Chemistry 10123 and 10125, **Exam 3** **Answer Key**
March 11, 2009

In the "**SHOW ALL WORK**" questions on this exam, include ***balanced, net-ionic equations for all equilibrium reactions***. ***Clearly state and justify any assumptions*** you make. Some ***selected equilibrium constants*** that are required in certain problems ***are listed on the last page*** of this exam.

1. (8 points) **SHOW ALL WORK.** Determine the molar solubility of $Mg(OH)_2$ in a solution that is buffered at pH = 8.50.

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2\ OH^-$

$K_{sp} = 2.06 \times 10^{-3} = [Mg^{2+}][OH^-]^2$

from the given pH: $[OH^-] = 10^{-5.50} = 3.16 \times 10^{-6}$ M

$2.06 \times 10^{-13} = [Mg^{2+}]\ (3.16 \times 10^{-6})^2$

$[Mg^{2+}]$ = molar solubility = 0.021 M

2. (10 points) **SHOW ALL WORK.** Determine the molar solubility of $Cd(OH)_2$ in a 1.50 M solution of KI.

K_{sp}: $Cd(OH)_2 \rightleftharpoons Cd^{2+} + 2\ OH^-$

K_f: $Cd^{2+} + 4\ I^- \rightleftharpoons CdI_4^{2-}$

K_{net}: $Cd(OH)_2 + 4I^- \rightleftharpoons CdI_4^{2-} + 2\ OH^-$

$K_{net} = K_{sp}\ K_f = (7.2 \times 10^{-15})(2.0 \times 10^{6}) = 1.44 \times 10^{-8}$

$K_{net} = 1.44 \times 10^{-8} = [CdI_4^{2-}]\ [OH^-]^2 / [I^-]^4 = (x)\ (2x)^2 / (1.50 - 4x)^4$

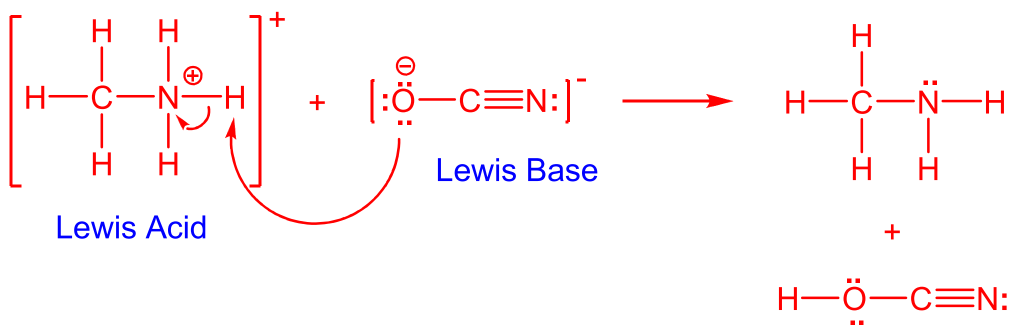
since K_{net} is small, assume 4x << 1.50

$1.44 \times 10^{-8} \sim (x)\ (2x)^2 / (1.50)^4$

$x \sim 2.6 \times 10^{-3}$ M (assumption is OK)

3. (10 points) Using acid-base concepts, predict the logical products of the following reaction in aqueous solution. Write ***Lewis electron dot formulas*** (including formal charges and/or resonance forms if needed) for all reactants and products. *Clearly indicate which reactant is the Lewis acid and which is the Lewis base.* Use arrow(s) to illustrate the formation and breaking of any bonds as the reaction proceeds from left to right.

$$CH_3NH_3^+(aq) \;+\; OCN^-(aq) \;\rightleftharpoons$$



4. (7 points) **SHOW ALL WORK.** Determine the equilibrium constant (K_c) for the reaction shown in question 3 above.

$CH_3NH_3^+ \rightleftharpoons CH_3CH_2 + H^+$ $\quad K_1 = K_w/K_b$ (for CH_3NH_2)

$OCN^- + H^+ \rightleftharpoons HOCN$ $\quad K_2 = 1 / K_a$ (for HOCN)

$CH_3NH_3^+ + OCN^- \rightleftharpoons CH_3NH_2 + HOCN$

$K_{net} = K_1 K_2 = K_w / K_a K_b = (10^{-14}) / (4.42 \times 10^{-4})(3.30 \times 10^{-4})$

$K_{net} = 6.86 \times 10^{-8}$

5. (8 points) **SHOW ALL WORK.** A 1.50 M solution of a certain diprotic acid, H_2A, is found to have a pH of 2.10 and an A^{2-} concentration of 3.80×10^{-9} M. For this acid, pK_{a1} = 4.38 and pK_{a2} = 8.42.

K_{a1}: $H_2A \rightleftharpoons HA^- + H^+$

K_{a2}: $HA^- \rightleftharpoons A^{2-} + H^+$

$[H^+] = 10^{-2.10} = 7.94 \times 10^{-3}$ M

$K_{a1} = (7.94 \times 10^{-3})^2 / [1.50 - (7.94 \times 10^{-3})]$

$= 4.21 \times 10^{-5}$ $\qquad pK_{a1} = 4.38$

$K_{a2} \sim [A^{2-}] = 3.80 \times 10^{-9}$ $\qquad pK_{a2} = 8.42$

6. (20 points) Indicate whether an aqueous solution of each of the following substances is acidic (A), basic (B), or neutral (N). For each solution, write a ***balanced net ionic equation for the major equilibrium reaction*** that is occurring in the solution.

(a) $(NH_4)_2SO_4$ Acidic

K_a: $NH_4^+ \rightleftharpoons NH_3 + H^+$

(b) $Mg(C_2H_3O_2)_2$ Basic

K_b: $C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$

(c) $(CH_3)_2NH$ Basic

K_b: $(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$

(d) $Ba(NO_3)_2$ Neutral

K_w: $H_2O \rightleftharpoons H^+ + OH^-$

(e) KClO Basic

K_b: $ClO^- + H_2O \rightleftharpoons HClO + OH^-$

7. (9 points) **SHOW ALL WORK.** Indium sulfide, In_2S_3 (325.8 g/mole) is so insoluble that a 20.0-L volume (about a 5-gallon can) of a saturated solution contains only 34 *pico*grams of In_2S_3. Determine K_{sp} for In_2S_3. [For those of you who have forgotten the metric system, *pico* = 10^{-12}!]

molar solubility of In_2S_3 = $(34 \times 10^{-12}$ g) (1 mole / 325.8 g) / (20.0 L)

= 5.218×10^{-15} M

$In_2S_3 \rightleftharpoons 2\ In^{3+} + 3\ S^{2-}$

$K_{sp} = [In^{3+}]^2 [S^{2-}]^3 = (2x)^2 (3x)^3 = 108\ x^5$

$K_{sp} = 108\ (5.218 \times 10^{-15})^5 = 4.2 \times 10^{-70}$

8. Assume that 500 mL of each of the following solutions (**A** - **D**) are available in your lab.

A: 2.50 M HBr | **C**: 0.50 M CH_3NH_3Br

B: 1.50 M $Ba(OH)_2$ | **D**: 1.00 M $HCHO_2$

(a) (3 points) The pH of solution **A** is - 0.40

(b) (3 points) The pH of solution **B** is 14.50

(c) (8 points) **SHOW ALL WORK.** Determine the pH of Solution **C**.

$$CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+$$

$K_a = K_w/K_b = x^2 / (0.50 - x)$ assume x << 0.5

$K_a = (10^{-14}) / (4.42 \times 10^{-4}) = 2.26 \times 10^{-11} \sim x^2 / 0.50$

$x = [H^+] \sim 3.36 \times 10^{-6}$ (assumption is OK)

pH = 5.47

(d) (6 points) If the entire 500 mL of solution **D** is mixed with a certain volume of one of the other solutions, a ***buffer solution*** with pH = 4.00 can be produced. Which solution (**A**, **B**, or **C**) should be used for this purpose? ***Briefly explain*** your answer, including a balanced chemical equation for any reaction that occurs upon mixing your chosen solution with **D**.

The weak acid, $HCHO_2$ in solution **D** must be partially neutralized by a strong base to produce some of its conjugate base, CHO_2^-. Therefore, some of solution **B**, the strong base, should be added to **D** to produce a buffer. The neutralization reaction is:

$$2\ HCHO_2 + Ba(OH)_2 \longrightarrow 2\ H_2O + Ba(CHO_2)_2$$

or simply: $HCHO_2 + OH^- \longrightarrow H_2O + CHO_2^-$

(e) (8 points) **SHOW ALL WORK.** Determine the volume (in mL) of the solution you selected in part (d) that must be added to solution **D** to yield a final pH of 4.00.

The main equilibrium in the resulting buffer solution is:

$$HCHO_2 \rightleftharpoons CHO_2^- + H^+$$

$[H^+] = K_a$ (moles $HCHO_2$) / (moles CHO_2^-)

initial moles of $HCHO_2$ = (0.50 L) (1 mole/L) = 0.50 moles

let x = moles OH^- added = moles CHO_2^- produced

$[H^+] = K_a (0.50 - x) / (x)$

$10^{-4.00} = (1.8 \times 10^{-4}) (0.50 - x) / x$

solve for x = 0.321 moles OH^-

Volume of $Ba(OH)_2$ solution =

(0.321 mole OH^-) [1 mole $Ba(OH)_2$ / 2 mole OH^-] (1000 mL / 1.50 mole)

= 107 mL

Substance	Equilibrium Constant(s)	
$HC_2H_3O_2$	$K_a = 1.75 \times 10^{-5}$	
$HCHO_2$	$K_a = 1.80 \times 10^{-4}$	
HCN	$K_a = 6.20 \times 10^{-10}$	
HOCN	$K_a = 3.30 \times 10^{-4}$	
H_2CO_3	$K_{a1} = 4.3 \times 10^{-7}$	$K_{a2} = 5.6 \times 10^{-11}$
H_2S	$K_{a1} = 8.9 \times 10^{-8}$	$K_{a2} = 1.0 \times 10^{-19}$
NH_3	$K_b = 1.76 \times 10^{-5}$	
CH_3NH_2	$K_b = 4.42 \times 10^{-4}$	
$HONH_2$	$K_b = 9.12 \times 10^{-9}$	
$Mg(OH)_2$	$K_{sp} = 2.06 \times 10^{-13}$	
$Cd(OH)_2$	$K_{sp} = 7.2 \times 10^{-15}$	
$Cu(OH)_2$	$K_{sp} = 2.2 \times 10^{-20}$	
$In(OH)_3$	$K_{sp} = 1.3 \times 10^{-37}$	
$Au(OH)_3$	$K_{sp} = 5.5 \times 10^{-46}$	
CuS	$K_{sp} = 1.3 \times 10^{-36}$	
$CdCO_3$	$K_{sp} = 1.0 \times 10^{-12}$	
$Cd(CN)_4^{2-}$	$K_f = 3.0 \times 10^{18}$	
CdI_4^{2-}	$K_f = 2.0 \times 10^{6}$	
$Cu(NH_3)_4^{2+}$	$K_f = 1.7 \times 10^{13}$	
$Cu(CN)_4^{2-}$	$K_f = 1.0 \times 10^{29}$	