Chemistry 10123, **Exam 3** **Answer Key**
March 20, 2019

In all of the "**SHOW ALL WORK**" questions, include ***balanced, net-ionic equations for all relevant chemical reactions and clearly indicate which ones are considered as equilibrium reactions***. ***Without the appropriate chemical reaction(s), no partial credit will be given!*** ***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. (10 points) Write a ***balanced chemical equation*** for the ***equilibrium*** reaction that corresponds to each of the following equilibrium constants. ***Indicate the proper phase (s, aq, etc.) of each species***.
[e. g., K_w for water would be: $2\ H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$]

(a) K_b for $H_2PO_3^-$

$$H_2PO_3^-{}_{(aq)} + H_2O \rightleftharpoons H_3PO_{3(aq)} + OH^-_{(aq)}$$

(b) K_{sp} for $Mg_3(PO_4)_2$

$$Mg_3(PO_4)_{2(s)} \rightleftharpoons 3\ Mg^{2+}_{(aq)} + 2\ PO_4^{3-}{}_{(aq)}$$

(c) K_b for H_2NNH_2

$$H_2NNH_{2(aq)} + H_2O \rightleftharpoons H_2NNH_3^+{}_{(aq)} + OH^-_{(aq)}$$

(d) K_f for $Cr(C_2O_4)_3^{3-}$

$$Cr^{3+}_{(aq)} + 3\ C_2O_4^{2-}{}_{(aq)} \rightleftharpoons Cr(C_2O_4)_3^{3-}{}_{(aq)}$$

(e) K_a for $Al(H_2O)_6^{3+}$

$$Al(H_2O)_6^{3+} \rightleftharpoons H^+_{(aq)} + Al(H_2O)_5(OH)^{2+}_{(aq)}$$

2. (10 points) **SHOW ALL WORK.** An unknown weak base (call it RNH_2) is dissolved in enough water to make 50.0 mL of solution. This solution is then titrated with 0.125 M HNO_3 and 40.0 mL of the HNO_3 solution is required to reach the equivalence point. Using a pH meter, the pH of the solution at the equivalence point is found to be 2.94. Determine the pK_b value of the unknown base.

At the equivalence point, all RNH_2 has been neutralized to RNH_3^+.

moles RNH_3^+ produced = moles HNO_3 added

= (0.040 L) (0.125 mole/L) = 0.00500 mole

total volume = 50.0 mL + 40.0 mL = 90.0 mL = 0.0900 L

M of RNH_3^+ = 0.00500 mole / 0.0900 L = 0.0556 M

$$RNH_3^+ \rightleftharpoons H^+ + RNH_2$$

$$K_a = [H^+][RNH_2] / [RNH_3^+] \approx (10^{-2.94})^2 / (0.0556) \approx 2.37 \times 10^{-5}$$

$pK_a = 4.63$

$pK_b = 14.00 - pK_a = 9.37$

3. (8 points) Indicate whether an aqueous solution of each of the following substances is acidic (A), basic (B), or neutral (N).

$NaClO_2$ B $(CH_3)_2NH_2Br$ A $Ba(NO_3)_2$ N HOCN A

4. (10 points) **SHOW ALL WORK.** Indium sulfide, In_2S_3 (molar mass = 326) is so insoluble that a 2.0-L volume of a saturated solution contains only 3.4 *pico*grams of In_2S_3. Determine K_{sp} for In_2S_3. (In case you have forgotten the metric system, *pico* = 10^{-12}!)

$In_2S_{3(s)} \rightleftharpoons 2\ In^{3+}{}_{(aq)} + 3\ S^{2-}{}_{(aq)}$

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

$x = (3.4 \times 10^{-12}\ g / 2.0\ L)(1\ mole / 326\ g) = 5.22 \times 10^{-15}\ M$

$K_{sp} = 108\ (5.22 \times 10^{-15})^5 = 4.2 \times 10^{-70}$

5. (7 points) **SHOW ALL WORK.** Determine the numerical value of the equilibrium constant (K_c) for the following reaction.

$Cr(OH)_{3(s)} + 3\ HCO_2H_{(aq)} \rightleftharpoons Cr^{3+}{}_{(aq)} + 3\ HCO_2^-{}_{(aq)} + 3\ H_2O$

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

$3\ \{ HCO_2H_{(aq)} \rightleftharpoons HCO_2^-{}_{(aq)} + H^+ \}$ $(K_a)^3$

$3\ \{ H^+{}_{(aq)} + OH^-{}_{(aq)} \rightleftharpoons H_2O \}$ $(1/K_w)^3$

$K_c = K_{sp}\ (K_a)^3\ (1 / K_w)^3$

$K_c = (6.3 \times 10^{-31})\ (1.80 \times 10^{-4})^3 / (1.00 \times 10^{-14})^3 = 3.67$

6. (10 points) **SHOW ALL WORK.** By doing the appropriate calculation, determine if a precipitate will form when 75.0 mL of an NaOH solution with pH = 11.40 is mixed with 125 mL of a 0.020 M $MgCl_2$ solution. Identify the precipitate, if any.

The possible precipitate is $Mg(OH)_2$ for which $K_{sp} = 2.06 \times 10^{-13}$.

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

Determine Q and compare to K_{sp}.

NaOH solution: pOH = 14.00 - pH = 2.60 $[OH^-] = 10^{-2.60} = 2.51 \times 10^{-3}\ M$

moles OH^- = $(0.075\ L)(2.51 \times 10^{-3}\ mole/L) = 1.88 \times 10^{-4}$ mole

after mixing: $[OH = (1.88 \times 10^{-4}\ mole) / (0.200\ L) = 9.41 \times 10^{-4}\ M$

moles Mg^{2+} = $(0.125\ L)(0.20\ mole/L) = 2.50 \times 10^{-3}$ moles

$[Mg^{2+}] = (2.50 \times 10^{-3}\ moles) / (0.200\ L) = 0.0125\ M$

$Q = [Mg^{2+}][OH^-]^2 = [0.0125][9.41 \times 10^{-4}]^2 = 1.18 \times 10^{-8}$

$Q > K_{sp}$ ∴ a precipitate of $Mg(OH)_2$ will form!

7. In a Gen Chem lab practical, you are given four labeled bottles that contain 500 mL each of the following solutions.

A: 0.300 M KOH	**B**: 0.300 M KNO_2	**C**: 0.300 M HOBr	**D**: 0.300 M HBr
pH = 13.48	pH = 8.41	pH = 4.54	pH = 0.52

(a) (7 points) Determine the pH of each of the above solutions and fill in the blanks accordingly. (*No partial credit will be given here and work need not be shown*.)

(b) (8 points) The main task of the lab practical is to prepare a ***buffer solution*** with a pH of 4.00. Think about which ***two*** solutions you would mix together to accomplish this. (Fill in the blanks with the correct letters.) I would mix the entire 500 mL of solution B with a smaller volume of solution D. ***Briefly explain*** your answers by giving specific reasons for selecting each of the two solutions. Include a ***balanced chemical equation*** for any reaction that occurs ***upon mixing*** your chosen solutions.

neutralization Rx: $H^+ + NO_2^- \longrightarrow HNO_2$

The reaction of H^+ (from the strong acid HBr) with excess NO_2^- will produce some of the conjugate acid HNO_2, thus yielding an HNO_2 / NO_2^- buffer solution! This buffer will have a pH comparable to pK_a for the weak acid HNO_2 (pK_a = 3.34). Using all of solution B with a smaller quantity of HBr (in moles) will insure that some of the NO_2^- remains along with HNO_2.

(c) (10 points) **SHOW ALL WORK.** Determine the volume (in mL) of the solution you selected in part (b) that must be added to 500 mL of the other solution to make the buffer with pH = 4.00.

neutralization Rx: $H^+ + NO_2^- \longrightarrow HNO_2$

initial moles NO_2^- = (0.500 L) (0.30 mole/L) = 0.15 moles

let x = moles HBr (i.e., H^+) added

after reaction: moles HNO_2 = x and moles NO_2^- = 0.15 - x

buffer solution: $HNO_2 \rightleftharpoons H^+ + NO_2^-$

$K_a = [H^+][NO_2^-] / [HNO_2] = 4.6 \times 10^{-4}$

$[H^+] = K_a [HNO_2] / [NO_2^-] = K_a$ (moles HNO_2) / (moles NO_2^-)

$10^{-4.00} = (4.6 \times 10^{-4})(x) / (0.15 - x)$ rearrange and solve for x!

x = 0.0268 mole H^+

(0.0268 mole HBr) (1000 mL / 0.300 moles) = 89.3 mL

8. (10 points) **SHOW ALL WORK.** A 3.75-g sample of codeine (a weak base with a pK_b of 5.79) was combined with 3.00 mL of 1.50 M HCl and the resulting solution was diluted to 500 mL. The measured pH of this solution was 8.46. Determine the molar mass of codeine.

let x = moles of base B (codeine)

moles H^+ added = moles of B neutralized = moles HB^+ produced

= (3.00 mL) (1.50 moles / 1000 mL) = 0.00450 mole

moles B remaining = x - 0.00450 and moles HB^+ produced = 0.00450

the resulting solution is a buffer in which the major equilibrium is

$$HB^+ \rightleftharpoons H^+ + B$$

$pK_a = 14 - pK_b = 14 - 5.79 = 8.21$

$[H^+] = K_a$ (moles HB^+) / (moles B)

$10^{-8.46} = (10^{-8.21})$ (0.00450) / (x - 0.00450)

x = 0.0125 moles B

molar mass = 3.75 g / 0.0125 mole = 300 g/mole

9. **SHOW ALL WORK.** Determine the molar solubility of Ag_2CrO_4 in each of following solutions.

(a) (5 points) 0.20 M $AgNO_{3(aq)}$

$$Ag_2CrO_{4(s)} \rightleftharpoons 2\ Ag^+_{(aq)} + CrO_4{}^{2-}{}_{(aq)}$$

let x = molar solubility of Ag_2CrO_4

$K_{sp} = 1.12 \times 10^{-12} = [Ag^+]^2 [CrO_4{}^{2-}] = (x + 0.20)^2 (x)$

since K_{sp} is very small, assume x << 0.20

$1.12 \times 10^{-12} \approx (0.20)^2 (x)$

$x \approx 2.8 \times 10^{-11}$ M (assumption is OK)

(b) (10 points) 0.20 M KSCN(aq)

K_{sp} $Ag_2CrO_{4(s)} \rightleftharpoons 2\ Ag^+_{(aq)} + CrO_4{}^{2-}{}_{(aq)}$

$(K_f)^2$ $2\ [\ Ag^+_{(aq)} + 2\ SCN^-_{(aq)} \rightleftharpoons Ag(SCN)_2{}^-{}_{(aq)}\ ]$

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net Rx: $Ag_2CrO_{4(s)} + 4\ SCN^-_{(aq)} \rightleftharpoons 2\ Ag(SCN)_2{}^-{}_{(aq)} + S^{2-}{}_{(aq)}$

$K_{net} = K_{sp} (K_f)^2 = (1.12 \times 10^{-12}) (1.2 \times 10^{10})^2 = 1.61 \times 10^8$

Since K_{net} is very large, the net reaction essentially goes to completion.
Thus, Ag_2CrO_4 will keep reacting (i.e., dissolving) until all of the SCN^- is consumed.

$\therefore$ molar solubility = (0.20 mole SCN^- / L) (1 mole Ag_2CrO_4 / 4 mole SCN^-)

= 0.050 mole/L

	IA (1)	IIA (2)	IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	. . . . . . (8)	VIIIB (9)	. . . . (10)	IB (11)	IIB (12)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	VIIIA (18)
1	1 **H** 1.0080																	2 **He** 4.0026
2	3 **Li** 6.9410	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.179
3	11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.066	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.880	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.690	29 **Cu** 63.546	30 **Zn** 65.380	31 **Ga** 69.723	32 **Ge** 72.610	33 **As** 74.922	34 **Se** 78.960	35 **Br** 79.904	36 **Kr** 83.800
5	37 **Rb** 85.468	38 **Sr** 87.620	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.940	43 **Tc** 98.907	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
6	55 **Cs** 132.91	56 **Ba** 137.33	57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.20	77 **Ir** 192.22	78 **Pt** 195.09	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.20	83 **Bi** 208.98	84 **Po** 208.98	85 **At** 209.99	86 **Rn** 222.02
7	87 **Fr** 223.02	88 **Ra** 226.03	89 **Ac** 227.03	104 Unq 261.11	105 Unp 262.11	106 Unh 263.12	107 Uns 262.12											

Substance	**Equilibrium Constant(s)**	
CH_3CO_2H	$K_a = 1.75 \times 10^{-5}$	
HCO_2H	$K_a = 1.80 \times 10^{-4}$	
$HOBr$	$K_a = 2.80 \times 10^{-9}$	
HNO_2	$K_a = 4.60 \times 10^{-4}$	
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	$K_b = 4.42 \times 10^{-4}$	
$HONH_2$	$K_b = 9.12 \times 10^{-9}$	
$Mg(OH)_2$	$K_{sp} = 2.06 \times 10^{-13}$	
$Cd(OH)_2$	$K_{sp} = 7.2 \times 10^{-15}$	
$Cr(OH)_3$	$K_{sp} = 6.3 \times 10^{-31}$	
$Cu(OH)_2$	$K_{sp} = 2.2 \times 10^{-20}$	
$Au(OH)_3$	$K_{sp} = 5.5 \times 10^{-46}$	
Ag_2S	$K_{sp} = 6.0 \times 10^{-51}$	
Ag_2CrO_4	$K_{sp} = 1.12 \times 10^{-12}$	
$CdCO_3$	$K_{sp} = 1.0 \times 10^{-12}$	
$Cd(CN)_4^{2-}$	$K_f = 3.0 \times 10^{18}$	
$Cu(NH_3)_4^{2+}$	$K_f = 1.7 \times 10^{13}$	
$Ag(CN)_2^-$	$K_f = 1.0 \times 10^{21}$	
$Ag(SCN)_2^-$	$K_f = 1.2 \times 10^{10}$	
$Cu(CN)_4^{2-}$	$K_f = 1.0 \times 10^{29}$	