Ionic Equilibrium

SOLUTIONS

EXERCISE - O

1. **Ans. (D)**

Conjugate acid of $O^{2\ominus}$ is $OH^{\ominus}$

2. **Ans. (D)**

$ClO_3^{\ominus}$ doesn't have acidic hydrogen, so it doesn't show acidic behaviour.

3. **Ans. (A)**

$NH_3 + H_2O \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$

Water is losing $H^{\oplus}$, so water is acting as an acid.

4. **Ans. (D)**

Conjugate base of $(CH_3)_2N^{\oplus}H_2$ is $(CH_3)_2NH$

5. **Ans. (C)**

$Cl^{\ominus}$ is weakest Bronsted Lowry base, as more HCl is strong acid. More stronger the acid, weaker is its conjugate base.

6. **Ans. (B)**

Hydrazoic acid $\Rightarrow HN_3$

Its conjugate base is $N_3^{\ominus}$

7. **Ans. (C)**

Conjugate base of HNO_3 is $NO_3^{\ominus}$

8. **Ans. (B)**

NH_3 & $S^{2\ominus}$ are bases in the reaction, as both are accepting $H^{\oplus}$.

9. **Ans. (A)**

To write conjugate acid add $H^{\oplus}$.

10. **Ans. (C)**

Lewis acid $\rightarrow$ Accepts lone pair of e.

Lewis base $\rightarrow$ Donates lone pair of e.

$$\underbrace{SiCl_4}_{\text{Lewis acid}} + \underbrace{2Cl^{\ominus}}_{\text{Lewis base}} \longrightarrow [SiCl_6]^{2\ominus}$$

$$\underbrace{CH_3^{\oplus}}_{\text{Lewis acid}} + {}^{\ominus}OC_2H_5 \longrightarrow \underbrace{CH_3OC_2H_5}_{\text{Methoxy ethane (a Lewis base)}}$$

11. **Ans. (D)**

Ionic product of water, K_w increases only with temperature.

12. Ans. (A)

$H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$

$K_d = \frac{[H^{\oplus}][OH^{\ominus}]}{[H_2O]} = \frac{10^{-14}}{55.4}$

$= (10^{14} \times 55.4)^{-1}$

13. Ans. (B)

pH + pOH = pKw

pH + pOH= 14

14. Ans. (A)

pH < 7, because as Temperature increases, K_w increases, pK_w decreases, so pH of H_2O will also decrease.

15. Ans. (D)

For pure water, $[OH^{\ominus}] = [H_3O^{\oplus}] = 10^{-6.7}$ M

$K_w = [H_3O^{\oplus}]\ [OH^{\ominus}]$

$= 10^{-6.7} \times 10^{-6.7} = 10^{-13.4}$

16. Ans. (D)

$[H_3O^{\oplus}]$ means $[H^{\oplus}] = 6.2 \times 10^{-9}$ mol/l

$pH = -\log(6.2 \times 10^{-9}) = 8.21$

17. Ans. (D)

$[H_3O^{\oplus}] \times [OH^{\ominus}] = K_w$ (constant at given constant temperature)

18. Ans. (D)

It is definition of Levelling effect.

19. Ans. (C)

$pH_1 = 3 \Rightarrow [H^{\oplus}]_1 = 10^{-3}$

$pH_2 = 6 \Rightarrow [H^{\oplus}]_2 = 10^{-6}$.

$\therefore \frac{[H^{\oplus}]_1}{[H^{\oplus}]_2} = \frac{10^{-3}}{10^{-6}} = 1000$

$\therefore$ $[H^{\oplus}]$ ion is reduced by 1000 times.

20. Ans. (C)

$[H_2SO_4] = \frac{1}{200}\text{mole}/\text{m}^3$

$= \frac{1}{200}\text{mole}/1000\text{L} \quad \because 1\ \text{m}^3 = 1000\ \text{L}$

$= \frac{1}{200 \times 1000}\text{mole}/\text{L}$

$= 0.5 \times 10^{-5}$ mole/L $= 5 \times 10^{-6}$ mole/L

$\therefore$ $[H^{\oplus}] = 2 \times 5 \times 10^{-6} = 10^{-5}$ mole/L = PH = 5

$\therefore$ POH = 14 – 5 = 9

21. Ans. (C)

V = 250 mL, PH = 13 $\Rightarrow [H^{\oplus}] = 10^{-13} \Rightarrow [OH^{\ominus}] = \frac{10^{-14}}{10^{-13}} = 10^{-1}$ M.

$\therefore$ $[NaOH] = [OH^{\ominus}] = 10^{-1}$ M

or, $\frac{n \times 1000}{250} = 0.1$ (where n = moles of NaOH)

or, $n = \frac{1}{40}$ mole

$\therefore$ mass of NaOH = n × 40 = $\frac{1}{40}$ × 40 g = 1g

22. Ans. (C)

pH = 14

23. Ans. (B)

NaOH = 8 g = $\frac{8}{40}$ mole = 0.2 mole $\Rightarrow OH^{\ominus}$ = 0.2 mole

H_2SO_4 = 4.9 g = $\frac{4.9}{98}$ mole $= \frac{1}{20}$ mole = 0.05 mole $\therefore$ $H^{\oplus}$ = 2 × 0.05 = 0.1 mole

$\because$ moles of $OH^{\ominus}$ > mole of $H^{\oplus}$

$\therefore$ $[OH^{\ominus}] = \frac{0.2-0.1}{1} = 0.1$ mole/L $\Rightarrow$ pOH = 1 $\Rightarrow$ pH = 13

24. Ans. (B)

$$[H^{\oplus}] = \frac{\frac{1}{200} \times 10 \times 2 + \frac{1}{200} \times 40 \times 2}{(10+40)} = \frac{0.1+0.4}{50} = \frac{0.5}{50} = 10^{-2}M$$

$\therefore$ pH = 2

25. Ans. (D)

(A) $[H^{\oplus}] = \frac{1}{100} \times 100 = 1$ mmole, $[OH^{\ominus}] = \frac{1}{10} \times 100$ = 10 mmole

$\because$ $[OH^{\ominus}] > [H^{\oplus}] \Rightarrow$ pH > 7

(B) $[H^{\oplus}] = \frac{1}{10} \times 55$ = 5.5 mmole, $[OH^{\ominus}] = 45 \times \frac{1}{10}$ = 4.5 mmole

$[H^{\oplus}] = \frac{5.5-4.5}{[55+45]} = \frac{1}{100} = 10^{-2} \Rightarrow pH = 2$

(C) $[H^{\oplus}] = \frac{1}{10} \times 10$ = 1 mmole, $[OH^{\ominus}] = \frac{1}{10} \times 90$ = 9 mmole

$\because$ $[OH^{\ominus}] > [H^{\oplus}] \Rightarrow$ pH > 7

(D) $[H^{\oplus}] = 75 \times \frac{1}{5} = 15$ mmole, $[OH^{\ominus}] = 25 \times \frac{1}{5} = 5$ mmole

$[H^{\oplus}] = \frac{(15-5)}{(75+25)} = \frac{10}{100} = 0.1 = 10^{-1}M$

$\therefore$ pH = 1

26. Ans. (B)

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

$$= \frac{1}{2}(9.229 - (-.523)$$

$$= 4.87$$

27. Ans. (A)

Strong electrolytes are completely ionised

28. Ans. (B)

Degree of ionisation of a compound depends on the nature of solute.

29. Ans. (B)

0.15 M solution of HOCl, $K_a = 9.6 \times 10^{-6}$

Assuming $\alpha \ll 1$,

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{9.6\times10^{-6}}{0.15}} \ll 1$$

So, $[H^{\oplus}] = \sqrt{K_aC} = \sqrt{9.6\times10^{-6}\times0.15}$

$[H^{\oplus}] = 1.2 \times 10^{-3}$ M

pH = 3 – log(1.2) = 2.92

30. Ans. (D)

pH = 2

$[H^{\oplus}] = 10^{-2}$

$10^{-2} = \sqrt{K_aC}$

$K_aC = 10^{-4}$

$4.5 \times 10^{-4} \times C = 10^{-4}$

$C = \frac{1}{45} = 0.2222$

31. Ans. (D)

For CH_3COOH, Normality = molarity.

$\therefore$ C = 0.1 M

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-5}}{0.1}} = 10^{-2}$$

32. Ans. (B)

$[NH_3] = C = 0.02$ M, $\alpha = \frac{5}{100} = 0.05.$

$[OH^{\ominus}] = C\alpha = 0.02 \times 0.05 = 0.0010 = 10^{-3}$ M.

$\therefore$ POH = 3 $\Rightarrow$ PH = 11

33. Ans. (C)

$C = 0.1$ M, $\alpha = \dfrac{2}{100} = 0.02$

$[H^{\oplus}] = C\alpha = 0.1 \times 0.02 = 2 \times 10^{-3}$ M.

$[OH^{\ominus}] = \dfrac{K_w}{[H^{\oplus}]} = \dfrac{10^{-14}}{2\times10^{-3}} = 0.5\times10^{-11} = 5\times10^{-12}\,M$

34. Ans. (C)

$CH_3COO^{\ominus} + H_2O \rightleftharpoons CH_3COOH + OH^{\ominus}$

$K_h = \dfrac{K_w}{K_a} = \dfrac{x^2}{C}$

$x = [OH^{\ominus}] = \left(\dfrac{K_w \times C}{K_a}\right)^{1/2}$

35. Ans. (C)

As it is salt of weak acid and strong base.

36. Ans. (A)

$pH = 7 + \dfrac{1}{2}\,[pK_a - pK_b]$

$= 7 + \dfrac{1}{2}\,[4 - 5]$

$= 6.5$

37. Ans. (A)

As temperature increases, K_w increases, pK_w decreases.

So, pH of neutral solution will decrease.

$pH < 7$

38. Ans. (D)

Hydrolysis of strong acid and strong base does not take place.

39. Ans. (A)

For NaCN solution, Normality = molarity.

$$C = \frac{1}{80}M$$

$h = \sqrt{\dfrac{K_h}{C}} = \sqrt{\dfrac{K_w}{K_a \times C}} = \sqrt{\dfrac{10^{-14}}{2\times10^{-9}\times\dfrac{1}{80}}} = \sqrt{4\times10^{-4}} = 0.02$

% hydrolysis = h × 100 = 0.02 × 100 = 2%

40. Ans. (D)

NH_4CH_3COO	$pH = 7 + \dfrac{1}{2}\,(pK_a - pK_b)$, salt of weak acid + weak base
NH_4Cl	Salt of strong acid + weak base $\Rightarrow$ pH < 7
$(NH_4)_2SO_4$	Salt of strong acid + weak base $\Rightarrow$ pH < 7
CH_3COONa	Salt of weak acid + strong base $\Rightarrow$ pH > 7

41. **Ans. (C)**

$$pH = 7 + \frac{1}{2}(pK_a - pK_b)$$

$$= 7+\frac{1}{2}(4.8-4.78)$$

$$= 7.01$$

42. **Ans. (B)**

$pH - pK_a = 1$

$$\log\frac{[\text{Conjugate base}]}{[\text{acid}]} = 1$$

[Conjugate base] = 10 × [acid]

43. **Ans. (A)**

$$\text{Buffer capacity} = \frac{0.02}{5.80-5.75} = \frac{0.02}{0.05} = 0.4$$

44. **Ans. (C)**

In option (C) (NH_4Cl + HCl), it is an acidic solution and it will not act as a buffer.

45. **Ans. (B)**

As blood is buffer solution.

46. **Ans. (C)**

keeping the pH constant.

47. **Ans. (B)**

$$(NH_4OH) = \frac{0.05}{2} = 0.025M = 2.5 \times 10^{-2}\ M$$

$$[NH_4Cl] = \frac{0.001}{2} = 0.0005\ M = 5 \times 10^{-4}\ M.$$

$K_b = 1.8 \times 10^{-5}$

$$\begin{array}{lcccc} NH_4OH\,(aq.) & \rightleftharpoons & NH_4^{\oplus}\,(aq.) & + & OH^{\ominus}(aq.) \\ 2.5 \times 10^{-2} - x & & 5 \times 10^{-4} + x & & x \end{array}$$

$$1.8 \times 10^{-5} = \frac{(5\times10^{-4}+x)x}{(2.5\times10^{-2}-x)}$$

$4.5 \times 10^{-7} - 1.8 \times 10^{-5}\ x = x^2 + 5 \times 10^{-4}\ x$

$x^2 + 5 \times 10^{-4}\ x + 1.8 \times 10^{-5}x - 4.5 \times 10^{-7} = 0$

or, $x^2 + 5.18 \times 10^{-4}\ x - 4.5 \times 10^{-7} = 0$

$$x = \frac{-5.18 \times 10^{-4} + \sqrt{(5.18\times10^{-4})^2 + 18\times10^{-7}}}{2}$$

$\because\ \ x > 0$

$$\text{or, } x = \frac{-5.18 \times 10^{-4} + 14.38\times10^{-4}}{2}$$

or, $x = 4.6 \times 10^{-4}$ M

$\therefore\ \ [OH^{\ominus}] = x = 4.6 \times 10^{-4}$ M

48. Ans. (C)

$NH_3 = 0.6 \times 600 = 360$ m mole | $K_b = 1.8 \times 10^{-5}$

$NH_4Cl = 0.5 \times 400 = 200$ m mole | $\therefore\ pK_b = 5 - \log 1.8 = 5 - 0.26 = 4.74$

$$pOH = pK_b + \log \frac{[NH_4^{\oplus}]}{[NH_3]}$$

$$\text{or, } pOH = 4.74 + \log \frac{200}{360}$$

or, $pOH = 4.74 - \log 1.8 = 4.74 - 0.26 = 4.48$

$\therefore\quad pH = 14 - 4.48 = 9.52$

49. Ans. (D)

$$pOH = pK_b + \log \frac{[NH_4^{\oplus}]}{[NH_4OH]}$$

$$= 4.74 + \log \frac{1}{1}$$

$= 4.74$

$pH = 14 - 4.74 = 9.26$

50. Ans. (B)

$$pOH_1 = pK_b + \log \frac{1}{1} = pK_b$$

$$pOH_2 = pK_b + \log \frac{2}{1} = pK_b + \log 2$$

$\Rightarrow\quad pOH_2 > pOH_1 \Rightarrow$ pOH increases $\Rightarrow$ pH decreases

51. Ans. (A)

Following three reactions will occurs :

$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$

$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O$

$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$

Therefore buffer solution will be :

(i) $H_3PO_4 + NaH_2PO_4$

(i) $NaH_2PO_4 + Na_2HPO_4$

(i) $Na_2HPO_4 + Na_3PO_4$

No. of buffer solutions = 3

52. Ans. (A)

$$pH = pK_{In} - \log \frac{[HIn]}{[In^{\ominus}]}$$

53. Ans. (A)

pH range of indicator is

$pK_{In} - 1 \le pH \le pK_{In} + 1$

$5 - 1 \le pH \le 5 + 1$

$4 \le pH \le 6$

54. Ans. (B)

$pK_b - 1 \le pOH \le pK_b + 1$

$11 - 1 \le pOH \le 11 + 1$

$3 - 1 \le pH \le 3 + 1$

55. Ans. (C)

Phenolphthalein is used for the titration of basic solution.

56. Ans. (D)

Phenolphthalein is weak acid.

57. Ans. (A)

pH range of methyl red indicator is 4.2 – 6.2

58. Ans. (A)

$pH = pK_{In} \pm 1$

pH range = 2.4 to 4.4 (range when indicator changes its colour)

59. Ans. (D)

pH range of phenolphthalein = 8.2 to 10

$\therefore$ We must take strong base to neutralise HCl.

60. Ans. (C)

phenolphthalein is used in the titration of

(i) Strong acid + Strong base

(ii) Weak acid + Strong base

It can't be used in a Redox titration.

61. Ans. (D)

For titration of weak acid-strong base phenolphthalein indicator is used.

62. Ans. (B)

$MX : K_{sp} = S_1^2 \Rightarrow S_1 = \sqrt{K_{sp}} = 2 \times 10^{-9}$ M

$QX_2 : K_{sp} = 4S_2^3 \Rightarrow S_2 = \left(\frac{K_{sp}}{4}\right)^{1/3} = 10^{-6}$ M

$S_2 > S_1$

63. Ans. (C)

$PbBr_2 \rightleftharpoons Pb^{2\oplus}(aq) + 2Br^{\ominus}(aq)$

$K_{sp} = 4S^3$

64. Ans. (B)

$$\begin{array}{lccccl} CuI(s) & \rightleftharpoons & Cu^{\oplus}(aq) & + & I^{\ominus}(aq); & K_{sp} \\ & & x & & (x + 0.1) \simeq 0.1 & \text{(from NaI)} \end{array}$$

$K_{sp} = [Cu^{\oplus}][I^{\ominus}] = x \times 0.1$

$x = \frac{K_{sp}}{0.1} = 5 \times 10^{-11}$ M

65. Ans. (A)

$CaF_2(s) \rightleftharpoons Ca^{2\oplus}(aq) + 2F^{\ominus}(aq); \quad K_{sp}$

$x \qquad 2x = 4 \times 10^{-4}$

$K_{sp} = x(2x)^2 = 2 \times 10^{-4} \times (4 \times 10^{-4})^2 = 3.2 \times 10^{-11}$

66. Ans. (D)

$A_2X_3(s) \rightleftharpoons 2A^{3\oplus}(aq.) + 3X^{2\ominus}(aq.)$

$2y \qquad 3y$

$K_{sp} = [A^{3\oplus}]^2 [x^{2\ominus}]^3 = (2y)^2 \times (3y)^3$

$= 4 \times 27 \times y^5 = 108 y^5$

67. Ans. (C)

$s = 1.43 \times 10^{-4}$ g/100 mℓ, Molar molar mass of AgCl = 143 g/mol

or, $s = \dfrac{1.43 \times 10^{-4}}{143} \times \dfrac{1000}{100}$ mole/L

$s = 10^{-5}$ mole/L

$AgCl\ (solid) \rightleftharpoons Ag^{\oplus}(aq.) + Cl^{\ominus}(aq.)$

$s \qquad s$

$= K_{sp} = [Ag^{\oplus}][Cl^{\ominus}] = s \times s = s^2 = (10^{-5})^2 = 10^{-10}$

68. Ans. (A)

$M_{CaCO_3} = 100g$

$s = \dfrac{7}{100}$ mole/L

$CaCO_3(s) \rightleftharpoons Ca^{2\oplus}(aq.) + CO_3^{2\ominus}(aq.)$

$s \qquad s$

$K_{sp} = s^2 = \left(\dfrac{7}{100}\right)^2 = 49 \times 10^{-4}$

$= 4.9 \times 10^{-3}$

69. Ans. (C)

$A_3B_2(s) \rightleftharpoons 3A^{2\oplus}(aq.) + 2B^{3\ominus}(aq.)$ Molar solubility 's' = $\dfrac{x}{M}$

$3s \qquad 2s$

$K_{sp} = (3s)^3 \times [B^{3\ominus}]^2$

or, $\dfrac{1}{27s^3} = \dfrac{[B^{3\ominus}]^2}{K_{sp}}$

or, $\dfrac{1}{27s^3 \times [B^{3\ominus}]} = \dfrac{[B^{3\ominus}]}{K_{sp}}$

or, $\dfrac{[B^{3\ominus}]}{K_{sp}} = \dfrac{1}{27s^3 \times 2s} = \dfrac{1}{54s^4} = \dfrac{1}{54} \times \dfrac{1}{\left(\dfrac{x}{M}\right)^4} = \dfrac{M^4}{54 \times x^4}$

70. Ans. (B)

$Ag_2CrO_4(s) \rightleftharpoons 2Ag^{\oplus}(aq.) + CrO_4^{2\ominus}(aq.)$

$2s \qquad (0.1 + s) \approx 0.1$

$K_{sp} = (2s)^2 \times 0.1$

or, $4 \times 10^{-13} = 4s^2 \times 0.1$

or $s^2 = \dfrac{10^{-13}}{0.1} = 10^{-12}$

or, $s = 10^{-6}$ mole/L

71. Ans. (D)

0.05 M $Na_2CO_3 \Rightarrow$ Common ion $CO_3^{2\ominus}$, so solubility decreases.

0.05 M $AgNO_3 \Rightarrow$ Common in $Ag^{\oplus}$, so solubility decreases.

In NH_3(aq.) solution, $Ag^{\oplus}$ form complex $[Ag(NH_3)_2]^{\oplus}$. So solubility will be maximum in NH_3(aq.)

72. Ans. (B)

$4 \times 10^{-19} = \dfrac{[Ag^{\oplus}](0.04)^2}{0.03} \Rightarrow [Ag^{\oplus}] = 7.5 \times 10^{-18}$ M

73. Ans. (B)

$AgCl \longrightarrow \underset{(x+y)}{Ag^{\oplus}} + \underset{x}{Cl^{\ominus}} \qquad AgCNS \longrightarrow \underset{(x+y)}{Ag^{\oplus}} + \underset{y}{CNS^{\ominus}}$

$\dfrac{K_{sp}\,(AgCl)}{K_{sp}\,(AgCNS)} = \dfrac{x}{y} = \dfrac{[Cl^{\ominus}]}{[CNS^{\ominus}]}$

So, $\dfrac{[Cl^{\ominus}]}{[CNS^{\ominus}]} = \dfrac{x}{y} = \dfrac{1.8 \times 10^{-10}}{1.6 \times 10^{-11}} = 1.125 \times 10 = 11.25$

$\Rightarrow \dfrac{x}{y} = 11.25$ or $x = 11.25\,y$.

$K_{sp}\,(AgCl) = [Ag^{\oplus}]\,[Cl^{\ominus}] = (x + y)\,x = 1.8 \times 10^{-10}$

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

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

So, $y = 1.14 \times 10^{-6}$

& $x = 11.25 \times 1.14 \times 10^{-6} = 12.83 \times 10^{-6}$

So, $[Ag^{\oplus}] = [x + y] = 12.83 \times 10^{-6} + 1.14 \times 10^{-6} = 13.97 \times 10^{-6} = 1.4 \times 10^{-5}$ M.

74. Ans. (A)

$Na_2CO_3(aq) + CaF_2(s) \rightleftharpoons 2NaF(aq) + CaCO_3(s)$

	$Na_2CO_3(aq)$	$CaF_2(s)$	$2NaF(aq)$	$CaCO_3(s)$
t = 0	2	–	0	–
t = eq	2 – a	–	2a	–

where a is very small

For $CaCO_3$, $K_{sp} = x = [Ca^{2\oplus}][CO_3^{2\ominus}] = [Ca^{2\oplus}] \times 2$ ($\because CO_3^{2\ominus}$ mainly coming from Na_2CO_3)

$\therefore \quad [Ca^{2\oplus}] = \dfrac{x}{2}$

For CaF_2, $K_{sp} = 4y^3 = \left(\dfrac{x}{2}\right)[F^{\ominus}]^2 \Rightarrow [F^{\ominus}] = \sqrt{\dfrac{8y^3}{x}}$

75. Ans. (B)

Let x mole Na_3PO_4 can be added in 10 L – $BaCl_2$ solution without any precipitation.

$\therefore \quad [Na_3PO_4] = [PH_4^{3\ominus}] = \dfrac{x}{10}M$, $[Ba^{2\oplus}] = 10^{-5}$ M, $M_{Na_3PO_4} = 164$

$Ba_3(PO_4)_2$ (solid) $\rightleftharpoons 3Ba^{2\oplus}(aq.) + 2PO_4^{3\ominus}$ (aq.)

$K_{sp} = [Ba^{2\oplus}]^3 [PO_4^{3\ominus}]^2$

or, $4\times10^{-23} = (10^{-5})^3 \times \left(\dfrac{x}{10}\right)^2$

or, $x^2 = \dfrac{4\times10^{-23}}{10^{-17}} = 4\times10^{-6}$

$\therefore \quad x = 2 \times 10^{-3}$ mole

$= 2 \times 10^{-3} \times 164 = 0.328$ gram

MULTIPLE CORRECT TYPE QUESTIONS

76. Ans. (D)

(A) Complete neutralization $\Rightarrow$ pH = 7.0

(B) $[H^+]_{final} = \dfrac{55\times0.1 - 45\times0.1}{100} = 0.01M$

(C) OH^- is in excess.

(D) $[H^+]_{final} = \dfrac{75\times\frac{1}{5} - 25\times\frac{1}{5}}{100} = 0.1$ M $\Rightarrow$ pH = 1.0

77. Ans. (B)

pH may decrease only on increasing $[H^+]$.

78. Ans. (ABCD)

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

(0.1–x)M   xM   (0.1+x)M

$\simeq$ 0.1 M $\simeq$0.1 M

Now, $1.8 \times 10^{-5} = \dfrac{x\times0.1}{0.1} \Rightarrow = 1.8 \times 10^{-5}$

and $\alpha = \dfrac{x}{0.1} = 1.8 \times 10^{-4}$

Now, $[H^T]_{from\ water} = [OH^-] = \dfrac{Kw}{[H^+]_{acid}} = 10^{-13}$ M

79. Ans. (BC)

(C) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$; $\Delta H° = +$ ve

(D) $HA + OH^- \rightleftharpoons A^- + H_2O$

$$\begin{array}{llll} & a & \frac{a}{2} & 0 \\ \text{Final} & \frac{a}{2} & & \frac{a}{2} \end{array}$$

$$P^H = P^{K_a} + \log\frac{a/2}{a/2} = P^{K_a}$$

80. Ans. (C)

$$\underset{C(1-\alpha)M}{HA} \rightleftharpoons \underset{C\alpha M}{H^+} + \underset{C\alpha M}{A^-}$$

$$K_a = \frac{C\alpha \bullet C\alpha}{C(1-\alpha)} = \frac{\alpha^2 \bullet C}{1-\alpha} \approx \alpha^2 \bullet C \Rightarrow = \sqrt{\frac{K_a}{C}}$$

$$\text{Now, } K_a = \frac{[H^+]\bullet C\alpha}{C(1-\alpha)} = \frac{[H^+]\bullet\alpha}{1-\alpha} \Rightarrow \alpha = \frac{K_a}{K_a + [H^+]}$$

$$= \frac{1}{1+\frac{[H^+]}{K_a}} = \frac{1}{1+10^{(P^{K_a} - P^H)}}$$

81. Ans. (ABC)

Dilution results in increased degree of dissociation but decrease in concentrations of all active components.

82. Ans. (AB)

Relation is valid only for conjugate pairs.

83. Ans. (D)

$$[H^+] >> [CO_3^{2-}]$$

84. Ans. (ABCD)

$RNH_2(g) + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$

1 bar xM xM

$$10^{-6} = \frac{x \bullet x}{1} \Rightarrow x = 10^{-3} \Rightarrow pOH = 3.0 \Rightarrow pH = 11.0$$

85. Ans. (D)

$NH_4OH(aq) \rightleftharpoons NH_4^+ + OH^-$

Addition of solid NH_4OH will increase NH_4OH(aq) concentration and hence, $[OH^-]$ will increase.

86. Ans. (ABD)

Theory based

87. Ans. (AC)

	$NH_4Cl + NaOH \rightleftharpoons NH_4OH + NaCl$			
	a	b	0	
For buffer :	(a–b)	≈0	b	$\Rightarrow$ a>b
	$CH_3\ COONa + HCl \rightleftharpoons CH_3COOH + NaCl$			
	a	b	0	
For buffer :	(a–b)	≈0	b	$\Rightarrow$ a>b

88. Ans. (ABCD)

KCN is a salt of weak acid (HCN) and strong base (KOH).

89. Ans. (BC)

	BOH	$+\ H^+$	$\rightleftharpoons$	$B^+ + H_2O$
	a mol	b mole		0
$\frac{1}{5}$th run	$a-\frac{a}{5}$	0		$\frac{a}{5}$
		$\simeq$		

Now, for 1/5th reaction, pOH = $pK_b + \log\frac{[B^-]}{[BOH]}$

or, (14 – 9) = $pK_b + \log\frac{a/5}{4a/5}$

$\therefore\ pK_b = 5.6 \Rightarrow K_b = 2.5 \times 10^{-6}$

At equivalent point: $pH \Rightarrow -\frac{1}{2}(pK_b + \log C)$

or, $4.5 \Rightarrow -\frac{1}{2}(5.6 + \log C) \Rightarrow C = 0.25$ M

Now, $n_{HCl\ used} = n_{B^+\ formed}$

or, $\frac{V \times 0.5}{1000} = \frac{(100+V)\times 0.25}{1000} \Rightarrow V_{HCl} = 100$ ml

Finally, $n_{BOH\ takes} = n_{HCl\ used\ for\ equivalent\ point}$

or, $\frac{w}{45} = \frac{100 \times 0.5}{1000} \Rightarrow w = 2.25\,gm$

$\therefore$ Percentage purity of base = $\frac{2.25}{2.5} \times 100 = 90\%$

90. Ans. (C)

At equivalent point, the solution should be acidic.

91. Ans. (C)

For precipitation of $Fe(OH)_2$, $[OH^-]_{min} = \sqrt{\frac{8\times 10^{-16}}{0.02}} = 2 \times 10^{-7}$

$\Rightarrow pOH_{max} = 6.7 \Rightarrow pH_{min} = 7.3$

For precipitation of $Fe(OH)_3$, $[OH^-]_{min} = \left(\frac{4 \times 10^{-28}}{0.05}\right)^{1/3} = 2 \times 10^{-9}$

$\Rightarrow pOH_{max} = 8.7 \Rightarrow pH_{min} = 5.3$

92. Ans. (ACD)

$$\underset{(0.5-x)M}{CO_3^{2-}} + H_2O \rightleftharpoons \underset{(x-y)M}{HCO_3^-} + \underset{(x+y)M}{OH^-} \; ; \; K_{h_1} = \frac{Kw}{K_{a_2}} = 2\times10^{-4}$$

Now, $2\times10^{-4} = \frac{(x-y)\cdot(x+y)}{(0.5-x)} \approx \frac{x\cdot x}{0.5} \Rightarrow x = 10^{-2}$

and $2.5\times10^{-9} = \frac{y\cdot(x+y)}{(x-y)} \approx \frac{y\cdot x}{x} \Rightarrow y = 2.5\times10^{-9}$

Now, $h = \frac{x}{0.5} = 0.02$

$pOH = -\log(x+y) \approx -\log(10^{-2}) = 2.0 \Rightarrow pH = 12.0$ and $[H_2CO_3] = y = 2.5\times10^{-9}$ M

93. Ans. (ABD)

$$\overset{+}{N}H_3CH_2COOH \xrightarrow{pK_{a1}=2.22} \overset{+}{N}H_3CH_2COO^- \xrightarrow{pK_{a2}=9.78} \overset{+}{N}H_3CH_2COO^-$$

$$P^H = \frac{1}{2}(P^{K_{a_1}} + P^{K_{a_2}}) = \frac{1}{2}(2.22+9.78) = 6.0$$

Now, $K_{a_1} = \frac{[\overset{\oplus}{N}H_3CH_2COO^-][H^+]}{[\overset{\oplus}{N}H_3CH_2COOH]}$

$\Rightarrow 10^{-2.22} = \frac{0.01\times10^{-6}}{[\overset{\oplus}{N}H_3CH_2COOH]}$

$\therefore [\overset{\oplus}{N}H_3CH_2COOH] = 10^{-5.78} = 1.7\times10^{-6}$ M

% of glycine in cationic form

$= \frac{1.7\times10^{-6}}{0.01}\times100 = 0.017\%$

COMPREHENSION TYPE QUESTIONS

94. Ans. (C)

$[CH_3COOH]_0 = \frac{0.7\times10^{-3}}{10\times10^3} = 7\times10^{-8}$M

The solution is so dilute that we may assume almost complete dissociation of acid.

$\therefore [H^+]_{acid} \approx 7\times10^{-8}$ M

Now, $H_2O \rightleftharpoons \underset{(7\times10^{-8}+x)M}{H^+} + \underset{xM}{OH^-}$

$10^{-14} = (7\times10^{-8}+x).x \Rightarrow x = 7\times10^{-8}$

$\therefore pH = -\log(7\times10^{-8}+x) = 6.85$

95. Ans. (B)

	CH_3COOH	$\rightleftharpoons$ CH_3COO^-	+ H^+
Eqn.	yM	7×10^{-8}M	$7\times10^{-8}+x$ $= 14\times10^{-8}$M

Now, $2.0\times10^{-5} = \frac{7\times10^{-8}\times14\times10^{-8}}{y}$

$\therefore y = 4.9\times10^{-10}$M

96. Ans. (A)

$$pH = pKa\,(NH_4^+) + \log\frac{[NH_3]_0}{[NH_4^+]}$$

$$= 9.3 + \log\frac{0.8}{0.2} = 9.9$$

97. Ans. (A)

	NH_4OH	+	H^+	$\rightleftharpoons$	$NH_4^+ + H_2O$
	0.8M		0.3M		0.2M
Final	0.5M		≈0		0.5M

$$pH = p^{K_a(NH_4^+)} + \log\frac{[NH_3]_0}{[NH_4^+]_0} = 9.3 + \log\frac{0.5}{0.5} = 9.3$$

98. Ans. (C)

H^+ added in excess. Final $[H^+] = 1.0 - 0.8 = 0.2M$

$\therefore$ pH = –log(0.2) = 0.7

99. Ans. (D)

$$pH = \frac{1}{2}\left(p^{K_{a_2}} + p^{K_{a_3}}\right) = \frac{1}{2}(8 + 13) = 10.5$$

100. Ans. (A)

For 2^{nd} equivalent point,

$$n_{NaoH} = 2 \times n_{H_3PO_4}$$

$$\frac{V \times 0.5}{1000} = 2 \times \frac{100 \times 0.1}{1000} \Rightarrow V = 40\text{ ml}$$

After adding HCl,

	HPO_4^{2-}	+	H^+	$\rightleftharpoons$	$H_2O_4^-$
	10 millimole		5 millimole		0
Final	5		≈0		5

$$\therefore pH = 8 + \log\frac{5}{5} = 8.0$$

101. Ans. (C)

$$S = \frac{K_{sp}}{[OH^-]^2} = \frac{4.0 \times 10^{-30}}{(10^{-6})^2} = 4.0 \times 10^{-18}\text{ M}$$

102. Ans. (C)

$$P^H = P^{K_a} + \log\frac{[HCO_3^-]_O}{[H_2CO_3]_O} = 6.4 + \log\frac{8}{1} = 7.3$$

103. Ans. (A)

$$7.4 = 6.4 + \log\frac{[HCO_3^-]_O}{[H_2CO_3]_O} \Rightarrow \frac{[H_2CO_3]_O}{[HCO_3^-]_O} = \frac{1}{10}$$

104. Ans. (B)

More CO_2 should dissolve in solution.

105. Ans. (B)

$$S = \frac{_{sp}[AgCN]}{[CN^-]} = \frac{1.0 \times 10^{-16}}{0.02} = 5.0 \times 10^{-15}\text{ M}$$

106. Ans. (D)

$$AgCN(s) + CN^{-} \rightleftharpoons Ag(CN)_2^{-}$$

$(0.02 - S)M \qquad SM$

$K_{eq} = K_{sp} \times K_f = 15$

$15 = \frac{s}{0.02 - s} \Rightarrow s = \frac{0.3}{16} = 1.875 \times 10^{-2}M$

107. Ans. (C)

$s = [Ag^+] + [Ag(Cu)_2^-]; \frac{K_{sp}}{[Cu^-]} + K_f. K_{sp} . [Cu^-]$

5M

For minimum solubility : $\frac{ds}{d[Cu^-]} = 0$

or, $-\frac{K_{sp}}{[Cu^-]^2} K_f. K_{sp} = 0$

$\Rightarrow [Cu^-] = \sqrt{\frac{1}{K_f}} = 2.58 \times 10^{-9}$ M

108. Ans. (C)

$$\overset{+}{N}H_3 - CH_3 - COOH \underset{K_{a_1} = 4 \times 10^{-3}}{\overset{K_{b_2} = 2.5 \times 10^{-12}}{\rightleftarrows}}$$

$$\overset{+}{N}H_3 - CH_3 - COO^- \underset{K_{b_1} = 6.25 \times 10^{-5}}{\overset{K_{a_2} = 1.6 \times 10^{-10}}{\rightleftarrows}}$$

$NH_2 - CH_2 - COO^-$

Required $K_b = K_{b_1} = 6.25 \times 10 \times 10^{-5}$

109. Ans. (C)

$\therefore pH = \frac{1}{2}(P^{K_{a_1}} + P^{H_{a_2}}) = \frac{1}{2}(2.4 + 9.8) = 6.1$

110. Ans. (C)

Phosphoric acid with three ionisable hydrogen ions is a tribasic acid.

111. Ans. (A)

If first step is taken only

$pH = \frac{1}{2}[pK_{a_1} - \log c]$

$C = \frac{0.5}{98} = 5.1 \times 10^{-3}$ M

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

112. Ans. (B)

$$\frac{[H^{\oplus}]^3[PO_4^{3\ominus}]}{[H_3PO_4]} = K_{a_1}K_{a_2}K_{a_3}$$

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

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

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

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

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

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

113. Ans. (B)

$Zn_3(PO_4)_2 \rightleftharpoons 3Zn^{2\oplus} + 2PO_4^{3\ominus}$

$\therefore \quad K_{sp} = [Zn^{2\oplus}]^3\ [PO_4^{3\ominus}]^2$

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

$[Zn^{2\oplus}]^3 = 1.88 \times 10^{-25}$; $[Zn^{2\oplus}] = 5.73 \times 10^{-9}$ M

114. Ans. (C)

(P) $[OH-]$ to just start precipitation = $\sqrt{\dfrac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\dfrac{2\times10^{-6}}{2\times10^{-3}}} = 10^{-15}$

$\therefore \quad pOH = 1.5 \Rightarrow P^H = 12.5$

(Q) $[OH-]_{max} = \left(\dfrac{K_{sp}}{[Al^{3+}]}\right)^{1/3} = \left(\dfrac{10^{-28}}{0.1}\right)^{1/3} = 10^{-9}$ M

$\therefore \quad p^{OH}_{min} = 9 \Rightarrow p^{H}_{max} = 5.0$

(R) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$\left(0.1 - 0.1\times\dfrac{10}{11}\right)$ M $\qquad 0.1\times\dfrac{10}{11}$ M

$= \dfrac{0.1}{11}$ M $\qquad = \dfrac{1}{11}$ M

Now, $K_a = 10^{-5} = \dfrac{\frac{1}{11}\times[H^+]}{\frac{0.1}{11}} \Rightarrow [H^+] = 10^{-6}$ M

(S) $[H^+] = \sqrt{K_a \cdot C} = \sqrt{10^{-7}\times0.001} = 10^{-5}$ M

$\Rightarrow pH = 5.0$

(T) $\underset{(6\times10^{-5}-x)\,M}{A^-} + H_2O \rightleftharpoons \underset{xM}{HA} + \underset{xM}{OH^-}$

$\dfrac{Kw}{K_a} = 2\times10^{-6}$

$2 \times 10^{-6} = \dfrac{x \cdot x}{(6\times10^{-5} - x)} \Rightarrow x = 1 \times 10^{-5}$

$\therefore \quad P^{OH} = 5 \Rightarrow pH = 9$

115. Ans. (B)

Theory based

116. Ans. (A)

(A) $pH = P^{K_{a_1}} + \log \frac{[H_2A^-]_0}{[H_3A]_0} = 4.0$

(B) $pH = P^{K_{a_2}} + \log \frac{[HA^{2-}]_0}{[H_2A^-]_0} = 8.0$

(C) $pH = P^{K_{a_3}} + \log \frac{[A^{3-}]_0}{[HA^{2-}]_0} = 12.0$

(D) $pH = \frac{1}{2}(P^{K_{a_1}} + P^{K_{a_2}}) = \frac{1}{2}(4+8) = 6.0$

(E) $pH = \frac{1}{2}(P^{K_{a_2}} + P^{K_{a_3}}) = \frac{1}{2}(8+12) = 10.0$

117. Ans. (B)

(A) $K_a(H_2O) = K_b(H_2O) = \frac{Kw}{[H_2O]} = \frac{10^{-14}}{\left(\frac{1000}{18}\right)} = 1.8 \times 10^{-16}$

(C) On increasing temperature, Kw increases and hence, P^{Kw} decreases.

EXERCISE - S

1. Ans. (0.209 M, 0.191 M, 9.13 × 10⁻³ M, 0)

$H_2SO_4(aq.) \longrightarrow H^+(aq.) + HSO_4^-(aq.)$

0.2   -   -

0   (0.2 + x)   (0.2 – x)

$HSO_4^-(aq.) \rightleftharpoons H^+(aq.) + SO_4^{2-}(aq.)$; K_2

0.2   0.2   -

(0.2 – x)   (0.2 + x)   x

$K_2 = 10^{-2} = \frac{(0.2+x)x}{(0.2-x)}$

$0.2 \times 10^{-2} - 10^{-2}x = 0.2\,x + x^2$

$x^2 + 0.21\,x - 2 \times 10^{-3} = 0$

$x = 9.13 \times 10^{-3}$ M

$\Rightarrow$ $[SO_4^{2-}] = x = 9.13 \times 10^{-3}$M

$[H_2SO_4] = 0$

$[H^+] = 0.2 + x = 0.209$ M

$[HSO_4^-] = 0.2 - x = 0.191$ M

2. Ans. ($[S^{2-}] = 2.5 \times 10^{-15}$M)

$H_2S(aq.) \rightleftharpoons 2H^+(aq.) + S^2(aq.); K_1 \times K_2$

$K_1 \times K_2 = \frac{[H^+]^2 \cdot [S^2]}{[H_2S]} = \frac{(2\times10^{-4})^2[S^{2-}]}{0.1}$

$[S^{2-}] = \dfrac{K_1 \times K_2 \times 0.1}{4 \times 10^{-8}} = 2.5 \times 10^{-15}\,M$

[H^+ is mainly given by HCl i.e. strong acid]

3. **Ans. ($K_b \simeq$ 1.73 × 10^{-5}, 5.27)**

(Weak base) let molarity of W.B. is M

BOH +	HCl →	BCl +	H_2O
(1) a = M × 50	0.1 × 10 = 1	-	-
a – 1	x	1	
(2) a = M × 50	0.1 × 25= 2.5	-	-
(a – 2.5)	x	2.5	

Both the two cases forms buffer

$pOH = pK_b + \log\left(\dfrac{S}{b}\right)$

$(14 - 9.84) = pK_b + \log\left(\dfrac{1}{a-1}\right)$ ....(1)

$(14 - 9.24) = pK_b\ \log\left(\dfrac{2.5}{a-2.5}\right)$ ....(2)

Equation (2)-(1) $\Rightarrow$ a = 5 $\Rightarrow pK_b$ = 4.76

$\Rightarrow$ M × 50 = 5 (from eqn. (2))

M = 0.1

$K_b = 10^{-4.76} = 1.7 \times 10^{-5}$

at equivalence point $\Rightarrow$ equal volumes will be added

BOH +	HCl $\longrightarrow$	BCl +	H_2O
$\dfrac{0.1}{2}M$	$\dfrac{0.1}{2}M$	-	-
0	0	$\dfrac{0.1}{2}M$	{when equal volumes are added concn. become half}

Salt of S.A. & W.B. undergoes hydrolysis

$pH = 7 - \dfrac{1}{2}pK_b - \dfrac{1}{2}\log C$

$= 7 - \dfrac{1}{2} \times 4.76 - \dfrac{1}{2}\log\left(\dfrac{0.1}{2}\right) = 5.27$

4. **Ans. (10^{-5}M)**

As S.A. & S.B. react so,

	HCl +	NaOH $\longrightarrow$	NaCl + H_2O
Milli-moles	2	1	-
	1	0	1

After reaction, $[HCl] = \dfrac{1}{10+10+10} = \dfrac{1}{30}M$

Finally [HA] = $\frac{0.1\times10}{10+10+10}=\frac{1}{30}$M

$HA(aq.) \rightleftharpoons H^+(aq.) + A^-(aq.) : K_a$

$\frac{1}{30}$ $\frac{1}{30}$ -

(from HCl)

$\left(\frac{1}{30}-x\right)\simeq\frac{1}{30}\left(\frac{1}{30}+x\right)\simeq\frac{1}{30}$ x

[x is negligible as $\frac{K_a}{C}<10^{-3}$]

$K_a = 10^{-5} = \frac{\frac{1}{30}.[A^-]}{\frac{1}{30}}$; $[A^-] = 10^{-5}$ M

5. **Ans. (pH = 11.48 , $[enH_2^{2+}]$ = 7.1 × 10⁻⁸ M)**

$en(aq.) + H_2O \rightleftharpoons enH^+ (aq.) + OH^-(aq.) ;\ K_{b_1}$

0.1 - -

0.1 – x (x – y) (x +y) ≃ x

$enH^+ (aq.) + H_2O \rightleftharpoons enH_2^{2+} (aq.) + OH^-(aq.) ;\ K_{b_2}$

(x–y) ≃ x y (x +y) ≃ x

(as $K_{b_1} >> K_{b_2} \Rightarrow x >> y$)

$K_{b_1}=\frac{x^2}{0.1-x}=\frac{x^2}{0.1}\left\{\begin{array}{l}\therefore\frac{K_{b_1}}{0.1}<10^{-3}\\ \Rightarrow(0.1-x)\simeq0.1\end{array}\right\}$

$[OH^-] = x = \sqrt{K_{b_1}C}=\sqrt{9\times10^{-5}\times0.1}$

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

pOH = 3 – log 3

pH = 14 – pOH = 11 + log 3 = 11.48

$K_{b_2}=\frac{x.y}{x}=y$

$[enH_2^{+2}] = y = 7.1 \times 10^{-8}$ M

6. **Ans. (10.6)**

As $K_{b_1} >> K_{10_2} \Rightarrow OH^-$ is given by I step only

$NiC(aq.) + H_2O \rightleftharpoons NiCH^+(aq.) + OH^- (aq.) ;\ K_{b_1}$

0.2 - -

(0.2 – x) = 0.2 x x

$\left[\because \frac{K_{b_1}}{0.2} < 10^{-3} \Rightarrow (0.2-x) \simeq 0.2\right]$

$K_{b_1} = \frac{x^2}{0.2}$

$[OH^-] = x = \sqrt{K_{b_1} \times 0.2} = \sqrt{16 \times 10^{-8}}$

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

pOH = 4 – log 4

pH = 14 – pOH = 10 + log 4 = 10.6

7. **Ans. (2×10^{-4}M)**

$NaOH(aq.) \longrightarrow Na^+ (aq.) + OH^-(aq.)$

0 10^{-4} 10^{-4}

$RNH_2(aq.) + H_2O \rightleftharpoons RNH_3^+ (aq.) + OH^-(aq.)$; K_b

10^{-2} - 10^{-4}

(from NaOH)

$(10^{-2} - x) = 10^{-2}$ x $(10^{-4} + x)$

$\left[\because \frac{K_b}{10^{-2}} < 10^{-3} \Rightarrow (10^{-2} - x) \simeq 10^{-2}\right]$

$K_b = 2 \times 10^{-6} = \frac{x(10^{-4} + x)}{10^{-2}}$

$2 \times 10^{-8} = 10^{-4}x + x^2$

$x^2 + 10^{-4} x - 2 \times 10^{-8} = 0$

$x = 10^{-4}$ M

$[OH^-] = 10^{-4} + x = 2 \times 10^{-4}$ M

8. **Ans. (pH = 10.52)**

Salt of strong base & weak acid

$C_6H_5O^-(aq.) + H_2O \rightleftharpoons C_6H_5OH (aq.) + OH^-(aq.)$

$(C-x) \simeq C = 10^{-3}$ M

$K_h = \frac{10^{14}}{K_a} = \frac{10^{-14}}{0.6 \times 10^{-10}} = \frac{10^{-4}}{0.6}$

$\frac{10^{-4}}{0.6} = \frac{x^2}{10^{-3}}$

$[OH^-] = x = \sqrt{\frac{10^{-4} \times 10^{-3}}{0.6}} = \frac{10^{-3}}{\sqrt{6}}$

pOH = $3 + \frac{1}{2}\log 6$

pH = 14 – pOH = $11 - \frac{1}{2}\log 6$ = 10.52

9. **Ans. ($[OH^-] = 3.73 \times 10^{-2}M$, $[H_3PO_4] = 6 \times 10^{-18}M$)**

$Na_3PO_4(aq.) \longrightarrow 3Na^+ (aq.) + PO_4^{3-}(aq.)$

0.1 M	-	-
-	0.3 M	0.1 M

Hydrolysis of PO_4^{3-}

$PO_4^{3-}(aq.) + H_2O \rightleftharpoons HPO_4^{2-}(aq.) + OH^- (aq.);\ K_{h_1}$,

$(0.1 - x) \simeq 0.1$ $(x-y) \simeq x$ $(x + y + z) \simeq x$

$HPO_4^-(aq.) + H_2O \rightleftharpoons H_2PO_4^- (aq.) + OH^-(aq.)\ ;\ K_{h_2}$

$(x - y) \simeq x$ $(y - z) \simeq y$ $(x+y+z) \simeq z$

as $K_{h_1} >> K_{h_2} >> K_{h_3} \Rightarrow x >> y >> z$

$$= K_{h_1} = \frac{10^{-14}}{K_3} = \frac{x^2}{0.1} \Rightarrow x = [OH^-] = \sqrt{\frac{10^{14}}{K_3} \times 0.1}$$

$= 3.73 \times 10^{-2}$ M

$$= K_{h_2} = \frac{10^{-14}}{K_2} = y; K_{h_3} = \frac{10^{-14}}{K_1} = \frac{x.z}{y}$$

10. **Ans. (8.35, 9.60, 4.66)**

All salts having amphiprotic anion so we can use direct formula for solution of amphiprotic anions

(i) $NaHCO_3 \Rightarrow$ pH $= \dfrac{pK_{a_1} + pK_{a_2}}{2}$

$= \dfrac{7 - \log 4.2 + 11 - \log 4.8}{2}$

$= 8.35$

(ii) $Na_2HPO_4 \Rightarrow$ pH $= \dfrac{pK_{a_2} + pK_{a_3}}{2}$

$= \dfrac{8 - \log 6.2 + 12}{2}$

$= 9.6$

(iii) $NaH_2PO_4 \Rightarrow$ pH $= \dfrac{pK_{a_1} + pK_{a_2}}{2}$

$= \dfrac{3 - \log 7.5 + 8 - \log 6.2}{2}$

$= 4.66$

11. **Ans. (10^{-3}M)**

HCN +	KOH $\longrightarrow$	KCN +	H_2O
150×0.5	$V_2 \times 1.5$		
= 75	= 75	-	
x	x	75 millimoles	

Concn. (C) $= \dfrac{75}{150 + V_2} = \dfrac{75}{200}$

$= 3.75 \times 10^{-1}$ M

Salt formed (KCN) undergoes hydrolysis

CN^- (aq.) + $H_2O \rightleftharpoons$ HCN (aq.) + OH^-(aq.) ; K_h

(C–x) C x x

$$K_h = \frac{10^{-14}}{K_a} = \frac{x^2}{C-x} = \frac{x^2}{C}$$

$$x = [HCN] = \sqrt{\frac{10^{-14}}{3.75\times10^{-9}}\times3.75\times10^{-1}} = 10^{-3}\ M$$

12. Ans. (83)

Amphiprotic anion

$$pH = \frac{pK_{a_1}+pK_{a_2}}{2} = \frac{7-\log5+11-\log5}{2} = 8.3$$

X = 8.3

10X = 8.3 × 10 = 83

13. Ans. (419)

$$pH = \frac{pK_{a_1}+pK_{a_2}}{2} = 4.19$$

X = 4.19 so 100 X = 419

14. Ans. (6)

$$K_h = \frac{x^2}{C} \Rightarrow x = [H^{\oplus}] = \sqrt{K_h.C}$$

$$[H^{\oplus}] = \sqrt{10^{-9}\times0.001} = 10^{-6}\ M$$

pH = 6

15. Ans. (6)

All salts are having amphiprotic anion ($HCO_3^{\ominus}$, $HPO_4^{2\ominus}$, $H_2PO_4^{\ominus}$)

So,

(i) $NaHCO_3 \Rightarrow pH = \frac{pK_{a_1}+pK_{a_2}}{2} = \frac{7-\log4.2+11-\log4.8}{2} = 8.35$

(ii) $Na_2HPO_4 \Rightarrow pH = \frac{pK_{a_2}+pK_{a_3}}{2} = \frac{8-\log6.2+12}{2} = 9.6$

(iii) $NaH_2PO_4 \Rightarrow pH = \frac{pK_{a_1}+pK_{a_2}}{2} = \frac{3-\log7.5+8-\log6.2}{2} = 4.66$

16. Ans. (25)

$$\%h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-14}}{K_2\times C}} = 0.25\%$$

17. Ans. (48)

$$K_h = \frac{x^2}{C} = \frac{(10^{-4})^2}{0.01} = 10^{-6}$$

$K_h = \dfrac{10^{-14}}{K_{b_2}} \Rightarrow 10^{-6} = \dfrac{10^{-14}}{K_{b_2}} \Rightarrow K_{b_2} = 10^{-8}$

a = 6

b = 8

a × b = 6 × 8 = 48

18. **Ans. (4.5)**

$pH = 7 - \frac{1}{2} - pK_b - \frac{1}{2}\log C$ (Salt of S, A & W.B.)

$= 7 - \frac{1}{2} \times (5 - \log 2) - \frac{1}{2}\log 2 = 4.5$

19. **Ans. (9.6)**

$pOH = pK_b + \log \dfrac{[NH_4Cl]}{[NH_3]}$

$(14-9) = 5 - \log 2 + \log\left(\dfrac{NH_4Cl}{0.25}\right)$

$\Rightarrow \dfrac{[NH_4Cl]}{0.25} = 2 \Rightarrow [NH_4Cl] = 0.5$ M

When KOH is added to buffer

	KOH +	NH_4Cl →	NH_4OH + (or NH_3)	KCl
initialy	(500×0.1) = 50	(200 × 0.5) = 100	(200 × 0.25) = 50	-
Finally	x	50	100	50

$\underbrace{50 \qquad 100}_{\text{Buffer sol.}}$

New pOH $= pK_b + \log\left(\dfrac{5}{b}\right)$

$= 5 - \log 2 + \log\left(\dfrac{50}{100}\right)$

$= 5 - 2\log 2$

New pH = 14 – pOH = 9 + 2 log 2

= 9.6

20. **Ans. (pH = 7.9 , pH = 7.3)**

pH of indicator = $pK_{I_n} + \log\dfrac{[I_{n^-}]}{[HI_n]}$ ...(1)

when half ionic form i.e. $[I_{n^-}] = [HI_n]$

$pH = 7.2 = pK_{I_n}$

when $\dfrac{[HI_n]}{[I_{n^-}]} = \dfrac{1}{5}$ then from formula ...(1)

$pH = 7.2 + \log\left(\frac{5}{1}\right) = 7.9$

for a new indicator when $\frac{(H_{I_n})}{(I_{n^-})} = \frac{1}{4}$

$7.2 + \log 5 = pK^1_{I_n} + \log 4$

$pK^1_{I_n} = 7.3$

for new indicator 50% ionised i.e. $[I_n-] = [HI_n] = 50\%$

$pH = pK^1_{I_n} = 7.3$

21. Ans. (2.8×10^{-3} mole)

Let solubility of AgBr is 'x' mol/L

$AgBr(s) \rightleftharpoons Ag^+(aq.) + Br^-(aq.)\ ;\ K_{sp}$

x x

$Ag^+(aq.) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.)\ ;\ K_f$

x	0.4	-
-	(0.4 – 2x)	x

$AgBr(s) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.) + Br^-(aq.)$

(0.4 – 2x) x x

$K_{sp} \times K_f = \frac{x^2}{(0.4-2x)^2}$

$\sqrt{K_{sp} \times K_f} = \frac{x}{0.4-2x}$

$x = 2.8 \times 10^{-3}$ M

22. Ans. (1.6×10^{-3})

Let solubility of PbI_2 be 's' mol/L. As salt is only 90% ionized so,

$PbI_2(s) \rightleftharpoons Pb^{+2}(aq.) + 2I^-(aq.)\ ;\ K_{sp}$

's' 0.9 S 1.8S

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

$1.4 \times 10^{-8} = (0.9\ S)\ (1.8\ S)^2$

$S = \left(\frac{1.4\times10^{-8}}{0.9\times(1.8)^2}\right)^{1/3}$

$= 1.6 \times 10^{-3}$ M

23. Ans. ($K_d = 1/K_f = 4.8 \times 10^{-4}$)

Overall formation const.

$K_f = K_1 \times K_2 \times K_3$

$= 130 \times 16 \times 1 = 2080$

$3SCN^- + Fe^{+3} \rightleftharpoons Fe(SCN)_3$; K_f

dissociation const. $(K_d) = \dfrac{1}{K_f}$

$K_d = \dfrac{1}{130 \times 16 \times 1} = 4.8 \times 10^{-4}$

24. **Ans. (0.284)**

$K_{sp} = 8 \times 10^{-8} = [Ba^{2\oplus}]\ [SO_4^{2\ominus}]$

$\because\ [Ba^{2\oplus}] = 2 \times 10^{-5}$

$[SO_4^{2\ominus}] = 4 \times 10^{-3}$ mol/L

Mass of Na_2SO_4 in 500 ml = $\dfrac{4 \times 10^{-3}}{2} \times 142 = 0.284$ gm

EXERCISE - JEE (Main) PYQ

1. **Ans. (3)**

POH = 14 – 8.26

$= pK_b + \log \dfrac{[NH_4^+]}{[NH_3]}$

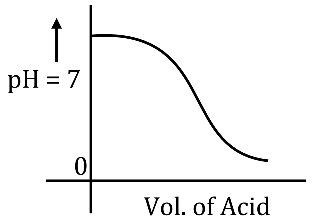
$= 5.74 = 4.74 + \log \dfrac{[NH_4^+]}{0.2} \Rightarrow [NH_4^+] = 2$

Hence

$NH_4Cl = 2 \times 53.5 = 107$ g

2. **Ans. (1)**

Titration curve of NH_4OH vs HCl (WB + SA).



3. **Ans. (3)**

$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$

m mole 2 2

\- - 2 mmole

$\left[NH_4^+\right] = \dfrac{2\text{mmole}}{60\,\text{ml}} = \dfrac{1}{30}$ M

$pH = \dfrac{pK_w - pK_b - \log C}{2} = \dfrac{14 - 5 + 1.48}{2} = 5.24$

4. Ans. (476)

Moles of CH_3COOH = 5 m mole

moles of NaOH = 2.5 m mole

$NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

2.5 m mole 2.5 m mole

0 2.5 m mole 2.5 m mole

so buffer is formed

$$pH = pKa + \log\left(\frac{2.5/75}{2.5/75}\right) = pKa$$

pH = 4.76

= 476×10^{-2}

5. Ans. (27)

K_a of Butyric acid $\Rightarrow 2\times10^{-5}$ PKa = 4.7

pH of 0.2 M solution

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

$$= \frac{1}{2}(4\cdot7)\frac{1}{2}\log(0.2)$$

= 2.35 + 0.35 = 2.7

pH = 27×10^{-1}

6. Ans. (10)

Buffer of HOAc and NaOAc

$$pH = pKa + \log\frac{0.1}{0.01}$$

5 = pKa + 1

pKa = 4

Ka = 10^{-4}

x = 10

7. Ans. (85)

Concentration of calcium lactate = 0.005 M,: concentration of lactate ion = (2 × 0.005) M.

Calcium lactate is a salt of weak acid + strong base

$\therefore$ Salt hydrolysis will take place.

$$pH = 7 + \frac{1}{2}(pKa + \log C)$$

$$= 7 + \frac{1}{2}(5 + \log(2\times0.005))$$

$$= 7 + \frac{1}{2}[5 - 2\log 10] = 7 + \frac{1}{2}\times3 = 8.5 = 8.5 \times 10^{-1}$$

8. Ans. (9079)

In resultant solution

$n_{NH_3} = 0.1 - 0.02 = 0.08$

$n_{NH_4Cl} = n_{NH_4^+} = 0.1 + 0.02 = 0.12$

$pOH = pK_b + \log\frac{[NH_4^+]}{[NH_3]}$

$= 4.745 + \log\frac{0.12}{0.08}$

$= 4.745 + \log\frac{3}{2}$

$= 4.745 + 0.477 - 0.301$

$pOH = 4.921$

$pH = 14 - pH$

$= 9.079$

9. **Ans. (2)**

$\Delta[H^+] = 1000$

$\Delta pH = -\log\Delta[H^+] = -\log 10^3$

$= -3$

10. **Ans. (5)**

$\because$ pH = 12

$\therefore$ $[H^+] = 10^{-12}$ M

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

$\therefore$ $[Ca(OH)_2] = 5 \times 10^{-3}$ M

$5 \times 10^{-3} = \frac{\text{milli moles of } Ca(OH)_2}{100\,\text{mL}}$

milli moles of $Ca(OH)_2 = 5 \times 10^{-1}$

Ans. = 5

11. **Ans. (186)**

Total milimoles of H^+ = (600×0.01) + (400×0.01×2)

= 1 4

$\left[H^+\right] = \frac{14}{1000} = 14 \times 10^{-3}$

pH = 3 – log 14

= 1.86

$= 186 \times 10^{-2}$

12. **Ans. (10)**

$AgCl(s) \rightarrow Ag^+(aq.) + Cl^-(aq.)$

S S

$K_{sp} = S^2 = \left(\frac{1.43}{143.4} \times 10^{-3}\right)^2 = 10^{-10}$

$-\log K_{sp} = 10$

13. **Ans. (2)**

(B) $pk_{In} = -\log(4 \times 10^{-10}) = 9.4$

Indicator range

$\Rightarrow pk_{In} \pm 1$

i.e. 8.4 to 10.4

(D) In acidic medium, phenolphthalein is in unionized form and is colourless.

14. **Ans. (3)**

Methyl orange is weak base.

Benzenoid structure	$\rightleftharpoons$	Quinonoid structure
(yellow coloured)		(Red coloured)
		(more intense)

Statement I – FALSE

Statement II – FALSE

15. **Ans. (233)**

K_2SO_4	$\longrightarrow$	$2K^+$	+	SO_4^{2-}
0.1 M		0.2M		0.1M

$BaSO_4$	$\rightleftharpoons$	Ba^{+2}	+	SO_4^{2-}
a–S		S		$S + 0.1 \approx 0.1$

$K_{SP} = S \times 10^{-1}$

$\Rightarrow 1 \times 10^{-10} = S \times 10^{-1}$

$\Rightarrow S = 10^{-9}$ mol L^{-1}

So, $S = 10^{-9} \times 233$ g L^{-1}

So, Answer : 233

16. **Ans. (9000)**

$(M_1 \times V_1)$	=	$(M_2 \times V_2)$
–1		–2
10×1		$10 \times V_2$

$V_2 = 10L$

Water added = 10 – 1

= 9 Litre

= 9000 mL

17. **Ans. (5)**

$$\left[Ba^{+2}\right] = \frac{25 \times 0.05}{50} = 0.025M$$

$$\left[F^{-}\right] = \frac{25 \times 0.02}{50} = 0.01M$$

$$\left[Ba^{+2}\right]\left[F^{-}\right]^2 = 25 \times 10^{-7}$$

$$K_{sp} = 5 \times 10^{-7} \text{ (given)}$$

Ratio = $\dfrac{\left[Ba^{+2}\right]\left[F^{-}\right]^2}{K_{sp}} = 5$

18. Ans. (458)

	CH_3COOH	+	NaOH	→	CH_3COONa	+	H_2O
Initially	5mmol		2mmol		0		0
after Rxn	3mmol		0		2 mmole		2 mmole

pH = $pKa + \log_{10}\dfrac{[salt]}{[acid]}$

pH = $4.76 + \log_{10}\dfrac{2}{3}$

pH = $4.58 = 458 \times 10^{-2}$

19. Ans. (4)

(A) pH of 10^{-8} M HCl is in acidic range (6.98).

(B) Conjugate Base of $H_2PO_4^-$ is HPO_4^{2-}

(C) K_w increases with increasing Temperature, as the temperature increases, the dissociation of water increases.

(D) At half neutralisation point, half of the acid is present in the form of salt.

pH = $Pk_a + \log\dfrac{1}{1} = Pk_a$

20. Ans. (1)

Indicator	pH range
Methyl orange	3.2 – 4.5
Phenolpthalein	8.3 – 10.5

Methyl orange may be used for a strong acid vs strong base and strong acid vs weak base titration.

Phenolpthalein may be used for a strong acid vs strong base and weak acid vs strong base titration.

EXERCISE - JEE (Advanced) PYQ

1. Ans. (7)

$AgCl \rightleftharpoons Ag^{\oplus} + Cl^{\ominus}$ $\quad K_{sp} = 1.6 \times 10^{-10}$

0.1M $\quad s_1 \quad s_1 + s_2$

$CuCl \rightleftharpoons Cu^{\oplus} + Cl^{\ominus}$ $\quad K_{sp} = 1 \times 10^{-6}$

0.1M $\quad s_2 \quad s_1 + s_2$

$$\frac{1.6\times10^{-10}}{1\times10^{-6}} = \frac{(s_1)(s_1+s_2)}{(s_2)(s_2+s_1)}$$

$s_2 = \frac{10^4}{1.6} s_1$

$\therefore \quad 1.6 \times 10^{-10} = (s_1)\,(s_1 + \frac{10^4}{1.6} s_1)$

$\therefore \quad s_1 = 1.6 \times 10^{-7} \quad \therefore \quad x = 7$

2. Ans. (A)

$$CH_3-\overset{\overset{O}{||}}{C}-OCH_3 + H_2O \xrightarrow{HA} CH_3-\overset{\overset{O}{||}}{C}-OH + CH_3OH$$

$R_1 = K_1\,[\text{Methylacetate}]\,[H^{\oplus}]_{WA}$

$R_2 = K_1\,[\text{Methylacetate}]\,[1]_{SA}$

$(\because \&[H^{\oplus}] = 1M)$

$R_1 = \frac{1}{100} R_2$

$\therefore \quad \frac{R_1}{R_2} = 1/100$

$1 = \frac{[H^{\oplus}]_{WA}}{[H^{\oplus}]_{SA}} = \frac{1}{100} \qquad [H^{\oplus}]_{WA} = 0.01$

$\therefore$	HA	$\rightleftharpoons$	$H^{\oplus}$	+	$A^{\ominus}$
	1M				
	$1-1\alpha$		1α		1α

$1\alpha = 0.01$

$Ka = \frac{(1\alpha)^2}{1-\alpha}$

$1 - \alpha \simeq 1$

$Ka = 10^{-4}$

3. Ans. (B)

Ag_2CrO_4	$\rightleftharpoons$	$2Ag^{\oplus}$	+	$CrO_4^{2\ominus}$	
s		$2s + 0.1$		s	(2s neglect)
Strong		$AgNO_3$	$\longrightarrow$	$Ag^{\oplus}$	+ $NO_3^{\ominus}$
electrolyte		0.1		0.1	0.1

$\therefore \quad Ksp = (0.1)^2 \times s$

$1.1 \times 10^{-12} = 10^{-2} \times s$

$s = 1.1 \times 10^{-10}$

4. Ans. (A)

CH_3COOH	+	$NaOH$	$\longrightarrow$	CH_3COONa	+	H_2O (Neutralization)
100 × 2 M		100 × 1M		100 × 1M		
0.1 moles left						

When 1 moles of SA is neutralized by SB 57kJ/mol energy is released

$\therefore$ 0.1 moles of SA is neutralized $\longrightarrow$ 5.7 kJ released and 5.7°C is increased

Hence in exp 2 when 0.1 mole of WA is neutralized by NaOH $\longrightarrow$ 5.6° C temp is increased

So, 5.6 kJ is released

Hence 0.1 is used to dissociate 0.1 mole CH_3COOH

∴ for 1 mole $\longrightarrow$ 1kJ is used

5. **Ans. (B)**

$$\begin{array}{llll} CH_3COOH & + \; NaOH & \longrightarrow & CH_3COONa + H_2O \\ 0.2 & \;\;\; 0.1 & & \\ 0.1 & \;\;\; \times & & 0.1 \end{array}$$

Buffer

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

pH = 4.7

6. **Ans. (4.47)**

$$AB \rightleftharpoons A^{\oplus} + B^{\ominus}$$

$$x \qquad x - y \rightarrow \text{react with } H^{\oplus}$$

$(x - y)x = 2 \times 10^{-10}$ ...(1)

$$\begin{array}{lllll} B^{\ominus} & + & H^{\oplus} & \rightleftharpoons & HB \\ x-y & & 10^{-3} & & y \end{array}$$

$$10^8 = \frac{y}{(x-y)\times 10^{-3}}$$

$$\frac{y}{x-y} = 10^5$$

$x - y = 10^{-5}y$ ...(2)

from (1) & (2)

$(x - y)y = 2 \times 10^{-10}$

$10^{-5}y^2 = 2 \times 10^{-10}$

$y = \sqrt{20} \times 10^{-3}$

∴ $(x)\,(x-\sqrt{20} \times 10^{-3}) = 2 \times 10^{-10}$

$x^2-\sqrt{20} \times 10^{-3}x - 2 \times 10^{-10} = 0$

on solving $x = \sqrt{20} \times 10^{-3}$

$x = 4.47 \times 10^{-3}$

∴ $Y \times 10^{-3} \Rightarrow y = 4.47$

7. **Ans. (D)**

P.
$$\begin{array}{lllll} CH_3COOH & + \; NaOH & \longrightarrow & CH_3COONa & + \; H_2O \\ 0.1\text{ M, 20 ml} & \;\; 0.1\text{ M, 10 ml} & & & \end{array}$$

$pH = pKa \Rightarrow [H^{\oplus}]$ will not change on dilution

correct match : P-1

Q.
$$\begin{array}{lllll} CH_3COOH & + \; NaOH & \longrightarrow & CH_3COONa & + \; H_2O \\ 0.1\text{ M, 20 ml} & \;\; 0.1\text{ M, 20 ml} & & & \\ — & \;\; — & & 0.05\text{ M} & \end{array}$$

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

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

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

correct match : Q-5

R. NH_4OH + HCl $\longrightarrow$ NH_4Cl

0.1 M, 20 ml   0.1 M, 20 ml   0.05 M

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

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

correct match : R-4

S. Because of dilution solubility does not change so $[H^{\oplus}]$ = constant

8. **Ans. (0.11)**

Vol. of NaOH used = 9.0 ml

gm equivalent of NaOH = gm equivalent of $H_2C_2O_4$

$M \times 9 \times 1 = 0.1 \times 5 \times 2$

$$M = \frac{1}{9} = 0.11$$

9. **Ans. (0.20)**

$K_{sp} = [Zn^{2\oplus}]\,[S^{2\ominus}]$

$1.25 \times 10^{-22} = 0.05 \times [S^{2\ominus}]$

$$[S^{2\ominus}] = \frac{1}{4} \times 10^{-20}$$

$H_2S(aq.) \rightleftharpoons 2H^{\oplus}(aq.) + S^{2\ominus}(aq.);\ K_1 \times K_2$

$$K_1 \times K_2 = \frac{[H^{\oplus}]^2[S^{2\ominus}]}{[H_2S]}$$

$$10^{-21} = \frac{[H^{\oplus}]^2\left[\frac{1}{4} \times 10^{-20}\right]}{(0.1)}$$

$[H^{\oplus}] = 0.2$ M

10. **Ans. (2.30 to 3.00)**

B	+	HA	$\longrightarrow$	$BH^{\oplus}$	+	$A^{\ominus}$
0.1 M, V ml						
0.1 V m mol		0.1V m mol		0.1 V		0.1 V

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

pH at eq. pt = 6 to 6.28

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

So $pK_b = 2.30 - 2.80$ Possible

Solution-2

at V = 6 ml

reaction is complete

So, V = 3 ml

is half of eq. pt

at which

pH = 11

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

$pK_b = 3$

11. **Ans. (10.02)**

	H_2CO_3 + NaOH	$\longrightarrow$	$NaHCO_3$	+ H_2O
Milli moles	10		10	–
At end	0	0	10 + 10 = 20	

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

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

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

$= 10.32 - \log 2 = 10.02$

12. **Ans. (6)**

$H_2SO_4 \rightleftharpoons HSO_4^{\ominus} + H^{\oplus}$

1   -   -

-    1M   1M

$Na_2SO_4 \longrightarrow 2Na^{\oplus} + SO_4^{2\ominus}$

1.8×10^{-2} M   -   -

3.6×10^{-2} M 1.8×10^{-2} M

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

1M   1M 1.8×10^{-2} M

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

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

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

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

$x = (1.8 \times 10^{-2} - 1.2 \times 10^{-2})M$

$\left[SO_4^{2\ominus}\right] = (1.8 \times 10^{-2} - 0.6 \times 10^{-2})M$

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

$PbSO_4$	$\longrightarrow$	$Pb^{2\oplus}$	+	$SO_4^{2\ominus}$
s		-		1.2×10^{-2} M
-		s		$(s + 1.2 \times 10^{-2})$

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

$(PbSO_4)$

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

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

$\Rightarrow s = \frac{1.6}{1.2} \times 10^{-6}\,M = X \times 10^{-Y}\,M$

$\Rightarrow Y = 6$

13. Ans. (B)

At pH = 7 $\Rightarrow$ pure water

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

At pH = 2

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

$\qquad s \qquad\qquad s-x$

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

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

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

$\Rightarrow s \simeq x$

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

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

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

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

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

$$\Rightarrow \frac{\dfrac{\sqrt{K_{sp}}}{10\sqrt{K_a}}}{\sqrt{K_{sp}}} = 10 \qquad \Rightarrow \frac{1}{10\sqrt{K_a}} = 10$$

$\Rightarrow \sqrt{K_a} = 10^{-2}$

$\Rightarrow K_a = 10^{-4}$

$\Rightarrow pK_a = 4$

JEE (Main) Practice Paper

SECTION–A

1. **Ans. (2)**

Bronsted acid is proton donor.

$CH_3COO^{\ominus}$ is a Bronsted base. It can accept a proton.

2. **Ans. (3)**

H_3PO_3 is a dibasic acid, so $HPO_3^{2\ominus}$ is not an amphiprotic species.

Amphiprotic species give both $H^{\oplus}$ and $OH^{\ominus}$ in water.

$H_2PO_4^{\ominus} \rightleftharpoons H^{\oplus} + HPO_4^{2\ominus}$

$H_2PO_4^{\ominus} + H_2O \longrightarrow H_3PO_4 + OH^{\ominus}$

$\Rightarrow H_2PO_4^{\ominus}$ is amphiprotic. Similarly, $HCO_3^{\ominus}$ is also amphiprotic.

3. **Ans. (2)**

On adding NH_3, conc. of $OH^{\ominus}$ increases $\Rightarrow [H_3O^{\oplus}]$ decrease.

4. **Ans. (3)**

$M_{eq.}$ of HCl = 20

$M_{eq.}$ of NaOH = 10

HCl	+	NaOH	$\rightarrow$	NaCl	+	H_2O
20		10				
10		–		10		

$[H^{\oplus}] = \dfrac{10}{100}$

$pH = -\log [H^{\oplus}] = 1$

5. **Ans. (2)**

Relative strength = $\sqrt{\dfrac{Ka_1}{Ka_2}} = \sqrt{\dfrac{3\times10^{-4}}{1.8\times10^{-5}}} \Rightarrow 4 : 1$

6. **Ans. (3)**

$2NH_3 \rightleftharpoons NH_2^{\ominus} + NH_4^{\otimes}$

x x

$K_{\text{self ionization const.}} = [NH_2^{\ominus}][NH_4^{\oplus}]$

$10^{-30} = x^2 \Rightarrow x = 10^{-15}$ mole/L

$\therefore [NH_4^{\oplus}] = 10^{-15}$ mole/L

$= 10^{-15} \times 6.022 \times 10^{23}$ ions/1000 ml

$= 6.022 \times 10^{8}$ ions/1000 ml.

$= \dfrac{6.022\times10^{8}\times100}{1000}$ ions / 100ml

$= 6.022 \times 10^7$ ions/100 ml.

7. **Ans. (1)**

Let weak acid is HA its sodium salt is NaA

$K_H = Ch^2 \Rightarrow 0.1 \times (0.03)^2$

$K_a = \dfrac{K_W}{K_H}$

$K_a = \dfrac{10^{-14}}{9\times10^{-5}}$ $K_a \approx 1 \times 10^{-10}$

8. **Ans. (3)**

$$H_2O(l) \underset{}{\overset{K_w}{\rightleftharpoons}} H^{\oplus}(aq.) + OH^-(aq.)$$

$$(\sqrt{5}\times10^{-7}+x) \qquad x$$

$10^{-14} = x(\sqrt{5}\times10^{-7}+x)$

or, $x^2 + \sqrt{5}\times10^{-7}x - 10^{-14} = 0$

or, $x = \dfrac{\sqrt{5}\times10^{-7} \pm \sqrt{5\times10^{-14}+4\times10^{-14}}}{2}$

$\because$ $x > 0 \Rightarrow x = \dfrac{-\sqrt{5}\times10^{-7}+3\times10^{-7}}{2}$

or, $x = \dfrac{10^{-7}(3-2.23)}{2}$

or $x = \dfrac{0.77}{2}\times10^{-7} = 0.385\times10^{-7}$

or, $x = 3.85 \times 10^{-8}$ M

$[H^{\oplus}]_{H_2O} = x = 3.85\times10^{-8}$ M

9. **Ans. (3)**

$pH = pKa + \log\dfrac{[salt]}{[acid]}$

$9 \Rightarrow 10 - \log 5 + \log\left(\dfrac{5\times v}{20}\right)$; $v = 2ml$

10. **Ans. (3)**

$pK_{b\,F^{\ominus}} = 10.4$

$\because$ $pK_{a\,HF} + pK_{b\,F^{\ominus}} = 14$ ($\because$ HF and $F^{\ominus}$ are conjugate acid-base pair)

$\therefore$ $pK_{a\,HF} = 14 - 10.4 = 3.6$

or, $K_{a\,HF} = 10^{-3.6} = 10^{-3-0.6} = \dfrac{10^{-3}}{10^{0.6}} = \dfrac{10^{-3}}{10^{2\times0.3}} = \dfrac{10^{-3}}{10^{2\times\log2}}$

$= \dfrac{10^{-3}}{10^{\log4}} = \dfrac{10^{-3}}{4} = 2.5\times10^{-4}$

11. **Ans. (2)**

$K_a = 1.8 \times 10^{-5}$

Required equilibrium const. = $\frac{1}{K_h} = \frac{K_a}{K_w} = \frac{1.8\times10^{-5}}{10^{-14}}$ = 1.8×10^{9}

12. **Ans. (4)**

Since, ionic product of salt is greater than K_{sp}, precipitation occurs.

13. **Ans. (2)**

For KCN, Normality = Molarity.

$K_h = \frac{10^{-14}}{1.6\times10^{-9}} = \frac{10^{-5}}{1.6} = \frac{10^{-4}}{16}$

$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-4}}{16\times\frac{1}{100}}} = \sqrt{\frac{10^{-2}}{16}} = \frac{0.1}{4} = 0.025$

$= 2.5 \times 10^{-2}$

14. **Ans. (3)**

NaCN	+	HCl	$\longrightarrow$	NaCl	+	HCN
0.01M, 40 ml		0.1 M, 20 ml				
4 m mole		2 m mole		0		0
4–2 = 2 m mole		0		2 m mole		2 m mole
(Salt of weak acid)						(Weak acid)

$\Rightarrow$ Acidic buffer solution.

15. **Ans. (3)**

(1) $Ag_2CO_3 \rightleftharpoons 2Ag^{\oplus} + CO_3^{2\ominus}$

$\qquad\qquad\qquad 2S \qquad\quad S$

(2) Solubility S = 10^{-4} mole/L

$K_{sp} = [Ag^{\oplus}]^2\,[CO_3^{2\ominus}]$

$K_{sp} = (2S)^2(S) = 4S^3 = 4\times10^{-12}$

$K_{sp} = 4\times10^{-12} = [Ag^{\oplus}]^2\,(0.1)$

$[Ag^{\oplus}] = 6.323\times10^{-6} = 2S$

$\therefore S = 3.16 \times 10^{-6}$ mole/litre

16. **Ans. (3)**

$CaF_2 \rightleftharpoons Ca^{2\oplus} + 2F^{\ominus}$

$K_{sp} = 3.4\times10^{-11} = (0.1)^2\,[Ca^{2\oplus}]$

$\therefore \quad [Ca^{2\oplus}] = \frac{3.4\times10^{-11}}{0.1\times0.1} = 3.4 \times 10^{-9}$ M

17. **Ans. (2)**

(1) $Mg(OH)_2 \rightleftharpoons Mg^{2\oplus} + 2OH^{\ominus}$

$\qquad\qquad\qquad S_1 \qquad\quad 2S_1$

$K_{sp} = [Mg^{2\oplus}][OH^{\ominus}]^2$;

$8.9 \times 10^{-13} = 4S_1^3$

$$S_1 = \left[\frac{8.9\times10^{-13}}{4}\right]^{1/3}$$

$$Al(OH)_3 \rightleftharpoons \underset{S_2}{Al^{3\oplus}} + \underset{3S_2}{3OH^{\ominus}}$$

$K_{sp} = [Al^{3\oplus}][OH^{\ominus}]^3$

$5 \times 10^{-33} = (S_2)(3S_2)^3$

$5 \times 10^{-33} = 27S_2^4$

$$S_2 = \left(\frac{5\times10^{-33}}{27}\right)^{1/4}$$

$$\frac{S_1}{S_2} = \frac{\left(\frac{8.9\times10^{-13}}{4}\right)^{1/3}}{\left(\frac{5\times10^{-33}}{27}\right)^{1/4}} = \frac{\left(\frac{0.89\times10^{-12}}{4}\right)^{1/3}}{\left(\frac{5}{270}\times10^{-32}\right)^{1/4}}$$

$$= \frac{\left(\frac{0.89}{4}\right)^{1/3}\times10^{-4}}{\left(\frac{5}{270}\right)^{1/4}\times10^{-8}}$$

$$= \frac{(0.222)^{1/3}}{(0.018)^{1/4}} \times 10^4$$

$$= \frac{0.60}{0.36} \times 10^4 = 1.66 \times 10^4$$

18. Ans. (2)

$pH = 9 \Rightarrow [H^{\oplus}] = 10^{-9} \Rightarrow [OH^{\ominus}] = \frac{K_{sp}}{[H^{\oplus}]} = \frac{10^{-14}}{10^{-9}} = 10^{-5}\,\text{mole / L}$

$[Mg^{2\oplus}] = 0.001\text{ M} = 10^{-3}\text{ M}$

$Mg(OH)_2\text{ (solid)} \rightleftharpoons Mg^{2}(aq.) + 2OH^{\ominus}(aq.)$

ionic product $= [Mg^{2\oplus}]\,[OH^{\ominus}]^2 = 10^{-3} \times (10^{-5})^2 = 10^{-13} < K_{sp}Mg(OH)_2$

$\Rightarrow$ no ppt.

19. Ans. (3)

Let V ml of NH_4Cl added into NH_4OH solution

$[NH_4Cl]$ in resultant solution $= \frac{0.2\times V}{100+V}$

$[NH_4OH]$ in resultant solution $= \frac{100\times0.1}{100+V}$

$pOH = pK_b + \log\frac{[NH_4^{\oplus}]}{[NH_4OH]}$;

$$5.3 = 4.7 + \log\left[\frac{\left(\frac{0.2\times V}{100+V}\right)}{\left(\frac{100\times0.1}{100+V}\right)}\right]$$

$\therefore\quad 4 = \frac{0.2\times V}{10} \Rightarrow V = 200\text{ ml}$

20. Ans. (2)

$pOH = \frac{1}{2}[pK_b - \log C]$

$9 = pK_b - \log(0.1)$

$pK_b = 8$

SECTION-B

1. Ans. (6)

$[H^{\oplus}] = 10^{-pH} = 10^{-13}$ mol/L

No. of $H^{\oplus} = \frac{10^{-13}}{1000} \times N_A = \frac{10^{-13}}{1000} \times 6.023 \times 10^{23}$

$= 6.023 \times 10^{7}$

2. Ans. (3)

When equal volume is mixed

$[H^{\oplus}]_{final} = \frac{10^{-5} \times v + 10^{-4} \times v}{v + v} = 5.5 \times 10^{-4}\,M$

$pH = 4 - \log(5.5) = 3.23$

3. Ans. (5)

Salt of S.B. & W.A.

$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{C}$

$x = [OH^-] = \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5}} \times 0.18} = 10^{-5}\,M$

4. Ans. (3)

CH_3COOH	$\rightleftharpoons$	$CH_3COO^{\ominus}$	+	$H^{\oplus}$
C		0		0
$C(1-\alpha)$		$C\alpha$		$C\alpha$

$K_a = \frac{C\alpha^2}{1-\alpha}$

$\Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}}$ $(\alpha << 0.1)$

$[H^{\oplus}] = C\alpha$

$[H^{\oplus}] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow pH = 3 - \frac{1}{2}\log 2 = 2.85$

5. Ans. (5)

NH_4Cl is a salt of strong acid and weak base for solutions of such salts.

$pH = \frac{1}{2}[pK_W - \log C - pK_b]$

$\Rightarrow 10.26 = 14 - \log C - 4.74$

$\Rightarrow \log C = 9.26 - 10.26 = -1.0$

$\therefore \quad C = 10^{-1}$ M

$[NH_4Cl] = 10^{-1}$ M

$W_{NH_4Cl} = 10^{-1} \times 53.5\ gL^{-1}$

$= 5.35\ gL^{-1}$

6. **Ans. (9)**

If 100 mL of 0.1 N NaOH is added to 100 mL of 0.1 N CH_3COOH, complete neutralization takes place and the concentration of $CH_3COONa = \frac{0.1}{2}$ M = 0.05 M

Now, $pH = 7 + \frac{1}{2}\ pK_a + \frac{1}{2}\log C = 8.72.$

7. **Ans. (2)**

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

If S is the solubility of $CaSO_4$ in moles L^{-1}

$K_{sp} = [Ca^{2\oplus}] \times [SO_4^{2\ominus}] = S^2$

$\therefore \quad S = \sqrt{K_{sp}} = \sqrt{9.0 \times 10^{-6}}$

$= 3 \times 10^{-3}\ mol\ L^{-1}$

$= 3 \times 10^{-3} \times 136\ gL^{-1} = 0.408\ gL^{-1}$

For dissolving 0.408 g of $CaSO_4$, water required = 1 L

$\therefore$ For dissolving 1g $CaSO_4$, water required $= \frac{1}{0.408}$ L = 2.45 L

8. **Ans. (4)**

$\frac{K_{sp}}{K_a} = \frac{x^2}{[H^{\oplus}]}$; x = solubility

$$x = \sqrt{\frac{K_{sp}}{K_a} \times (H^{\oplus})} = \sqrt{\frac{8\times10^{-10}}{5\times10^{-10}} \times 10^{-3}} = 4\times10^{-2}M$$

9. **Ans. (2)**

m moles of $OH^{\ominus} = 400 \times \frac{1}{200} \times 2 = 4$

m moles of $H^{\oplus} = 400 \times \frac{1}{50} \times 1 = 8$

	$H^{\oplus}$	+	$OH^{\ominus}$	$\rightarrow$	H_2O
t = 0	8		4		
t = t	4		–		

m moles of $H^{\oplus}$ remaining = 4

$[H^{\oplus}] = \frac{4}{800+200} \Rightarrow \frac{4}{1000} = 4 \times 10^{-3}\ mmol\ mL^{-1}(molL^{-1})$

pH = 3 – log 4 ⇒ 2.4

10. **Ans. (7)**

$[OH^{\ominus}]$ from NaOH $= 10^{-7}$M

As the $[OH^{\ominus}]$ coming from NaOH is less than 10^{-6} M, we have to consider $[OH^-]$ coming from water as well.

$$\begin{array}{cccc} H_2O & \rightleftharpoons & OH^{\ominus} & + & H^{\oplus} \\ & & (x + 10^{-7}) & & x \end{array}$$

$K_w = [H^{\oplus}][OH^{\ominus}] = 10^{-14} = x(x + 10^{-7})$

$x^2 + 10^{-7}x - 10^{-14} = 0$

$\Rightarrow \quad x = \dfrac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \quad (\sqrt{5} = 2.236)$

$[OH^{\ominus}] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$

pOH = 7 – log(1.618) = 6.79

pH = 14 – 6.79 = 7.21

JEE (Advanced) Practice Paper

1. Ans. (A)

$pH = 5 \Rightarrow (H^{\oplus}) = 10^{-5}M$; VL

$pH = 3 \Rightarrow (H^{\oplus}) = 10^{-3}M$; VL

finally $[H^{\oplus}] = \dfrac{10^{-5}V + 10^{-3}V}{V+V}$

$= \dfrac{10^{-5} + 10^{-3}}{2} \simeq \dfrac{10^{-3}}{2}M$

pH = 3 + log 2 = 3.3

2. Ans. (C)

$pH = 2 \Rightarrow (H^{\oplus}) = 10^{-2}M$; M_1

$pH = 3 \Rightarrow (H^{\oplus}) = 10^{-3}M$; M_2

Moles of HCl removed = $\underset{(\text{moles})}{n_{H^{\oplus}(\text{initial})}} - \underset{(\text{moles})}{n_{H^{\oplus}(\text{final})}}$

$= 10^{-2} \times 1 - 10^{-3} \times 1$

$= 9 \times 10^{-3} = 0.009$

3. Ans. (B)

At 25° C $[H^{\oplus}] = 10^{-8}$ M

$pH = -\log[H^{\oplus}]$

pH = 8

4. Ans. (A)

$$\begin{array}{lcccc} & HCOOH & + & NaOH \longrightarrow & HCOONa \\ \alpha = 50\% & a & & & x \\ \text{neutralization} & a - \dfrac{a}{2} & & x & \dfrac{a}{2} \end{array}$$

It became buffer solution

$pH = pK_a + \log\dfrac{\text{Salt}}{\text{Acid}}$

$[H^{\oplus}] = 2 \times 10^{-4}$

5. **Ans. (D)**

In all three cases concentration of NH_3 is double than HCl

$$\begin{array}{lllll} HCl & + & NH_3 & \longrightarrow & NH_4Cl \\ [a] & & [2a] & & \\ \times & & [a] & & [a] \end{array}$$

Hence all have same conc. of $H^{\oplus}$ ions.

6. **Ans. (B)**

$$\begin{array}{lllll} AgCl & \longrightarrow & Ag^{\oplus} & + & Cl^{\ominus} \\ S_1 & & S_1 & & S_1 \\ & & (S_1+S_2) & & (S_1) \\ AgCNS & \longrightarrow & Ag^{\oplus} & + & CNS^{\ominus} \\ S_2 & & S_2 & & S_2 \\ & & (S_1+S_2) & & (S_2) \end{array}$$

$K_{AgCl} = (S_1)(S_1+S_2) = 1.7 \times 10^{-10}$ ...(1)

$K_{AgCNS} = (S_2)(S_1+S_2) = 1 \times 10^{-12}$ ...(2)

Equation (1) ÷ (2)

$\frac{S_1}{S_2} = \frac{1.7\times10^{-10}}{1\times10^{-12}}$ ...(3)

$\frac{[Cl^{\ominus}]}{[CNS^{\ominus}]} = 1.7 \times 10^2$

From equation (3)

$S_1 = 170\ S_2$

$(170\ S_2)(171\ S_2) = 1.7 \times 10^{-10}$

$S_2^2 = \frac{1.7\times10^{-10}}{170\times171}$

$S_2^2 = \frac{10^{-12}}{171}$

$S_2 = \frac{10^{-6}}{13.07}$

$S_2 = 0.076 \times 10^{-6}$

$S_1 = 12.92 \times 10^{-6}$

$[S_1+S_2] = 13.036 \times 10^{-6}$

$[S_1+S_2] = 1.3036 \times 10^{-5}$ M

7. **Ans. (C)**

$$\begin{array}{lllll} Na_2CO_3 & + & HCl & \longrightarrow & NaHCO_3 + NaCl \\ a & & \frac{a}{4} & & - \quad\quad - \\ \frac{3a}{4} & & x & & \left(\frac{a}{4}\right) \end{array}$$

Buffer solution

$$pH = pK_a + \log\left(\frac{S}{a}\right) = 11 + \log\left(\frac{3\frac{a}{4}}{\frac{a}{4}}\right)$$

$pH = 11 + \log 3$

8. **Ans. (C)**

$$pH = pK_{In} + \log\left(\frac{In^{\ominus}}{HIn}\right)$$

	HIn (Red)	$In^{\ominus}$(blue)
Case 1:	75%	25%
Case 2:	25%	75%

$$pH_1 = pK_{In} + \log\left(\frac{25}{75}\right)$$

$$pH_2 = pK_{In} + \log\left(\frac{75}{25}\right)$$

$\Delta pH = pH_2 - pH_1 = 2\log 3 = 0.954$

9. **Ans. (D)**

$Fe(OH)_3$ has max solubility in

Acid $[H_2SO_4] \longrightarrow 2H^{\oplus}$

0.1 M 0.2 M

As H_2SO_4 releases $[H^{\oplus}]$, which react with $[OH^{\ominus}]$ of $Fe(OH)_3$, due to this solubility is maximum.

10. **Ans. (B,C)**

2.5 gm impure sample have BOH weak monoacidic base

Assume moles of BOH present = a

Conc. of BOH = 10a

BOH	+	HCl	$\longrightarrow$	BCl	+	H_2O
10a		0.5 V				
$10a - \frac{1}{5} \times 10a$				$\frac{1}{5} \times 10a$		
8a				2a		

Basic Buffer

$$pH = 14 - (pKb + \log\frac{Salt}{Base})$$

$$9 = 14 - pKb - \log\frac{1}{4}$$

$pKb = 5 + 2 \times 0.3 = 5.6$

$K_b = 10^{-5.6}$

At equivalent point

BOH	+	HCl	$\longrightarrow$	BCl	+	H_2O	$\because$ a = 0.5 V
a		0.5V		a			

Conc. BCl = $\frac{a}{0.1+V}$ $\longrightarrow$ Salt hydrolysis

$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$

$4.5 = 7 - \frac{1}{2} \times 5.6 - \frac{1}{2}\log\frac{a}{0.1+V}$

$-0.3 = \frac{1}{2}\log\left(\frac{a}{0.1+V}\right)$

$2\log\left(\frac{1}{2}\right) = \log\left(\frac{a}{0.1+V}\right) = \frac{a}{0.1+V} = \frac{1}{4}$

$\Rightarrow$ 0.5V × 4 = 0.1 + V   V = 100 ml of HCl

2V = 0.1 + V

V = 0.1

Salt conc. = $\frac{0.5\times0.1}{0.1+0.1}$ = 0.25 M

$\therefore$ moles of Base = 0.5 V

= 0.5 × 0.1

= 0.05 moles

wt = 0.05 × 45 = 2.25

wt% = $\frac{2.25}{2.5}$ × 100 = 90%

11. Ans. (A,B,C)

(A) For SA and WB methyl orange is used as indicator.

(B) $pH = pK_{In} + 1$

$pH = pK_{In} + \log 10$

$\therefore$ % = $\frac{In^{\ominus}}{In^{\ominus}+HIn}$ × 100

= $\frac{10}{10+1}$ × 100

~ 91%

(C) pH at eq. point = $7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$

For titration of salt of (weak base + Strong Acid)

(D) for polyprotic acids

$Na_3PO_4 \longrightarrow 3Na^{\oplus} + PO_4^{3\ominus}$

$PO_4^{3\ominus} + H_2O \rightleftharpoons HPO_4^{2\ominus} + OH^{\ominus}$

At 2nd $HPO_4^{2\ominus} + H_2O \rightleftharpoons H_2PO_4^{\ominus} + OH^{\ominus}$

Eq. point $H_2PO_4^{\ominus} + H_2O \rightleftharpoons H_3PO_4 + OH^{\ominus}$

$pH = \frac{1}{2}[pKa_1 + pKa_2]$

12. Ans. (A,B,C)

(A) $[OH^{\ominus}] = \sqrt{K_b.C} = \sqrt{10^{-5}\times 0.1} = 10^{-3}$ M &

(B) pOH = 3 ; pH = 14 – 3 = 11

(C) Salt of S.A. & W.B. is acidic solution.

(D) for phenolphthalein indicator can be used when strong base is present.

13. Ans. (B,C)

(A) $[H^{\oplus}] = \sqrt{K_{a_1}C} = \sqrt{10^{-5}\times 0.1} = 10^{-3}M$

&

(B) pH = 3

But $[A^{2\ominus}] = K_{a_2} = 10^{-8}$

(for diprotic weak acid)

(C) H_2A + NaHA $\Rightarrow$ buffer solution

5 millimoles 5 millimoles

$$pH = pK_a + \log\left(\frac{S}{a}\right) = 5 + \log\left(\frac{5}{5}\right) = 5$$

$\Delta pH = 5 - 3 = 2$

(D) $H_2A + 2NaOH \longrightarrow Na_2A + 2H_2O$

5 5

Cannot neutralise completely

14. Ans. (D)

$AgNO_3 + 2NH_3 \rightarrow [Ag(NH_3)_2]^{\oplus} + NO_3^{\ominus}$

0.8×2 = 1.6 1.6×2

$Ag^{\oplus}$ left 5×10^{-8}

$$\therefore K_{dis} = \frac{[Ag^{\oplus}][NH_3]^2}{[AgNH_3]^{\oplus}}$$

$$10^{-8} = \frac{5\times 10^{-8}\times (NH_3)^2\times 2}{1.6\times (2)^2}$$

NH_3 free $= \sqrt{\frac{3.2}{5}} = 0.8$

NH_3 in complex = 1.6 × 2 = 3.2

$\therefore$ Total = 3.2 + 0.8 = 4

15. Ans. (C)

(A) 1M CH_3COOH, 100 ml

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

1×100 ml 1×25ml

= 100 mmoles 25 mmoles

= 75 0 25

$$\text{Buffer pH} = pKa + \log\frac{25}{75} = pKa + \log\left(\frac{1}{3}\right)$$

(B) CH_3COOH + $NaOH \longrightarrow CH_3COONa$

= 100 mmoles   1 × 50 mmoles

50 mmoles   0   50 mmoles

$$pH = pKa + \log\frac{50}{50} = pKa$$

(C) CH_3COOH + $NaOH \longrightarrow CH_3COONa$

100 mmoles   1×75 mmoles

100 – 75   0   75

$$pH = pKa + \log\frac{75}{25} = pKa + \log(3)$$

(D) CH_3COOH + $NaOH \longrightarrow CH_3COONa$

100 mmoles   1 × 100 mmoles

0   0   100 (Salt of WA + SB)

$$pH = 7 + \frac{1}{2}(pKa - \log C)$$

$$= 7 + \frac{1}{2}pKa - \frac{1}{2}\log 100$$

$$= 7 + \frac{1}{2}(pKa - 2)$$

16. Ans. (A)

(A) Specific gravity = 1.225

Volume = 200 ml

wt = 1.225 × 200 = 245 gm

wt of H_2SO_4 = 0.25 × 245 = 61.25

$$\text{moles} = \frac{61.25}{98} = 0.625$$

H_2SO_4 + $X(OH)_3$

0.625   0.8 × 0.525 = 0.42

↓   ↓

$2H^{\oplus}$ $3OH^{\ominus}$

= 1.250   = 1.260

$H^{\oplus}$ + $OH^{\ominus} \longrightarrow H_2O$

1.25   1.26

–   0.01

∴ pOH = – log (0 .01) = 2

pH = 12

Hence (Malachite green is used)

(B)

$$\left.\begin{array}{l}\text{50 ml of 0.1 M } HCO_3^{\ominus}\\ \text{50 ml of 0.8 M } CO_3^{2\ominus}\end{array}\right\}\text{Buffer}$$

$pH = PKa_2 + \log\frac{[CO_3^{2\ominus}]}{[HCO_3^{\ominus}]}$ $[CO_3^{2\ominus}] = \frac{50\times0.8}{100}$

$pH = 11 - \log(2) + \log(8)$ $[HCO_3^{\ominus}] = \frac{50\times0.1}{100}$

pH = 11.6 (Malachite green is used)

(C) $HCl + NaOH \longrightarrow NaCl + H_2O$

50×0.1	100×0.13M	↓	
5mmoles	13 mmole	5mmoles	

$NaOH + HA \longrightarrow NaA + H_2O$

8mmoles	50×0.2 = 10 mmoles	8 mmoles	
–	2 mmoles		

∴ Buffer is formed

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

$= 5 + \log\frac{8}{2}$

= 5.6 (Propyl red is used)

17. Ans. (A)

On dilution volume increase hence concentration of $[H^{\oplus}]$ decreases on dilution degree of ionisation increases but increase in volume is more.

18. Ans. (B)

pH of HA & NaOH titration falls in the range of phenolphthalein indicator hence it is used.

19. Ans. (10.00)

$$CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}$$

1

When C = 1 M $\quad 1-1\alpha_1 \quad \alpha_1 \quad \alpha_1$

$Ka_1 = \frac{\alpha_1^2}{1-\alpha_1}$

$$CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}$$

When $C = \frac{1}{100}$ $\quad \frac{1}{100} - \frac{1}{100}\alpha_2 \quad \frac{\alpha_2}{100} \quad \frac{\alpha_2}{100}$

$Ka_1 = \frac{\left(\frac{\alpha_2}{100}\right)^2}{\left(\frac{1}{100}\right)(1-\alpha_2)}$

Both Ka_1 are same

$\frac{\alpha_1^2}{1-\alpha_1} = \frac{\alpha_2^2}{(100)^2\times\frac{1}{100}(1-\alpha_2)}$ $\quad 1-\alpha_1 \sim 1$

$1-\alpha_2 \sim 1$

$\frac{\alpha_2^2}{\alpha_1^2} = 100$

$\therefore \frac{\alpha_2}{\alpha_1} = 10$

20. Ans. (2.50)

$H_2S(aq.) \rightleftharpoons 2H^{\oplus}(aq.) + S^{2\ominus}(aq.); K_1 \times K_2$

$K_1 \times K_2 = \dfrac{[H^{\oplus}]^2 \cdot [S^{2\ominus}]}{[H_2S]} = \dfrac{(2\times10^{-4})^2[S^{2\ominus}]}{0.1}$

$[S^{2\ominus}] = \dfrac{K_1 \times K_2 \times 0.1}{4\times10^{-8}} = 2.5\times10^{-15}\,M$

[$H^{\oplus}$ is mainly given by HCl i.e. strong acid]

Important Notes

Important Notes