**CHM1311 D: Principles of Chemistry (Prof. N. Goto)**
**Assignment #7**
**Due Nov 23rd, at the beginning of class. Late assignments will not be accepted.**

Assignments can be submitted individually, or by groups of up to 4 students.

**1) Last Name:** ________________ **First Name:** ______________ **Student ID:** ______________

**2) Last Name:** ________________ **First Name:** ______________ **Student ID:** ______________

**3) Last Name:** ________________ **First Name:** ______________ **Student ID:** ______________

**4) Last Name:** ________________ **First Name:** ______________ **Student ID:** ______________

Solutions must be written legibly, in the space provided. Adequate detail to the calculation (including units, appropriate sig figs) must be provided to make it possible for other students to understand how you arrived at the final solution. If more space is needed, use the back of the page. Do not add extra pages, as they will not be marked. Assignment pages must be stapled together.

**NOTE:** For each question a hint, reference to an Office Hours video, or an Interactive LearningWare (ILW) problem in WileyPLUS is given in brackets.

**You will need to use the data in Appendix E of the textbook for some of the questions.**

**Question 1. (ILW 16.13)**

What mass of acetic acid ($CH_3CO_2H$) must be added to 1.45 L of 0.40 M sodium acetate to make a buffer solution whose pH=5.25? (3 marks)

$pK_a = 4.75$

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

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{pH-pK_a} = 10^{5.25-4.75} = 3.16$$

$$[CH_3COOH] = \frac{[CH_3COO^-]}{3.16} = \frac{0.40\ M}{3.16} = 0.12\bar{6}\ M$$

$$m = nM = cVM = (0.12\bar{6}\ M)(1.45\ L)(60.05\ g\ mol^{-1})$$

$$= 11\ g$$

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**Question 2. (Similar to problem covered Nov 9th, 5th slide)**

Consider a buffer solution that contains 0.30 M $NH_4Cl$ and 0.10 M $NH_3$.

a) Calculate its pH. (2 marks)

$pK_b = 4.75$

$pK_a = 14 - 4.75 = 9.25$

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]}$$

$$= 9.25 + \log\left(\frac{0.10M}{0.30M}\right)$$

$$= 8.77$$

b) Calculate the change in pH if 0.100 g of solid NaOH is added to 200.0 mL of this solution. (4 marks)

$$C_{OH} = \frac{m}{MV} = \frac{0.100g}{(39.997\ g\ mol^{-1})(0.2000L)}$$

$$= 0.0125\ mol\ L^{-1}$$

| | $NH_4^+$ | $+ OH^-$ | $\rightarrow NH_3 + H_2O$ |
|---|---|---|---|
| I | 0.30 | 0.0125 | 0.10 |
| C | -0.0125 | -0.0125 | 0.0125 |
| F | 0.287$\bar{2}$ | $\emptyset$ | 0.11$\bar{2}$5 |

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]}$$

$$= 9.25 + \log\frac{(0.112\bar{5})}{0.2\bar{8}72}$$

$$= 8.84$$

c) If the acceptable buffer range of the solution is ±0.10 pH units, calculate how many moles of $H_3O^+$ can be neutralized by 250 mL of the initial buffer. (4 marks)

$$H_3O^+ + NH_3 \longrightarrow NH_4 + H_2O$$

WE WANT TO KNOW HOW MUCH $H_3O^+$ CAN BE ADDED TO LOWER pH BY MORE THAN 0.10 - NEW pH WOULD BE 8.77 - 0.10 = 8.67

NEW $[NH_3] = [NH_3]_0 - [H_3O^+]_{ADDED}$

$[NH_4^+] = [NH_4^+]_0 + [H_3O^+]_{ADDED}$

PUT INTO H-H EQUATION:

$$pH = pK_a + \log\frac{[NH_3]_0 - [H_3O^+]_{ADDED}}{[NH_4^+]_0 + [H_3O^+]_{ADDED}}$$

$$\frac{[NH_3] - [H_3O^+]}{[NH_4^+] + [H_3O^+]} = 10^{pH - pK_a} = 10^{8.67-9.25} = 0.264\bar{8}$$

$$[NH_3] - [H_3O^+] = 0.264\bar{8}([NH_4^+] + [H_3O^+])$$

$$\frac{[NH_3] - 0.2648[NH_4^+]}{1.264\bar{8}} = [H_3O^+]_{ADDED}$$

$$[H_3O^+]_{ADDED} = 0.0162\bar{6}\ M$$

$$n = cV$$

$$= (0.0162\bar{6}\ M)(0.250\ L)$$

$$= 4.07 \times 10^{-3}\ mol$$

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**Question 3. (Video 16.23)**

Metolazone is a weakly basic ($pK_b$ = 4.30) diuretic used to treat congestive heart failure. For analysis of the metolazone content of a generic brand pill, a titration is carried out with strong acid. It takes 50.00 mL of 0.100 M acid to reach the stoichiometric point. The initial metalazone concentration is 0.025 M and the solution volume is 200. mL. Calculate the pH of this solution at the following points:

a) Initial pH. (3 marks)

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad K_b = 5.01\times10^{-5}$$

| | B | | $BH^+$ | $OH^-$ |
|---|---|---|---|---|
| I | 0.025 | | ∅ | ≈0 |
| C | −x | | x | x |
| E | 0.025 − x | | x | x |

$$K_b = \frac{x^2}{0.025-x} \approx \frac{x^2}{0.025}$$

$$x = \sqrt{0.025\,K_b} = 1.12\times10^{-3}\text{ M} = [OH^-]$$

pOH = 2.95

pH = 11.05

$[B]_{eq} \approx [B]_0$ VALID?

$$\%\text{ERROR} = \frac{x}{0.025-x}\times100\%$$

$= 4.7\%$

∴ VALID

b) After addition of 19.50 mL of acid (4 marks)

$$n_{H_3O^+} = C_{H_3O^+}V_{H_3O^+} = (0.100\text{ M})(19.50\times10^{-2}\text{ L}) = 1.950\times10^{-3}\text{ mol}$$

$$n_B = C_BV_B = (0.025\text{ M})(0.200\text{ L}) = 0.005\text{ mol}$$

$$n_{B,EXCESS} = n_B - n_{H_3O^+} = 0.005\text{ mol} - 0.00195\text{ mol} = 0.00305\text{ mol}$$

$$[B] = \frac{n_{B,EXCESS}}{V_B + V_{H_3O^+}} = \frac{0.00305\text{ mol}}{0.200\text{ L} + 0.01950\text{ L}} = 0.0139\text{ M}$$

$$[BH^+] = \frac{n_{H_3O^+}}{V_{TOTAL}} = \frac{0.01950\text{ mol}}{0.21950\text{ L}} = 0.00888\text{ M}$$

$$pK_a = 14.00 - pK_b = 9.70$$

$$pH = pK_a + \log\frac{[B]}{[BH^+]} = 9.70 + \log\left(\frac{0.0139}{0.00888}\right) = 9.89$$

c) After addition of 25.00 mL of base solution. (1 mark)

∵ 25.00 mL IS HALF-WAY TO STOICHIOMETRIC POINT

∴ $n_B = n_{BH^+}$

∴ $\frac{[B]}{[BH^+]} = 1$ ∴ $pH = pK_a$

$= 9.70$

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d) At the stoichiometric point. (5 marks) ALL B CONVERTED TO $BH^+$

$$[BH^+] = \frac{n_B}{V_{H_3O^+} + V_B} = \frac{0.005 \text{ mol}}{0.200 L + 0.050 L} = 0.02 \text{ M}$$

| | $BH^+$ | $+ H_2O \rightleftharpoons$ | $B$ | $+ H_3O^+$ |
|---|---|---|---|---|
| I | 0.20 | | 0 | ≈0 |
| C | −x | | x | x |
| E | 0.20 −x | | x | x |

$$K = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20} \quad x = \sqrt{K_a (0.20)}$$
$$= \sqrt{10^{-9.7}(0.20)}$$
$$= 1.998 \times 10^{-6} M$$
$$= [H_3O^+]$$
$$\therefore pH = 5.7$$

e) After addition of 56.8 mL base solution. (3 marks)

$$C_{H_3O^+, EXCESS} = \frac{n_{H_3O^+} - n_B}{V_{H_3O^+} + V_B} = \frac{C_{H_3O^+} V_{H_3O^+} - n_B}{V_T}$$
$$= \frac{(0.100 M)(0.0568 L) - 0.005 \text{ mol}}{0.2568 L}$$
$$= 2.65 \times 10^{-3} M$$
$$pH = 2.58$$

f) Choose an indicator from Table 6.2 of the textbook (Chapter 16, slide 30) that would be most appropriate for this titration. (1 mark)

∵ pH @ STOICHIOMETRIC POINT IS 5.7

∴ USE BROMOCRESOL PURPLE (ITS $pK_a$ IS CLOSEST @ 6.3)

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**Question 4. (ILW 16.37)**

How many grams of $CaCO_3$ will dissolve in 0.875 L of 0.200 M $Ca(NO_3)_2$ solution? (4 marks)

$CaCO_{3(s)} \rightarrow Ca^{2+} + CO_3^{2-}$

I: — 0.200 ∅

C: +s +s

E: — 0.200+s s

$K_{sp} = 3.36\times10^{-9} = (0.200+s)s \approx 0.200s$

$\therefore s = 1.68\times10^{-8}$ M = SOLUBILITY OF $CaCO_3$ IN 0.200M $Ca(NO_3)_2$

$m = nM = cVM$

$= (1.68\times10^{-8}\,M)(0.875L)(100.09\,\frac{g}{mol})$

$= 1.47\times10^{-6}$ g

$= 1.47$ µg

**Question 5. (Calculate Q)**

If 0.21 g of solid $BaF_2$ is added to 400 mL of water, will all the solid dissolve? (4 marks)

$n_{BaF_2} = \frac{m}{M} = \frac{0.21g}{175.34\ g/mol} = 1.20\times10^{-3}$ mol

$n_{Ba^{2+}} = n_{BaF_2}$

$n_{F^-} = n_{BaF_2} \times \frac{2\,mol\,F^-}{1\,mol\,BaF_2} = 0.00240$ mol

$[Ba^{2+}] = \frac{n}{V} = \frac{0.00120\ mol}{0.400L} = 2.99\times10^{-3}$ M

$[F^-] = \frac{n}{V} = \frac{0.00538\ mol}{0.400L} = 0.00599$ M

$Q_{sp} = [Ba^{2+}][F^-]^2$

$= (2.99\times10^{-3})(5.99\times10^{-3})^2$

$= 1.1\times10^{-7}$

$K_{sp} = 1.8\times10^{-7}$

$\because Q_{sp} < K_{sp}$

$\therefore BaF_{2(s)}$ WILL ALL DISSOVE

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**Question 6. (Hint: Calculate the maximum concentration of hydroxide ions that can be present in the solution before each ion precipitates)**

a) Can $Cr^{3+}$ be separated from $Ca^{2+}$ by the addition of an NaOH solution to an acidic solution that contains 0.530 M $Ca^{2+}$ and 0.130 M $Cr^{3+}$? Assume that the initial concentration of OH- is zero for these calculations. (5 marks)

$K_{sp} = 5.0\times10^{-6}$

$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$

| | $Ca^{2+}$ | $OH^-$ |
|---|---|---|
| I | 0.530 | Ø |
| C | +x | +2x |
| E | 0.530+x | 2x |

$K_{sp} = 4x^2(0.530+x) \approx 4x^2(0.530)$

$x = 0.00154$ M $[OH^-] = 2(0.00154\text{ M}) = 0.00307$ M

$Cr(OH)_{3(s)} \rightleftharpoons Cr^{3+}_{(aq)} + 3OH^-_{(aq)}$

$K_{sp} = 6.3\times10^{-31}$

| | $Cr^{3+}$ | $OH^-$ |
|---|---|---|
| I | 0.130 | Ø |
| C | +x | +3x |
| E | 0.130+x | 3x |

$K_{sp} = (0.130+x)(3x)^3$

$\approx 0.130(9x^3)$

$x = 5.61\times10^{-11}$

$[OH^-] = 3x = 1.69\times10^{-10}$ M

∴ IT IS POSSIBLE TO PRECIPITATE THE CHROMIUM BY RAISING THE [OH⁻] UP TO THE CONCENTRATION FOUND @ THE SOLUBILITY LIMIT OF $Ca(OH)_2$.

b) At what hydroxide ion concentration will the second cation precipitate? (i.e. the cation of the more soluble salt.) This was calculated in part (a). (1 mark)

WE WOULD START TO SEE PRECIPITATION OF $Ca(OH)_2$ WHEN $[OH^-] = 0.00307$M

c) What is the concentration of the less soluble cation at the hydroxide ion concentration in (b)? (2 marks)

$K_{sp} = [Cr^{3+}][OH^-]^3$

$[Cr^{3+}] = \dfrac{K_{sp}}{[OH^-]^3}$

$= \dfrac{6.3\times10^{-31}}{(0.00307)^3}$

$= 2.17\times10^{-23}$ M