Chem201, Winter 2006
Midterm N2
02/21/06

Name Answer Key_____

SID_____

1. For a 0.1 M aqueous solution of a sodium acetate, CH_3COONa, one mass balance is simply $[Na^+] = 0.1M$. Write a mass balance involving acetate (7 pt).

$$[CH_3COO^-] + [CH_3COOH] = 0.1\,M$$

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

$$PbO + H_2O \Leftrightarrow Pb^{2+} + 2OH^- \qquad K = 5.0 \cdot 10^{-16}$$

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

$$K_w = 10^{-14} = [H_3O^+][OH^-] \quad \Rightarrow \quad [OH^-] = \frac{K_w}{10^{-10.5}} = \frac{10^{-14}}{10^{-10.5}} = 10^{-3.5}\,M$$

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

3. A 0.045 M solution of benzoic acid has a pH of 2.78. Calculate pK_a for this acid. (5 pts)

$$HA \Leftrightarrow H^+ + A^- \quad \Rightarrow \quad [H^+] = 10^{-2.78}$$

HA: F-$10^{-2.78}$; H^+: $10^{-2.78}$; A^-: $10^{-2.78}$

$$K_a = \frac{(10^{-2.78})^2}{(0.045 - 10^{-2.78})} = 6.4 \cdot 10^{-5} \qquad pK_a = 4.19$$

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

$$\underbrace{HA}_{F-x} \Leftrightarrow \underbrace{H^+}_{x} + \underbrace{A^-}_{x}$$

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

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

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

5. Consider the diprotic acid H_2A with $K_1 = 1.0\times10^{-4}$ and $K_2 = 1.0\times10^{-8}$ Find the pH and concentrations of H_2A, HA- and A^{2-} in:

(a) 0.1 M H_2A, (7 pts)

$$\underbrace{H_2A}_{F-x} \Leftrightarrow \underbrace{H^+}_{x} + \underbrace{HA^-}_{x}$$

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

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

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

(b) 0.1 M NaHA (7 pts)

$$[H^+] = \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}} = 1 \cdot 10^{-6} M \quad \Rightarrow \quad pH = 6.0$$

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

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

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

(c) 0.1 Na_2A (7 pts)

$$\underbrace{A^{2-}}_{0.1 - x} + H_2O \Leftrightarrow \underbrace{HA^-}_{x} + \underbrace{OH^-}_{x}$$

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

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

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

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

(a) 0 mL (10 pts)

$$\underbrace{B}_{0.03 - x} + H_2O \Leftrightarrow \underbrace{BH^+}_{x} + \underbrace{OH^-}_{x} \qquad K_b = \frac{K_w}{K_a} = 10^{-4.65} = \frac{x^2}{0.03 - x}$$

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

(b) Ve (10 pts)

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

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

$$BH^+ \Leftrightarrow B + H^+$$

$$0.01875 - x \quad x \quad x$$

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

7. Calculate α_{Y4-} for EDTA ($K_1 = 1.0$, $K_2 = 0.032$, $K_3 = 0.010$, $K_4 = 0.0022$, $K_5 = 6.9\times10^{-7}$, $K_6 = 5.8\times10^{-11}$) at:

(a) pH 3.6 (7 pts)

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

$$\alpha_{Y^{4-}} = \frac{K_1K_2K_3K_4K_5K_6}{[H^+]^6 + [H^+]^5K_1 + [H^+]^4K_1K_2 + [H^+]^3K_1K_2K_3 + [H^+]^2K_1K_2K_3K_4 + [H^+]K_1K_2K_3K_4K_5 + K_1K_2K_3K_4K_5K_6}$$

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

(b) pH 11.0. (7 pts)

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

$$\alpha_{Y^{4-}} = \frac{K_1K_2K_3K_4K_5K_6}{[H^+]^6 + [H^+]^5K_1 + [H^+]^4K_1K_2 + [H^+]^3K_1K_2K_3 + [H^+]^2K_1K_2K_3K_4 + [H^+]K_1K_2K_3K_4K_5 + K_1K_2K_3K_4K_5K_6}$$

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

8. A 50 mL sample containing La^{3+} was treated with sodium oxalate to precipitate $La_2(C_2O_4)_3$, which was washed, dissolved in acid, and titrated with 18.04 mL of
0.006363 M $KMnO_4$. Calculate the molarity of La^{3+} in the unknown. (16 pts)

$$2 \times \left| MnO_4^- + 8H^+ + 5e \Leftrightarrow Mn^{2+} + 4H_2O \right.$$

$$5 \times \left| C_2O_4^{2-} \Leftrightarrow 2CO_2 + 2e \right.$$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \Leftrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$$n_{MnO_4^-} = 18.04\ mL \cdot 0.006363\ M = 0.1148\ mmoles$$

$$n_{C_2O_4^{2-}} = \frac{5}{2} n_{MnO_4^-} = 0.2870\ mmoles$$

$$n_{La^{3+}} = \frac{2}{3} n_{C_2O_4^{2-}} = 0.1913\ mmoles$$

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