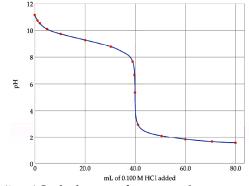
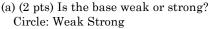
## EXAM FOUR<br/>CHM 205 (Dr. Mattson)<br/>28 MARCH 2008Academic Integrity Pledge:<br/>In keeping with Creighton University's ideals and with the Academic Integrity Code<br/>adopted by the College of Arts and Sciences, I pledge that this work is my own and that I<br/>have neither given nor received inappropriate assistance in preparing it.

**Instructions:** Show all work whenever a calculation is required! You will receive credit for <u>how</u> you worked each problem as well as for the correct answer. If you need more space, you may use the back of your periodic table — Write: "See PT" in box and then attach the periodic table. BOX YOUR ANSWERS! Write legibly.

## CHAPTER 15. APPLICATIONS OF AQUEOUS EQUILIBRIA

1. The following graph results from the titration of 50.00 mL of a base with 0.100 M HCl(aq).





(b) (3 pts) What is the molarity of the base?

(c) (3 pts) What is K<sub>b</sub> for the base?

(d) (2 pts) Which indicator would be best to use to signal the equivalence point for this titration? i. Indicator C,  $pK_a = 7.0$  (blue to red) ii. Indicator D,  $pK_a = 9.0$  (colorless to blue) iii. Indicator A,  $pK_a = 3.0$  (blue to yellow) iv. Indicator B,  $pK_a = 5.0$  (red to colorless)

- 2. (2 pts each) Consider the titration of 25.00 mL of the diprotic acid,  $H_2A$  with 0.200 M NaOH(aq). Suppose the first equivalence point was observed after the addition of 24 mL NaOH(aq).
- (a) Which of these species is dominant at the first equivalence point? Circle: H<sub>2</sub>A HA<sup>-</sup> A<sup>-2</sup>

(b) At what volume of OH<sup>-</sup> added would you look to determine pK<sub>21</sub>?

(c) At what volume of OH<sup>-</sup> added would you look to determine pK<sub>a2</sub>?

(d) At what volume of OH<sup>-</sup> added do you expect for the second equivalence point?

(e) At what volume range of OH<sup>-</sup> added does the HA<sup>-</sup> + A<sup>-2</sup> buffer exist?

A. 
$$0 < V < 24 \text{ mL}$$
B.  $24 < V < 48 \text{ mL}$ C.  $0 < V < 25 \text{ mL}$ D.  $0 < V < 48 \text{ mL}$ 

3. (5 pts) Determine the molar solubility of Ca(OH)<sub>2</sub>. [K<sub>sp</sub> =  $4.7 \ge 10^{-6}$ ]

4. (5 pts) What is the molar solubility of  $Ca(OH)_2$  in a solution that is 0.090 M NaOH?

5. (5 pts) Will a precipitate form when 100 mL 0.020 M calcium nitrate and 100 mL 0.0040 M sodium hydroxide are poured together? Don't forget they mutually dilute each other to a combined volume of 200 mL!

- 6. (4 pts) Which is more soluble,  $Fe(OH)_2 [K_{sp} = 4.9 \times 10^{-17}]$  or  $Cu(OH)_2 [K_{sp} = 1.6 \times 10^{-19}]$ ? Calculate or explain.
- 7. (4 pts) Which is more soluble,  $CaSO_4[K_{sp} = 7.1 \text{ x} 10^{-5}]$  or  $Ca(OH)_2 [K_{sp} = 4.7 \text{ x} 10^{-6}]$ ? Calculate or explain.
- 8. (15 pts) Predict the sign of  $\Delta$ H,  $\Delta$ S, and  $\Delta$ G for each of these processes. Write "-," "0," or "+." If it is not possible to predict the sign, write "?"

	$\Delta S$	$\Delta H$	$\Delta G$
Water freezing at 0 °C:			
$\mathrm{H_{2}O(l)} \not \rightarrow \mathrm{H_{2}O(s)}$			
$CH_4(g) + 2 O_2(g) \rightarrow$			
$\rm CO_2(g)$ + 2 H <sub>2</sub> O(g)			
Iron rusting (unbalanced):			
$\text{Fe} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_x(\text{O})_y$			
Commercial synthesis of $NH_3$ :			
3 H <sub>2</sub> (g) + N <sub>2</sub> (g) → 2 NH <sub>3</sub> (g)			
Reaction we've studied:			
$2 \operatorname{NO}_2(g) \rightarrow \operatorname{N}_2\operatorname{O}_4(g)$			

9(a and b). (5 pts each) Calculate  $\Delta H^0$  and  $\Delta S^0$  for the reaction shown in the boxes below.

	$\Delta H_{f}^{0}$ (kJ/mol)	S <sup>0</sup> (J/mol K)
0 <sub>2</sub> (g)	0	205
0 <sub>3</sub> (g)	143	239

2 O<sub>3</sub>(g) → 3 O<sub>2</sub>(g) 
$$\Delta$$
H<sup>o</sup> =

 $2 \text{ O}_3(g) \rightarrow 3 \text{ O}_2(g) \Delta S^0 =$ 

9(c). (4 pts) Calculate  $\Delta G^{o}$  for the reaction.

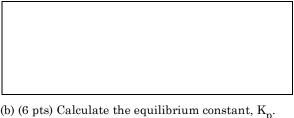
9(d). (2 pts) Under what temperature conditions will this reaction be spontaneous?(A) high temperatures only (B) all temperatures

(C) low temperatures only (D) never

10. Consider the reaction for which  $\Delta H^{0}$  = +26.5 kJ and  $\Delta G^{0}$  = +1.7 kJ

 $\mathrm{H}_{2}(\mathrm{g}) + \mathrm{I}_{2}(\mathrm{s}) \not \rightarrow 2 \ \mathrm{HI}(\mathrm{g})$ 

(a) (5 pts) Calculate  $\Delta {\rm S}^{\rm 0}$ 



(c) (6 pts) Calculate  $\Delta$ G if the initial pressures of H<sub>2</sub> and HI are P<sub>H2</sub> = 2.5 atm and P<sub>HI</sub> = 0.17 atm.

(d) (3 pts) The little "o" on  $\Delta \mathrm{G}^{\mathrm{0}}$  indicates the

temperature is \_\_\_\_\_, the pressures are

\_\_\_\_ and the concentrations are: \_\_\_\_\_

(e) (5 pts) At what temperature does  $\Delta G = 0$ ?

(1 pts) Print your name here and sign Academic Integrity Statement on other side.

**Your exam score (100 possible):** Determine your grade:  $A+ \ge 95; A \ge 90; B+ \ge 85; B \ge 80; C+ \ge 75; C \ge 70; D \ge 60$ 

## **Useful Formulas:**

 $\Delta \mathbf{G} = \Delta \mathbf{G^o} + \mathbf{R} \ \mathbf{T} \ \mathbf{lnQ}$   $\mathbf{R} = 8.314 \ J/mol \ \mathbf{K} = 0.0821 \ \mathbf{L} \ atm/mol \ \mathbf{K}$ 

## **Answers**:

- 1. (a) Weak
- (b) 0.080 M
- (c)  $\rm K_b$  for 3 x  $10^{-5}$

(d) iv

- 2. (a) HA<sup>-</sup>
- (b) 12 mL
- (c) 36 mL
- (d) 48 mL

(e) B

- 3. x = 1.05 x  $10^{-2}$  mol/L
- 4.  $x = 5.8 \times 10^{-4} \text{ mol/L}$
- 5.  $Q_{sp} = [0.010][0.0020]^2 =$ .  $Q_{sp} < K_{sp}$ , therefore, no precipitate is expected.
- 6. Fe(OH)\_2 , since both salts are of the same form, 1:2, we can simply compare  $\rm K_{sp}$  values.
- 7. Since the salts are not of the same form, we must compare x values.  $Ca(OH)_2$  is more soluble.

8.			
	$\Delta S$	ΔH	ΔG
Water freezing at 0 °C: H <sub>2</sub> O(l) $\rightarrow$ H <sub>2</sub> O(s)	-	-	0
$\begin{array}{c} \operatorname{CH}_4(g) + 2 \operatorname{O}_2(g) \rightarrow \\ & \operatorname{CO}_2(g) + 2 \operatorname{H}_2 \operatorname{O}(g) \end{array}$	?	-	-
Iron rusting (unbalanced): Fe + $O_2$ + $H_2O \rightarrow Fe(OH)_x(O)_y$	-	-	-
Commercial synthesis of NH <sub>3</sub> : 3 H <sub>2</sub> (g) + N <sub>2</sub> (g) $\rightarrow$ 2 NH <sub>3</sub> (g)	-	-	-
Reaction we've studied: $2 \operatorname{NO}_2(g) \rightarrow \operatorname{N}_2\operatorname{O}_4(g)$	-	-	?

9(a and b)  $\Delta H^{0}$  = - 286 kJ and  $\Delta S^{0}$  = 137 J/K

9(c)  $\Delta G^0 = -327 \text{ kJ}$ 

9(d). (B)

- 10. (a)  $\Delta \mathrm{S}^{\mathrm{o}} = +83.2 \ \mathrm{J/K}$
- (b)  $K_p = 0.50$
- (c)  $\Delta G$  -9.35 kJ

(d) The little "o" on  $\Delta \mathrm{G}^{\mathrm{0}}$  indicates the temperature

is 298 K, the pressures are 1.0 atm and the

concentrations are: 1.0 M.

(e) 318 K