SOLUTIONS

EXERCISE # O-I

1. $H_2O \rightarrow H^+ + OH^+$ $\Delta H = +ve$

k_w if T $K_{eq} = K_w$

2. $K_w = [H^+] \times [OH^-]$

for pure water $[H^+] = [OH^-]$

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

3. $pH_i = 3$ Þ $[H^+]_i = 10^{-3}$ M

$pH_f = 6$ Þ $[H^+]_f = 10^{-6}$ M

$[H^+]_i V_i = [H^+]_f V_f$

$10^{-3} \times V_i = 10^{-6} \times V_f$

$V_f = 1000\ V_i$

$C_i = 1000\ C_f$

4. $pH_i = 2 \Rightarrow [H^+]_i = 10^{-2}$ M

$pH_f = 6 \Rightarrow [H^+]_f = 10^{-6}$ M

$$\frac{[H^+]_i}{[H^+]_f} = \frac{10^{-2}}{10^{-6}}$$

$[H^+]_i = 10^4 [H_+]_f$

5. pH = 13, so pOH = 1 $\Rightarrow$ $[OH^-] = 0.1$

$$0.1 = \frac{\text{Moles of } OH^-}{0.25}$$

Moles of OH^- = 0.025

Mass of NaOH = 0.025 × 40 = 1 g

6. pH of acid < 7

So pH sol should Þ 6 – 7

7. $[H^+]_i = 10^{-2}$ $[H^+]_f = 10^{-3}$

initial moles = 10^{-2} final moles of $H^+ = 10^{-3}$

Moles of H^+ should be removed = $10^{-2} - 10^{-3} = 0.009$

8. $$[H^+]_f = \frac{10 \times \frac{1}{200} \times 2 + 40 \times \frac{1}{200} \times 2}{50} = \frac{1}{100} \Rightarrow pH = 2$$

9. **Higher the** K_a, stronger the acid

10. NH_3 is base, so $[OH^-]$, $[H^+]$ ˉ

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

$0.1\ (1-\alpha) \qquad 0.1\ \alpha \qquad 0.1\ \alpha$

$10^{-5} = \dfrac{0.1\alpha \times 0.1\alpha}{0.1(1-\alpha)}$

$10^{-5} = \dfrac{0.1\alpha^2}{1-\alpha} \Rightarrow \qquad \dfrac{\alpha^2}{1-\alpha} = 10^{-4} \quad \Rightarrow a = 10^{-2}$

13. $NH_4OH \rightarrow NH_4^+ + OH^-$

$c(1-\alpha) \qquad c\alpha \qquad c\alpha$

$[OH^-] = c\alpha \qquad = 0.02 \times \dfrac{5}{100} = 10^{-3}$

$pOH = 3 \qquad \Rightarrow pH = 11$

15. $[H^+]_f = \dfrac{10^{-3}+10^{-5}}{2} = \dfrac{101}{2} \times 10^{-5}$

$pH = 5 - \log\dfrac{101}{2} = 3.3$

16. $[H^+] \quad = \sqrt{Ka_1C_1 + Ka_2C_2} = \sqrt{3\times10^{-4}\times0.03 + 1\times10^{-10}\times0.1} = 3 \times 10^{-3}$ M

$[A^-] = \dfrac{3\times10^{-4}\times0.03}{3\times10^{-3}} = 3 \times 10^{-3}$ M

$[B^-] = \dfrac{1\times10^{-10}}{3\times10^{-3}} = 3.33 \times 10^{-9}$ M

17. $[OH^-] \quad = \sqrt{Ka_1C_1 + Ka_2C_2} = \sqrt{6.4\times10^{-5}\times\dfrac{0.1}{2} + 1.8\times10^{-5}\times\dfrac{4}{45}\times\dfrac{1}{2}} = \sqrt{\dfrac{8}{2}\times10^{-6}} = 2 \times 10^{-3}$ M

$pOH = 3 - \log 2$

$pH = 11 + \log 2 = 11.3$

18. $RNH_2 + H_2O \longrightarrow RNH_3^+ + OH^-$

$0.01-x \qquad x \qquad x$

$2 \times 10^{-6} = \dfrac{x-(x+10^{-4})}{0.01-x}$

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

$x = 10^{-4}$

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

20. 0.1 M HCl + 0.1 M H_3PO_4 (a << 1)

$H_3PO_4 \rightleftharpoons H^+ + H_2PO^-$

$0.1(1-\alpha)$ $\quad 0.1 + 0.1\alpha \quad 0.1\alpha$

» 0.1

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

$Ka_1 = \dfrac{0.1 \times 0.1\alpha}{0.1} \Rightarrow a = 10\,K\alpha_1$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$

$0.1\alpha \quad 0.1 \quad \alpha_2$

$Ka_2 = \dfrac{0.1 \times [HPO_4^{2-}]}{0.1\alpha}$

$[HPO_4^{2-}] = \alpha K_2 = 10\,Ka_1\,Ka_2$

21. $[HPO_4^{2-}] = 10\,Ka_1\,Ka_2$

$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$

$10\,Ka_1\,Ka_2 - x \quad x + 0.1 \quad x$

» 0.1

$Ka_3 = \dfrac{0.1 \times x}{10Ka_1Ka_2 - x} = \dfrac{0.1 \times x}{10Ka_1Ka_2}$

$[PO_4^{3-}] = x = 100\,Ka_1\,Ka_2\,Ka_3$

22. $NH_2^- + H^+ \rightarrow NH_3$

Base C.A.

24. Bronsted acid $\rightarrow$ which can given H^+

24. $NHO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$

Acid Base C.A C.B.

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

$$Keq = \frac{1}{Kh} = \frac{Ka}{Kw} = \frac{1.8\times10^{-5}}{10^{-14}} = 1.8 \times 10^{9}$$

26. $Ka\ HF \times Kb\ F^- = Kw$

$pKa = 14 - 10.83 = 3.17$

$Ka = 10^{-3.17} = 6.75 \times 10^{-4}$

28. At 85ºC neutral pH < 7

29. $[H^+] = \frac{0.01}{100} = 10^{-3}\ M \Rightarrow pH = 3$

30.
(A) 0.1 M NaCl $\Rightarrow pH = 7$
(B) 0.1 M NH_4Cl $\Rightarrow pH < 7$
(C) 0.1 M CH_3COONa $\Rightarrow pH > 7$
(D) 0.1 M HCl $\Rightarrow pH = 1$

31 $h = \sqrt{\frac{Kw}{Ka}\times C} = \sqrt{\frac{10^{-14}\times 1/80}{1.3\times10^{-9}}} = \sqrt{\frac{10^{-6}}{8\times1.3}}$

$CN^- + H_2O \rightarrow HCN + OH^-$

$1/80(1-h)$ $h/80$ $h/80$

$\frac{10^{-14}}{1.3\times10^{-9}} = \frac{h^2}{80(1-h)}$ Þ $h^2 = \frac{8}{1.3}\times10^{-4}$

$h = 2.48 \times 10^{-2}$

% h = 2.48

32. $CN^- + H_2O \rightarrow HCN + OH^-$

$0.01(1-h)$ $0.01h$ $0.01h$

$$\frac{10^{-14}}{1.4\times10^{-9}} = \frac{0.01h^2}{1-h}$$

$h^2 = \frac{10}{1.4}\times10^{-4}$

$h = 2.67 \times 10^{-2}$

% h = 2.67%

$K_{b_3} > K_{b_2} > K_{b_1}$

33. $Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+$

34. $S^{2-} + H_2O \rightarrow HS^- + OH^-$

35. $A^{3-} + H_2O \rightarrow HA^{2-} + OH^-$

$Kh_1 = \frac{Kw}{Ka_3}$

$pH = \frac{1}{2}(pK_w + pKa_3 + \log C)$

36. $\frac{h}{1-h} = \sqrt{Kh}$ (for salt of WA + WB)

h does not depend on conc.

37. $pH = \frac{1}{2}(pK_w + pK_a - pK_b) = \frac{1}{2} \times (14 + 4.8 - 4.78) = 7.01$

38. Amphiprotic species ® which can given as well as take H^+ ion.

41. For 1 M NaCl & 1 M HCl solution

$\Rightarrow pH < 7$

42. $pOH = pK_b = 4.74$

$pH = 9.26$

43. $[OH^-] = K_b \times \frac{[NH_3]}{[NH_4^+]} = 1.8 \times 10^{-5} \times \frac{0.05}{0.001} = 9.0 \times 10^{-4}$

44. $pOH = 5 - \log 1.85 + \log \frac{500 \times 0.5}{300 \times 0.3}$

$= 5 + \log \frac{25}{16.2} = 5.188$

$pH = 14 - 5.188 = 8.812$

45. $pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$

$= 4.82 + \log\frac{3}{2} = 5$

46. $pH = 5 + \log\frac{10\times1}{50\times2} = 5 - 1 = 4$

47. $pH = 10 - \log5 + \log\frac{5\times V_{mL}}{10\times2} = 9$

$\log\frac{5V_{mL}}{20} = \log0.5$

$V_{mL} = 2$ mL

48. $4.74 = 5 - \log1.34 + \log\frac{x}{0.02}$

$x = 1.5 \times 10^{-2}$ mol

49. $4 = 3.7 + \log\frac{0.1\times V_{mL}}{50\times0.05}$

$2 = \frac{0.01\times V_{mL}}{50\times0.05}$ $\Rightarrow V_{mL} = 50$ mL

50. If $[NH_4OH]^-$, $[OH^-]^-$, pH $^-$

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

$Ph - pKa = \log\frac{[C.B]}{[Acid]} = 5 = \log 10^5$

$[C.B.] = 10^5 \times [Acid]$

52.

HA	+	NaOH	$\rightarrow$	NaA	+	H_2O
10 mmol		x mmol		10 mmol		–
10–x		0		10+x		–

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

$5.5 = 5 + \log \frac{10+x}{10-x}$

$3.16 = \frac{10+x}{10-x} \Rightarrow x = 5.2$

Mass of NaOH added = $5.2 \times 40 \times 10^{-3}$g= 2.08×10^{-1}g

53. On moderate dilution pH of buffer solution does not change.

54. Buffer capacity = $\frac{0.02}{0.05} = 0.4$

56. Moles of OH^- = $\frac{8}{40} = \frac{1}{5}$

Moles of H^+ = $\frac{4.9}{98} \times 2 = \frac{1}{10}$

$[OH^-] = \frac{0.1}{1} = 0.1$

pOH = 1 $\Rightarrow$ pH = 13

57. $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + H_2O$

0.5 mmol 1 mmol

0 0 1 mmol

Solution will be neutral so pH = 7

58. M Moles of H^+ = 15

M Moles of OH^- = 5

$[H^+]_f = \frac{10}{100} = \frac{1}{10}$ Þ $pH_f = 1$

64. NaCN + HCl ¾→ HCN + NaCl

	NaCN	HCl	HCN	NaCl
mmi	4	2	0	0
mmf	2	0	2	2

60. (A) $H_3PO_4 + NaH_2PO_4$ (W.A + its salt)

(B) $H_2CO_4 + NaHCO_3$ (W.A + its salt)

(C) $NH_4Cl + HCl$ (W.A + its salt)

(A) $CH_3COOH + CH_3COONa$ (W.A + its salt)

61. $HCOOH + KOH \rightarrow HCOOK + H_2O$

mm :	16	8	0	0
mmf	8	0	8	-

$pH = 3.7 + \log \frac{8}{8} = 3.7$

$pOH = 10.3$

62. $pH = 4.74 + \log \frac{0.6}{0.4} = 4.916$

63. $pH = pKa = 3.7$

64. $pH = 5 + \log \frac{25}{75}$ (25% neutralization)

$= 5 + \log \frac{1}{3}$

$pH = 5$ (50% neutralization)

$pH = 5 + \log \frac{75}{25}$ (75% neutralization)

$= 5 - \log 3$

65. $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$

mmi	2	2	0	0
mm_f	0	0	2	-

$[CH_3COOH] = \frac{2}{20} = 0.1$

$$\underset{0.1-x}{CH_3COOH} \longrightarrow \underset{x}{CH_3COO^-} + \underset{x}{H^+}$$

$1.8 \times 10^{-5} = \frac{x^2}{0.1 - x}$

$[H^+] = x = \sqrt{1.8} \times 10^{-3}$

$pH = 2.88$

66. For 0.1 M NaHA

$$pH = \frac{7+11}{2} = 9$$

for 0.1 M H_2A $pH < 7$

for 0.1 M Na_2A $pH > 7$

for 0.1 M NaHA + 0.1 M $Na_2A \Rightarrow$ $pH = pKa_2 = 11$

67. $N_3PO_4 + NaH_2PO_4$

$NaH_2PO_4 + Na_2HPO_4$

$Na_2HPO_4 + Na_3PO_4$

68. $H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$

mmi	9	5	0	0
mm_f	4	0	5	-

$$pH = 3 + \log\frac{5}{4} = 3.1$$

69.

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

70. $pH = pKIn \pm 1$

71. pH range of methyl red
$\Rightarrow 4.2 – 6.3$

72. pH at equivalence point is (5.5 – 11)

73. For HCl Vs $NH_4OH \Rightarrow$ pH range (3 – 8.5)

74. For NaOH Vs $H_2C_2O_4$ titration
pH range is (11 – 5.5)

75. Oxalic acid Vs $KMnO_4$ titration is a redox titration.

76. For WA Vs SB titration
pH range is 5.5 – 11. So suitable indicator is Hph.

78. $pH_i = pKa + \log\frac{20}{80}$

$pH_f = pKa + \log\frac{80}{20}$

$\Delta pH = 2\log 4 = 1.2$

79. $2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + CO_2\uparrow + H_2O\uparrow$

a mol a/2 mol

$Na_2CO_3 + HCl \xrightarrow{HPh} NaHCO_3 + NaCl$

$\frac{a}{2} = 0.1 \times 0.5$

a = 0.1 mol

w = 0.1 × 84 = 8.4 gm

% purity = $\frac{8.4}{10} \times 100 = 84\%$

81. $K_{sp} = (28)^2 \times (3s)^3 = 108\ s^5$

82. $K_{sp} = s^2 = 64 \times 10^{-6}$

$s = 8 \times 10^{-3}$ M

$= 8 \times 10^{-3}$ mol/L

$= 8$ mol/m^3

83. $s = \frac{14.3\times10^{-4}}{143} = 10^{-5}$ M

$K_{sp} = s^2 = 10^{-10}$ M^2

84. $s = \frac{7}{100} = 7 \times 10^{-2}$ M

$K_{sp} = s^2 = 4.9 \times 10^{-3}$

85. (A) $K_{sp} = s^2$

$s = \sqrt{80} \times 10^{-19}$ M

(B) $K_{sp} = s^2$

$s = \sqrt{7} \times 10^{-8}$ M

(C) $K_{sp} = 108\ s^5 = 1 \times 10^{-72}$

$s = \left(\frac{1000}{108}\right)^{1/5} \times 10^{-15}$ M

(D) $K_{sp} = 27\ s^4$

$$s = \left(\frac{180}{27}\right) \times 10^{-5}\ M$$

86. $4s^3 = 8.64 \times 10^{-13}$

$s^3 = 216 \times 10^{-15}$

$s = 6 \times 10^{-5}$ M (in water)

$$Ag_2CrO_4 \text{ ¾}\!\!\longrightarrow \underset{2s}{2Ag^+} + \underset{\substack{s+0.6\\ \approx 0.6}}{CrO_4^{2-}}$$

$(2s)^2 \times 0.6 = 8.64 \times 10^{-13}$

$4s^2 = 14.4 \times 10^{-13}$

$s^2 = 3.6 \times 10^{-13}$

$s = 6 \times 10^{-7}$ M

87. 0.1 M $CaBr_2$ $\Rightarrow [Br^-] = 0.2$ M

0.1 M NaBr $\Rightarrow [Br^-] = 0.1$ M

0.1 M $AgNO_3 \Rightarrow [Ag^+] = 0.1$ M

In case of 0.1 M $CaBr_2$, morality of common ion is maximum so. There maximum common ion effect.

88. $SrCO_3 \rightarrow \underset{s_1}{Sr^{2+}} + \underset{s_1+s_2}{CO_3^{2-}}$

$ZnCO_3 \rightarrow \underset{s_2}{Zn^{2+}} + \underset{s_2+s_1}{CO_3^{2-}}$

$$\frac{(s_1+s_2)s_1}{(s_1+s_2)s_2} = \frac{10^{-10}}{1.5\times 10^{-11}} = \frac{100}{15}$$

$$\frac{s_1}{s_2} = \frac{20}{3}$$

89. $[Ba^{2+}]\,[CO_3^{2-}] = K_{sp}$

$5.1 \times 10^{-9} = [Ba^{2+}] \times 10^{-4}$

$[Ba^{2+}] = 5.1 \times 10^{-5}$ M

90. $K_{sp} = [Mg^{2+}]\,[OH^-]^2$

$1 \times 10^{-11} = 0.1 \times [OH^-]^2$

$[OH^-] = 10^{-5}$ M

pOH = 5 Þ pH = 9

91. $Q_{IP} = 10^{-3} \times 10^{-10} = 10^{-13}$

$Q_{IP} < K_{sp}$ (no ppt)

92. $Ag^+ + Br^- \rightarrow AgBr$

C_i $\quad 10^{-7}$ M $\quad 10^{-7}$ M $\quad 0$

$Q_{ip} = 10^{-7} \times 10^{-7} = 10^{-14}$, $Q_{ip} < K_{eq}$,

So there will be no precipitation

93. $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

	10mmol	80mmol
5	0	75
	$\frac{x}{500}$	$\frac{75}{500}$

then $\left(\frac{x}{500}\right)^2\left(\frac{75}{500}\right) = 15 \times 10^{-12}$

$\frac{x}{500} = 10^{-5}$

$x = 5 \times 10^{-3}$

$[Ag^+] = \frac{5\times10^{-3}}{500} = 10^{-5}$

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

$y \quad\quad x - y \quad\quad 4 \times 10^{-5} - y$

$4 \times 10^{-5} - y = 10^{-5}$

$y = 3 \times 10^{-5}$

$(x - y)(4 \times 10^{-5} - y) = 10^{-10}$

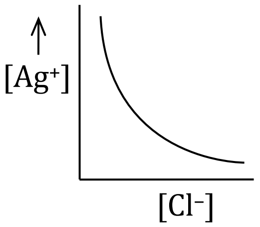
$(x - y)(10^{-5}) = 10^{-10}$

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

$x - 3 \times 10^{-5} = 10^{-5}$

$x = 4 \times 10^{-5}$

95. $K_{sp} = [Ag^+][Cl^-]$



96. $CN^- + H_2O \rightarrow HCN + OH^-$

Solubility if $[OH^-]^-$, $[H^+]$, pH^-

97. Solubility of Ag_2CO_3 will be max. in NH_3 due to complex formation.

98. $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$

x 0.8 0.1

$Ag\,(NH_3)_2^+ \rightleftharpoons Ag\,(NH_3)^+ + NH_3$

0.1 – x x 0.8 + x

~0.1 ~0.8

$$\frac{1}{K_{f_2}} = \frac{1}{10^4} = \frac{(0.8)x}{0.1} \Rightarrow x = 1.25 \times 10^{-5}$$

99. $Ag\,A\,(s) \xrightleftharpoons{K_{sp}} Ag^+\,(aq) + A^-(aq)$

S S–x

$A^-(aq) + H_2O \xrightleftharpoons{K_w/K_a} AH\,(aq) + OH^-(aq)$

S–x x x

$$10^{-4} = \frac{K_w}{K_a} = \frac{x^2}{S-x} \Rightarrow \frac{10^{-10}}{S-x} \qquad \Rightarrow (S-x) = \frac{10^{-10}}{10^{-4}} = 10^{-6}$$

$\Rightarrow S = x + 10^{-6}$ {but $x = 10^{-5}$}$\Rightarrow S = (1.1 \times 10^{-5})$

$K_{sp} = [Ag^+\,(aq)]\,[A^-(aq)] \Rightarrow 1.1 \times 10^{-5} \times 10^{-6}$

$K_{sp} = 1.1 \times 10^{-11}$

EXERCISE:S-1

1. pH = 13

$[H^+] = 10^{-13}$ M

$= 10^{-13}$ mol/L

$= 10^{-13}\times6\times10^{23}$ ions/L

Q 1 L contains 6×10^{10} ions

10^{-3} L will contain $= 6\times10^{10}\times10^{-3}$

$= 6\times10^{7}$ ions

2. (i) $K_w = [H^+][OH^-] = 9\times10^{-14}$

In pure water

$[H^+] = [OH^{-2}] = 3\times10^{-7}$

pH = 7 – log3 = 6.52

(ii) At 60°C neutral pH = 6.52

If pH < 6.52 then solution will be acidic and pH > 6.52. Then solution will be basic.

3. $2H_2O \rightarrow H_3O^+ + OH^-$

$C(1-\alpha)$ $\quad C\alpha \quad C\alpha$

$[H^+] = \dfrac{1000}{18}\times3.6\times10^{-9} = 2\times10^{-7}$ M

$K_w = [H^+][OH^-]= 2\times10^{-7}\times2\times10^{-7} = 4\times10^{-14}$

4. $2NH_3 \rightarrow NH_4^+ + NH_2^-$

$\left[NH_4^+\right]\left[NH_2^-\right] = 10^{-30}$

$\left[NH_2^-\right]=\left[NH_4^+\right] = 10^{-15}$ M

$\left[NH_2^-\right] = 10^{-15}\times6\times10^{23}$ ions/L

1 L contains 6×10^{5} NH_2^- ions

10^{-6} L (1 mm^3) will contain= $6\times10^{8}\times10^{-6}$ = 600 NH_2^- ions

5. (a) $[H^+] = 10^{-1} \Rightarrow$ pH = 1

(b) $[OH^-] = \dfrac{10^{-3}}{100} = 10^{-5}$M

$pOH = 5 \Rightarrow pH = 9$

(c) $[OH^-] = \frac{1}{10} \times \frac{2}{10} = 2 \times 10^{-3}$

$pOH = 3 - \log 2$

$pH = 11 + \log 2 = 11.3$

(d) $H_2O \rightarrow H^+ + OH^-$

$X + 10^{-8} \quad x$

$K_w = (x + 10^{-8})x = 10^{-14}$

$x = 9.5 \times 10^{-8}$

$[H^+] = 10.51 \times 10^{-8}$ M

$pH = 8 - \log 10.51 = 8 - 1.03 = 6.97$

(e)

$H_2O \rightarrow H^+ + OH^-$

$x \quad 10^{-10} + x$

$K_w = (x + 10^{-10})x = 10^{-14}$

$x » 10^{-7}$

$pH = 7$

6. If $V \rightarrow ¥$, then solution will almost neutral. So $pH = 7$

7. $HCl \rightarrow H^+ + Cl^-$

$x+y \quad x$

$H_2O \rightarrow H^+ + OH^-$

$x+y \quad y$

$x + y = 10^{-6.95}$

$(x + y) \times y = 10^{-14}$

$y = 10^{-7.05}$

$x + y = 11.22\times10^{-8}$

$y = 8.9\times10^{-8}$

$x = 2.32\times10^{-8}$ M

8. (b) $CH_3COOH \rightarrow CH_3COO^- + H^+$

$0.1-x \qquad x \qquad x$

$$1.8\times10^{-5} = \frac{x^2}{0.1-x}$$

$x^2 = 1.8\times10^{-6}$

$[H^+] = x = 1.36\times10^{-3}$

pH = 3 – log1.3 = 2.87

(c) $NH_4OH \rightarrow NH_4^+ + OH^-$

$0.1-x \qquad x \qquad x$

$$1.8\times10^{-5} = \frac{x^2}{0.1-x}$$

$[OH^-] = x = 1.34\times10^{-3}$

pOH = 2.87 $\Rightarrow$ pH = 11.13

(f) 10^{-7} M CH_3COOH

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

Acid will completely dissociate, so a » 1

Taking contribution of water

$[H^+] = 1.62 \times 10^{-7} \Rightarrow$ pH = 6.78

(g) $\frac{K_a}{C} = \frac{1.8\times10^{-5}}{10^{-8}} = 1.8\times100$

Acid will completely dissociate, so a » 1

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

$10^{-8} \qquad 10^{-8} + x$

$H_2O \rightarrow H^+ \quad + \quad OH^-$

$10^{-8} + x \qquad x$

$K_w = (10^{-8} + x)x = 10^{-14}$

$x = 9.51\times10^{-8}$

$[H^+] = 10.51\times10^{-8} \Rightarrow pH = 6.97$

9. (a) $HA \rightarrow H^+ + A^-$

$10^{-4.5} \quad 10^{-4.5}$

$$K_a = \frac{10^{-4.5}\times10^{-4.5}}{0.1-10^{-4.5}} = \frac{10^{-9}}{0.1} = 10^{-8}$$

(b) $BOH \longrightarrow B^+ + OH^-$

$10^{-3.5} \; 10^{-3.5}$

$$K_b = \frac{10^{-3.5}\times10^{-3.5}}{0.1-10^{-3.5}} = 10^{-6}$$

10. $$\frac{C_1\alpha_1^2}{1-\alpha_1} = \frac{C_2\alpha_2^2}{1-\alpha_2}$$

$$\alpha_1^2 = 10^{-2}\alpha_2^2 \Rightarrow \frac{\alpha_2^2}{\alpha_1^2} = 100 \Rightarrow \frac{\alpha_2}{\alpha_1} = 10$$

11. $$1.8\times10^{-5} = \frac{1\times\alpha_1^2}{1-\alpha_1} = 1\times\alpha_1^2$$

$$6.2\times10^{-10} = \frac{1\times\alpha_1^2}{1-\alpha_2} = 1\times\alpha_2^2$$

$$\frac{\alpha_1^2}{\alpha_2^2} = \frac{1.5\times10^{-5}}{6.2\times10^{-10}} = 2.9\times10^{-4}$$

$$\frac{\alpha_1}{\alpha_2} = 1.70\times10^2$$

12. $NH_4OH \longrightarrow NH_4^+ + OH^-$

$10^{-4} \quad 10^{-4}$

$$10^{-5} = \frac{10^{-8}}{C-10^{-4}}$$

$C - 10^{-4} = 10^{-3}$

$C = 1.1\times10^{-3}$ M

13. $HA \longrightarrow H^+ + A^-$

$10^{-3} \quad 10^{-3}$

$$K_a = \frac{10^{-6}}{10^{-2} - 10^{-3}} = \frac{10^{-6}}{9\times10^{-3}} = \frac{1}{9}\times10^{-3}$$

14. $5.9\times10^{-10} = \dfrac{x^2}{0.3 - x}$

$x^2 = 5.9\times0.3\times10^{-10}$

$x = \sqrt{1.77}\times10^{-5}$

$pH = 5 - \log\sqrt{1.77} = 4.87$

15. $[H^+] = \dfrac{10^{-4}}{2} + \dfrac{19}{2}\times10^{-4} = 10\times10^{-4} = 10^{-3}$

$\Rightarrow \quad pH = 3$

16. (a) $[H^+] = \dfrac{10+20}{100} = \dfrac{30}{100}$

$pH = 1 - \log 3 = 0.52$

(b) $[H^+] = \sqrt{2\times10^{-5}\times0.1 + 4\times10^{-5}\times0.1} = \sqrt{6}\times10^{-3}$

$pH = 3 - 0.39 = 2.61$

17. $HCOOH \longrightarrow H^+ + HCOO^-$

$0.05-x \quad x \quad x$

$1.8\times10^{-4} = \dfrac{x^2}{0.05 - x}$

$x^2 = 1.8\times10^{-4}\times0.05$

$x^2 = 9\times10^{-6}$

$pH_i = 2.52$

$HCOOH \longrightarrow H^+ + HCOO^-$

$0.05-x \quad 0.1+x \quad x$

$1.8\times10^{-4} = \dfrac{(0.1+x)x}{0.05 - x}$

$x^2 + 0.1x - 9\times10^{-6} = 0$

$x = 0.9\times10^{-4}$

$[H^+] = 0.1$

$pH_f = 1$

$\Delta pH = 1 - 2.52 = -1.52$

$1.8\times10^{-4} = \dfrac{0.1\times[HCOO^-]}{0.05}$

$[HCOO^-] = 0.9\times10^{-4} = 9\times10^{-5}$ M

18. $CHCl_2COOH \longrightarrow CHCl_2COO^- + H^+$

$0.01-x \qquad x \qquad x+0.01$

$3\times10^{-2} = \dfrac{x(x+0.01)}{0.01-x}$

$x^2 + 4\times10^{-2}x - 3\times10^{-4} = 0$

$x = 0.64\times10^{-2}$

$[H^+] = 1.64\times10^{-2}$ M

$[CHCl_2COO^-] = x = 0.64\times10^{-2}$ M

19. $[H^+] = \sqrt{1.8\times10^{-5}\times0.02+6.4\times10^{-5}\times0.01} = 10^{-3}$ M

$1.8\times10^{-5} = \dfrac{[CH_3COO^-]\times10^{-3}}{0.02-10^{-3}}$

$[CH_3COO^-] = 1.8\times10^{-2}\times19\times10^{-3} = 3.42\times10^{-4}$ M

$6.4\times10^{-5} = \dfrac{\left[C_7H_5O_2^-\right]\times10^{-3}}{0.01-10^{-3}}$

$\left[C_7H_5O_2^-\right] = 6.4\times10^{-2}\times9\times10^{-3} = 5.76\times10^{-4}$ M

20. $H_2C_2O_4 \longrightarrow H^+ + HC_2O_4^-$

$0.1-x \qquad x+y \qquad x-y$

$HC_2O_4^- \longrightarrow H^+ + C_2O_4^{2-}$

$x-y \qquad x+y \qquad y$

$10^{-2} = \dfrac{(x+y)(x-y)}{0.1-x}$

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

$10^{-5} = \dfrac{x \times y}{x}$

$K_{a1} >> K_{a2}$,so $x >> y$

$10^{-2} = \dfrac{x^2}{0.1-x}$

$x^2 + 10^{-2}x - 10^{-3} = 0$ Þ $x = 2.7\times10^{-2}$

$[H^+] = [HC_2O_4^-] = 2.7\times10^{-2}$ M

$[C_2O_4^{2-}] = 10^{-5}$ M

$[H_2C_2O_4] = 7.3\times10^{-2}$ M

21. $H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$

$10^{-2}-x \quad\quad x+y+z \quad\quad x-y$

$H_2PO_4^- \longrightarrow H^+ + HPO_4^{2-}$

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

$HPO_4^{2-} \longrightarrow H^+ + PO_4^{3-}$

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

$K_{a1} >> K_{a2} >> K_{a3}$, so $x >> y >> z$

$10^{-3} = \dfrac{(x+y+z)(x-y)}{10^{-2}-x}$

$10^{-3} = \dfrac{x^2}{10^{-2}-x}$

$x^2 + 10^{-3}x - 10^{-5} = 0$ Þ $x = 2.7\times10^{-3}$

$10^{-8} = \dfrac{(x+y+z)(y-z)}{x-y}$

$10^{-8} = \dfrac{x \times y}{x}$ Þ $y = 10^{-8}$

$10^{-13} = \dfrac{(x+y+z)\times z}{y-z}$

$10^{-13} = \frac{x \times z}{y} = \frac{2.7\times10^{-3}\times2}{10^{-8}}$

$z = \frac{1}{2.7}\times10^{-18} = 3.7\times10^{-19}$

$[H^+] = [H_2PO_4^-] = 2.7\times10^{-3}$ M

$[HPO_4^-] = 10^{-8}$ M

$[PO_4^{3-}] = 3.7\times10^{-19}$

$H_3PO_4 = 7.3\times10^{-3}$ M

22. $H_2SO_4 \longrightarrow H^+ + HSO_4^-$

0.2 0.2 0.2

$H_2SO_4^- \longrightarrow H^+ + SO_4^{2-}$

0.2–x 0.2+ x 0.2

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

$x^2 + 21 \times 10^{-2}x - 2 \times 10^{-3} = 0$

$x = 0.9127 \times 10^{-2}$

$[H^+] = 0.209127$ M

$[SO_4^{2-}] = 0.009127$ M

$[HSO_4^-] = 0.190873$ M

23. $en + H_2O \longrightarrow enH^+ + OH^-$ $k_{b1} = 8.5 \times 10^{-5}$

0.1–x x–y x+y

$\approx x$ $\approx x$

$enH^+ + H_2O \longrightarrow enH_2^{2+} + OH^-$ $k_{b2} = 7.1 \times 10^{-8}$

x–y y x+y

$\approx x$ $\approx x$

$k_{b1} >> k_{b2}$ so $x >> y$

$8.5 \times 10^{-5} = \frac{x^2}{0.1-x}$ $\Rightarrow$ $x^2 = 8.5 \times 10^{-6} \Rightarrow x = 2.91 \times 10^{-3}$

$[OH^-] = 2.91 \times 10^{-3}$ M $\Rightarrow$ pH = 11.46

$7.1 \times 10^{-8} = \frac{x \times y}{x}$ $\Rightarrow$ $y = 7.1 \times 10^{-8}$

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

24. All cations (Cu^{2+}, NH_4^+)are acid and all anions ($C_2H_5O^-$, F^-, SO_3^{2-})are base

Solution of salt of SA + SB $\longrightarrow$ Neutral (KNO_3)

Solution of salt of SA + WB $\longrightarrow$ Acidic ($ZnCl_2$)

Solution of salt of WA + SB $\longrightarrow$ Basic ($NaOCl$, CH_3COONa, Na_2CO_3)

25. $K_a(HOCl) = \frac{10^{-14}}{4 \times 10^{-10}} = 3.5 \times 10^{-5}$

26. $H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$

$H_2PO_4^- \longrightarrow H^+ + HPO_4^{2-}$

$HPO_4^{-2} \longrightarrow H^+ + PO_4^{3-}$

(i) Dissociation constant of $HPO_4^{2-} = K_{a_3} = 10^{-12}$

(ii) $K_a\, H_2PO_4^- \times K_b\, HPO_4^{-2} = K_w$

$K_b\, HPO_4^{-2} = \frac{10^{-14}}{10^{-8}} = 10^{-6}$

(iii) $K_aH_3PO_4 \times K_b\, H_2PO_4^- = K_w$

$K_b\, H_2PO_4^- = \frac{10^{-14}}{10^{-3}} = 10^{-11}$

(iv) $K_b\, PO_4^{3-} = \frac{K_w}{K_{a_3}} = \frac{10^{-14}}{10^{-12}} = 10^{-2}$

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

$0.08 - x$ $\quad x \quad x$

$\frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.08 - x}$

$\frac{10^{-9}}{1.8} = \frac{x^2}{0.08}$

$x^2 = \frac{0.08}{1.8} \times 10^{-9} = 0.44 \times 10^{-10}$

$x = [OH^-] = 0.66 \times 10^{-5}$ M

28. $NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$

$2-x \qquad\qquad x \qquad x$

$$\frac{10^{-14}}{1.8\times10^{-5}} = \frac{x^2}{2-x}$$

$$x^2 = \frac{2\times10^{-9}}{1.8}$$

$$x = [H^+] = \frac{10}{3}\times10^{-5} \Rightarrow pH = 4.48$$

29. $C_6H_5NÅ + H_2O \longrightarrow C_5H_5N + H_3O^+$

$0.25-x \qquad\qquad x \qquad x$

$$\frac{10^{-14}}{K_b} = \frac{4\times10^{-6}}{0.25-2\times10^{-3}}$$

$$\frac{10^{-14}}{K_b} = \frac{4\times10^{-6}}{0.25}$$

$$K_b = \frac{0.25\times10^{-14}}{4\times10^{-6}} = \frac{1}{16}\times10^{-8} = 6.25\times10^{-10}$$

30. $CN^- + H_2O \longrightarrow HCN + OH^-$

$0.06(1-h) \qquad\qquad 0.06h \qquad 0.06h$

$$\frac{10^{-14}}{6\times10^{-10}} = \frac{0.06h^2}{1-h}$$

$$\frac{1}{6}\times10^{-14} = \frac{0.06h^2}{1-h}$$

$$0.06h^2 = \frac{1}{6}\times10^{-4}$$

$$h^2 = \frac{1}{36}\times10^{-2}$$

$$h = \frac{1}{60} = 0.0166 = 1.66\ \%$$

31. $C_6H_5O^- + H_2O \longrightarrow C_6H_5OH + OH^-$

$10^{-3}-x \qquad\qquad x \qquad x$

$$\frac{10^{-14}}{1.05\times10^{-10}}=\frac{x^2}{10^{-3}-x}$$

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

$x^2 + 10^{-4}x - 10^{-7} = 0$

$[OH^-] = x=\frac{\sqrt{41}-1}{2}\times10^{-4} = 2.7 \times 10^{-4}$

pH = 10 + log2.7 = 10.3

32. $\underset{0.1-x}{PO_4^{3-}}+H_2O\longrightarrow \underset{x}{HPO_4^{2-}}+\underset{x}{OH^-}$

$$\frac{10^{-14}}{4.5\times10^{-13}}=\frac{x^2}{0.1-x}$$

$$\frac{x^2}{0.1-x}=\frac{1}{45}$$

$45x^2 + x - 0.1 = 0$

$[OH^-] = x = 4.911 \times 10^{-1}$

$[H_2PO_4^-] = 6.2 \times 10^{-8}$ M

$H_2PO_4^- + H_2O \longrightarrow H_3PO_4 + OH^-$

33. $CrO_4^{2-} + H_2O \longrightarrow HCrO_4^- + OH^-$

0.005–x x x

$$kh_1 = \frac{k_w}{k_{a_2}}\ \frac{10^{-14}}{3.1\times10^{-7}}=\frac{x^2}{0.005-x}$$

$$\frac{10^{-7}}{3.1}=\frac{x^2}{5\times10^{-3}} \Rightarrow x^2 = \frac{5\times10^{-10}}{3.1}$$

$x = h = 1.26\times10^{-5}$

$$h = \frac{1.26\times10^{-5}}{5\times10^{-3}} = 2.52\times10^{-3}$$

34. $PuO_2^{2+} + H_2O \longrightarrow PuO_2OH^+ + H^+$

0.01–x x x

= 10^{-4} = 10^{-4}

$$K_b = \frac{10^{-8}}{0.01-10^{-4}} = \frac{10^{-8}}{0.01} = 10^{-6}$$

$K_a(PuO_2^{2+}) \times K_b(PuO_2OH^+) = K_w$

$K_a\, PuO_2^{2+} = 10^{-6}$

$$K_b\, PuO_2OH^+ = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

35. (a) $Zn^{2+} + H_2O \longrightarrow Zn(OH)^+ + H^+$

0.001–x x x

$$10^{-9} = \frac{x^2}{10^{-3}-x}$$

$x^2 = 10^{-12}$

$x = [H^+] = 10^{-6}\, M \Rightarrow pH = 6$

(b) $K_a\, Zn^+ \times K_b\, Zn(OH)^+ = K_w$

$10^{-9} \times K_b\, Zn(OH)^+ = 10^{-14}$

$K_w\, Zn(OH)^+ = 10^{-5}$

36. $pH = \frac{1}{2}(pK_w + pK_a - pK_b)$

pH = 7

37. $pH = \frac{pK_2 + pK_1}{2} = \frac{10.34 + 6.34}{2} = 8.34$

38. $pH = \frac{pK_2 + pK_1}{2} = \frac{5.44 + 2.94}{2} = 4.19$

39. $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$

$$1.8\times10^{-5} = \frac{0.1\times[OH^-]}{5\times10^{-2}}$$

$[OH^-] = 1.8\times5\times10^{-6} = 9\times10^{-6}$ M

40. Moles of $(NH_4)_2SO_4 = x$

Moles of $NH_3 = 1$

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

$$4.74 = 4.74 + \log\frac{2x}{0.1}$$

$$2x = 0.1 \text{ Þ } x = \frac{0.1}{2} = 0.05$$

41. (a) $C_5H_5N + H_2O \longrightarrow C_5H_5N^+ + OH^-$

$0.2-x \qquad x \qquad x$

$$1.5\times10^{-9} = \frac{x^2}{0.2-x}$$

$x^2 = 3\times10^{-10}$

$[OH^-] = x = \sqrt{3}\times10^{-5}$ M

$$pOH = 5 - \frac{1}{2}\log3 \Rightarrow pH = 9 + \frac{1}{2}\log3 = 9.15$$

(b) Equilibrium will shift to backward reaction so $[OH^-]^{-}$, pOH , pH^{-}

(c) $$pOH = pK_b + \log\frac{[C_5H_5NH^+]}{[C_5H_5N]}$$

$$= 9 - \log1.5 + \log\frac{0.3}{0.1} = 9 - \log1.5 + \log3 = 9.3$$

pH = 4.7

42. (a) $NH_4OH + NaOH \longrightarrow NH_4OH^- + NaCl$

0.1	0.05	0.1	–	(initial moles)
0.05	0	0.15	–	(moles at equilibrium)

$pOH_i = 4.74 \Rightarrow pH_i = 9.26$

$$pOH_f = 4.74 + \log\frac{0.05}{0.15} = 4.74 - \log3$$

$pH_f = 9.26 + \log3 = 9.74$

(b) $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

0.1	0.05	0.1	(initial moles)
0.05	0	0.05	(moles at equilibrium)

$pOH_i = 4.74 \Rightarrow pH_i = 9.26$

$pOH_f = 4.74 + \log\frac{0.05}{0.15} = 4.74 + \log 3$

$pH_f = 9.26 - \log 3 = 8.78$

43. (a) millimoles of $OH^- = 8$

millimoles of $H^+ = 3$

$[OH^-] = \frac{5}{50} = 0.1$

$pOH = 1 \Rightarrow pH = 13$

(b) millimoles of $H^+ = 0.2$

millimoles $OH^- = 0.2$

Hence solution will be neutral, so pH = 7

(d) millimoles of $H^+ = 1\times2$

millimoles of $OH^- = 1$

$[H^+] = \frac{1}{20}$

$pH = \log 20 = 1.3$

44. In case of (iii) buffer can be prepared

In case of (iv) and (v) buffer can be prepared if moles of weak acid or weak base is more

45. $CH_3COOH + NaOH \longrightarrow CH_3COO\times1a + H_2O$

10m mol	5m mol	–	–
5m mol	0	5m mol	–

$pH = pK_a = 4.74$

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

7.5m mol	5m mol	–	–
2.5m mol	0	5m mol	–

$pOH = 4.74 + \log\frac{2.5}{5} = 4.74 - \log 2$

$pH = 9.26 + \log 2 = 9.56$

47. $NH_3 + HCl \longrightarrow NH_4Cl$

20m mol 15m mol –

5m mol 0 15m mol

$pOH = 4.74 + \log\frac{15}{5} = 4.74 + \log 3$

$pH = 9.26 - \log 3 = 8.78$

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

10m mol 7.5m mol – –

2.5m mol 0 5m mol –

$pOH = 4.74 + \log\frac{2.5}{5} = 4.74 + \log\frac{1}{2}$

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

0.1–x x x

$\frac{10^{-14}}{10^{-5}} = \frac{x^2}{0.1-x}$

$10^{-9} = \frac{x^2}{0.1}$

$x^2 = 10^{-10}$

$x = [OH^-] = 10^{-5}$

$pOH = 5 \Rightarrow pH = 9$

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

0.05–x x x

$\frac{10^{-14}}{1.8\times10^{-5}} = \frac{x^2}{0.05-x}$

$x^2 = 0.05\times10^{-14} = 1.8\times10^{-5}$

$[OH^-] = x = 0.52\times10^{-5}$

$[H^+] = 1.92\times10^{-9}$ M $\Rightarrow pH = 8.71$

51. $NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$

0.2–x x x

$$\frac{10^{-14}}{1.8\times10^{-5}}=\frac{x^2}{0.2-x}$$

$x^2=\frac{1}{9}\times10^{-9}$

$[H^+]$ = x = $1.05\times10^{-5} \Rightarrow$ pH = 4.98

52. (i) $CH_3COOH \longrightarrow CH_3COO^- + H^+$

0.1–x x x

$2\times10^{-5}=\frac{x^2}{0.1-x}$

$x^2 = 2\times10^{-6}$

$[H^+]$ = x = $\sqrt{2}\times10^{-3}$

pH = 3 – 0.15 = 2.85

(ii) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

5mmol 1mmol –

4mmol 0 1mmol

pH = 4.7 + $\log\frac{1}{4}$ = 4.7 – 0.6 = 4.1

(iii) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

5mmol 2mmol –

3mmol 0 2mmol

pH = 4.7 + $\log\frac{2}{3}$ = 4.52

(iv) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

5mmol 2.5mmol –

2.5mmol 0 2.5mmol

pH = pK_a = 4.7

(v) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

5mmol 4mmol –

1mmol 0 4mmol

pH = 4.7 + log4 = 5.3

(vi) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

5mmol 5mmol –

0 0 5mmol

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

0.05–x x x

$$\frac{10^{-14}}{2\times10^{-15}} = \frac{x^2}{0.05-x}$$

$$x^2 = \frac{1}{2}\times10^{-9}\times0.05 = \frac{1}{4}\times10^{-10}$$

$$[OH^-] = x = \frac{1}{2}\times10^{-5}$$

pOH = 5 + log2

pH = 9 – log2 = 8.7

53. $pK_{In} = 2$

$K_{In} = 10^{-2}$

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \Rightarrow 10^{-2} = \frac{4\times10^{-3}[In^-]}{[HIn]}$$

$$\frac{[In^-]}{[HIn]} = \frac{10}{4} = 2.5$$

$$\%\text{ of }[HIn] = \frac{1}{3.5}\times100 = 28.57\ \%$$

54. $pH_i = pK_a + \log\frac{25}{75} = pK_a = \log\frac{1}{3}$

$pH_f = pK_a + \log\frac{75}{25} = pK_a + \log3$

$\Delta pH = 2\log3 = 0.96$

55. $$K_{In} = \frac{[H^+]\times[Basic]}{[Acidic]}$$

$$6\times10^{-5} = \frac{10^{-5}\times[Basic]}{[Acidic]}$$

$$\%\text{ of }[Basic] = \frac{6}{7}\times100 = 85.71\ \%$$

56. pH = $pK_{In} \pm 1$

pH range of indicator = 2.4 – 4.4

57. At equivalence point H_3BO_3 will present in solution.

$$\underset{0.05-x}{H_3BO_3} + H_2O \longrightarrow \underset{x}{B(OH)_4^-} + \underset{x}{H^+}$$

$$7.2\times10^{-10} = \frac{x^2}{0.05-x}$$

$$x^2 = \frac{7.2}{20}\times10^{-10}$$

$$[H^+] = x = \sqrt{\frac{7.2}{20}}\times10^{-5}\ M$$

$$pH = 5 - \frac{1}{2}\log\frac{7.2}{20} = 5.44$$

pH range of titration = 4.44 – 6.44

So suitable indicator methyl red (4.2 – 6.3)

58. **(018)**

59. $A_3X_3(s) \longrightarrow 2A^{3+}(aq) + 3X^{2-}(aq)$

$\qquad\qquad\qquad 2s \qquad\qquad 3s$

$K_{sp} = (2s)^2\times(3s)^3 = 108s^5 = 1.08\times10^{-23}$

$s = 10^{-5}$ M

60. $s = \dfrac{0.038}{3.04} = 1.25\times10^{-3}$ M

$K_{sp} = s^2 = (1.25)^2\times10^{-8} = 1.56\times10^{-8}$ M

61. $CaF_2 \longrightarrow Ca^{2+} + 2F^-$

$\qquad 4.1\times\dfrac{10^{-4}}{2} \qquad 4.1\times10^{-4}$

$$K_{sp} = \frac{4.1\times10^{-4}}{2}\times(4.1\times10^{-4})^2 = 3.44\times10^{-11}$$

62. $s = \frac{2.4\times10^{-5}}{60}\times10 = 4\times10^{-6}$ M

$K_{sp} = 4s^3 = 4\times(4\times10^{-6})^3$

$= 2.56\times10^{-16}$

63. For MX

$s^2 = K_{sp} = 4\times10^{-18}$

$s = 2\times10^{-9}$ M

For QX_2

$4s^2 = K_{sp} = 4\times10^{-18}$

$s = 10^{-6}$ M

Solubility of QX_2 is more

64. $CuI \longrightarrow Cu^+ + I^-$

$\quad\quad s \quad\quad s+0.1 \approx 0.1$

$s\times0.1 = 5\times10^{-12}$

$[Cu^+] = s = 5\times10^{-11}$ M

65. $AgCl \longrightarrow Ag^+ + Cl^-$

$\quad\quad s \quad\quad s+0.2$

$s\times0.2 = 1\times10^{-10}$

$s = 5\times10^{-10}$ M

66. $AgSCN \longrightarrow Ag^+ + SCN^-$

$\quad\quad s_1+s_2 \quad\quad s_1$

$AgBr \longrightarrow Ag^+ + Br^-$

$\quad\quad s_1+s_2 \quad\quad s_2$

$(s_1 + s_2)s_1 = 1.1\times10^{-12}$

$(s_1 + s_2)s_2 = 5\times10^{-13}$

$(s_1 + s_2)^2 = 1.6\times10^{-12}$

$s_1 + s_2 = \sqrt{1.6}\times10^{-6}$

$s_1 = \frac{1.1\times10^{-12}}{\sqrt{1.6}\times10^{-6}} = 9\times10^{-7}$ M

$s_2 = \frac{5\times10^{-13}}{\sqrt{1.6}\times10^{-6}} = 4\times10^{-7}$ M

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

$s_1 \quad 2(s_1+s_2)$

$MgF_2 \longrightarrow Mg^{2+} + 2F^-$

$s_2 \quad 2(s_1+s_2)$

$s_1 \times 2(s_1 + s_2) = 4\times10^{-9}$

$s_2 \times 2(s_1 + s_2) = 9.5\times10^{-9}$

$3(s_1 + s_2)^2 = 13.5\times10^{-9}$

$(s_1 + s_2)^2 = \frac{13.5}{3}\times10^{-10} = 45\times10^{-10}$

$s_1 + s_2 = \sqrt{45}\times10^{-5}$

$[F^-] = 2(s_1 + s_2) = 2\times\sqrt{45}\times10^{-5}\,M = 1.34\times10^{-4}\,M$

68. For pptn $\qquad K_{sp} = Q_{IP}$

(a) $Q_{IP} = 10^{-3} \times(10^{-5})^2 = 10^{-13}$

So $Q_{IP} < K_{sp}$ No pptn

(b) $Q_{IP} = 10^{-3}\times10^{-6} = 10^{-9}$

$Q_{IP} > K_{sp}$ pptn will occur

69. $\frac{8\times10^{-6}\times v}{v+1}\times\frac{10^{-4}}{v+1} = 2\times10^{-10}$

$(v-1)^2 = 0 \Rightarrow v = 1\,L$

70. $K_{sp} = 4s^3 = 4 \times (10^{-3})^3 = 4 \times 10^{-9}$

$4 \times 10^{-9} = [Ag^+]^2\,[CrO_4^{2-}]$

$= [Ag^+]^2\,[10^{-1}]$

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

$[Ag^+]$ moles precipitated $= 2 \times 10^{-3} - 2 \times 10^{-4} = 18 \times 10^{-4}$

moles of Ag_2CrO_4 precipitated $= 9 \times 10^{-4}$

71. $Pb^{2+} + 2Cl^- \longrightarrow PbCl_2(s) \qquad k = \frac{1}{ksp}$

0.1x	0.75 M	0
x	0.55 M	0.1M

$$\frac{1}{1.7\times10^{-4}}=\frac{1}{x\times(0.55)^2}$$

$$x=\frac{1.7}{(0.55)^2}\times10^{-4} = 5.6\times10^{-4}$$

$[Pb^{2+}] = 5.6 \times 10^{-4}$

Moles of $Pb^{2+} = 5.6 \times 10^{-5}$

Mass of Pb^{2+} $= 5.6 \times 208 \times 10^{-5} = 1.2 \times 10^{+3} \times 10^{-2}$ mg$=$ 12 mg

72. $CaCO_3 \longrightarrow Ca^{2+} + CO_3^{2-}$

7×10^{-5}

$BaCO_3 \longrightarrow Ba^{2+} + CO_3^{2-}$

7×10^{-5}

$$\frac{7\times10^{-5}\times[CO_3^{2-}]}{7\times10^{-5}\times0.1\times[CO_3^{2-}]}=\frac{45\times10^{-10}}{K_{sp}(BaCO_3)}$$

$K_{sp}(BaCO_3) = 4.9\times10^{-10}$

73. $Fe^{3+} + 3SCN^- \longrightarrow Fe(SCN)_3$

$K_f = K_1\times K_2\times K_2 = 130\times16\times1 = 2080$

$K_d = \frac{1}{K_f} = 4.8\times10^{-4}$

74. $AgBr \longrightarrow \underset{x}{Ag^+} + \underset{s}{Br^-}$ $\qquad x \times s = 5 \times 10^{-13}$

$$\underset{\substack{s\\x}}{Ag^+} + \underset{\substack{0.4\\0.4-2s}}{2NH_3} \longrightarrow \underset{\substack{0\\s}}{Ag(NH_3)_2^+} \qquad k_{eq} = 1\times10^8$$

$$\frac{s}{x(0.4-2s)}=1\times10^8$$

$$\left(\frac{s}{0.4-2s}\right)^2 = 10^8 \times 5 \times 10^{-13}$$

$$\frac{s}{0.4-2s}=\sqrt{50}\times10^{-3}$$

$s = \sqrt{50} \times 10^{-3} \times 0.4 = 2.82 \times 10^{-3}$ M

75. (a) $[Ag^+] = 10^{-2}$ (b) $[CO_3^{2-}] = 4\times10^{-2}$ (d) $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$

As $[H^+]$ increases, solubility of Ag_2CO_3 increases.

d > c > a > b

EXERCISE # O-II

1. $H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$

$H_3PO_4^- \longrightarrow H^+ + H_2PO_4^{2-}$

$HPO_4^{2-} \longrightarrow H^+ + PO_4^{3-}$

if $K_1 >> K_2$

$[H^+] = [H_2PO_4^-]$ $[HPO_4^{2-}] = K_2$

$[H^+] = \sqrt{K_1(H_3PO_4)}$ $[H^+] >> [PO_4^{3-}]$

2. (A) **TRUE** $K_b\ A^- = \dfrac{Kw}{KaHA} = \dfrac{10^{-14}}{10^{-6}} = 10^{-8}$

(B) **TRUE** If T $\uparrow$, Kw $\uparrow$

(C) **TRUE** Acidic strength $\propto Ka \propto \dfrac{1}{pKa}$

(D) **TRUE** Salt of SA + WB (NH_4Cl) undergoes cationic hydrolysis.

3. (A) If T increases, then $[H^+]$ increases, pH^-

(B) If T increases , then $[OH^-]$ increases ,pOH^-

(C) For 10^{-4} M HCl, pH = 4

$10^{-5} = \dfrac{0.01x^2}{1-x} \Rightarrow x^2 = 10^{-4} \Rightarrow x = 10^{-2} \Rightarrow pH = 2$

(D) $HA \longrightarrow H^+ + A^-$

$C(1-\alpha)$ $c\alpha$ $c\alpha$

$K_a = \dfrac{C\alpha^2}{1-\alpha} \Rightarrow \alpha \propto \dfrac{1}{\sqrt{C}}$

4. (A) **FALSE** At half equivalence point pH = pKa

(B) **TRUE** $pH = 4.74 + \log\dfrac{0.1}{0.01} = 5.74$

(C) **TRUE** $pH = pKa + \log\frac{[C.B.]}{[Acid]}$

(D) **FALSE** Buffer capacity is max when $\frac{S}{a} = 1$

5. (A) As, T increases , Kw increases and $[H^+]$ $[OH^-]$ also increase, so neutral pH < 7

If pOH =7, then pH < 7 solution will be acidic.

(B) $pH = -\log [H^+]$

(C) For $CH_3COONa(aq)$

$[OH^-] = \sqrt{\frac{kw}{K_a} \times C}$ Þ $[OH^-] \propto \sqrt{C}$

On dilution $[OH^-]$¯, pOH, pH¯

(D) Buffer capacity = 2.303 $\frac{s.a}{s+a}$

6. 0.1 M BOH ($K_b = 10^{-5}$), it is weak base.

For salt BCl

$$B^+ + H_2O \longrightarrow BOH + H^+$$

0.1–x x x

$10^{-9} = \frac{x^2}{0.1x}$ $\Rightarrow$ $x^2 = 10^{-10} \Rightarrow x = 10^{-5} \Rightarrow pH = 5$

7. For ppt Q_{ip} ³ K_{sp}

K_{sp} of AgCl = 1.8×10^{-10}

(A) $Q_{ip} = \frac{10^{-4}}{2} \times \frac{10^{-4}}{2} = \frac{1}{4} \times 10^{-8}$

$Q_{ip} > k_{sp}$ (ppt will take place)

(B) $Q_{ip} = \frac{10^{-5}}{2} \times \frac{10^{-5}}{2} = \frac{1}{4} \times 10^{-10}$

$Q_{ip} < k_{sp}$ (ppt does not take place)

(C) $Q_{ip} = \frac{10^{-6}}{2} \times \frac{10^{-6}}{2} = \frac{1}{4} \times 10^{-12}$

$Q_{ip} < k_{sp}$ (ppt does not take place)

(D) $Q_{ip} = \frac{10^{-10}}{2} \times \frac{10^{-10}}{2} = \frac{1}{4} \times 10^{-20}$

$Q_{ip} < k_{sp}$ (ppt does not take place)

8. (A) **TRUE** Ksp AgCl > Ksp AgBr

So AgBr will ppt first

(B) **TRUE** For M_2x $Ksp = 4s^3$

For Qy_2 $Ksp = 4s^3$

For Pz_3 $Ksp = 27s^3$

(C) **FALSE** $Li_3Na_3(AlF_6)_2 \longrightarrow 3Li^+ + 3Na^+ + 2AlF_6^{3-}$

3s 3s 2s

$K_{sp} = 2916 \times s^8$

9. (A) **TRUE** due to common – ion effect of Cl^-.

(B) **TRUE**

(C) **TRUE** Due hydrolysis of CH_3COOH solubility increases.

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

(D) **TRUE**

10. In original solution

$[H^+] = \sqrt{K_a \times C} = \sqrt{10^{-6} \times 1} = 10^{-3}M$

11. Let resulting solution (After dilution) have concentration Co

CH_3COOH	$\rightleftharpoons$	CH_3COO^- +	H^+
Co		0	0
Co–X		X	X

pH = 2 × 3 = 6 $[H^+] = x = 10^{-6}$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x.x}{(Co - x)}$$

$$10^{-6} = \frac{(10^{-6})^2}{Co - 10^{-6}}$$

$Co = 2 \times 10^{-6}$ M

Now, for CH_3COOH

1 M × 1 litre = 2×10^{-6} M × V

V = 5×10^5 litre.

12. $CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

2×10^{-6} ,V   0.5 × 10–6, V

$\frac{1.5 \times 10^{-6} \times V}{2V}$ 0 $\frac{0.5 \times 10^{-6} \times V}{2V}$

$$pH = pKa + \log_{10}\left(\frac{\text{anion}}{\text{acid}}\right)$$

$= 6 - \log_{10} 3 = 5.523$

13. pH at I half equivalence point = $p^{K_{a_3}} = 12$

pH at I equivalence point = $\frac{p^{K_{a_2}} + p^{K_{a_3}}}{2} = 10$

$\Rightarrow p^{K_{a_2}} = 8$

pH at II equivalence point = $\frac{p^{K_{a_1}} + p^{K_{a_2}}}{2} = 6$

$\Rightarrow p^{K_{a_1}} = 4$

At III equivalence point

$Na_3OP_4 + 3HCl \longrightarrow 3NaCl + H_3PO_4$

100	300	–	–
×	×	100	100

$$C = \frac{100}{400} = \frac{1}{4}M$$

$$Ka_1 = 10^{-4} = \frac{(H^+)^2}{C} \Rightarrow (H^+) = \sqrt{ka_1C}$$

$$= \frac{10^{-2}}{2}$$

$= 5 \times 10^{-3}$

pH = 3 – log 5

14. at II half equivalence point

$Na_2HPO_4 + HCl \longrightarrow NaCl + NaH_2PO_4$

100	50	–	–
50	×	50	50

$$pH = p^{K_{a_2}} + \log\frac{50}{50} = p^{K_{a_2}} = 8$$

15. Equilibrium constant = Kw / k_{a_3}

16. Let moles of HA is x and moles of HB is (1-x) which reacts with NaOH

$x \times 11.8 + (1-x) \times 12.4 = 12.25$

17. $[H^+] = \sqrt{k_{a_1}C_1 + k_{a_2}C_2} = \sqrt{1\times10^{-5} + 9\times10^{-5}} = 10 \times 10^{-3} = 10^{-2}$

pH = 2

18. Number of moles Cu oxidised $= \frac{7.04}{64} \times 10^{-3}$

$= 1.1 \times 10^{-4}$

19. $Cu + 2Ag^+ \rightleftharpoons Cu^{+2} + 2Ag$

Since equilibrium constant is very large

$[Ag^+] = 2.2 \times 10^{-4}$

20. $K_{sp} = [Ag^+]^2 [BrO_3]$

$= 4.84 \times 10^{-8}$

21. (A) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

10 mmol	2.5 mmol	0	0
7.5 mmol	0	2.5 mmol	

$$pH = pK_a + \log\frac{2.5}{7.5} = pK_a - \log 3$$

(B) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

10 mmol	5 mmol	
5 mmol	0	5 mmol

at half equivalence point pH = pK_a

(C) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

10 mmol	7.5mmol	–	–
2.5 mmol	0	7.5 mmol	

$pH = pK_a + \log 3$

(D) It volume of final solution is doubled then conc. will be half.

$$pH = \frac{1}{2}(pK_w + pK_a + \log\frac{1}{2}) = \frac{1}{2}(pK_w + pK_a - 2)$$

22. (P) $NaOH + HCl \longrightarrow NH_4Cl + H_2O$

0.2 V	0.2V	0	–
0	0	0.2V	–

$[NH_4Cl] = 0.1$ M

$$pH = \frac{1}{2}(pK_w - pK_b - \log C) = \frac{1}{2}(14 - 5 - \log 0.1) = 5$$

(Q) $CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$

0.2 V	0.2V	0	–
0	0	0.2V	–

$[CH_3COOH] = 0.1$ M

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

0.1 – x	x	x

$$10^{-5} = \frac{x_2}{0.1 - x}$$

$x = 10^{-3} \quad \Rightarrow \quad pH = 2$

(R) 0.1 M Na_2HPO_4

$$pH = \frac{pK_{a_3} + pk_{a_2}}{2} = \frac{10+6}{2} = 5$$

(S) $pH = pK_{a1} + \log\frac{[HCO_3^-]}{[H_2CO_3]}$

at half equivalence point

$[HCO_3^-] = [H_2CO_3] \Rightarrow pH = 5$

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

s 2s

$4s^3 = 5 \times 10^{-16}$

$s^3 = \frac{1}{8} \times 10^{-15}$ Þ $s = \frac{1}{2} \times 10^{-5}$

$[OH^-] = 10^{-5}$

$\Rightarrow pOH = 5$

$\Rightarrow pH = 10$

Exercise: S-II

1. $H_2S \rightarrow H^+ + HS^-$

$0.1 - x \quad x + 2\times10^{-4} \quad x - y$

$\approx 2\times10^{-4} \quad \approx x$

$HS^- \longrightarrow H^+ + S^{2-}$

$x - y \quad 2\times10^{-4} \quad y$

$\approx x$

$$10^{-7} = \frac{2\times10^{-4}\times x}{0.1 - x} = \frac{2\times10^{-4}\times x}{0.1}$$

$x = [HS^-] = 5 \times 10^{-5}$ M

$$10^{-14} = \frac{2\times10^{-4}\times y}{5\times10^{-5}}$$

$y = [S^{2-}] = 2.5 \times 10^{-15}$ M

2. $NiC(aq) + H_2O \rightleftharpoons NiCH^+ + OH^-$ $\quad kb_1 = 7 \times 10^{-7}$

$0.02 - x \quad x - y \quad x + y$

$\approx x \quad \approx x$

$NiCH^+ + H_2O \rightleftharpoons NiCH_2^{2+} + OH^-$ $\quad kb_2 = 10^{-10}$

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

$\approx x \quad \approx x$

$kb_1 >> kb_2$, $x >> y$

$$7\times10^{-7} = \frac{x^2}{0.02 - x} \Rightarrow x^2 = 1.4 \times 10^{-8} \Rightarrow x = \left[OH^-\right] = \sqrt{1.4} \times 10^{-4}$$

$[OH^-] = 7 \times 10^{-6} \Rightarrow pH = 10.073$

3. For $NaHCO_3$

$$pH = \frac{pka_2 + pka_1}{2} = \frac{6.38 + 10.32}{2}$$

For Na_2HPO_4

$$pH = \frac{pka_3 + pka_2}{2} = \frac{12 + 7.2}{2} = 9.6$$

For NaH_2PO_4

$$pH = \frac{pka_2 + pka_1}{2} = \frac{7.2 + 2.12}{2} = 4.66$$

4. (a) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

6	3	0	(initial mmoles)
3	0	3	(equilibrium mmoles)

pH = pka_1 = 3 – log 7.5= 2.12

(b) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

6	6	0	(initial mmoles)
0	0	6	(equilibrium mmoles)

$$pH = \frac{pka_2 + pka_1}{2} = \frac{7.2 + 2.12}{2} = 4.66$$

(c) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

4.8	7.2	0	(initial mmoles)
0	2.4	4.8	(equilibrium mmoles)

$NaHPO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

4.8	2.4	0	(initial mmoles)
2.4	0	2.4	(equilibrium mmoles)

pH = pka_2 = 7.2

(d) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

4	10	0	(initial mmoles)
0	6	4	(equilibrium mmoles)

$NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

4	6	0	(initial mmoles)
0	2	4	(equilibrium mmoles)

$NaHPO_4 + NaOH \longrightarrow Na_3PO_4 + H_2O$

4	2	0	(initial mmoles)
2	0	2	(equilibrium mmoles)

pH = pka_3 = 12

5. (a) $pH = 5 - \log 1.34 + \log \frac{0.015}{0.02} = 5 - \log 1.34 + \log 0.75 = 4.75$

(b)

$C_3H_5O_2Na$	+ HCl	$\longrightarrow$ $C_3H_5O_2H$ + $NaCl$	
1.5×10^{-4}	0.1×10^{-4}	2×10^{-4}	(initial moles)
1.4×10^{-4}	0	2.1×10^{-4}	(equilibrium moles)

$pH = 4.87 + \log \frac{1.4\times10^{-4}}{2.1\times10^{-4}} = 4.693$

(c)

$C_3H_5O_2H$	+ $NaOH$	$\longrightarrow$ $C_3H_5O_2Na$ + H_2O	
2×10^{-4}	0.1×10^{-4}	1.5×10^{-4}	(initial moles)
1.9×10^{-4}	0	1.6×10^{-4}	(equilibrium moles)

$pH = 4.87 + \log \frac{1.6\times10^{-4}}{1.9\times10^{-4}} = 4.795$

(d) % change in case of b

$\Delta pH = \frac{4.75 - 4.693}{4.75} \times 100 = 1.2\%$

% change in case of c

$$\Delta pH = \frac{4.75 \times 4.75}{4.75} \times 100 = 0.94\%$$

6. $BOH + HCl \longrightarrow BCl + H_2O$

50C	1	0	0	(initial moles)
50C–1	0	1	–	(equilibrium moles)

$14 - 9.84 = pk_b + \log \frac{1}{50C - 1}$ (i)

$BOH + HCl \longrightarrow BCl + H_2O$

50C	2.5	0	0	(initial moles)
50C–2.5	0	2.5	–	(equilibrium moles)

$14 - 9.24 = pk_b + \log \frac{2.5}{50C - 2.5}$ (ii)

(i) – (ii)

$0.6 = \log \frac{2.5(50C - 1)}{50C - 2.5} = \log 4 \Rightarrow C = 0.1$

$pkb = 4.75$, $ka = 1.8 \times 10^{-5}$

at equivalence point

$pH = \frac{1}{2}(pk_w - pk_b - \log C) = \frac{1}{2}(14 - 4.76 - \log 0.05) = 5.27$

7. $pH = pkIn = 7.2$

$pH = 7.2 + \log \frac{5}{1} = 7.2 + 0.7 = 7.9$

for new indicator

$7.9 = pkIn + \log 21 \quad \Rightarrow pkIn = 7.3$

$pH = pkIn = 7.3$ (when 50% is ionized)

9. When MnS start to ppt, FeS has already ppted for pptⁿ of MnS

$0.01 \times [S^{2-}] = 2.5 \times 10^{-13}$

$[S^{2-}] = 2.5 \times 10^{-11} = 25 \times 10^{-12}$

$9.6 \times 10^{-21} = \dfrac{[H^+]^2 \times 25 \times 10^{-12}}{0.1}$

$[H^+]^2 = \dfrac{9.6}{25} \times 10^{-10}$ Þ $[H^+] = \sqrt{\dfrac{9.6}{25}} \times 10^{-5}$

pH = 5.21

10. $\dfrac{[Ca^{2+}][CO_3^{2-}]}{[Ca^{2+}][F^-]^2} = \dfrac{x}{4y^3}$

$\dfrac{2}{[F^-]^2} = \dfrac{x}{4y^3} \Rightarrow [F^-] = \sqrt{\dfrac{8y^3}{x}}$

11. $CuCO_3(s) + 4\,NH_3 \rightarrow \left[Cu(NH_3)_4\right]^{2+}(aq) + CO_3^{2-}(aq)$

0.1	x	0	0
≈ 0	x–0.4	0.1	0.1

$\dfrac{\left[Cu(NH_3)\right]^{2+}\left[CO_3^{2-}\right]}{\left[NH_3\right]_4} = ksp \times kf = 2.8 \times 10^3$

$\dfrac{0.1 \times 0.1}{(x-0.4)^4} = 2.8 \times 10^3 \Rightarrow x = 0.444$ M

12. $MnS \longrightarrow Mn^{2+} + S^{2-}$

$\qquad\qquad s \qquad s$

$S^{2-} + H_2O \longrightarrow HS^- + OH^-$

$\dfrac{kw}{k_2} = \dfrac{[HS^-][OH^-]}{[S^{2-}]}$

$[HS^-] = \dfrac{kw}{k_2} \times \dfrac{[S^{2-}]}{[OH^-]} = [S^{2-}] \times \dfrac{[H^+]}{k_2}$

$HS^- + H_2O \longrightarrow H_2S + OH^-$

$\dfrac{kw}{k_1} = \dfrac{[H_2S][OH^-]}{[HS^-]}$

$$[H_2S] = \frac{kw}{k_1} \times \frac{[HS^-]}{[OH^-]} = \frac{[H^+]}{k_1}[HS^-]$$

$$[H_2S] = \frac{[H^+]^2}{k_1k_2}[S^{2-}]$$

$$s = [S^{2-}]_f + [HS^-]_f + [H_2S]_f$$

$$s = [S^{2-}]_f \left[1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1k_2}\right]$$

$$k_{sp} = \frac{s \cdot s}{1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1k_2}}$$

$$s = \sqrt{ksp\left(1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1k_2}\right)}$$

EXERCISE # JEE-MAINS

1. Ksp $= 4s^3 = 4 \times (1.0 \times 0^{-5})^3 = 4 \times 10^{-15}$

2. Ksp $= 4s^3$

$= 4x^3$

3. $MX_4 \longrightarrow M^{4+} + 4X^-$

$\quad\quad s \quad\quad 4s$

Ksp $= s \times (4s)^4$

$= 256\ s^5$

$$s = \left(\frac{Ksp}{256}\right)^{1/5}$$

4. $H_2PO_4^- \longrightarrow H^+ + HPO_4^{2-}$

Acid C.B.

5. pH = 5.4

$[H^+] = 10^{-5.4} = 10^{0.6} \times 10^{-6} = 4 \times 10^{-6}$

6. $MX_2 \longrightarrow M^{2+} + 2x^-$

$\quad\quad s \quad\quad 2s$

$Ksp = 4s^3 = 4 \times 10^{-12}$

$s = 10^{-3}$ M

$[M^{2+}] = 10^{-3}$ M

7. $OH^- \longrightarrow H^+ + O^{2-}$

Acid C.B.

8. $H_2A \longrightarrow H^+ + HA^-$ Ka_1

$HA^- \longrightarrow H^+ + A^{2-}$ Ka_2

$H_2A \longrightarrow 2H^+ + A^{2-}$ $K_{overall} = Ka_1 \times Ka_2$

9. $pH = pKa + \log\frac{[A^-]}{[HA]}$

pH = pKa= 4.5(if acid is half ionize)

pOH = 9.5

10. $Ksp = s^2 = 1.0 \times 10^{-8}$

$s = 0^{-4}$ M

$= 10^{-6} \times 283$ g/L

$= 283 \times 10^{-5}$ g/100 mL

$= 2.83 \times 10^{-3}$ g/100 mL

11. $pH = \frac{1}{2}(pKw + pKa - pKb) = \frac{1}{2}(14 + 4.8 - 4.78)$

$= \frac{1}{2} \times 14.02 = 7.01$

12. For pptⁿ to start

Ksp = Qip

$[Ba^{2+}] \times 10^{-4} = 5.1 \times 10^{-9}$

$[Ba^{2+}] = 5.1 \times 10^{-5}$ M

13. For pptⁿ to start

Ksp = Qip

$0.05 \times [Br] = 5 \times 10^{-13}$

$[Br^-] = 10^{-11}$ M

moles of Br^- = 1×10^{-11}

mass of KBr = $1 \times 10^{-11} \times 120$ = 1.2×10^{-9} g

14. $K_1 >> K_2$

$H_2CO_3 \longrightarrow H^+ + HCO_3^-$

c – x x x – y

» x

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

x – y x + y y

» x » x

$[H^+]$ » $[HCO_3^-] = 1.2 \times 0^{-6}$ M

$[CO_3^{2-}] = Ka_2 = 4.8 \times 10^{-11}$ M

15. Ksp = Qip

$10^{-3} \times [OH^-]^2 = 1.1 \times 10^{-11}$

$[OH^-]_{min} = 10^{-4}$

pOH = 4 $\Rightarrow$ pH = 10

16. In reaction (ii) $H_2PO_4^{2-}$ given H^+ ion.

17. $Ksp = 27s^3$

$27s^3 = 1.6 \times 10^{-30}$

$$s = \left(\frac{1.6\times10^{-30}}{27}\right)^{1/3}$$

18. $HA \rightleftharpoons H^+ + A^-$ pH = 5

1 – x x x $[H^+] = 10^{-5}$

$$Ka = \frac{10^{-5}\times10^{-5}}{1} = 10^{-10}$$

19. If Ksp < Qip

$Ksp = 1.7 \times 10^{-10}$

For option (4)

$Qip = 1 \times 10^{-2} \times (1 \times 10^{-3})^2$ = 10^{-8}

20. $HQ \longrightarrow H^+ + Q^-$ pH = 3

$0.1 - x \quad x \quad x$ $[H^+] = 10^{-3}$

$$Ka = \frac{10^{-3} \times 10^{-3}}{0.1} = 10^{-5}$$

21. For pptⁿ to start

Ksp = Qip

$5.1 \times 10^{-9} = [Ba^{2+}] \times [CO_3^{2-}]$

$[Ba^{2+}] \times 10^{-4} = 5.1 \times 10^{-9}$

$[Ba^{2+}] = 5.1 \times 10^{-5}$ M

22. $[OH^-] = 5 \times 10^{-2}$

pOH = 2 – log5

Þ pH = 12 + log5 = 12.7

23. $Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^-$

$\quad s \quad 2s$

$Ksp = 4s^3$ Þ $s = \left(\frac{Ksp}{4}\right)^{1/3}$

$Cr_2(SO_4)_3 \longrightarrow 2Cr^{3+} + 3SO_4^{2-}$

$\quad 2s \quad 3s$

$Ksp = 108s^5$ Þ $s = \left(\frac{Ksp}{108}\right)^{1/5}$

For $BaSO_4$ $Ksp = s^2$ Þ $s = (Ksp)^{1/2}$

For $CrCl_3$ $Ksp = 27s^4$ Þ $s = \left(\frac{Ksp}{27}\right)^{1/4}$

24. Moles of $CH_3COOH = \frac{5}{60} = 0.083$

Moles of $CH_3COONa = \frac{7.5}{62} = 0.091$

$$pH = 4.76 + \log\frac{0.091}{0.083}$$

pH > 4.76

Range of pH Þ pKa ± 1

25. pHi = 1 $[H^+]_i = 0.1$

$pH_f = 2[H^+]_f = 0.01$

$M_iV_i = M_fV_f$

$0.1 \times 1 = 0.01 \times V_f \Rightarrow V_f = 10$ L

water should be added = 9L

26. Refer notes.

27. $Zr_3(PO_4)_4 \longrightarrow 3Zr^{+4} + 4PO_4^{3-}$

3s 4s

$Ksp = (3s)^3 \times (4s)^4 = 6912\ s^7$

$$s = \left(\frac{Kps}{6912}\right)^{1/7}$$

28. $pH = \frac{1}{2}(pKw + pKa - pKb)$

$= \frac{1}{2}(14 + 3.2 - 3.4)$

$= \frac{1}{2} \times 13.8 = 6.9$

29. pH range of methy orange = 3.1 – 4.4

in titration of W.A. Vs SA at end point pH should be less than 7.

30. pptⁿ to start

Ksp = Qip

$[Ba^{2+}]_f [SO_4^{2-}]_f = Ksp\ BaSO_4$

$$\frac{50 \times 1}{500} \times \frac{Mi \times 450}{500} = 1 \times 10^{-10}$$

$M_i = 1.1 \times 10^{-9}$ M

31. $H_2S \rightleftharpoons H^+ + HS^-$ $Ka_1 = 1.0 \times 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-}$ $Ka_2 = 1.2 \times 10^{-13}$

$H_2S \rightleftharpoons 2H^+ + S^{2-}$ $Ka = 1.2 \times 10^{-20}$

$$1.2 \times 10^{-20} = \frac{[H^+]^2 \times [S^{2-}]}{[H_2S]}$$

$$1.2 \times 10^{-20} = \frac{(0.2)^2 \times [S^{2-}]}{0.1}$$

$[S^{2-}] = 3 \times 10^{-20}$ M

32. CH_3COOK is salt of WA + S.B.

So pH > 7

33. Ksp $PbCl_2 = 3.2 \times 10^{-8} = 4s^3$

$s = 2 \times 10^{-3}$ M = 0.414 g/L

Vol. of water require to dissolve 1g of $PbCl_2 = \frac{0.1}{0.414} = 0.241$ L

34. (i) M Mol of $H^+ = 15$

M Mol of $OH^- = 5$

$[H^+]_f = \frac{10}{100} = 0.1 \Rightarrow$ pH = 1

35. $2NH_4OH + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + H_2O$

6	2	0	–
2	0	2	–

$$pOH = pKb + \log\frac{[NH_4^+]}{[NH_4OH]} = 4.7 + \log\frac{4}{2} = 4.7 + \log 2$$

pH = 9.3 – log2 = 9

36. $Ca(OH)_2 + Na_2SO_4 \longrightarrow CaSO_4 + 2NaOH$

$Ca(OH)_2$	Na_2SO_4	$CaSO_4$	2NaOH
0.1 m mole	0.014 m mole	0	0
0.086 m mole	0	0.014 m mol	0.014 m mole

Mass of $CaSO_4 = 0.014 \times 136 = 1.90$ g

$$[OH^-] = \frac{0.014}{0.2} = 0.28 \text{ M}$$

37. $Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$

$s_1 \qquad 2s_1 + 0.1 \qquad s_1$

» 0.1

$8 \times 10^{-12} = (0.1)^2 \times s_1$

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

38. $Zr_3(PO_4)_4 \longrightarrow 3Zr^{4+} + 4PO_4^{3-}$

$s \qquad 3s \qquad 4s$

$K_{sp} = 6912\, s^7$

$$s = \left(\frac{K_{sp}}{6912}\right)^{1/7}$$

39. Initial pH > 7 ,at equivalence point pH = 7

40. (a) $[H^+] = \dfrac{400 \times 0.1 \times 2 - 400 \times 0.1}{800} = 0.05$ M

pH = 1.3

(b) $K_w = [H^+]\,[OH^-]$

T , Kw

(c) $HA \longrightarrow H^+ + A^-$

$c(1 - a) \qquad ca \qquad ca$

$K_a = \dfrac{c\alpha^2}{1-\alpha}$ Þ $10^{-5} = 10^{-5} \times \dfrac{\alpha^2}{1-\alpha}$ Þ $\alpha = \dfrac{1}{2}$

(d) Le-Chatelier principle is applicable to common ion effect.

41. $pH = \dfrac{1}{2}(pK_w - pK_b - \log c) = \dfrac{1}{2}(14 - 5 - \log 2 \times 10^{-2}) = 5.35$

42. $Al(OH)_3 \longrightarrow Al^{3+} + 3OH^-$

s 3s + 0.2

» 0.2

$(0.2)^3 \times s = 2.4 \times 10^{-24}$ $\Rightarrow s = 3 \times 10^{-22}$ M

43. $Ksp = 4s^3 = 4 \times (1.84 \times 10^{-5})^3$

$Cd(OH)_2 \rightleftharpoons Cd^{2+} + 2OH^-$

s 28 + 0.01

» 0.01

$s \times (0.01)^2 = 4 \times (1.84 \times 10^{-5})^3$

$s = 2.49 \times 10^{-10}$ M

44. pH of 0.01 M HCl = 2

pH of 0.01 M NaOH = 12

pH of 0.01 M $CH_3COONa > 7$

pH of 0.01 M NaCl = 7

order of pOH : A > D > C > B

45. Acidic buffer solution contains weak acid and its salt with strong base.

Option (A) : Solution is containing strong acid and its salt with strong base.

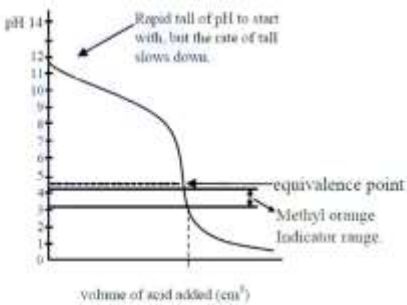
Option (B) : $\underset{0}{\overset{0.1\times100\text{mm}}{HCl_{(aq)}}} + \underset{10\text{mm}}{\overset{0.1\times200\text{mm}}{CH_3COONa_{(aq)}}} \longrightarrow \underset{10\text{mm}}{CH_3COOH_{(aq)}} + NaCl_{(aq)}$

Resulting solution contains weak acid and its salt with strong base.

Option (C) : $\underset{0}{\overset{0.1\times100\text{mm}}{CH_3COOH_{(aq)}}} + \underset{0}{\overset{0.1\times100\text{mm}}{NaOH_{(aq)}}} \longrightarrow \underset{10\text{mm}}{CH_3COONa_{(aq)}} + H_2O_{(l)}$

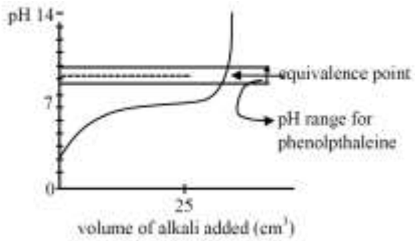
Resulting solution contains only salt of weak acid and strong base.

46. Titration curve for strong acid and weak base initially a buffer of weak base and conjugate acid is:



Formed, thus pH falls slowly and after equivalence point, so the pH falls sharply so methyl arrange,

having pH range of 3.2 to 4.4 will weak as indicator. So statement-I is correct.



Titration curve for weak acid and strong base (NaOH) Initially weak acid will form a buffer so pH

increases slowly but after equivalence point. It rises sharply covering range of phenolphthalein so it will

be suitable indicator so statement-II is false.

50. Let moles added = a

$$Ag^{+}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons Ag(NH_3)^{+}_{2(aq.)}$$

t = 0 $\quad 0.8 \quad \left(\frac{a}{2}\right)$

t = ∞ $\quad 5\times10^{-8} \quad \left(\frac{a}{2}-1.6\right) \quad 0.8$

$$\frac{0.8}{(5\times10^{-8})\left(\frac{a}{2}-1.6\right)^2} = 10^8$$

$$\Rightarrow \frac{a}{2} - 1.6 = 0.4 \Rightarrow a = 4$$

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

pH of 0.2 M solution

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

$$= \frac{1}{2}(4.7)\frac{1}{2}\log(0.2)$$

= 2.35 + 0.35 = 2.7

pH= 27×10^{-1}

52. $HCl + H_2SO_4$

$$\left[H^+\right] = \frac{(0.01\times 200)+(0.01\times 2\times 400)}{600}$$

$$= \frac{2+8}{600} = \frac{10}{600} = \frac{1}{60}$$

$$pH = -\log\left[\frac{1}{60}\right]$$

= 1.78

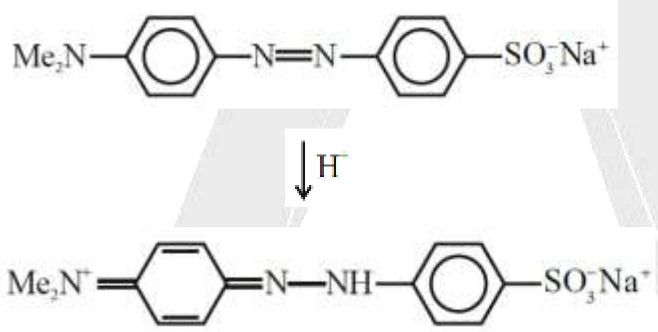
53. pOH = 14 – 8.26

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

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

Hence, NH_4Cl = 2 × 53.5 = 107 g

54.



(QUINONOID FORM)

55. In deionized water no common ion effect will take place so maximum solubility

EXERCISE # JEE-ADVANCED

1. $HCl + NaOH \longrightarrow NaCl + H_2O$

2m mol 3mmol 10 -

0 1mmol 2m mol -

$[OH^-] = \dfrac{1}{500} = 2\times10^{-3}$

pH = 11 + log2 = 11.3

2. pH = 8 $\Rightarrow$ pOH = 6

$[OH^-] = 10^{-6}$ M

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

$K_{sp} = 4s^2 = 4\times(6.7)^3\times10^{-18} = 1.2\times10^{-15}$

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

s $2s+10^{-6}$

$s(2s + 10^{-6}) = 1.2\times10^{-15}$

$s\times10^{-2} = 1.2\times10^{-15}$

$s = 1.2\times10^{-3}$ M

4. HCl $\Rightarrow$ pH < 7 NaCl $\Rightarrow$ pH = 7

NaCN $\Rightarrow$ pH > 7 $NH_4Cl \Rightarrow$ pH < 7

NaCN < NaCl > NH_4Cl > HCl

5. Amount of SO_2 in atmosphere = $\dfrac{10}{10^6} = 10\times10^{-6}$

Molar conc. of SO_2 in water = Amount of SO_2 × Solubility of SO_2

$= 10\times10^{-6}\times1.3653$

$= 1.3653\times10^{-5}$ M

$H_2SO_3 \longrightarrow H^+ + HSO_3^-$

$1.3653\times10^{-5} - x$ x x

$K_a = \dfrac{x^2}{1.3653\times10^{-5} - x} = 10^{-1.92}$

$x = 1.364\times10^{-5}$ pH = 4.865

6. Equation of $H_2C_2O_4.2H_2O$ = Equation of NaOH

$$\frac{10}{250}\times\frac{63}{126}\times 2 = 0.1\times V(L)$$

$$V(L) = \frac{1}{25}$$

V(mL) = 40

7. $A_pB_q(s) \longrightarrow pA^{q+}(aq) + qB^{p-}(aq)$

s ps qs

$K_{sp} = (ps)^p(qs)^q$

$= p^pq^q(s)^{p+q}$

8. $[CH_3COOH]_f = 0.1$ M

$[HCl]_f = 0.1$ M

(a) $CH_3COOH \longrightarrow CH_3COO^- + H^+$

0.1–x x x+0.1

$$1.75\times10^{-5} = \frac{x(x+0.1)}{0.1-x}$$

$x = 1.75\times10^{-5}$

$0.1\times\alpha = 1.75\times10^{-5}$

$a = 1.75\times10^{-4}$

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

(b) Moles of NaOH = $\frac{6}{40}$ = 0.15 mol

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

	CH_3COOH	NaOH	CH_3COONa	H_2O
n_i	0.1	0.05	0	-
n_f	0.05	0	0.05	-

0.1 moles NaOH will be consumed by 0.1 mol of HCl

$pH = pK_a = 4.75$

9. T increases , K_w increases , H^+, pH $^-$

10. Which has minimum value of K_{sp} i.e. HgS

11. $X^- + H_2O \longrightarrow 4X + OH^-$

$0.1(1-h) \quad\quad 0.1\,h \quad 0.1\,h$

$K_h = \frac{K_w}{K_a(HX)} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$

$K_h = \frac{Ch^2}{1-h} = \frac{0.1h^2}{1-h} = 10^{-9}$

$0.1\,h^2 = 10^{-9}$

$h^2 = 10^{-8}$

$h = 10^{-4}$

$\%\,h = 0.01\,\%$

12. At end point HA will completes reacts with NaOH

$HA + NaOH \longrightarrow NaOH + H_2O$

$[A^-] = 0.05\ M$

$pH = \frac{1}{2}(pK_w + pK_a + \log C)$

$= \frac{1}{2}(14 + 6 - \log 5 + \log 0.05)$

$= \frac{1}{2}(20 - \log 5 - \log 20)$

$\Rightarrow pH = 9$

13. $CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+Cl^-$

0.1 mol	0.08 mol	0
0.02 mol	0	0.05 mol

$[OH^-] = K_b \times \frac{[CH_3NH_2]}{[CH_3NH_3^+]}$

$= 5\times10^{-4} \times \frac{0.02}{0.08} = \frac{5}{4}\times10^{-4}$

$[H^+] = \frac{K_w}{[OH^-]} = \frac{4}{5}\times10^{-10} = 8\times10^{-11}\ M$

14. $CO_2 + H_2O \longrightarrow HCO_3^- + H^+$

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

15. For MX

$K_{sp} = s^2 = 4\times10^{-8}$

$s = 2\times10^{-4}$ M

For MX_2

$K_{sp} = 4s^2 = 32\times10^{-14}$

$s^2 = 8\times10^{-15}$

$s = 2\times10^{-5}$ M

For M_3X

$K_{sp} = 27s^4 = 2.7\times10^{-15}$

$s = 10^{-14}$ M

$MX > M_3X > MX_2$

16. $BOH + HCl \longrightarrow BCl + H_2O$

It equivalence point

Moles of BOH = moles of HCl

$$2.5\times\frac{2}{5} = \frac{2}{15}\times V(mL)$$

V(mL) = 7.5 mL

V_f = 10 mL

$$[BCl] = \frac{1}{10} = 0.1\ M$$

$$\underset{0.1(1-h)}{B^+} + H_2O \longrightarrow \underset{0.1-h}{BOH} + \underset{0.1-h}{H^+}$$

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

$$10^{-2} = \frac{0.1-h^2}{1-h}$$

h = 0.27

Þ $[H^+] = 0.1\times h = 0.027$ M

17. $$pH = \frac{1}{2}(pK_w + pK_a + \log C)$$

$= \frac{1}{2}(14 + 4 + \log 0.01) = \frac{1}{2} \times 16 = 8$

18. (A) $HNO_3 + CH_3COOH$ (S.A. + W.A.)

It can't be a buffer

(B) $KOH + CH_3COONa$ (S.B. + Salt)

It can't be a buffer

(C) $CH_3COONa + HNO_3 \longrightarrow CH_3COOH + NaNO_3$

It can form buffer if volume of CH_3COONa and HNO_3 is different.

(D) $CH_3COOH + CH_3COONa$

It is a buffer

19. For CuCl

$K_{sp} = s^2 = 10^{-6}$

$s = 10^{-3}$

$AgCl(s) \longrightarrow As^+(aq) + Cl^-(aq)$

$\quad s \quad s+10^{-3}$

$s(s + 10^{-3}) = 1.6\times10^{-10}$

$s\times10^{-3} = 1.6\times10^{-10}$

$s = 1.6\times10^{-7}$

20. For Ag_2CrO_4 $\quad K_{sp} = 1.1\times10{-12}$

$Ag_2CrO_4 \longrightarrow 2Ag^+(aq) + CrO_4^{2-}$

$\quad 2s+0.1 \quad s$

$\quad » 0.1$

$(0.1)^2 \times s = 1.1\times10^{-12}$

$8 = 1.1\times10^{-10}$ M

21. $r \propto [H^+]^1$

$$\frac{\sqrt{K_a \times C}}{1} = \frac{1}{100}$$

$\sqrt{K_a \times C} = 10^{-2}$

$K_a = 10^{-4}$

22. From exp.-1

$5.7\times1000 = C\times5.7$

From exp-2

$q = C\times5.6$

$q = 5.65$ kJ

$\Delta H = -\frac{5.6}{0.1} = -56$ kJ. / mol

$\Delta H_{ion} = -56 + 57 = 1$ kJ/ mol

23. $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

0.2 mol	0.1 mol	0	0
0.1 mol	0	0.1 mol	0

$pH - pK_a = 4.7$

24. $s = \sqrt{K_{sp}\left(\frac{H^+}{K_a}+1\right)}$

$= \sqrt{20\times10^{-10}\left(\frac{10^{-3}}{10^{-8}}+1\right)}$

$= \sqrt{2\times10^{-5}} = 4.47\times10^{-3}$ M

25. (P) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

2m mol	1m mol	0	-
1m mol	0	1m mol	-

If forms a buffer and pH does not change with dilution.

(Q) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

2m mol	2m mol	0	-
0	0	2m mol	-

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

$CH^+ = \sqrt{\frac{K_w \times K_a}{C}}$

$[H^+] \propto \frac{1}{\sqrt{C}}$

(R) $NH_3 + HCl \longrightarrow NH_4Cl$

2m mol 2m mol 0

0 0 2m mol

$NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$

$[H^+] = \sqrt{\frac{K_w}{K_b} \times C}$ Þ $[H^+] \propto \sqrt{C}$

(S) $Ni(OH)_2(s) \longrightarrow Ni^{2+}(aq) + 2OH^-(aq)$

On dilution $[OH^-]$ remains same in saturated solution of $Ni(OH)_2$

26. $B + HA \longrightarrow BH^{\oplus} + A^-$

0.1M 0.1M

0mL pH = 13

3 mL → 50% Neutralization pH = 11

6 mL → equivalence point pH = 3 to 9

Equivalence point

B	+	HA	$\longrightarrow$	$BH^+ + A^-$
0.1×6		0.1×6		
$= 0.6$ m mol		$= 0.6$ m mol		
0		0		0.6 m mol

Total volume $= 12$ml

Concentration of Salt $= \frac{0.6}{12}$

$pH = 6 = \sqrt{\frac{k_w}{k_b} \times c} = \sqrt{\frac{10^{-14} \times 0.6}{k_b \times 12}}$ $\{pH = 0.6, [H^+] = 10^{-6}\}$.

$\Rightarrow [H^+] = 10^{-6} = \sqrt{\frac{K_w}{K_b} \times \frac{0.1 \times 6}{12}}$

$10^{-12} = \frac{10^{-14} \times 10^{-1}}{K_b} \times \frac{1}{2}$

$k_b = 5 \times 10^{-4}$

$pk_b = -\log k_b = -\log(5 \times 10^{-4}) = -\log 5 + 4\log 10$

$pk_b = 4 - 0.7$

$pk_b = 3.3$

27. $[Zn^{+2}][S^{2-}] \le K_{sp}(ZnS)$

$[S^{2-}] \le \frac{5}{4} \times \frac{10^{-22}}{0.05}$

$H_2S \Leftrightarrow 2H^+ + s^{2-}$

$[S^{2-}] = \frac{K_{net} \times [H_2S]}{[H^+]^2}$

$\frac{K_{net} \times [H_2S]}{[H^+]^2} \leq \frac{5}{4} \times \frac{10^{-22}}{10^{-2} \times 5}$

$[H^+]^2 \geq \frac{10^{-21} \times 10^{-1} \times 4}{10^{-20}}$

$[H^+] \geq 2 \times 10^{-1} = 0.2$

Alternate:

$[Zn^{+2}][S^{2-}] \leq K_{sp}$

$[S^{2-}] \leq \frac{5}{4} \times \frac{10^{-22}}{0.05} = \frac{1}{4} \times 10^{-20}$

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

$[H^+]^2 = \frac{K_1 K_2 \times [H_2S]}{[S^{2-}]} = \frac{10^{-21} \times 0.1}{[S^{2-}]}$

$[S^{2-}] = \frac{10^{-22}}{[H^+]^2} \leq \frac{1}{4} \times 10^{-20}$

$[H^+] \geq 0.2$

28. First acid base reaction between H_2CO_3 and NaOH takes place.
In the final solution, we have 0.01 mole Na_2CO_3 and 0.02 moles of $NaHCO_3$.
Here, we have a buffer of $NaHCO_3$ and Na_2CO_3.

$\therefore pH = pK_{a_2} + \log \frac{[\text{ Salt }]}{|\text{ Acid }]}$

$= 10.32 + \log \frac{\left(\frac{0.01}{0.1}\right)}{\left(\frac{0.02}{0.1}\right)}$

$= 10.32 + \log \frac{1}{2}$

$= 10.32 - \log 2$

$= 10.32 - 0.3$

$= 10.02$

$\therefore pH = 10.02$

29. $H_2SO_4 \longrightarrow \underset{1M}{H_M^+} + HSO_4^{2-}$ (K_{a_1} is very large)

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}\ ^{1M^4}K_{a_2} = 1.2 \times 10^{-2}$

$[SO_4^{2\ 2}]$ coming from $Na_2SO_4 = 1.8 \times 10^{-2}$

$\frac{[SO_4^2][H^+]}{[HSO_4]} = \frac{1.8 \times 10^2 \times 1}{1} > K_{a_2}$

$\therefore$ Rather than dissociation of $HSO_4{}^-$into $H^+$and$SO_4{}^{2-}$ ions, association between already present $H^+$and $SO_4{}^{2-}$ will take place.

$\therefore [SO_4^{2-}] = 1.8 \times 10^{-2} - x$

$$\left.\begin{array}{r}[H^+] = 1 - x \approx 1 \\ [HSO_4^-] = 1 + x \approx 1\end{array}\right\}(\text{assuming } x << 1)$$

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

$\Rightarrow x = 0.6 \times 10^{-2}$

$[SO_4^{2-}] = 1.2 \times 10^{-2} M$

$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

If solubility of $PbSO_4 = sM$

$\therefore [Pb^{2+}] = s$

$[SO_4^{2}] = s + 1.2 \times 10^{-2} \approx 1.2 \times 10^{-2}$

(assuming $s \ll 1.2 \times 10^{-2}$)

$\therefore s \times 1.2 \times 10^{-2} = 1.6 \times 10^{-8}$

$$s = \frac{1.6}{1.2} \times 10^{-6} = 1.33 \times 10^{-6}$$

On comparing with $X \times 10^{-Y}$

$Y = 6$

30. $MX \rightleftharpoons M^{\oplus} + X^{\ominus}$

$X^{\ominus} + H^{\oplus} \rightleftharpoons HX$

$$S = \sqrt{K_{sp}\left(+\frac{H^{\oplus}}{K_a}\right)}$$

$$10^{-4} = \sqrt{K_{sp}\left(1 + \frac{10^{-7}}{K_a}\right)}$$

$$10^{-3} = \sqrt{K_{sp}\left(1 + \frac{10^{-2}}{K_a}\right)}$$

Squaring Equation [(1)/(2)] gives

$$10^{-2} = \frac{\left(1 + \frac{10^{-7}}{K_a}\right)}{\left(1 + \frac{10^{-2}}{K_a}\right)}$$

$$10^{-2}+\frac{10^{-4}}{K_a}=1+\frac{10^{-7}}{K_a}$$

$$\frac{10^{-4}-10^{-7}}{K_a}=0.99$$

$$\frac{10^{-4}}{K_a}=0.99$$

$$K_a=\frac{10^{-4}}{0.99}=\frac{1}{99}\times 10^{-2}$$

$$\mathrm{K}_a=2+\log\ 99=4$$