2}]}$

$10^{-7} = \dfrac{[PO_4^{-3}]}{[HPO_4^{-2}]} \qquad\qquad \Rightarrow \quad [PO_4^{-3}] = 10^{-7}\,[HPO_4^{-2}]$

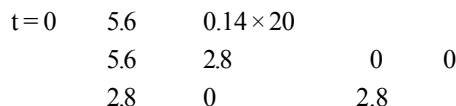$[HPO_4^{-2}] + [PO_4^{-3}] = 10^{-4} \Rightarrow [1 + 10^{-7}]\,[HPO_4^{-2}] = 10^{-4}$

$[PO_4^{-3}] = 10^{-7} \Rightarrow [HPO_4^{-2}] = \mathbf{10^{-11}\, M}$

37. **(a)** At eq. point

No. of milieq. of Base = No. of milieq. of HCl

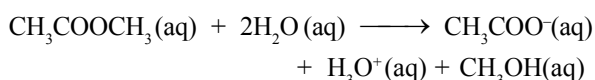$\dfrac{0.252 \times 1000}{Molar mass} = 0.14 \times 40$

∴ Molar mass of base = **45**

(b) $\qquad$ BOH + HCl $\longrightarrow$ BCl + H_2O

$t = 0 \qquad$ 5.6 $\qquad$ 0.14 $\times$ 20

$\qquad\qquad$ 5.6 $\qquad$ 2.8 $\qquad\qquad$ 0 $\qquad$ 0

$\qquad\qquad$ 2.8 $\qquad$ 0 $\qquad\qquad$ 2.8

$\qquad$ Basic buffer

$\qquad\qquad\qquad$ pH = 10.7 $\qquad$ So pOH = 3.3

$\qquad$ pOH = pK_b = 3.3

$K_b =$ Anti log (– 3.3) = Anti log (1 – 0.3) $\times 10^{-4} = \mathbf{5 \times 10^{-4}}$

38. $K_b(NH_3) = 1.8 \times 10^{-5}$

$$CH_3COOCH_3(aq) + 2H_2O(aq) \longrightarrow CH_3COO^-(aq) + H_3O^+(aq) + CH_3OH(aq)$$

$[NH_4^+]_0 = 0.1$ M, $[NH_3] = 0.06$ M, $[CH_3COOCH_3]_0 = 0.02$ M

$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]} = 4.74 + \log\left(\frac{0.1}{0.06}\right)$$

$(pOH)_{initial} = 4.74 + 0.22 = 4.96$ $\quad\therefore\quad (pH)_{initial} = \mathbf{9.04}$

$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$$
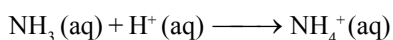
| 0.06 | 0.02 | 0.1 | mole |
| 0.04 | – | 0.12 | mole |

$$(pOH)_{final} = 4.74 + \log \frac{0.12}{0.04} = 4.74 + \log\left(\frac{0.12}{0.04}\right)$$

$= 4.74 + \log 3 = 4.74 + 0.48 = 5.22$

$\therefore (pH)_{final} = \mathbf{8.78}$

$\Delta pH = 9.04 - 8.78 = 0.26$

Yes this is satisfactory buffer.

40. Let V mL of NH_4OH be mixed with NH_4Cl to have a buffer of pH 8.65.

The total volume after mixing becomes $(V + 30)$ mL.

m mole of $NH_4OH = 0.3 \times V$

$$\therefore [NH_4OH] = \frac{0.3 \times V}{(V + 30)}$$

m mole of $NH_4Cl = 0.2 \times 30$

$$\therefore [NH_4Cl] = \frac{0.2 \times 30}{(V + 30)}$$

Also pOH of buffer mixture is given by :

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

$$14 - 8.65 = 4.74 + \log \frac{(0.2 \times 30)/(V + 30)}{(0.3 \times V)/(V + 30)} \quad (pOH = 14 - pH).$$

$$0.6 = \log \frac{6}{0.3V}.$$

$\therefore$ V = **5 mL.**

Similarly calculate

$$\left(14 - 10 = 4.74 + \log \frac{0.2 \times 30/(V_1 + 30)}{0.3 \times V_1/(V_1 + 30)}\right) \text{ for pH} = 10 ;$$

V = **111.11 mL.**

41. Initial pH of solution when,

$$[NH_3] = \frac{0.1}{1} \quad \text{and} \quad [NH_4Cl] = \frac{0.1}{1}$$

$$pOH = -\log 1.8 \times 10^{-5} + \log \frac{[Salt]}{[Base]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1} = 4.74$$

$\therefore$ pH = **9.26**

(i) Now 0.02 mole of HCl are added then

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

Mole before reaction	0.02	0.1	0.1
Mole after reaction	0	0.08	(0.1 + 0.02)

$\therefore$ Volume = 1 litre

$$\therefore [NH_4OH] = \frac{0.08}{1} \quad \text{and} \quad [NH_4Cl] = \frac{0.12}{1}$$

$$\therefore pOH_1 = -\log 1.8 \times 10^{-5} + \log \frac{0.12}{0.08} = 4.92$$

$\therefore$ pH_1 = **9.08**

Change in pH $= pH - pH_1 = 9.26 - 9.08 = +0.18$

$\therefore$ Change in pH = **0.18** and pH decreases

(ii) Now 0.02 mole of NaOH are added

$$NaOH + NH_4Cl \longrightarrow NaCl + NH_4OH$$

Mole before reaction	0.02	0.1	0	0.1
Mole after reaction	0	0.08	0.02	0.12

$$\therefore pOH_2 = -\log 1.8 \times 10^{-5} + \log \frac{0.08}{0.12} = 4.57$$

$\therefore$ pH_2 = **9.43**

Change in pH $= pH - pH2 = 9.26 - 9.43 = -0.18$

$\therefore$ Change in pH = **0.18 unit** i.e., pH **increases.**

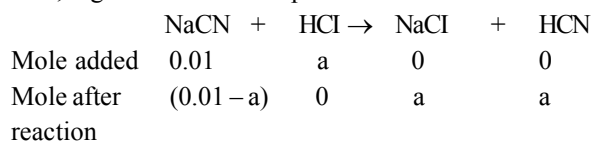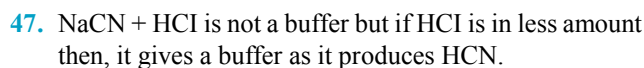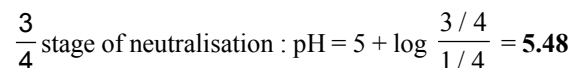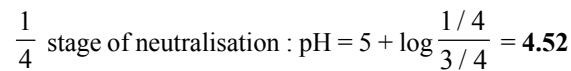**42.** Let V mL of 0.1 M HCOONa be mixed to 50 mL of 0.05 M HCOOH.
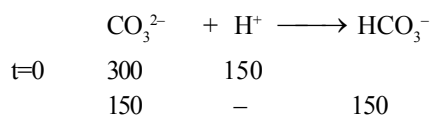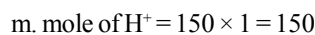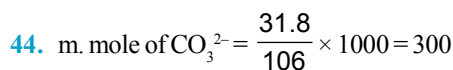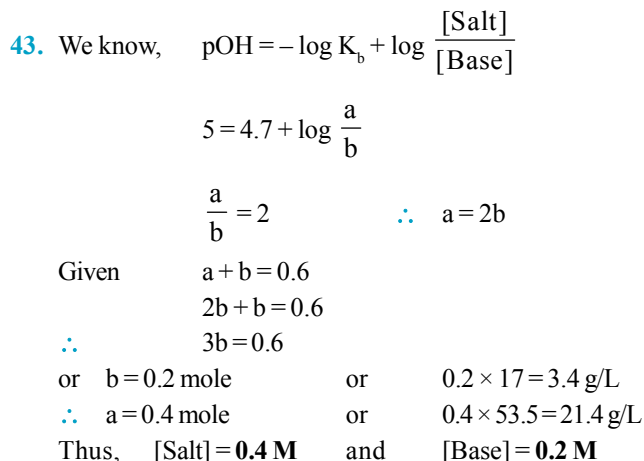
$$\therefore \text{ In mixture } [HCOONa] = \frac{0.1 \times V}{(V + 50)}$$

$$[HCOOH] = \frac{50 \times 0.05}{V + 50}$$
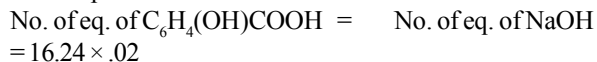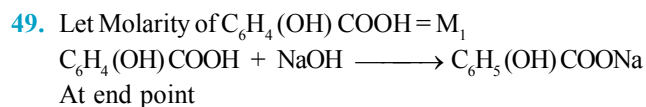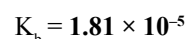
$$\therefore pH = -\log K_a + \log \frac{[Salt]}{[Acid]}$$

$$\therefore 4.0 = 3.7 + \log \frac{(0.1 \times V)/(V + 50)}{2.5/(V + 50)}$$

$\therefore$ V = **50 mL**

43. We know, $\quad pOH = -\log K_b + \log \dfrac{[Salt]}{[Base]}$

$$5 = 4.7 + \log \dfrac{a}{b}$$

$$\dfrac{a}{b} = 2 \qquad \therefore \quad a = 2b$$

Given $\quad a + b = 0.6$
$\qquad\qquad 2b + b = 0.6$
$\therefore \qquad\qquad 3b = 0.6$

or $\quad b = 0.2$ mole $\qquad$ or $\qquad 0.2 \times 17 = 3.4$ g/L
$\therefore \quad a = 0.4$ mole $\qquad$ or $\qquad 0.4 \times 53.5 = 21.4$ g/L

Thus, $\quad$ [Salt] = **0.4 M** $\quad$ and $\quad$ [Base] = **0.2 M**

44. m. mole of $CO_3^{2-} = \dfrac{31.8}{106} \times 1000 = 300$

m. mole of $H^+ = 150 \times 1 = 150$

$$CO_3^{2-} \quad + \quad H^+ \longrightarrow HCO_3^-$$

t=0 $\qquad$ 300 $\qquad\quad$ 150
$\qquad\quad$ 150 $\qquad\quad$ – $\qquad\qquad$ 150

so $\quad pH = pK_a + \log \dfrac{[CO_3^{2-}]}{[HCO_3^-]} = 10.3$.

45. $K_a = c\alpha^2 = 0.1 \times (0.01)^2 = 10^{-5}$.

$$HA \rightleftharpoons H^+ \quad + \quad A^-.$$
$0.1(1-\alpha) \qquad\quad 0.1\,\alpha \qquad 0.1\alpha + 0.2$.

$$10^{-5} = \dfrac{0.1\alpha \times (0.1\alpha + 0.2)}{0.1}$$

$\alpha = 5 \times 10^{-5} \qquad$ (Therefore, 0.1α is neglected).

46. pH of $CH_3COOH = \dfrac{1}{2}\,(pK_a - \log c)$

$$3 = \dfrac{1}{2}\,(pK_a - \log 0.1) \qquad \therefore \quad pK_a = 5$$

$\dfrac{1}{4}$ stage of neutralisation : $pH = 5 + \log \dfrac{1/4}{3/4} = \textbf{4.52}$

$\dfrac{3}{4}$ stage of neutralisation : $pH = 5 + \log \dfrac{3/4}{1/4} = \textbf{5.48}$

47. NaCN + HCI is not a buffer but if HCI is in less amount then, it gives a buffer as it produces HCN.

	NaCN +	HCI →	NaCI +	HCN
Mole added	0.01	a	0	0
Mole after reaction	(0.01 – a)	0	a	a

This is buffer of HCN + NaCN
Let a mole of HCI be used for this purpose

$\therefore \qquad pH = -\log K_a + \log \dfrac{0.01 - a}{a}$

$$8.5 = -\log (4 \times 10^{-10}) + \log \dfrac{0.01 - a}{a}$$

$\therefore \qquad$ a = **8.89×10^{-3} mole of HCI**

48. Case I: $\qquad\qquad BOH \;+\; HCI \;\rightarrow\; BCI +\; H_2O$

Millimole before reaction $\quad$ a $\qquad 0.1 \times 5 = 0.5 \quad 0 \qquad 0$
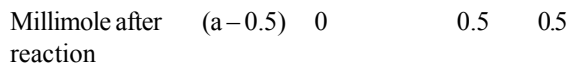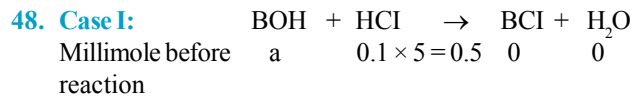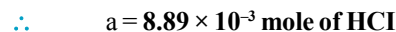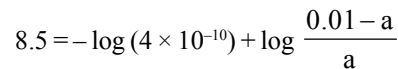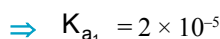
Millimole after reaction $\quad$ (a – 0.5) $\quad$ 0 $\qquad\quad 0.5 \qquad 0.5$

$\therefore \quad pH = 10.04$

$\therefore \quad pOH = -\log K_b + \log \dfrac{[BCI]}{[BOH]} \qquad$ ....(1)

$\therefore \quad pOH = 3.96$

$\therefore \quad 3.96 = -\log K_b + \log \dfrac{0.5}{(a - 0.5)} \qquad$ ...(2)

Case II : $\qquad\qquad BOH \;+\; HCI \;\rightarrow\; BCI \;+\; H_2O$

Millimole before reaction $\quad$ a $\qquad 0.1 \times 20 = 2$

Millimole after reaction $\quad$ (a – 2) $\qquad$ 0 $\qquad\quad 2 \qquad 2$

$\therefore \quad pH = 9.14$

$\therefore \quad pOH = -\log K_b + \log \dfrac{[BCI]}{[BOH]} \qquad$ ...(3)

$\therefore \quad pOH = 4.86$

$\therefore \quad 4.86 = -\log K_b + \log \dfrac{2}{a - 2} \qquad$ ...(4)

$\qquad\qquad K_b = \textbf{1.81} \times \textbf{10}^{-5}$

49. Let Molarity of $C_6H_4(OH)COOH = M_1$

$C_6H_4(OH)COOH \;+\; NaOH \longrightarrow C_6H_5(OH)COONa$

At end point

No. of eq. of $C_6H_4(OH)COOH = \quad$ No. of eq. of NaOH
$= 16.24 \times .02$

$$25 \times M_1 = 0.3248 \implies M_1 = \dfrac{0.3248}{25} = 0.013$$

Half neutrilazation

$C_6H_4(OH)COOH \;+\; NaOH \longrightarrow C_6H_5(OH)COONa$
$\;0.3248 \qquad\qquad 0.1624 \qquad\qquad 0 \qquad 0$
$\;0.1624 \qquad\qquad 0 \qquad\qquad\quad 0.1624$

$pH = pK_{a_1} + \log \dfrac{[C_6H_5(OH)COONa]}{[C_6H_5(OH)COOH]} \implies 4.7 = pK_{a_1}$

$\implies K_{a_1} = 2 \times 10^{-5}$

Complate Neutrilization

$$C_6H_5(OH)COOH + NaOH \longrightarrow C_6H_5(OH)COONa + H_2O$$

| 0.3248 | 0.3248 | 0 |
| 0 | 0 | 0.3248 |

$$[C_6H_5(OH)COONa] = \frac{0.3248}{41.24} = 7.88 \times 10^{-3}$$
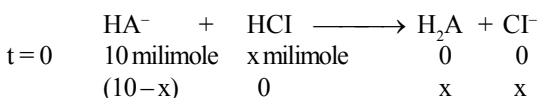
$C_6H_5(OH)COONa$ This species is amphiprotic species.

So $pH = \dfrac{pK_{a1} + pK_{a2}}{2} \Rightarrow 7.5 = \dfrac{4.7 + pK_{a2}}{2}$

$15 - 4.7 = pK_{a2} \qquad\qquad \Rightarrow pK_{a2} = 10.3$

$\Rightarrow K_{a2} = 5 \times 10^{-11}$

50. Let $\qquad\qquad$ Acid is H_2A

$H_2A \xrightarrow{\;K_{a1}\;} HA^- \xrightarrow{\;K_{a2}\;} A^{-2}$

For HA^-, $\qquad pK_{a2} = 9.7$

and $\qquad\qquad pK_b = 11.7 \quad$ So $pK_{a1} = 14 - 11.7 = 2.3$

$$HA^- + HCl \longrightarrow H_2A + Cl^-$$

| $t = 0$ | 10 milimole | x milimole | 0 | 0 |
| | $(10-x)$ | 0 | x | x |

This solution Act as Buffer solution

So $pH = pK_{a1} + \log \dfrac{[HA^-]}{[H_2A]} \Rightarrow 2.6 = 2.3 + \log \dfrac{[HA^-]}{[H_2A]}$

$0.3 = \log \dfrac{(10-x)}{x} \Rightarrow 2 = \left[\dfrac{10-x}{x}\right] \Rightarrow 2x = 10$

$-x$

$3x = 10 \qquad \Rightarrow x = 3.33$ milimole

51. $pK_a = 11 - \log 4.7 = 11 - \log 4.7 \qquad = 11 - 0.672 = 10.328$

$pH = pK_a + \log\left(\dfrac{n_{Na_2CO_3}}{0.3}\right)$

$10 = 10.328 + \log\left(\dfrac{n_{Na_2CO_3}}{0.3}\right)$

$\log \dfrac{0.3}{n_{Na_2CO_3}} = 0.328 \qquad \Rightarrow \dfrac{0.3}{n_{Na_2CO_3}} = 2.13$

$W_{Na_2CO_3} = \left[\dfrac{0.3}{2.13}\right] \times 106 = 14.94 \approx 15$ gram

52. $pH_1 = pK_a + \log \dfrac{x}{a}$

$pH_2 = pK_a + \log \dfrac{y}{a}$.

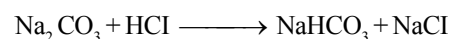$pH_2 - pH_1 = 0.6 = \log \dfrac{y}{x}$.

$y = x \, 10^{0.6} = 4x.$

$x : y = 1 : 4.$

53. We know that pH of a mixture of solution containing weak acid and strong base can be calculated as below

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

$$= 7 + \frac{1}{2} \times 4.72 + \frac{1}{2} \log 0.05 = 7 + 2.36 - 0.65 = 8.71$$

54. Let $NaHCO_3 + Na_2CO_3 + KCl$

$\qquad\qquad xg \qquad\quad yg$

At Ist equivalent point

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

Milimole HCl consumed $= 0.15 \times 10 = 1.5$

$$\left[\frac{Y}{106}\right] \times 1 \times 10^3 = 1.5 \qquad y = \frac{1.5 \times 106}{1000} = 0.159\,g$$

At IInd equivalent point

m. eq. of Na_2CO_3 + m. eq. of $NaHCO_3$ = m. eq. of $HCl = 35 \times 0.15$

$\Rightarrow \left[\dfrac{x}{84}\right] + \left[\dfrac{y}{106}\right] \times 2 = 0.15 \times 35 \times 10^{-3}$

$\Rightarrow \dfrac{x}{84} + (1.5 \times 10^{-3}) \times 2 = 5.25 \times 10^{-3}$

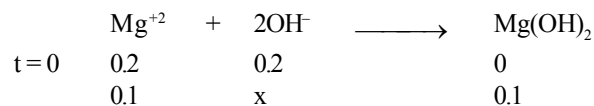$\Rightarrow x = \dfrac{(2.25 \times 84)}{1000} = 0.189\,g$

mass of $KCl = 0.152\,g$

mass % of $Na_2CO_3 = \dfrac{0.159 \times 100}{0.5} = 31.8\%$

mass % of $NaHCO_3 = \dfrac{0.189 \times 100}{0.5} = 37.8\%$

mass % of $KCl = \dfrac{0.152 \times 100}{0.5} = 30.4\%$
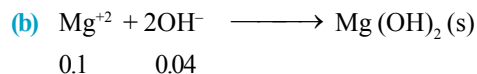
55. As the value of K_{sp} is very law so we.

(a) can assume that almost all the $Mg(OH)_2$ will Present in solid state.

$$Mg^{+2} + 2OH^- \longrightarrow Mg(OH)_2$$

| $t = 0$ | 0.2 | 0.2 | 0 |
| | 0.1 | x | 0.1 |

At the end of reaction $[Mg^{+2}] = 0.1$

$K_{sp}[Mg(OH)_2] = [Mg^{+2}][OH^-]^2 = 1.6 \times 10^{-12}$

$\Rightarrow [OH^-]^2 = \dfrac{1.6 \times 10^{-12}}{0.1} \Rightarrow [OH^-] = 4 \times 10^{-6}\,M$

$\Rightarrow pOH = 6 - \log 4 \Rightarrow pH = 14 - 6 + 0.6 = \textbf{8.6}$

(b) $Mg^{+2} + 2OH^- \longrightarrow Mg(OH)_2(s)$

$\quad\quad 0.1 \quad\quad 0.04$

At the end of reaction $[Mg^{+2}] = 0.1 - \dfrac{0.04}{2} = 0.08$

$K_{sp}(Mg(OH)_2) = [Mg^{+2}][OH^-]^2 = 1.6 \times 10^{-12}$

$[OH^-]^2 = \dfrac{1.6 \times 10^{-12}}{0.08} \Rightarrow [OH^-] = 4.47 \times 10^{-6}$

$\therefore pOH = 6 - \log 4.47 \quad = 5.35$

$pH = 14 - 5.35 = \mathbf{8.65}$

(c) $Mg(OH)_2 + 2HCl \longrightarrow Mg^{+2} + 2Cl^- + 2H_2O$

$\quad 0.1 \quad\quad\quad 0.04 \quad\quad\quad 0.1 \quad\quad - \quad\quad -$

$\quad 0.1 - 0.02 \quad\quad 0 \quad\quad\quad 0.1 + 0.02$
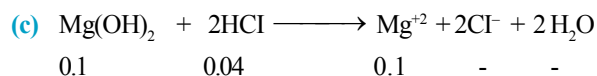
$[Mg^{+2}] = 0.12\,M$

$K_{sp}[Mg(OH)_2] = [Mg^{+2}][OH^-]^2 = 1.6 \times 10^{-12}$

$[OH^-]^2 = \dfrac{1.6 \times 10^{-12}}{0.12} = \dfrac{4}{3} \times 10^{-11}\,M^2$

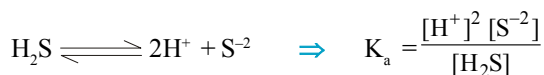$\Rightarrow [OH^-] = \sqrt{\dfrac{4}{3} \times 10^{-11}}\,M$

$\Rightarrow pOH = 5.44 \quad\quad \Rightarrow pH = 14 - \mathbf{5.44} = \mathbf{8.56}$

58. (a) $pK_a(CH_3COOH) = 4.74$

$[CH_3COOH] = 0.25\,M, \quad\quad [CH_3COONa] = 0.15\,M$

$[H^+] = \dfrac{K_a[CH_3COOH]}{[CH_3COO^-]}$

$= \dfrac{1.8 \times 10^{-5} \times 0.25}{0.15} = 3 \times 10^{-5}\,M$

$H_2S \rightleftharpoons 2H^+ + S^{-2} \quad \Rightarrow \quad K_a = \dfrac{[H^+]^2[S^{-2}]}{[H_2S]}$

$[S^{2-}] = \dfrac{9 \times 10^{-21} \times 0.1}{9 \times 10^{-10}} = 10^{-12}\,M$

$IP(MnS) = [Mn^{+2}][S^{-2}] = 1.5 \times 10^{-2} \times 10^{-12} = 1.5 \times 10^{-14}$

$IP < K_{sp} \rightarrow$ So No PPT is formed.

(b) For precipitation of MnS the minimum concentration of $[S^{2-}]$

$[Mn^{+2}][S^{2-}] = K_{sp}$

$1.5 \times 10^{-2} \times [S^{2-}] = 2.4 \times 10^{-13} \quad \Rightarrow \quad [S^{2-}] = 1.6 \times 10^{-11}\,M$
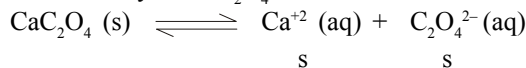
For this $[S^{2-}]$

$[H^+]^2 = \dfrac{K_a[H_2S]}{[S^{2-}]} = \dfrac{9 \times 10^{-21} \times 0.10}{1.6 \times 10^{-11}} = 7.5 \times 10^{-6}\,M$

$[H^+] = \dfrac{K_a[CH_3COOH]}{[CH_3COO^-]} \quad \Rightarrow \quad 7.5 \times 10^{-6}$

$= \dfrac{1.8 \times 10^{-5} \times 0.25}{[CH_3COO^-]}$

$[CH_3COONa] = \mathbf{0.60\,M}$

59. Let solubility of CaC_2O_4 is s mole/lit

$CaC_2O_4(s) \rightleftharpoons Ca^{+2}(aq) + C_2O_4^{2-}(aq)$

$\quad\quad\quad\quad\quad\quad\quad s \quad\quad\quad s$

$C_2O_4^{2-}$ react with H^+ to produce $HC_2O_4^-$ & $H_2C_2O_4$
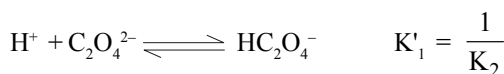
$H^+ + C_2O_4^{2-} \rightleftharpoons HC_2O_4^- \quad\quad K_1' = \dfrac{1}{K_2}$

$\dfrac{1}{K_2} = \dfrac{[HC_2O_4^-]}{[H^+][C_2O_4^{2-}]} \Rightarrow [HC_2O_4^-] = \dfrac{[H^+][C_2O_4^{2-}]}{K_2}$

Again this $HC_2O_4^-$ react with H^+ as.

$HC_2O_4^- + H^+ \rightleftharpoons H_2C_2O_4 \quad K_1' = \dfrac{1}{K_1}$
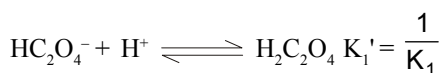
$\dfrac{1}{K_1} = \dfrac{[H_2C_2O_4]}{[HC_2O_4^-][H^+]}$

$\Rightarrow [H_2C_2O_4] = \dfrac{[HC_2O_4^-][H^+]}{K_1}$

Puting the value of $[HC_2O_4^-]$

$\Rightarrow [H_2C_2O_4] = \dfrac{[H^+]^2[C_2O_4^{2-}]}{K_1 K_2}$

Now $[C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4] = s$

$[C_2O_4^{2-}]\left[1 + \dfrac{[H^+]^+}{K_2} + \dfrac{[H^+]^2}{K_1 K_2}\right] = s$

$[C_2O_4^{2-}]\left[1 + \dfrac{10^{-4}}{5 \times 10^{-5}} + \dfrac{10^{-8}}{25 \times 10^{-7}}\right] = s$

$[C_2O_4^{2-}] = \left(\dfrac{s}{3}\right) \quad \Rightarrow \quad K_{sp} = [Ca^{+2}][C_2O_4^{2-}] = 2.7 \times 10^{-9}$
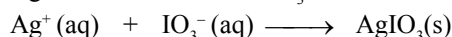
$\dfrac{s^2}{3} = 2.7 \times 10^{-9} \quad\quad \Rightarrow \quad s = \mathbf{9 \times 10^{-5}\,M}$

60. Initial moles of $Ag^+ = 0.01$; Initial moles of $IO_3^- = 0.005$
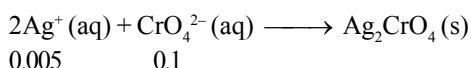
Initial moles of $CrO_4^{2-} = 0.1$

Ksp of $AgIO_3 << Ksp$ of CrO_4^{2-}

Ag^+ first combined with IO_3^-

$Ag^+(aq) + IO_3^-(aq) \longrightarrow AgIO_3(s)$

moles of Ag^+ left after the above reaction $= 0.01 - 0.005$
$$= 0.005$$

Now
$$2Ag^+ (aq) + CrO_4^{2-} (aq) \longrightarrow Ag_2CrO_4 (s)$$
$$0.005 \qquad 0.1$$
moles of CrO_4^{2-} left after the above reaction $= 0.1 - 0.0025$
$$= 0.0975$$
At equilibrium
$$[CrO_4^{2-}] = \textbf{0.0975 M}$$

$$[Ag^+] = \sqrt{\frac{Ksp \text{ of } Ag_2CrO_4}{[CrO_4^{2-}]}} = \sqrt{\frac{10^{-8}}{0.0975}} = \textbf{3.2} \times \textbf{10}^{-4}\,\textbf{M}$$

$$[IO_3^-] = \frac{Ksp \text{ of } AgIO_3}{[Ag^+]} = \frac{10^{-13}}{3.2 \times 10^{-4}} = \textbf{3.125} \times \textbf{10}^{-10}\,\textbf{M}$$

Total moles of precipitate formed $= 0.005 + 0.0025$
$$= \textbf{0.0075}$$

61. $\qquad [Sr(OH)_2] \longrightarrow Sr^{2+} + 2OH^-$
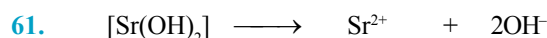
$$[Sr(OH)_2] = \frac{19.23}{121.62 \times 1} = 0.158\,M$$

$\therefore \quad [OH^-] = 2 \times 0.158\,M = \textbf{0.316 M}$

or pOH $= 0.5.$ $\qquad \therefore \quad$ **pH $= 13.5$**

$\quad [Sr^{2+}] = \textbf{0.158 M.}$

62. $\qquad Co^{2+} + N_2H_4 \rightleftharpoons Co(N_2H_4)^{2+}$

$t = 0 \qquad 0.01 \qquad 0.02$

$t_{eq.} \qquad 0.01-x \qquad 0.02-x \qquad x$

$\qquad = 0.06$

$\therefore \qquad x = 4 \times 10^{-3}\,M$

$\therefore \qquad [N_2H_4] = 0.016\,M$

$\therefore \qquad K_f = \dfrac{(4 \times 10^{-3})}{(0.006)\,(0.016)} = 41.67$

63. $\qquad Cu^{2+} + 4NH_3\,(\ell) \rightleftharpoons [Cu(NH_3)_4]^{2+}$

Initial mole $\quad 0.005 \quad 0.5 \times 0.4 \qquad 0$

$\qquad\qquad\qquad = 0.2$

$K_f = 5.6 \times 10^{11}$

K_f is large and thus all the Cu^{2+} will give $[Cu(NH_3)_4]^{2+}$

Let Cu^{2+} left is a, than

$[Cu(NH_3)_4]^{2+} = 0.005\,mole = \dfrac{0.005}{0.5}\,M \qquad (0.005 \gg a)$

$[Cu^{2+}] = \dfrac{a}{0.5}\,M \qquad (Let)$

$[NH_3] = 0.2 - 4 \times 0{,}005 + 2a$

$\qquad = 0.2 - 0.02 + 2a \qquad (0.18 \gg 2a)$

$\qquad = 0.18\,mole = \dfrac{0.18}{0.5}\,M$

$\therefore \quad K_f = 5.6 \times 10^{11} = \dfrac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$

$$= \frac{\dfrac{0.005}{0.5}}{[Cu^{2+}] \times \left[\dfrac{0.18}{0.5}\right]^4}$$

$\therefore \quad [Cu^{2+}] = \textbf{1.06} \times \textbf{10}^{-12}\,\textbf{M}$

64. $\qquad BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$
$$\qquad\qquad\qquad\quad s \qquad\quad s$$
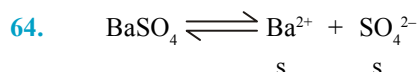
(where s M/litre is soluble of $BaSO_4$)

(i) $\quad K_{SP} = s \times s$

$\therefore \quad s = \sqrt{K_{SP}} = \sqrt{1.6 \times 10^{-9}} = \textbf{4} \times \textbf{10}^{-5}\,\textbf{mol litre}^{-1}$

(ii) In presence of 0.10 M $BaCl_2$, let s mol/litre $BaSO_4$ is disolved
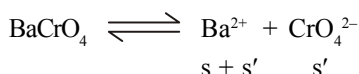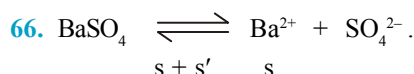
$K_{SP} = [Ba^{2+}]\,[SO_4^{2-}]$

$1.6 \times 10^{-9} = (0.1+s)\,(s) \qquad [(0.1+s) = 0.1 \text{ as } s \lll 0.1]$

$\therefore \quad s = \textbf{1.6} \times \textbf{10}^{-8}\,\textbf{M}$

65. $Pb^{2+} + 2Cl^- \longrightarrow PbCl_2.$

$\qquad \dfrac{10}{101} - x \qquad \dfrac{1}{101} - 2x \approx 0.$

$[Pb^{2+}] = \left(10 - \dfrac{1}{2}\right) \times \dfrac{1}{101} = \dfrac{9.5}{101} = \textbf{9.4} \times \textbf{10}^{-2}\,\textbf{M.}$

66. $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}.$
$$\qquad\quad s + s' \qquad\quad s$$

$\qquad BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{2-}$
$$\qquad\qquad\quad s + s' \qquad\quad s'$$

$[Ba^{2+}] = 1.4 \times 10^{-5} = \sqrt{K_{sp1} + K_{sp2}}$

$\therefore \quad K_{sp1} + K_{sp1} = (1.4 \times 10^{-5})^2$

$\& \quad \dfrac{K_{sp1}}{K_{sp2}} = \dfrac{1}{2.5}$

On solving, $K_{sp1} = \textbf{5.6} \times \textbf{10}^{-11}$
$$K_{sp2} = \textbf{1.4} \times \textbf{10}^{-10}$$

Solubility of $BaSO_4$ in 0.01 M $Na_2SO_4 = \dfrac{5.6 \times 10^{-11}}{0.01}$

$$= \textbf{5.6} \times \textbf{10}^{-9}\,\textbf{M.}$$

67. Taking density of water to be 1 g/cc.

$$[CaSO_4] = \frac{136}{10^6} \times \frac{1000}{136} = 10^{-10} \text{ M.}$$

Concentration of $CaSO_4$ in saturated solution.

$$= \sqrt{K_{SP}} = 3 \times 10^{-3}.$$

$M_1V_1 = M_2V_2.$
$10^{-10} \times V_1 = 3 \times 10^{-3} \times V_2.$

$$\frac{V_2}{V_1} = \frac{1}{3} \quad \Rightarrow \quad \frac{V_1 - V_2}{V_1} = 0.67.$$

68. For the precipitation of $Mg(OH)_2$
$[Mg^{2+}][OH^-]^2 = K_{sp}$
$[OH^-] = 5 \times 10^{-5}.$
For NH_3 - NH_4^+ buffer solution,

$$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} \Rightarrow [NH_3] = \frac{(5 \times 10^{-6})(0.4)}{2 \times 10^{-5}} = 0.1 \text{ M.}$$

69. Let final concentration of SO_4^{2-} in solution $= [SO_4^{2-}]_{left} = x$
Mole balance equation for SO_4^{2-}

$$[SO_4^{2-}]_{initial} = [SO_4^{2-}]_{left} + [SO_4^{2-}]_{combined}$$

$$\frac{0.3 \times 10}{30} = 0.1 = [SO_4^{2-}]_{left} + [SO_4^{2-}]_{combined}$$

$0.1 = x + [Ca^{2+}]_{combined} + [Sr^{2+}]_{combined}$
$\Rightarrow 0.1 = x + ([Ca^{2+}]_{initial} - [Ca^{2+}]_{left}) + ([Sr^{2+}]_{initial} - [Sr^{2+}]_{left})$

$$\Rightarrow 0.1 = x + \left(\frac{0.2}{3} - \frac{K_{sp} \text{ of } CaSO_4}{[SO_4^{2-}]_{left}} \right) +$$

$$\left(\frac{0.2}{3} - \frac{K_{sp} \text{ of } SrSO_4}{[SO_4^{2-}]_{left}} \right)$$

$$\Rightarrow 0.1 = x + \left(\frac{0.2}{3} - \frac{2.4 \times 10^{-5}}{x} \right) + \left(\frac{0.2}{3} - \frac{7.6 \times 10^{-7}}{x} \right)$$

$\Rightarrow 3x^2 + 0.1x + 7.428 \times 10^{-5} = 0$
on solving, $x = [SO_4^{2-}]_{left} = \mathbf{7.26 \times 10^{-4} \text{ M}}$

$$[Ca^{2+}]_{left} = \frac{2.4 \times 10^{-5}}{7.26 \times 10^{-4}} = \mathbf{0.033 \text{ M}}$$

$$[Sr^{2+}]_{left} = \frac{7.6 \times 10^{-7}}{7.26 \times 10^{-4}} = \mathbf{1.05 \times 10^{-3} \text{ M}}$$

70. $[Ag^+]$ concentration $= \dfrac{100}{350} \times 2 \times \sqrt[3]{\dfrac{1.4 \times 10^{-5}}{4}}$

$$= 8.68 \times 10^{-3}.$$

$[SO_4^{2-}]$ concentration $= \dfrac{100}{350} \times \sqrt[3]{\dfrac{1.4 \times 10^{-5}}{4}}$

$$= 4.34 \times 10^{-3}.$$

$[Pb^{2+}] = \dfrac{250}{350} \times \sqrt{2.8 \times 10^{-13}} = 3.78 \times 10^{-7}.$

$[CrO_4^{2-}] = 3.78 \times 10^{-7}.$
$[Ag^+]^2 [CrO_4^{2-}] = 2.85 \times 10^{-11} > K_{SP}$ of Ag_2CrO_4.
$[Pb^{2+}] [SO_4^{2-}] = 1.64 \times 10^{-9} < K_{SP}$ of $PbSO_4$.
Only Ag_2CrO_4 will precipitate.

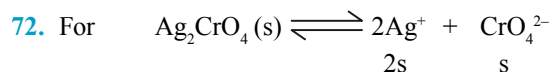**71.** For $CaSO_4$, Let solubility be s mol/litre

Them $s = \sqrt{K_{SP}} = \sqrt{9 \times 10^{-6}} = 3 \times 10^{-3}$ mol litre^{-1}

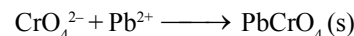Thus, 3×10^{-3} mole of $CaSO_4$ is soluble in water = 1 litre

$\therefore \dfrac{1}{136}$ mole (1 g) of $CaSO_4$ is soluble in

$$= \frac{1}{136 \times 3 \times 10^{-3}} = \mathbf{2.45 \text{ litre water}}$$

72. For $\quad Ag_2CrO_4 (s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$
$\qquad\qquad\qquad\qquad\quad 2s \qquad\quad s$
$\qquad K_{SP} = 4s^3 \Rightarrow s = 2 \times 10^{-4}$ mol/lt.
Now,

$$CrO_4^{2-} + Pb^{2+} \longrightarrow PbCrO_4 (s)$$

m. moles of CrO_4^{2-} = m. moles of Pb^{2+}
$\qquad 50 \times 2 \times 10^{-4} = 20 \text{ X}$
$\therefore \qquad X = 5 \times 10^{-4}$ M.

73. Let solubility of $Mg(OH)_2$ be s mol litre^{-1}
$\qquad\quad Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$
$\therefore \quad [Mg^{2+}] [OH^-]^2 = K_{SP}$
$\qquad 4s^3 = 8.9 \times 10^{-12}$
$\therefore \quad s = 1.305 \times 10^{-4}$ mol litre^{-1}
$\therefore \quad [OH^-] = 2 \times 1.305 \times 10^{-4}$ mol litre^{-1}
$\therefore \quad pOH = 3.58$
$\therefore \quad pH = \mathbf{10.42}$
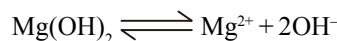
74. Mole balance equation
$\qquad [HCO_3^-]_0 = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$
$\Rightarrow [HCO_3^-]_0$

$$= [H_2CO_3] + \frac{K_{a1}[H_2CO_3]}{[H^+]} + \frac{K_{a1}K_{a2}[H_2CO_3]}{[H^+]^2}$$

$$\Rightarrow [HCO_3^-]_0 = [H_2CO_3]\left(1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2}\right)$$

$$\Rightarrow [HCO_3^-]_0$$

$$= [H_2CO_3]\left(1 + \frac{4.9 \times 10^{-7}}{10^{-8}} + \frac{4.9 \times 10^{-7} \times 10^{-12}}{(10^{-8})^2}\right)$$

$$\Rightarrow [HCO_3^-]_0 = [H_2CO_3](1 + 49 + 4.9 \times 10^{-3})$$

$$\therefore [H_2CO_3] = \frac{[HCO_3^-]_0}{50}$$

$$\Rightarrow n_{H_2CO_3} = \frac{0.0005}{50} = 10^{-5} \text{ mole}.$$

$$[HCO_3^-] = \frac{K_{a1}[H_2CO_3]}{[H^+]}$$

$$\Rightarrow n_{HCO_3^-} = \frac{4.9 \times 10^{-7} \times 10^{-5}}{10^{-8}} = 4.9 \times 10^{-4} \text{ mole}$$

$$[CO_3^{2-}] = \frac{K_{a1}K_{a2}[H_2CO_3]}{[H^+]^2}$$

$$n_{CO_3^{2-}} = \frac{4.9 \times 10^{-7} \times 10^{-12} \times 10^{-5}}{(10^{-8})^2}$$

$$= 4.9 \times 10^{-8} \text{ mole}$$

75. $PbBr_2 \rightleftharpoons Pb^{2+} + 2Br^-$.
$\qquad\qquad 0.8\,s \quad 2 \times 0.8s$

$8 \times 10^{-5} = 4 \times (0.8)^3 \times s^3 \Rightarrow s = 5 \times 10^{-3} \text{ mol/lt.}$
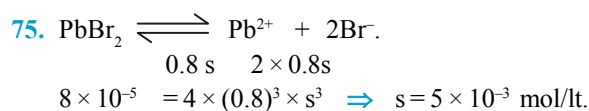
solubility of salt $= 5 \times 10^{-3} \times 368 = $ **1.84 g/lt**.

76. milli moles of $I^- = 25 \times 2 \times \sqrt[3]{\dfrac{7.1 \times 10^{-9}}{4}}$.

milli moles of $Ag^+ = 13.3 \times M$.

$Ag^+ (aq) + I^- (aq) \longrightarrow AgI (s)$
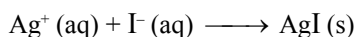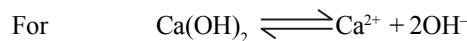
Equating both $M = 4.55 \times 10^{-3}$.

77. $[F^-]$ concentration when $[Sr^{2+}]$ is 2.5×10^{-3}

$= \sqrt{\dfrac{2.8 \times 10^{-9}}{2.5 \times 10^{-3}}} = 1.058 \times 10^{-3} \text{ M}.$

Total m. moles of F^- added $= 100 \times [1.058 \times 10^{-3} + 2\,(0.016 - 0.0025)] = 2.8$

Mass of NaF added $= 2.8 \times 10^{-3} \times 42 = 0.1776$ g.

78. $[Ag^+][Cl^-] = 1.75 \times 10^{-10}$
$\qquad [Ag^+][Br^-] = 5.25 \times 10^{-13}$

$$\Rightarrow [Br^-] = \frac{5.25 \times 10^{-13}}{1.75 \times 10^{-10}} \times [Cl^-]$$

$$= \frac{5.25 \times 10^{-13}}{1.75 \times 10^{-10}} \times (0.075) = 2.25 \times 10^{-4} \text{ M}.$$

79. 500 mL of 0.4 M NaOH are mixed with 500 mL of $Ca(OH)_2$ a saturated solution having $Ca(OH)_2$ solubility as s M.

For $\qquad Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$
$\qquad\qquad\qquad K_{SP} = s \times (2s)^2 = 4s^3$
Then, $\qquad\qquad 4s^3 = 4.42 \times 10^{-5}$

$$\therefore \qquad s = \sqrt[3]{\left(\frac{4.42 \times 10^{-5}}{4}\right)} = 0.0223\text{M}$$

Now $Ca(OH)_2$ + NaOH are mixed

$\therefore$ Solution has Ca^{2+} and OH^- out of which some Ca^{2+} are precipiated

On mixing, $\quad [Ca^{2+}] = \dfrac{0.0223 \times 500}{1000} = 0.01115$

$\qquad\qquad\qquad\qquad = 111.5 \times 10^{-4} \text{ M}$

$$[OH^-] = \frac{0.0223 \times 2 \times 500}{1000} + \frac{500 \times 0.4}{1000} = 0.2223 \text{ M}$$

$\qquad\qquad$ [from $Ca(OH)_2$] [from NaOH]

$\therefore \qquad [Ca^{2+}][OH^-]^2 = K_{SP}$
$\qquad [Ca^{2+}]_{left}[0.2223]^2 = 4.42 \times 10^{-5}$

$$[Ca^{2+}]_{left} = \frac{4.42 \times 10^{-5}}{[0.2223]^2} = 8.94 \times 10^{-1} \text{ mol litre}^{-1}$$

$\therefore$ Mole of $Ca(OH)_2$ precipitated = Mole of $[Ca^{2+}]$ precipitated

$\qquad = 111.5 \times 10^{-4} - 8.94 \times 10^{-4} = 102.46 \times 10^{-4}$

$\therefore$ Wt. of $Ca(OH)_2$ precipitated from $Ca(OH)_2$ solution
$\qquad = 102.46 \times 10^{-4} \times 74 = 7582.04 \times 10^{-4}$ g = **759 mg**

80. For $\qquad CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$

$\qquad\qquad [Ca^{2+}][SO_4^{2-}] = K_{SP}$

Let $[SO_4^{2-}] = a$, just sufficient to precipitate $CaSO_4$ from a solution having $[Ca^{2+}] = 0.005$ M

Then, $\quad [0.005][a] = 2.4 \times 10^{-5} \quad \therefore a = \dfrac{2.4 \times 10^{-5}}{0.005}$
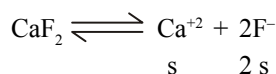
$\qquad [SO_4^{2-}] = $ **4.8 × 10⁻³ mol litre⁻¹**

81. Concentration of $CaCO_3 = \left[\dfrac{7 \times 10^{-3}}{100}\right]$ mole/lit

$= 7 \times 10^{-5}$ mole/lit

K_{sp} of $CaCO_3 = 49 \times 10^{-5}$ mole/lit

when only $[Ba^{+2}]$ is 90% precipitated then only $CaCO_3$ starts precipitation

then if & solution contain a mole/lit of Ca^{+2} & Ba^{+2}

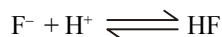$[Ca^{+2}][CO_3^{-2}] = 49 \times 10^{-10}$ $[CO_3^{-2}] = \left[\dfrac{49 \times 10^{-10}}{a}\right]$

Now for $BaCO_3$ $K_{sp} = [Ba^{+2}][CO_3^{-2}]$

$= \dfrac{a \times 10}{100} \times \dfrac{49 \times 10^{-10}}{a} = 4.9 \times 10^{-10}$

82. $CaF_2 \rightleftharpoons Ca^{+2} + 2F^-$

Let Solubility is s mole/lit

$$CaF_2 \rightleftharpoons Ca^{+2} + 2F^-$$
$$ s \qquad 2s$$

The F^- react with H^+ to produce HF

$F^- + H^+ \rightleftharpoons HF$

$$K_1 = \dfrac{1}{K_a} = \dfrac{[HF]}{[F^-][H^+]}$$

$$\Rightarrow [HF] = \dfrac{[F^-][H^+]}{K_a} = \dfrac{[F^-][H^+]}{3.45 \times 10^{-4}}$$

$[HF] = 2.9 \times 10^3 [F^-][H^+]$

(A) at pH = 7 $[HF] = 2.9 \times 10^{-4}[F^-]$

But the solution contain $[HF + F^-] = 2[Ca^{+2}]$

$[2.9 \times 10^{-4} + 1][F^-] = 2s$ $[F^-] = 2s$

$K_{sp} = 4s^3 = 0.4 \times 10^{-11}$ $s = (10 \times 10^{-12})^{1/3} = 2.15 \times 10^{-4}$

(b) At pH = s

$[HF] = 2.9 \times 10^3[F^-] \times 10^{-5} = 2.9 \times 10^{-2}[F^-]$

$[F^-] + HF = 2s$ $\Rightarrow$ $[F^-] + 0.029[F] = 2s$

$[F][1.029] = 2s$ $\Rightarrow$ $[F^-] = \left(\dfrac{1}{1.029}\right) \times 2s$

$K_{sp} = 4 s^3\left(\dfrac{1}{1.029}\right)^2 = 4 \times 10^{-11}$ $\Rightarrow$ $s^3 = (1.29)^2 \times 10^{-11}$
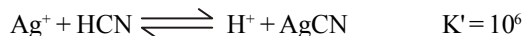
$s = (10.6 \times 10^{-12})^{\frac{1}{3}} = 2.2 \times 10^{-4}$

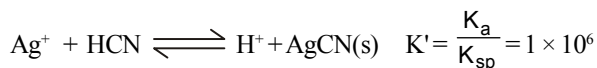**83.** Volume of both $AgNO_3$ & HCN are equal so. There concentration is half

$[AgNO_3] = 0.01$ M $\qquad\qquad$ $[HCN] = 0.01$ M

$HCN \rightleftharpoons H^+ + CN^-$ $\qquad K_a = 4 \times 40^{-10}$ .... **(i)**

$Ag^+ + CN^- \rightleftharpoons AgCN$ $K = \dfrac{1}{K_a}$ .... **(ii)**

on adding equation **(i)** & equation **(ii)**

$Ag^+ + HCN \rightleftharpoons H^+ + AgCN$ $\qquad K' = 10^6$

As the volue of K' is very high so almost all Ag^+ & HCN converted in product

$Ag^+ + HCN \rightleftharpoons H^+ + AgCN(s)$ $\quad K' = \dfrac{K_a}{K_{sp}} = 1 \times 10^6$
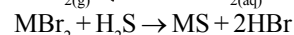
$\begin{array}{cccc} 0.01 & 0.01 & 0 & 0 \\ x & x & \approx 0.01 & \approx 0.01 \end{array}$

$K' = \dfrac{0.01}{(x)^2} = 10^6$

$X^2 = 10^{-8} \Rightarrow X = 10^{-4}$

Conc. of $[Ag^+] = \mathbf{10^{-4}}$

84. Given, $MBr_{2(g)} \rightleftharpoons MBr_{2(aq)} \rightarrow M^{2+} + 2Br^-$

$MBr_2 + H_2S \rightarrow MS + 2HBr$

K_{SP} of $MS = [M^{2+}][S^{2-}]$

$6 \times 10^{-21} = [0.05][S^{2-}]$

$\therefore$ $[S^{-2}] = 1.2 \times 10^{-19}$ M

Thus, MS will be precipitated if H_2S provides 1.2×10^{-19} M ions of S^{2-}

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

$$K_1 \times K_2 = \dfrac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$10^{-7} \times 1.3 \times 10^{-13} = \dfrac{[H^+]^2[1.2 \times 10^{-19}]}{[0.1]}$$

$\therefore$ $[H^+] = 1.04 \times 10^{-1}$ and pH = **0.983**

85. When $Mg(OH)_2$ starts precipitation, then,

$[Mg^{2+}][OH^-]^2 = K_{SP}$ of $Mg(OH)_2$

$[0.1][OH^-]^2 = 1 \times 10^{-11}$

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

$\therefore$ pOH = 5

$\therefore$ pH = 14 − pOH

pH = 14 − 5 = 9

86. The minimum $[OH^-]$ at which there will be no precipitation of $Mg(OH)_2$ obtained by

$K_{SP} = [Mg^{2+}][OH^-]^2$

$6.0 \times 10^{-12} = [0.05][OH^-]^2$

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

Thus, a solution having $[OH^-] = 1.34 \times 10^{-5}$ M will not show precipitation of $Mg(OH)_2$ in 0.05 M Mg^{2+} solution. These hydroxyl ions are to be derived by a buffer of NH_4Cl and NH_4OH i.e.,
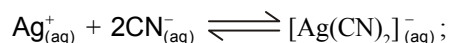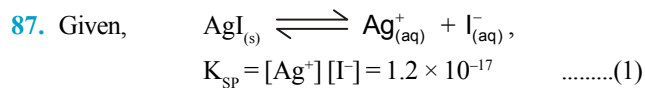
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$
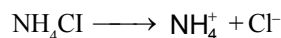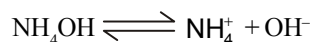
For NH_4OH $\quad K_b = \dfrac{[NH_4^+][OH^-]}{[NH_4OH]}$

In presence of NH_4Cl; all the $[NH_4^+]$ are provided by NH_4Cl since common ion effect decreases dissociation of NH_4OH.

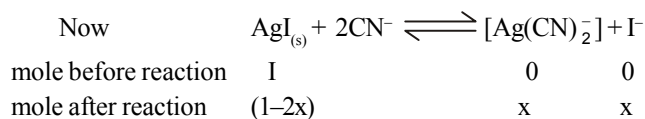$\therefore \quad 1.8 \times 10^{-5} = \dfrac{[NH_4^+][1.34 \times 10^{-5}]}{[0.05]}$

$\therefore \quad [NH_4^+] = 0.067$ M or $\quad [NH_4Cl] = \mathbf{0.067\ M}$

87. Given, $\quad AgI_{(s)} \rightleftharpoons Ag^+_{(aq)} + I^-_{(aq)}$,

$K_{SP} = [Ag^+][I^-] = 1.2 \times 10^{-17}$ ....(1)

$Ag^+_{(aq)} + 2CN^-_{(aq)} \rightleftharpoons [Ag(CN)_2]^-_{(aq)}$;

$K_f = \dfrac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = 7.1 \times 10^{19}$ ....(2)

Let x mole of AgI be dissolved in CN^- solution then,

Now $\quad AgI_{(s)} + 2CN^- \rightleftharpoons [Ag(CN)_2^-] + I^-$

mole before reaction $\quad$ I $\qquad\qquad$ 0 $\qquad$ 0

mole after reaction $\quad$ (1–2x) $\qquad\quad$ x $\qquad$ x

By Eqs. (1) and (2), $\qquad K_{eq} = K_{SP} \times K_f$
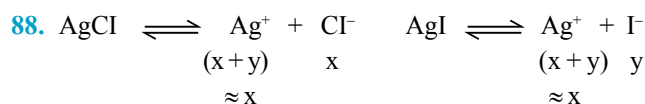
$= \dfrac{[Ag(CN)_2^-][I^-]}{[CN^-]^2} = 1.2 \times 10^{-17} \times 7.1 \times 10^{19}$

$K_{eq} = 8.52 \times 10^2$ ....(3)

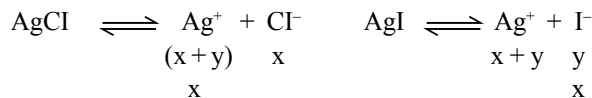$\therefore \quad K_{eq} = 8.52 \times 10^2 = \dfrac{x \cdot x}{(1-2x)^2} = \dfrac{x^2}{(1-2x)^2}$ or

$\dfrac{x^2}{1-2x} = 29.2$

Thus, $\quad x = 29.2 - 52.4x \qquad$ or $\quad x = \mathbf{0.49\ mole}$

88. $AgCl \rightleftharpoons Ag^+ + Cl^- \qquad AgI \rightleftharpoons Ag^+ + I^-$
$\qquad\quad (x+y) \quad x \qquad\qquad (x+y) \quad y$
$\qquad\qquad \approx x \qquad\qquad\qquad\qquad\quad \approx x$

$\dfrac{K_{sp}(AgCl)}{K_{sp}(AgI)} = \dfrac{x}{y} = \dfrac{1 \times 10^{-10}}{8.5 \times 10^{-17}} = \dfrac{10}{8.5} \times 10^{+6}$
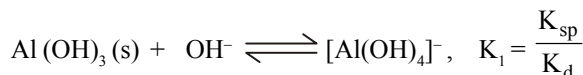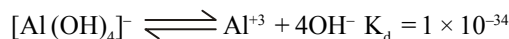
$x = 1.8 \times 10^6\, y$

$AgCl \rightleftharpoons Ag^+ + Cl^- \qquad AgI \rightleftharpoons Ag^+ + I^-$
$\quad (x+y) \quad x \qquad\qquad\qquad x+y \quad y$
$\qquad\quad x \qquad\qquad\qquad\qquad\qquad\quad x$

$x^2 = 10^{-10} \qquad\qquad\qquad xy = 8.5 \times 10^{-17}$
$x = 10^{-5} \qquad\qquad\qquad\quad y = 8.5 \times 10^{-12}$

89. $K_{sp} = 4 \times (6.7 \times 10^{-6})^3 = 1.203 \times 10^{-15}$
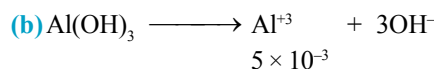$s \times (10^{-6})^2 = 1.203 \times 10^{-15}$
$s = 1.203 \times 10^{-3}$ M

90. $Al(OH)_3\,(s) \rightleftharpoons Al^{+3} + 3\,OH^- \quad K_{SP} = 5 \times 10^{-33}$

$[Al(OH)_4]^- \rightleftharpoons Al^{+3} + 4OH^- \quad K_d = 1 \times 10^{-34}$

$Al(OH)_3\,(s) + OH^- \rightleftharpoons [Al(OH)_4]^-,\quad K_1 = \dfrac{K_{sp}}{K_d}$

$\quad 1 \times 10^{-3} \qquad\qquad 0$
$\qquad 0 \qquad\qquad\qquad 1 \times 10^{-3}$

$K_1 = \dfrac{[Al(OH)_4]^-}{[OH^-]} = \dfrac{5 \times 10^{-33}}{1 \times 10^{-34}} = 50 \Rightarrow [OH^-]$

$= \dfrac{1 \times 10^{-3}}{50} = 2 \times 10^{-5}$

$pOH = 5 - \log 2 \quad = 4.7 \quad \Rightarrow \quad pH = 14 - 4.7 = 9.3$
$\Rightarrow \quad pH = 9.3$

(b) $Al(OH)_3 \longrightarrow Al^{+3} + 3OH^-$
$\qquad\qquad\qquad\qquad 5 \times 10^{-3}$

$[Al^{+3}][OH^-]^3 = K_{SP}$
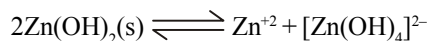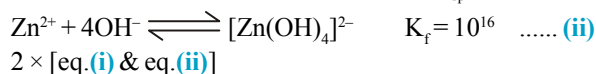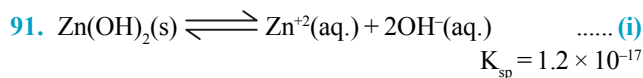
$[OH^-]^3 = \dfrac{5 \times 10^{-33}}{5 \times 10^{-3}}$

$[OH^-]^3 = 1 \times 10^{-30}$
$[OH^-] = 10^{-10}$
$pOH = 10$
$pH = 4$

91. $Zn(OH)_2(s) \rightleftharpoons Zn^{+2}(aq.) + 2OH^-(aq.)$ ...... **(i)**
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad K_{sp} = 1.2 \times 10^{-17}$

$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-} \qquad K_f = 10^{16}$ ...... **(ii)**

$2 \times [eq.\mathbf{(i)}\ \&\ eq.\mathbf{(ii)}]$

$2Zn(OH)_2(s) \rightleftharpoons Zn^{+2} + [Zn(OH)_4]^{2-}$
$K' = (K_{sp})^2\ K_f \Rightarrow K' = 1.44 \times 10^{-18}$

$2Zn(OH)_2(s) \rightleftharpoons Zn^{+2}\,(aq.) + [Zn(OH)_2]^{2-}$
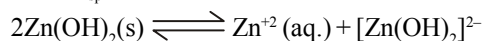
$\qquad\qquad\qquad \left(\dfrac{s}{2}\right) \qquad\qquad \left(\dfrac{s}{2}\right)$

$\left(\dfrac{s^2}{4}\right) = 1.44 \times 10^{-18} \qquad K' = 1.44 \times 10^{-18}$

$s^2 = 4 \times 144 \times 10^{-20} \Rightarrow \qquad s = \mathbf{2.4 \times 10^{-9}}$ M

But $K_{sp}[Zn(OH)_2] = [Zn^{2+}][OH^-]^2 = 1.2 \times 10^{-17}$

$\Rightarrow$ $(1.2 \times 10^{-9})[OH^-]^2 = 1.2 \times 10^{-17}$

$[OH^-] = \mathbf{10^{-4}\,M}$

EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

1. Conjugate base is formed by the removal of H' from acid

$$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$$
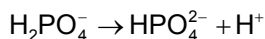
2. $MX_4 \text{ (solid)} \rightleftharpoons M^{4+}_{(aq)} + 4X^-_{(aq)}$ Solubility product, $K_{sp} = s \times (4s)^4 = 256\,s^5$

$\therefore$ $s = \left(\dfrac{K_{ps}}{256}\right)^{1/5}$

3. $MX_{2(s)} \rightleftharpoons M^{2+}\,(aq) + 2X^-\,(aq)$
$K_{sp} = s \cdot (2s)^2 = 4s^3$ $\Rightarrow$ $4 \times 10^{-12} = 4s^3$
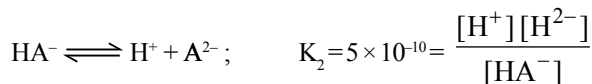$\Rightarrow$ $s^3 = 1 \times 10^{-12}$
$\Rightarrow$ $s = 1 \times 10^{-4}\,M$ $\Rightarrow$ $[M^{2+}] = 1 \times 10^{-4}\,M$

4. Conjugate base of OH^- $\quad OH^- \rightleftharpoons O^{2-} + H^+$

5. $pH = -\log[H^+]$ $\Rightarrow$ $[H^+] = \text{antilog } (-pH)$
$= \text{antilog}(-5.4) = 3.98 \times 10^{-6}$

6. $H_2A \rightleftharpoons H^+ + HA^-$; $\quad K_1 = \dfrac{[H^+][HA^-]}{[H_2A]} = 1 \times 10^{-5}$

$HA^- \rightleftharpoons H^+ + A^{2-}$; $\quad K_2 = 5 \times 10^{-10} = \dfrac{[H^+][H^{2-}]}{[HA^-]}$

$K = \dfrac{[H^+]^2\,[H^{2-}]}{[H_2A]} = K_1 \times K_2 = 1 \times 10^{-5} \times 5 \times 10^{-15}$

7. For acidic buffer, $pH = pK_a + \dfrac{[A^-]}{[HA]}$

when the acid is 50% ionised, $[A^-] = [HA]$ $\qquad$ or
$pH = pK_a + \log 1$ or $pH = pK_a$
given $pK_a = 4.5$ $\qquad \therefore$ $pH = 4.5$
$\therefore$ $pOH = 14 - 4.5 = 9.5$.

8. $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$ $\qquad$ [s = Solubility]
$\quad K_{sp} = s^2$
or
$s = 1.0 \times 10^{-4}$ mol/lit $= 1.0 \times 10^{-4} \times 283$ g/lt $= 2.83 \times 10^{-3}$ gm/100 ml.

9. $pH = 7 + \dfrac{1}{2}pK_a - \dfrac{1}{2}pK_b = 7 + \dfrac{4.8}{2} - \dfrac{4.78}{2} = 7.01$
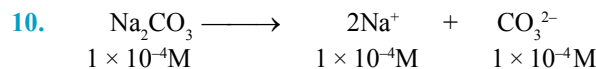
10. $\quad Na_2CO_3 \longrightarrow \quad 2Na^+ \quad + \quad CO_3^{2-}$
$\quad 1 \times 10^{-4}M \qquad\qquad 1 \times 10^{-4}M \qquad 1 \times 10^{-4}M$
$K_{sp}[BaCO_3] = [Ba^{+2}][CO_3^{2-}]$
$5.1 \times 10^{-9} = [Ba^{+2}] \times 1 \times 10^{-4}$
$[Ba^{+2}] = 5.1 \times 10^{-5}M$

11. $K_{sp} = [Ag^+][Br^-] = 5.0 \times 10^{-13}$
$[Ag^+] = 0.05\,M$
$[0.05][Br^-] = 5.0 \times 10^{-13}$

$[Br^-] = \dfrac{5.0 \times 10^{-13}}{0.05} = 1 \times 10^{-11}\,M$

moles of KBr $= M \times V = 1 \times 10^{-11} \times 1 = 1 \times 10^{-11}$
weight of KBr $= 1 \times 10^{-11} \times 120 = 1.2 \times 10^{-9}$ g

12. $K_{SP} = 1.0 \times 10^{-11} = (Mg^{+2})(OH^-)^2$
$1.0 \times 10^{-11} = (0.001)(OH^-)^2$
$(OH^-) = 10^{-4}$
$P^{OH} = 4$
$P^H = 14 - 4 = 10$.

13. In IInd equation $H_2PO_4^-$ give H^+ ion to the H_2O therefore in the IInd equation it act as an acid.

14. $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $\qquad\qquad K_1 = 4.2 \times 10^{-7}$
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $\qquad\qquad K_2 = 4.8 \times 10^{-11}$
$K_1 \gg K_2$
$\therefore$ $[H^+] = [HCO_3^-]$

$K_2 = \dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$

but $\quad [H^+] = [HCO_3^-]$
$\quad [CO_3^{2-}] = K_2 = 4.8 \times 10^{-11}$

15. $pH = 1$ $\quad [H^+] = 10^{-1} = 0.1\,M$;
$pH = 2$ $\quad [H^+] = 10^{-2} = 0.01\,M$
for dilution of HCl $M_1V_1 = M_2V_2$
$\qquad\qquad 0.1 \times 1 = 0.01 \times V_2$
$\qquad\qquad V_2 = 10\,lt$
Volume of water added $= 10 - 1 = 9$ litre

16. $CH_3COOK + H_2O \longrightarrow CH_3COOH + KOH$
$\qquad\qquad\qquad\qquad$ Weak acid $\quad$ Strong base

Hence nature of solution is basic

17. $[H_2S] = 0.10\,M$
$[HCl] = 0.20\,M$ $\qquad\qquad \Rightarrow \qquad [H^+] = 0.2\,M$

(1) $H_2S \rightleftharpoons HS^- + H^+$ $K_1 = 1.0 \times 10^{-7}$

(2) $HS^- \rightleftharpoons S^{2-} + H^+$ $K_2 = 1.2 \times 10^{-13}$

So,

$H_2S \rightleftharpoons S^{2-} + 2H^+$ $= K_1 \times K_2$
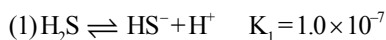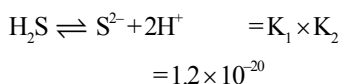
$= 1.2 \times 10^{-20}$
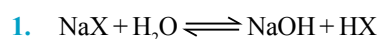
So,

$[S^{2-}] = \dfrac{1.2 \times 10^{-20} \times [H_2S]}{[H^+]^2}$

$= \dfrac{1.2 \times 10^{-20} \times 10^{-1}}{4 \times 10^{-2}} = 3 \times 10^{-20} M$

*All the [H$^+$] will come from strong acid [HCl] only.

Part # II : IIT-JEE ADVANCED

1. $NaX + H_2O \rightleftharpoons NaOH + HX$

In it HX is weak acid, so NaX is a salt of weak acid and strong base.

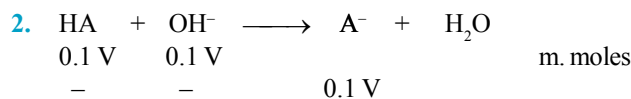∴ Hydrolysis constant of NaX is $K_h = \dfrac{K_w}{K_a} = \dfrac{1 \times 10^{-14}}{10^{-5}}$

$= 1 \times 10^{-9}$

For this type of salt $K_h = Ch^2$

C = molar concentration, h = degree of hydrolysis

∴ $1 \times 10^{-9} = 0.1 \times h^2$

or $h^2 = \dfrac{1 \times 10^{-9}}{0.1} = 1 \times 10^{-8}$ $h = 1 \times 10^{-4}$

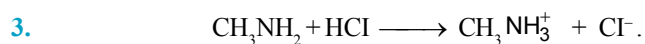∴ percentage hydrolysis of NaX salt $= 1 \times 10^{-4} \times 100$

$= 1 \times 10^{-2} = 0.01\%$

2. $HA + OH^- \longrightarrow A^- + H_2O$

0.1 V   0.1 V   m. moles

  –   –   0.1 V

$[A^-] = \dfrac{0.1 V}{2V} = \dfrac{0.1}{2} M$,

$pH = 7 + \dfrac{1}{2}(pK_a + \log c) = 7 + \dfrac{1}{2}(6 - \log 5.6) +$

$\dfrac{1}{2}\log\left(\dfrac{0.1}{2}\right) \approx 9$

3. $CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+ + Cl^-$.

Initial moles   0.1   0.08

moles after   0.02   0

0.08 mole in 1 lt reaction

$K_b = \dfrac{[OH^-][CH_3NH_3^+]}{[CH_3NH_2]}$

or, $5 \times 10^{-4} = \dfrac{[OH^-] \times 0.08}{0.02}$ or, $[OH^-] = \dfrac{5}{4} \times 10^{-4}$.

∵ $[H^+] = \dfrac{K_w}{[OH^-]}$ or,

$[H^+] = \dfrac{10^{-14} \times 4}{5 \times 10^{-4}} = 8 \times 10^{-11} M$.

4. $BOH + HCl \longrightarrow BCl + H_2O$ (in titration)

$B^+ + H_2O \rightleftharpoons BOH + H^+$
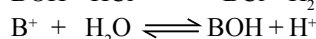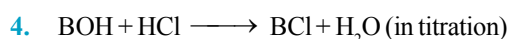
For titration

$N_{acid} V_{acid} = N_{base} V_{base}$

$\dfrac{2}{15} \times V = 2.5 \times \dfrac{2}{5}$

$V = 3 \times 2.5 = 7.5 mL$

In resulting solution

$[B^+] = \dfrac{\dfrac{2}{5} \times 2.5}{10} = \dfrac{2}{20} = 0.1$

$K_h = \dfrac{K_w}{K_b} = \dfrac{10^{-14}}{10^{-12}} = 10^{-2}$

or $K_h = \dfrac{0.1 h^2}{(1-h)} = 10^{-2}$ (solve quadratic equation to

get 'h', as we can't write $1 - h \approx 1$ since h is > 0.1)

or $h = 0.27$

$[H^+] = 0.1 \times 0.27 = 2.7 \times 10^{-2}$

5.

MX	MX$_2$	M$_3$X
$s_1^2 = 4 \times 10^{-8}$	$4s_2^3 = 3.2 \times 10^{-14}$	$27s_3^4 = 2.7 \times 10^{-15}$
$s_1 = 2 \times 10^{-4}$	$s_2^3 = 8 \times 10^{-15}$	$s_3^4 = 10^{-16}$
	$s_2 = 2 \times 10^{-5}$	$s_3 = 10^{-4}$

⟹ $s_1 > s_3 > s_2$

⟹ $MX > M_3X > MX_2$

6. Given $K_a = 10^{-4}$

$pK_a = 4$

$C = 0.01 M$
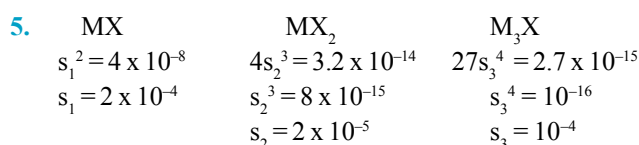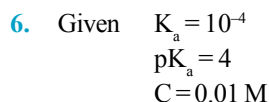
$pH = 7 + \dfrac{1}{2}pK_a + \dfrac{1}{2}\log C = 7 + \dfrac{1}{2}(4) + \dfrac{1}{2}(-2)$

$= 8$ **Ans.**

7. Basic solutions will convert red litmus blue.

$\left.\begin{array}{l} \text{KCN} \\ \text{K}_2\text{CO}_3 \\ \text{LiCN} \end{array}\right\}$, their aqueous solution will be basic due to anionic hydrolysis.
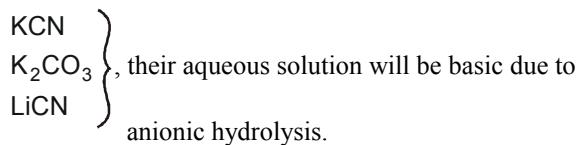
8. **(C)** $HNO_3 + CH_3COONa$ mixture can act as buffer solution if volume of HNO_3 solution taken is lesser than volume of CH_3COONa solution because of following reaction :
$CH_3COONa + HNO_3 \longrightarrow CH_3COOH + NaNO_3$
(D) $CH_3COOH + CH_3COONa$ - mixture will act as buffer.
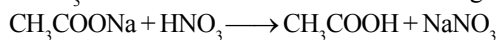
9. $AgCl\,(s) \rightleftharpoons Ag^+ + Cl^-$ $\qquad K_{sp}(AgCl) = 1.6 \times 10^{-10}$
$\qquad\qquad\qquad Z \qquad Z + Y$
$CuCl\,(s) \rightleftharpoons Cu^+ + Cl^-$ $\qquad K_{sp}(CuCl) = 10^{-6}$
$\qquad\qquad\qquad Y \qquad Z + Y$

$Z\,(Z+Y) = 1.6 \times 10^{-10}$
$Y\,(Z+Y) = 10^{-6}$
$\Rightarrow (Z+Y)^2 = 1.6 \times 10^{-10} + 10^{-6} \Rightarrow (Z+Y)^2 \approx 10^{-6}$
$\Rightarrow Z + Y = 10^{-3}$ $\qquad\qquad\qquad \Rightarrow Z(Z+Y) = 1.6 \times 10^{-10}$
$\Rightarrow Z \times 10^{-3} = 1.6 \times 10^{-10}$ $\qquad \Rightarrow Z = 1.6 \times 10^{-7}$
$\Rightarrow 1.6 \times 10^{-x} = 1.6 \times 10^{-7}$ $\qquad \Rightarrow x = 7$

10. As ester hydrolysis is first order with respect to $[H^+]$.

$\dfrac{R_{HA}}{R_{HX}} = \dfrac{[H^+]_{HA}}{[H^+]_{HX}}$

$\dfrac{1}{100} = [H^+]_{HA}$

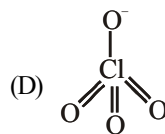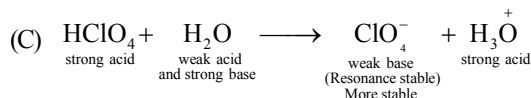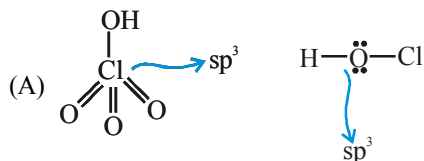$\begin{array}{cccc} HA & \rightleftharpoons & H^+ + & A^- \\ 1 - 0.01 & & 0.01 & 0.01 \\ \approx 1 & & & \end{array}$

$K_a = \dfrac{0.01 \times 0.01}{1} = 10^{-4}$

11. $MX_2 \rightleftharpoons M^{2+} + 2X^-$
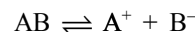$\quad m_0(1-\alpha) \qquad m_0\alpha \;\; 2m_0\alpha \qquad ; \qquad m = m_0(1+2\alpha)$

$\dfrac{(-\Delta T_f)_{observed}}{(-\Delta T_f)_{undissociated}} = i = \dfrac{m}{m_0} = 2$

12. **A, C, D**

(A)
$$\overset{OH}{\underset{O}{\overset{|}{\underset{\|}{\overset{}{C}l}}}}\!\!\!\underset{O}{\diagup}\!\diagdown O \to sp^3 \qquad H-\ddot{\underset{\cdots}{O}}-Cl$$
$$sp^3$$

(C) $\underset{\substack{\text{strong acid}}}{HClO_4} + \underset{\substack{\text{weak acid} \\ \text{and strong base}}}{H_2O} \longrightarrow \underset{\substack{\text{weak base} \\ \text{(Resonance stable)} \\ \text{More stable}}}{ClO_4^-} + \underset{\substack{\text{strong acid}}}{H_3\overset{+}{O}}$

(D)
$$\overset{O^-}{\underset{O}{\overset{|}{\underset{\|}{Cl}}}}\diagup\diagdown O$$

13.
$$AB \rightleftharpoons A^+ + B^-$$
Solubility $\qquad x \qquad x \quad x - y$
$2 \times 10^{-10} = x\,(x-y)$ $\qquad$ ....(1)
$B^- + H^+ \rightleftharpoons HB$
$x - y \quad 10^{-3} \qquad y$

$10^8 = \dfrac{y}{(x-y)10^{-3}}$

$\dfrac{y}{x-y} = 10^5$

$x - y = 10^{-5} y$ $\qquad$ ....(2)
From (1) & (2)
$2 \times 10^{-10} = x^2 - 2 \times 10^{-5}$
$x^2 = 2 \times 10^{-5}$
$x = \sqrt{20} \times 10^{-3}$
$\quad = 4.47 \times 10^{-3}$

14.

(P) $NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$
M.Mole $\quad 1 \qquad 2$
Now solution contains 1 m mole CH_3COOH & 1 m. mole CH_3COONa in 30 ml solution. It is a Buffer solution
$\therefore [H^+]$ does not charge with dilution.

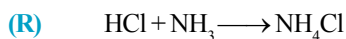**(Q)** $NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$
M.Mole $\quad 2 \qquad 2$
Now solution contains 2 m mole CH_3COONa in 40 ml solution (salt of weak acid strong base)

$[H^+]_{initial} = \sqrt{\dfrac{K_w Ka}{C}}$

Now on dilution upto 80 ml, now can. Becomes $\dfrac{C}{2}$

$\therefore [H^+]_{new} = \sqrt{\dfrac{K_w K_a}{C/2}} = [H^+]_{initial} \times \sqrt{2}$
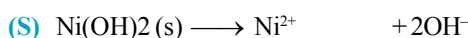
(R) $HCl + NH_3 \longrightarrow NH_4Cl$

M.Mole   2   2

Now solution contain 2 m. mole of NH_4Cl in 40 ml solution (salt of SA & WB)

$$[H^+]_{initial} = \sqrt{\frac{K_w C}{K_b}}$$

Now on dilution upto 80 ml, new conc. becomes $\dfrac{C}{2}$

$$\therefore \quad [H^+]_{new} = \sqrt{\frac{K_w C}{K_b 2}} = \frac{[H^+]_{initial}}{\sqrt{2}}$$

(S) $Ni(OH)2 \,(s) \longrightarrow Ni^{2+} \qquad +2OH^-$

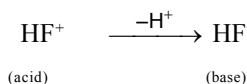$\because$ it is sparingly soluble salt

$\therefore$ on dilution $[OH^-]$ conc. is saturated solution of $Ni(OH)2$ remains const.

$\therefore [H^+]_{new} = [H^+]_{initial}$

<div align="center">

◀ MOCK TEST ▶

</div>

2. Conjugate acid base pair are differ by an proton (H^+).

$$HF^+ \xrightarrow{\;-H^+\;} HF$$

   (acid)   (base)

6. $K = [HCOOH_2^+][HCOO^-] = 10^{-3} \times 10^{-3} = 10^{-6}$

7. $K_a = 10^{-6}$ for $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

Thus K for reverse reaction is $\dfrac{1}{10^{-6}} = 10^6$

9. **(A)** At 25ºC, $[H^+]$ in a solution of 10^{-8} M HCl $> 10^{-7}$ M.
(B) $[H^+] = 10^{-8}$ M.
(C) $[OH^-] = 4 \times 10^{-6}$ M $\Rightarrow [H^+] = 2.5 \times 10^{-9}$ M.
(D) $[H^+] = 10^{-9}$ M.

10. (a)   HCl   NaOH

No. of mili eq. $= \dfrac{1}{10} \times 100 = 10 \qquad \dfrac{1}{10} \times 100 = 10$

So solution is Neutral

(b) $\dfrac{1}{10} \times 55 = 5.5 \qquad\qquad \dfrac{1}{10} \times 45 = 4.5$

$[H^+] = \dfrac{1}{100} = 10^{-2}$ M, pH $= 2$

(c) $\dfrac{1}{10} \times 10 = 1 \qquad\qquad \dfrac{1}{10} \times 90 = 9$ Basic

(d) $\dfrac{1}{5} \times 75 = 15 \qquad\qquad \dfrac{1}{5} \times 25 = 5$

$[H^+] = 0.1$ M, pH $= 1$

12. Concentration of Solutions are same therefore $[H^+]$ depends only on Dissociation constant.

14. pH of 0.1 M H_2S solution can be derived by :

$$H_2S \rightleftharpoons H^+ + HS^- \,; K_1 = 1 \times 10^{-7}$$
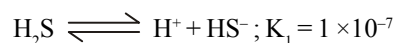
$$\therefore \quad [H^+] = C\alpha = C\sqrt{\frac{K_1}{C}} = \sqrt{K_1 \times C} = \sqrt{1 \times 10^{-7} \times 0.1}$$

$$= \sqrt{10^{-8}} = 10^{-4} \quad \therefore \quad pH = 4$$

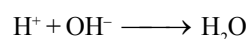**15. (A)** In 0.6 m M HCOOH solution

$$K_a = \frac{[H^+]^2}{C - [H^+]} \quad \Rightarrow \quad 8 \times 10^{-4} = \frac{[H^+]^2}{6 \times 10^{-4} - [H^+]}$$

$$\therefore \quad [H^+] = \mathbf{4 \times 10^{-4}\, M.}$$

So solution in **(A), (C)** & **(D)** are ISOHYDRIC.

16. (A) $[H^+] = 10^{-2}$ and $[OH^-] = 10^{-2}$

$$H^+ + OH^- \longrightarrow H_2O$$

This leads complete neutralisation

so, $\;pH = 7 = \dfrac{2 + 12}{2}$

(D) $[H^+] = 10^{-5}$ and $[OH^-] = 10^{-5}$

$$[H^+] + [OH^-] \longrightarrow H_2O$$
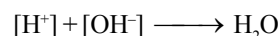
This leads complete neutralisation

so, $\;pH = 7 = \dfrac{5 + 9}{2}$

18. On the basis of ostwald dilution law, number of H^+ ions will increase but increase in volume will be more. Therefore, $[H^+]$ decreases, pH increases.

20. Since K_a of HCN is less than that of HF, so CN^- is stronger base than F^-

22. Due to common ion effect, $[H^+]$ increases therefore ionization of HCOOH decreased.

24. Since K_a of CH_3COOH & K_b of NH_4OH are same so degree of hydrolysis of CH_3COO^- & NH_4^+ are exactly same.

25. (A) $[H^+]$ in HCl solution $= 10^{-5}$ M

$[H^+]$ in H_2S solution $= \sqrt{K_a \times C} = 10^{-4}$ M

so $[H^+]$ in HCl solution $< [H^+]$ in H_2S solution

& $[OH^-]$ in HCl solution $> [OH^-]$ in H_2S solution

& degree of dissociation of water in HCl solution > degree of dissociation of water in H_2S solution

pH of HCl solution > pH of H_2S solution.

(B) At pH = 4.74 in CH_3COOH solution, $[CH_3COO^-] = [CH_3COOH]$

∴ degree of dissociation of $CH_3COOH = \dfrac{1}{2}$

At pH = 9.26 i.e. pOH = 4.74 in NH_4OH solution, $[NH_4^+] = [NH_4OH]$

∴ degree of dissociation of CH_3COOH = degree of dissociation of NH_4OH

degree of dissociation of water in CH_3COOH solution > degree of dissociation of water in NH_4OH solution.

(C) $[H^+]$ in CH_3COOH solution $= \sqrt{1.8 \times 10^{-5} \times 0.1}$

$$= \sqrt{1.8} \times 10^{-3} \text{ M}$$

$[H^+]$ in HCOOH solution $= \sqrt{1.8 \times 10^{-4} \times 1}$

$$= \sqrt{1.8} \times 10^{-2} \text{ M}$$

so, degree of dissociation of CH_3COOH = degree dissociation of HCOOH.

(D) $[H^+]$ in HA_1 solution $= \sqrt{10^{-5} \times 0.1} = 10^{-3} \text{ M}$

$[H^+]$ in HA_2 solution $= \sqrt{10^{-6} \times 0.01} = 10^{-4} \text{ M}$

so $[OH^-]$ in solution of $HA_1 < [OH^-]$ in solution of HA_2

pH in solution of $HA_1 <$ pH in solution of HA_2

& degree of dissociation of water $HA_1 <$ degree of dissociation of water HA_2.

27. (i) $CH_3COOH = 0.2 \text{ M}$

$[H^+] = \sqrt{K_a \times C} = \sqrt{2 \times 10^{-5} \times 0.2} = \sqrt{4 \times 10^{-6}}$

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

$$pH = 3 - \log 2 = \textbf{2.7}$$

$C\alpha = [H^+] \Rightarrow \alpha = \dfrac{2 \times 10^{-3}}{2 \times 10^{-1}} \Rightarrow \alpha = \textbf{0.01}$

(ii) $HCl \longrightarrow H^+ + Cl^-$

$\quad 0.1 \qquad\qquad 0.1 \quad\ 0.1$

$[H^+] = 0.1 \qquad\qquad pH = 1$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$\quad 0.2 \qquad\qquad\quad O \qquad\quad 0.1$

$\quad 0.2(1-\alpha) \qquad\quad 0.2\alpha \qquad 0.1 + 0.2\alpha = 0.1$

$K_a = \dfrac{0.2\alpha \times 0.1}{0.2} = 2 \times 10^{-5} \qquad \alpha = 2 \times 10^{-4}$

(iii) $[CH_3COO^-] = 0.2 \times 2 \times 10^{-4} = \textbf{4} \times \textbf{10}^{-5}$

(iv) % change in $\alpha = \dfrac{1 \times 10^{-2} - 2 \times 10^{-4}}{1 \times 10^{-2}} \times 100$

$$= \left|1 - \dfrac{2}{100}\right| \times 100 = \textbf{98 \%}$$

28. $HA + NaOH \rightarrow NaA + H_2O;$ or $HA + OH^- \rightarrow A^- + H_2O$

$$K_{eq.} = 10^9 = \dfrac{[A^-][H_2O]}{[HA][OH^-]}$$

Also $HA \rightleftharpoons H^+ + A^- \quad K_a = \dfrac{[H^+][A^-]}{[HA]}$

∴ $\dfrac{K_{eq}}{K_a} = \dfrac{1}{K_w}$ or $K_a = 10^9 \times 10^{-14} = 10^{-5}$ Thus for

$$A^- + H_2O \rightleftharpoons HA + OH$$

$$[OH^-] = Ch = C\sqrt{\dfrac{K_H}{C}} = \sqrt{\dfrac{K_w C}{K_a}} = \sqrt{\dfrac{10^{-14} \times 0.1}{10^{-5}}} = 10^{-5} M$$

∴ $[H^+] = 10^-$ and pH = 9

30. $Asc^- + H_2O \rightleftharpoons HAsc + OH^-$

∴ $[OH^-] = C.h = C\sqrt{\dfrac{K_h}{C}} = \sqrt{K_h.C} = \sqrt{\dfrac{K_w}{K_a}.C}$

$$= \sqrt{\dfrac{10^{-14} \times 0.02}{5 \times 10^{-5}}} = 2 \times 10^{-6}$$

∴ $[H^+] = \dfrac{1 \times 10^{-14}}{2 \times 10^{-6}} = 5 \times 10^{-9} \text{ M}$

Also $h = \sqrt{\left[\dfrac{K_h}{C}\right]} = \sqrt{\dfrac{K_w}{K_a \times C}} = \sqrt{\dfrac{10^{-14}}{5 \times 10^{-5} \times 0.02}}$

$$= \textbf{10}^{-4} \text{ or } \textbf{0.01 \%}$$