SOLUTIONS

EXERCISE # O-I

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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

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

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

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

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

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

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

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

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

$pOH = 3 \Rightarrow pH = 11$

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

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

16. $[H^+] = \sqrt{Ka_1C_1 + Ka_2C_2} = \sqrt{3\times10^{-4}\times0.03 + 1\times10^{-10}\times0.1} = 3 \times 10^{-3}$ 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. $[OH^-] = \sqrt{Ka_1C_1 + Ka_2C_2} = \sqrt{6.4\times10^{-5}\times\dfrac{0.1}{2} + 1.8\times10^{-5}\times\dfrac{4}{45}\times\dfrac{1}{2}} = \sqrt{\dfrac{8}{2}\times10^{-6}} = 2 \times 10^{-3}$ M

$pOH = 3 - \log 2$

$pH = 11 + \log 2 = 11.3$

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

0.01-x x 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)

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

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

» 0.1

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

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

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

0.1α 0.1 α_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. $[HPO_4^{2-}] = 10\ Ka_1\ Ka_2$

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

$10\ Ka_1\ Ka_2 - x$ $x + 0.1$ 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.

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

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

1/80(1 – h) h/80 h/80

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

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

$\% h = 2.48$

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

$0.01(1-h) \quad 0.01h \quad 0.01h$

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

$h^2 = \dfrac{10}{1.4} \times 10^{-4}$

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

$\% h = 2.67\%$

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

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

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

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

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

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

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

h does not depend on conc.

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

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

41. For 1 M NaCl & 1 M HCl solution

$\Rightarrow pH < 7$

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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. $pH = 5 + \log \frac{10 \times 1}{50 \times 2} = 5 - 1 = 4$

47. $pH = 10 - \log 5 + \log \frac{5 \times V_{mL}}{10 \times 2} = 9$

$\log \frac{5V_{mL}}{20} = \log 0.5$

V_{mL} = 2 mL

48. $4.74 = 5 - \log 1.34 + \log \frac{x}{0.02}$

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

49. $4 = 3.7 + \log \frac{0.1 \times V_{mL}}{50 \times 0.05}$

$2 = \frac{0.01 \times V_{mL}}{50 \times 0.05}$ $\Rightarrow V_{mL} = 50$ mL

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

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

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

$pOH = 1 \Rightarrow pH = 13$

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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

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

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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. $N_3PO_4 + NaH_2PO_4$

$NaH_2PO_4 + Na_2HPO_4$

$Na_2HPO_4 + Na_3PO_4$

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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

$w = 0.1 \times 84 = 8.4$ gm

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

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

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

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

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

85. (A) $K_{sp} = s^2$ $\quad s = \sqrt{80} \times 10^{-19}$ M

(B) $K_{sp} = s^2$ $\quad s = \sqrt{7} \times 10^{-8}$ M

(C) $K_{sp} = 108\ s^5 = 1 \times 10^{-72}$ $\quad s = \left(\dfrac{1000}{108}\right)^{1/5} \times 10^{-15}$ M

(D) $K_{sp} = 27\ s^4$ $\quad s = \left(\dfrac{180}{27}\right) \times 10^{-5}$ M

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

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

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

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

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

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

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

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

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

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

$$\frac{(s_1+s_2)s_1}{(s_1+s_2)s_2} = \frac{10^{-10}}{1.5\times10^{-11}} = \frac{100}{15}$$

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

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	10^{-7} M	10^{-7} M	0

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

So there will be no precipitation

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

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

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

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

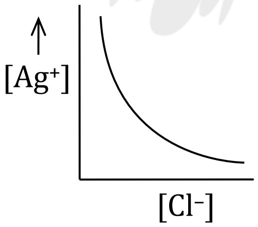
$(x - y)(10^{-5}) = 10^{-10}$

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

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

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

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.

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

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

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

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