

1. For a 0.1 M aqueous solution of a sodium acetate,  $\text{CH}_3\text{COONa}$ , one mass balance is simply  $[\text{Na}^+] = 0.1\text{M}$ . Write a mass balance involving acetate (7 pt).

$$[\text{CH}_3\text{COO}^-] + [\text{CH}_3\text{COOH}] = 0.1\text{ M}$$

2. How many moles of  $\text{PbO}$  will dissolve in 1.00 L of water if pH is fixed at 10.5? (12 pts) Consider the equilibrium:

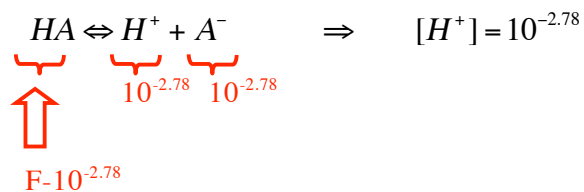


$$K = 5.0 \cdot 10^{-16} = [\text{Pb}^{2+}][\text{OH}^-]^2$$

$$K_w = 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \Rightarrow \quad [\text{OH}^-] = \frac{K_w}{10^{-10.5}} = \frac{10^{-14}}{10^{-10.5}} = 10^{-3.5}\text{ M}$$

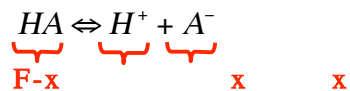
$$\text{Solubility} = [\text{Pb}^{2+}] = \frac{K}{[\text{OH}^-]^2} = \frac{5.0 \cdot 10^{-16}}{(10^{-3.5})^2} = 5.0 \cdot 10^{-9}\text{ M}$$

3. A 0.045 M solution of benzoic acid has a pH of 2.78. Calculate  $\text{p}K_a$  for this acid. (5 pts)



$$K_a = \frac{(10^{-2.78})^2}{(0.045 - 10^{-2.78})} = 6.4 \cdot 10^{-5} \quad \text{p}K_a = 4.19$$

4. A 0.045 M solution of HA is 0.6 % dissociated. Calculate pKa for this acid. (5 pts)



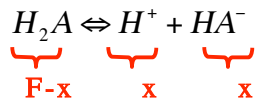
$$\alpha = 0.006 = \frac{x}{F}$$

$$x = 0.006 \times 0.045 = 0.00027$$

$$K_a = \frac{x^2}{F - x} = \frac{(0.00027)^2}{0.045 - 0.00027} = 1.6 \cdot 10^{-6} \quad pK_a = 5.79$$

5. Consider the diprotic acid H<sub>2</sub>A with K<sub>1</sub> = 1.0×10<sup>-4</sup> and K<sub>2</sub> = 1.0×10<sup>-8</sup> Find the pH and concentrations of H<sub>2</sub>A, HA<sup>-</sup> and A<sup>2-</sup> in:

(a) 0.1 M H<sub>2</sub>A, (7 pts)



$$K_1 = 1.0 \cdot 10^{-4} = \frac{x^2}{F - x} \Rightarrow x = 3.11 \cdot 10^{-3} = [H^+] = [HA^-] \Rightarrow pH = 2.51$$

$$[H_2A] = 0.1 - x = 0.0969 M$$

$$[A^{2-}] = \frac{K_2[HA^-]}{[H^+]} = 1 \cdot 10^{-8} M$$

(b) 0.1 M NaHA (7 pts)

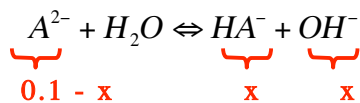
$$[H^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}} = 1 \cdot 10^{-6} M \Rightarrow pH = 6.0$$

$$[HA^-] \approx 0.1M$$

$$[H_2A] = \frac{[H^+][HA^-]}{K_1} = 1 \cdot 10^{-3} M$$

$$[A^{2-}] = \frac{K_2[HA^-]}{[H^+]} = 1 \cdot 10^{-3} M$$

(c) 0.1 Na<sub>2</sub>A (7 pts)



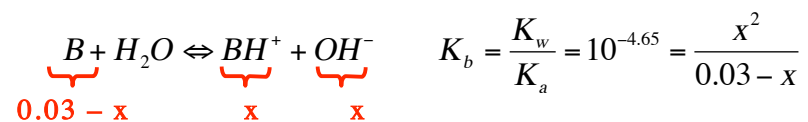
$$\frac{x^2}{0.1 - x} = \frac{K_w}{K_2} = \frac{10^{-14}}{1 \cdot 10^{-8}} = 10^{-6} \Rightarrow x = [OH^-] = [HA^-] = 3.16 \cdot 10^{-4} M \Rightarrow pH = 10.5$$

$$[A^{2-}] = 0.1 - x = 9.97 \cdot 10^{-2} M$$

$$[H_2A] = \frac{[H^+][HA^-]}{K_1} = 1 \cdot 10^{-10} M$$

6. A 50 mL solution of 0.03 M benzylamine (pK<sub>a</sub> = 9.35) was titrated with 0.05 M HCl. Calculate the pH at the following volumes of added acid:

(a) 0 mL (10 pts)

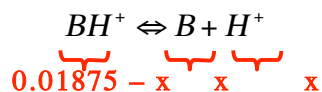


$$x = 8.31 \cdot 10^{-4} M \Rightarrow pH = 10.92$$

(b) Ve (10 pts)

$$V_e = \frac{50 \text{ mL} \cdot 0.03 \text{ M}}{0.05 \text{ M}} = 30 \text{ mL}$$

$$[BH^+] = \left( \frac{50 \text{ mL}}{50 \text{ mL} + 30 \text{ mL}} \right) \times 0.03 = 0.01875 \text{ M}$$



$$\frac{x^2}{0.01875 - x} = K_a = 10^{-9.35} \Rightarrow x = 2.96 \cdot 10^{-6} \text{ M} \Rightarrow \text{pH} = 5.53$$

7. Calculate  $\alpha_{Y^{4-}}$  for EDTA ( $K_1 = 1.0$ ,  $K_2 = 0.032$ ,  $K_3 = 0.010$ ,  $K_4 = 0.0022$ ,  $K_5 = 6.9 \times 10^{-7}$ ,  $K_6 = 5.8 \times 10^{-11}$ ) at:

(a) pH 3.6 (7 pts)

$$[H^+] = 10^{-3.6} \text{ M}$$

$$\alpha_{Y^{4-}} = \frac{K_1 K_2 K_3 K_4 K_5 K_6}{[H^+]^6 + [H^+]^5 K_1 + [H^+]^4 K_1 K_2 + [H^+]^3 K_1 K_2 K_3 + [H^+]^2 K_1 K_2 K_3 K_4 + [H^+] K_1 K_2 K_3 K_4 K_5 + K_1 K_2 K_3 K_4 K_5 K_6}$$

$$\alpha_{Y^{4-}} = 5.66 \cdot 10^{-10}$$

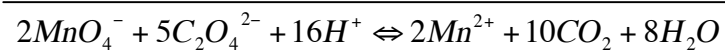
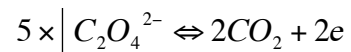
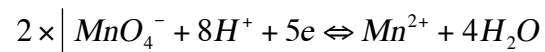
(b) pH 11.0. (7 pts)

$$[H^+] = 10^{-11} \text{ M}$$

$$\alpha_{Y^{4-}} = \frac{K_1 K_2 K_3 K_4 K_5 K_6}{[H^+]^6 + [H^+]^5 K_1 + [H^+]^4 K_1 K_2 + [H^+]^3 K_1 K_2 K_3 + [H^+]^2 K_1 K_2 K_3 K_4 + [H^+] K_1 K_2 K_3 K_4 K_5 + K_1 K_2 K_3 K_4 K_5 K_6}$$

$$\alpha_{Y^{4-}} = 0.85$$

8. A 50 mL sample containing  $\text{La}^{3+}$  was treated with sodium oxalate to precipitate  $\text{La}_2(\text{C}_2\text{O}_4)_3$ , which was washed, dissolved in acid, and titrated with 18.04 mL of 0.006363 M  $\text{KMnO}_4$ . Calculate the molarity of  $\text{La}^{3+}$  in the unknown. (16 pts)



$$n_{\text{MnO}_4^-} = 18.04 \text{ mL} \cdot 0.006363 \text{ M} = 0.1148 \text{ mmoles}$$

$$n_{\text{C}_2\text{O}_4^{2-}} = \frac{5}{2} n_{\text{MnO}_4^-} = 0.2870 \text{ mmoles}$$

$$n_{\text{La}^{3+}} = \frac{2}{3} n_{\text{C}_2\text{O}_4^{2-}} = 0.1913 \text{ mmoles}$$

$$[\text{La}^{3+}] = \frac{n_{\text{La}^{3+}}}{50 \text{ mL}} = \frac{0.1913 \text{ mmoles}}{50 \text{ mL}} = 3.826 \text{ mM}$$