



SOLUTIONS

EXERCISE # O-I

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$$K_w \quad \text{if} \quad T \quad K_{\text{eq}} = K_w$$

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

for pure water $[\text{H}^+] = [\text{OH}^-]$

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

3. $p\text{H}_i = 3 \Rightarrow [\text{H}^+]_i = 10^{-3} \text{ M}$

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

$$[\text{H}^+]_i V_i = [\text{H}^+]_f V_f$$

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

$$V_f = 1000 V_i$$

$$C_i = 1000 C_f$$

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

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

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

$$[\text{H}^+]_i = 10^4 [\text{H}^+]_f$$

5. $\text{pH} = 13, \text{ so } p\text{OH} = 1 \Rightarrow [\text{OH}^-] = 0.1$

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

$$\text{Moles of OH}^- = 0.025$$

$$\text{Mass of NaOH} = 0.025 \times 40 = 1 \text{ g}$$

6. pH of acid < 7

So pH sol should be 6 – 7

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

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

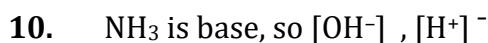
$$\text{Moles of H}^+ \text{ should be removed} = 10^{-2} - 10^{-3} = 0.009$$

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

9. Higher the K_a , stronger the acid



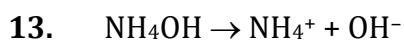
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$$0.1(1-\alpha) \quad 0.1\alpha \quad 0.1\alpha$$

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

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



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

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

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

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

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

16. $[H^+] = \sqrt{K_a_1 C_1 + K_a_2 C_2} = \sqrt{3 \times 10^{-4} \times 0.03 + 1 \times 10^{-10} \times 0.1} = 3 \times 10^{-3} M$

$$[A^-] = \frac{3 \times 10^{-4} \times 0.03}{3 \times 10^{-3}} = 3 \times 10^{-3} M$$

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

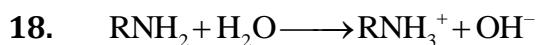
17. $[OH^-] = \sqrt{K_a_1 C_1 + K_a_2 C_2} = \sqrt{6.4 \times 10^{-5} \times \frac{0.1}{2} + 1.8 \times 10^{-5} \times \frac{4}{45} \times \frac{1}{2}} = \sqrt{\frac{8}{2} \times 10^{-6}} = 2 \times 10^{-3} M$

$$pOH = 3 - \log 2$$

$$pH = 11 + \log 2 = 11.3$$



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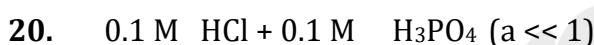
$$0.01-x \quad x \quad x$$

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

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

$$x = 10^{-4}$$

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



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

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

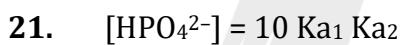
$$K_{a1} = \frac{0.1 \times 0.1\alpha}{0.1} \Rightarrow a = 10 K_{a1}$$



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

$$K_{a2} = \frac{0.1 \times [\text{HPO}_4^{2-}]}{0.1\alpha}$$

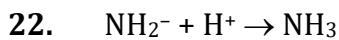
$$[\text{HPO}_4^{2-}] = \alpha K_2 = 10 K_{a1} K_{a2}$$



$$10 K_{a1} K_{a2} - x \quad x + 0.1 \quad x \\ \gg 0.1$$

$$K_{a3} = \frac{0.1 \times x}{10 K_{a1} K_{a2} - x} = \frac{0.1 \times x}{10 K_{a1} K_{a2}}$$

$$[\text{PO}_4^{3-}] = x = 100 K_{a1} K_{a2} K_{a3}$$



$$\text{Base} \quad \text{C.A.}$$



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24. Bronsted acid → which can give H⁺



Acid Base C.A C.B.



$$K_{\text{eq}} = \frac{1}{K_h} = \frac{K_a}{K_w} = \frac{1.8 \times 10^{-5}}{10^{-14}} = 1.8 \times 10^9$$

26. Ka HF × Kb F⁻ = Kw

$$pK_a = 14 - 10.83 = 3.17$$

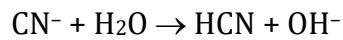
$$K_a = 10^{-3.17} = 6.75 \times 10^{-4}$$

28. At 85°C neutral pH < 7

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

30. (A) 0.1 M NaCl $\Rightarrow \text{pH} = 7$
 (B) 0.1 M NH₄Cl $\Rightarrow \text{pH} < 7$
 (C) 0.1 M CH₃COONa $\Rightarrow \text{pH} > 7$
 (D) 0.1 M HCl $\Rightarrow \text{pH} = 1$

31. $h = \sqrt{\frac{K_w \times C}{K_a}} = \sqrt{\frac{10^{-14} \times 1/80}{1.3 \times 10^{-9}}} = \sqrt{\frac{10^{-6}}{8 \times 1.3}}$



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

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



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

$$\% h = 2.48$$



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

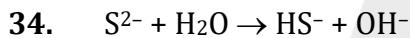
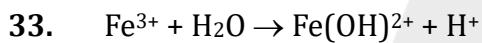
$$\frac{10^{-14}}{1.4 \times 10^{-9}} = \frac{0.01h^2}{1-h}$$

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

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

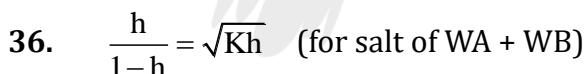
$$\% h = 2.67\%$$

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

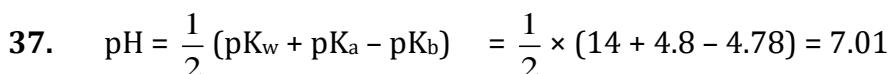


$$Kh_1 = \frac{K_w}{K_{a_3}}$$

$$\text{pH} = \frac{1}{2} (\text{pK}_w + \text{pK}_{a_3} + \log C)$$



h does not depend on conc.



38. Amphiprotic species @ which can give as well as take H⁺ ion.

41. For 1 M NaCl & 1 M HCl solution

$$\Rightarrow \text{pH} < 7$$



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

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

$$V_{mL} = 2 \text{ mL}$$

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

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

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

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

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



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

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

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



10 mmol	x mmol	10 mmol	-
10-x	0	10+x	-

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

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

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

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

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

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

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

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

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

$$\text{pOH} = 1 \Rightarrow \text{pH} = 13$$



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0.5 mmol 1 mmol

0 0 1 mmol

Solution will be neutral so pH = 7



M Moles of OH⁻ = 5

$$[\text{H}^+]_f = \frac{10}{100} = \frac{1}{10} \quad \text{p} \quad \text{pH}_f = 1$$



mmi	4	2	0	0
mmf	2	0	2	2



mm : 16 8 0 0

mmf 8 0 8 -

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

$$\text{pOH} = 10.3$$

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

63. $\text{pH} = \text{pKa} = 3.7$



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

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

$$\text{pH} = 5 \quad (50\% \text{ neutralization})$$

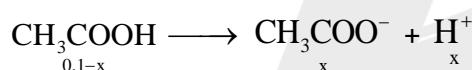
$$\text{pH} = 5 + \log \frac{75}{25} \quad (75\% \text{ neutralization})$$

$$= 5 - \log 3$$



mmi	2	2	0	0
mmf	0	0	2	-

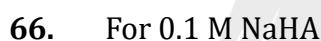
$$[\text{CH}_3\text{COOH}] = \frac{2}{20} = 0.1$$



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

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

$$\text{pH} = 2.88$$

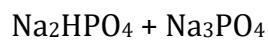
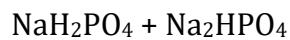


$$\text{pH} = \frac{7+11}{2} = 9$$

for 0.1 M H₂A pH < 7

for 0.1 M Na₂A pH > 7

for 0.1 M NaHA + 0.1 M Na₂A \Rightarrow pH = pK_{a2} = 11





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$$\begin{array}{ccccc} \text{mmi} & 9 & 5 & 0 & 0 \\ \text{mm}_f & 4 & 0 & 5 & - \end{array}$$

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

69.

$$\text{pH} = \text{pK}_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

70. $\text{pH} = \text{pK}_{\text{In}} \pm 1$

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

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

73. For HCl Vs NH₄OH \Rightarrow pH range (3 – 8.5)

74. For NaOH Vs H₂C₂O₄ titration
pH range is (11 – 5.5)

75. Oxalic acid Vs KMnO₄ titration is a redox titration.

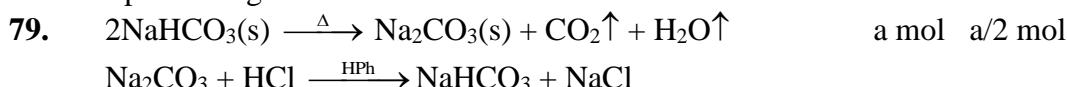
76. For WA Vs SB titration

pH range is 5.5 – 11. So suitable indicator is Hph.

78. $\text{pH}_i = \text{pK}_a + \log \frac{20}{80}$

$$\text{pH}_f = \text{pK}_a + \log \frac{80}{20}$$

$$\Delta \text{pH} = 2 \log 4 = 1.2$$



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

$$a = 0.1 \text{ mol}$$

$$w = 0.1 \times 84 = 8.4 \text{ gm}$$

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



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

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

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

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

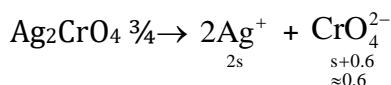
(D) $K_{sp} = 27 s^4$

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

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

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

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



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

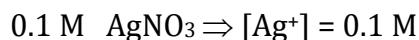
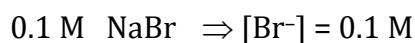
$$4s^2 = 14.4 \times 10^{-13}$$

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

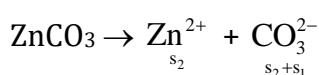
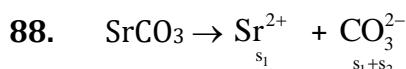
$$s = 6 \times 10^{-7} M$$



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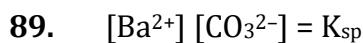


In case of $0.1 \text{ M } \text{CaBr}_2$, morality of common ion is maximum so. There maximum common ion effect.



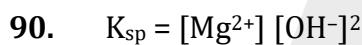
$$\frac{(s_1 + s_2)s_1}{(s_1 + s_2)s_2} = \frac{10^{-10}}{1.5 \times 10^{-11}} = \frac{100}{15}$$

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



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

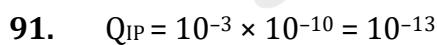
$$[\text{Ba}^{2+}] = 5.1 \times 10^{-5} \text{ M}$$



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

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

$$\text{pOH} = 5 \text{ p } \text{pH} = 9$$



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



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

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

So there will be no precipitation



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

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

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

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

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



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

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

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

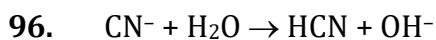
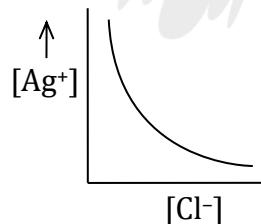
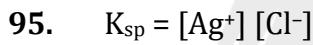
$$(x - y)(4 \times 10^{-5} - y) = 10^{-10}$$

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

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

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

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



Solubility if $[\text{OH}^-]$, $[\text{H}^+]$, pH^-

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



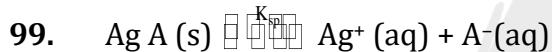
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$$\begin{array}{ccc} x & 0.8 & 0.1 \\ \text{Ag}(\text{NH}_3)_2^+ & \rightleftharpoons & \text{Ag}(\text{NH}_3)^+ + \text{NH}_3 \end{array}$$

$$\begin{array}{ccc} 0.1 - x & x & 0.8 + x \\ \sim 0.1 & & \sim 0.8 \end{array}$$

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



$$\begin{array}{ccc} S & S-x & \\ \text{A}^-(\text{aq}) + \text{H}_2\text{O} & \rightleftharpoons & \text{AH}(\text{aq}) + \text{OH}^-(\text{aq}) \end{array}$$

$$\begin{array}{ccc} S-x & x & x \end{array}$$

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

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

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

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