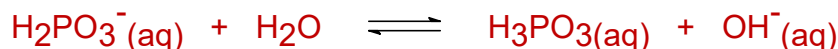


In all of the "SHOW ALL WORK" questions, include balanced, net-ionic equations for all relevant chemical reactions and clearly indicate which ones are considered as equilibrium reactions. Without the appropriate chemical reaction(s), no partial credit will be given! Clearly state and justify any assumptions 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:  $2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$ ]

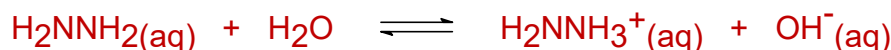
- (a)  $K_b$  for  $\text{H}_2\text{PO}_3^-$



- (b)  $K_{sp}$  for  $\text{Mg}_3(\text{PO}_4)_2$



- (c)  $K_b$  for  $\text{H}_2\text{NNH}_2$



- (d)  $K_f$  for  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$



- (e)  $K_a$  for  $\text{Al}(\text{H}_2\text{O})_6^{3+}$



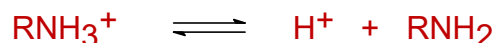
2. (10 points) **SHOW ALL WORK.** An unknown weak base (call it  $\text{RNH}_2$ ) is dissolved in enough water to make 50.0 mL of solution. This solution is then titrated with 0.125 M  $\text{HNO}_3$  and 40.0 mL of the  $\text{HNO}_3$  solution is required to reach the equivalence point. Using a pH meter, the pH of the solution at the equivalence point is found to be 2.94. Determine the  $\text{p}K_b$  value of the unknown base.

At the equivalence point, all  $\text{RNH}_2$  has been neutralized to  $\text{RNH}_3^+$ .

$$\begin{aligned} \text{moles RNH}_3^+ \text{ produced} &= \text{moles HNO}_3 \text{ added} \\ &= (0.040 \text{ L}) (0.125 \text{ mole/L}) = 0.00500 \text{ mole} \end{aligned}$$

$$\text{total volume} = 50.0 \text{ mL} + 40.0 \text{ mL} = 90.0 \text{ mL} = 0.0900 \text{ L}$$

$$\text{M of RNH}_3^+ = 0.00500 \text{ mole} / 0.0900 \text{ L} = 0.0556 \text{ M}$$



$$K_a = [\text{H}^+][\text{RNH}_2] / [\text{RNH}_3^+] \approx (10^{-2.94})^2 / (0.0556) \approx 2.37 \times 10^{-5}$$

$$\text{p}K_a = 4.63$$

$$\text{p}K_b = 14.00 - \text{p}K_a = 9.37$$

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



4. (10 points) **SHOW ALL WORK.** Indium sulfide, In<sub>2</sub>S<sub>3</sub> (molar mass = 326) is so insoluble that a 2.0-L volume of a saturated solution contains only 3.4 picograms of In<sub>2</sub>S<sub>3</sub>. Determine K<sub>sp</sub> for In<sub>2</sub>S<sub>3</sub>. (In case you have forgotten the metric system, *pico* = 10<sup>-12</sup>!)

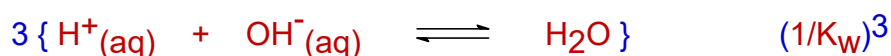
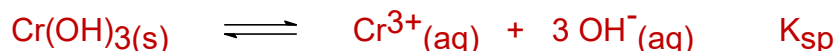
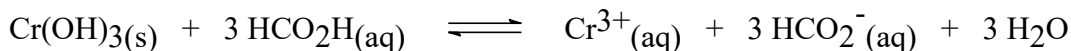


$$K_{\text{sp}} = [\text{In}^{3+}]^2 [\text{S}^{2-}]^3 = (2x)^2(3x)^3 = 108 x^5 \quad \text{where, } x = \text{molar solubility}$$

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

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

5. (7 points) **SHOW ALL WORK.** Determine the numerical value of the equilibrium constant (K<sub>c</sub>) for the following reaction.



$$K_{\text{c}} = K_{\text{sp}} (K_{\text{a}})^3 (1 / K_{\text{w}})^3$$

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

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<sub>2</sub> solution. Identify the precipitate, if any.

The possible precipitate is Mg(OH)<sub>2</sub> for which K<sub>sp</sub> = 2.06 × 10<sup>-13</sup>.



Determine Q and compare to K<sub>sp</sub>.

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

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

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

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

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

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

$$Q > K_{\text{sp}} \quad \therefore \text{ a precipitate of Mg(OH)}_2 \text{ will form!}$$

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<sub>2</sub>

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.



The reaction of H<sup>+</sup> (from the strong acid HBr) with excess NO<sub>2</sub><sup>-</sup> will produce some of the conjugate acid HNO<sub>2</sub>, thus yielding an HNO<sub>2</sub> / NO<sub>2</sub><sup>-</sup> buffer solution! This buffer will have a pH comparable to pK<sub>a</sub> for the weak acid HNO<sub>2</sub> (pK<sub>a</sub> = 3.34). Using all of solution B with a smaller quantity of HBr (in moles) will insure that some of the NO<sub>2</sub><sup>-</sup> remains along with HNO<sub>2</sub>.

(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.



$$\text{initial moles NO}_2^- = (0.500 \text{ L}) (0.30 \text{ mole/L}) = 0.15 \text{ moles}$$

$$\text{let } x = \text{moles HBr (i.e., H}^+) \text{ added}$$

$$\text{after reaction: moles HNO}_2 = x \text{ and moles NO}_2^- = 0.15 - x$$



$$K_a = [\text{H}^+][\text{NO}_2^-] / [\text{HNO}_2] = 4.6 \times 10^{-4}$$

$$[\text{H}^+] = K_a [\text{HNO}_2] / [\text{NO}_2^-] = K_a (\text{moles HNO}_2) / (\text{moles NO}_2^-)$$

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

$$x = 0.0268 \text{ mole H}^+$$

$$(0.0268 \text{ mole HBr}) (1000 \text{ mL} / 0.300 \text{ moles}) = 89.3 \text{ mL}$$

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.

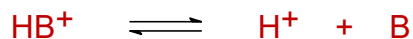
let  $x$  = moles of base B (codeine)

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

$$= (3.00 \text{ mL}) (1.50 \text{ moles} / 1000 \text{ mL}) = 0.00450 \text{ mole}$$

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

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



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

$$[H^+] = K_a (\text{moles } HB^+) / (\text{moles } B)$$

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

$$x = 0.0125 \text{ moles } B$$

$$\text{molar mass} = 3.75 \text{ g} / 0.0125 \text{ mole} = 300 \text{ g/mole}$$

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

(a) (5 points) 0.20 M  $AgNO_3(aq)$



let  $x$  = molar solubility of  $Ag_2CrO_4$

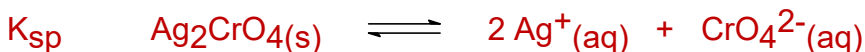
$$K_{sp} = 1.12 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}] = (x + 0.20)^2 (x)$$

since  $K_{sp}$  is very small, assume  $x \ll 0.20$

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

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

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



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

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.

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

$$= 0.050 \text{ mole/L}$$

IA (1)												VIIIA (18)						
1	<b>H</b> 1.0080																<b>He</b> 4.0026	
2	<b>Li</b> 6.9410	<b>Be</b> 9.0122											<b>B</b> 10.811	<b>C</b> 12.011	<b>N</b> 14.007	<b>O</b> 15.999	<b>F</b> 18.998	<b>Ne</b> 20.179
3	<b>Na</b> 22.990	<b>Mg</b> 24.305	IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIIB (7)	VIIIIB (8)	VIIIIB (9)	VIIIIB (10)	IB (11)	IIB (12)	<b>Al</b> 26.982	<b>Si</b> 28.086	<b>P</b> 30.974	<b>S</b> 32.066	<b>Cl</b> 35.453	<b>Ar</b> 39.948
4	<b>K</b> 39.098	<b>Ca</b> 40.078	<b>Sc</b> 44.956	<b>Ti</b> 47.880	<b>V</b> 50.942	<b>Cr</b> 51.996	<b>Mn</b> 54.938	<b>Fe</b> 55.847	<b>Co</b> 58.933	<b>Ni</b> 58.690	<b>Cu</b> 63.546	<b>Zn</b> 65.380	<b>Ga</b> 69.723	<b>Ge</b> 72.610	<b>As</b> 74.922	<b>Se</b> 78.960	<b>Br</b> 79.904	<b>Kr</b> 83.800
5	<b>Rb</b> 85.468	<b>Sr</b> 87.620	<b>Y</b> 88.906	<b>Zr</b> 91.224	<b>Nb</b> 92.906	<b>Mo</b> 95.940	<b>Tc</b> 98.907	<b>Ru</b> 101.07	<b>Rh</b> 102.91	<b>Pd</b> 106.42	<b>Ag</b> 107.87	<b>Cd</b> 112.41	<b>In</b> 114.82	<b>Sn</b> 118.71	<b>Sb</b> 121.75	<b>Te</b> 127.60	<b>I</b> 126.90	<b>Xe</b> 131.29
6	<b>Cs</b> 132.91	<b>Ba</b> 137.33	<b>La</b> 138.91	<b>Hf</b> 178.49	<b>Ta</b> 180.95	<b>W</b> 183.85	<b>Re</b> 186.21	<b>Os</b> 190.20	<b>Ir</b> 192.22	<b>Pt</b> 195.09	<b>Au</b> 196.97	<b>Hg</b> 200.59	<b>Tl</b> 204.38	<b>Pb</b> 207.20	<b>Bi</b> 208.98	<b>Po</b> 208.98	<b>At</b> 209.99	<b>Rn</b> 222.02
7	<b>Fr</b> 223.02	<b>Ra</b> 226.03	<b>Ac</b> 227.03	Unq 261.11	Unp 262.11	Unh 263.12	Uns 262.12											

**Substance****Equilibrium Constant(s)**