Part 1. Answer 6 of the following 7 questions. If you answer more than 6 questions, cross out the one you wish not to be graded. Otherwise only the first 6 will be graded. 5 points each.

1. Which of the following is always positive when a spontaneous process occurs?
   a. ΔS
   b. ΔS_{surr}
   c. ΔS_{tot} (or ΔS_{universe})
   d. ΔH_{universe}
   e. ΔH_{surr}  

Second Law

2. Of the following, the entropy of gaseous _______ ___ is the largest at 25°C and 1 atm.
   a. C_2H_6
   b. C_2H_2
   c. CH_4
   d. C_2H_4

3. During the titration of a monoprotic weak acid with a standard base, when exactly half of the required amount of base has been added to reach the equivalence point:
   a. pH = \sqrt{c_A K_a} with c_A the starting concentration of the weak acid
   b. pH = pK_a/2
   c. pH = pK_a - \log(1/2)
   d. pH = pK_a
   e. pH = \sqrt{c_b K_b} with c_b the final concentration of the conjugate base

50:50 buffer half-way to equivalence point

4. Which of the following does not act as a Lewis acid in aqueous solution?
   a. Cr^{3+}
   b. H^+
   c. K^+
   d. SO_3
   e. Cu^{2+}

forms complexes with OH

Arrhenius and Brønsted-Lowry acids are Lewis acids

ineffective or negligible in aqueous solution

acidic oxide: SO_3 + H_2O → H_2SO_4

forms complexes with NH_3

5. The K_{sp} for Zn(OH)_2 is 5.0x10^{-17}. Determine the molar solubility of Zn(OH)_2 in a buffer solution with a pH of 11.5.  
   a. 5.0x10^{-6} M
   b. 1.2x10^{-12} M
   c. 1.6x10^{-14} M
   d. 5.0x10^{-12} M
   e. 5.0x10^{-17} M

\[ K_{sp} = [Zn^{2+}][OH^-]^2 \quad \text{and} \quad s = [Zn^{2+}] \]
6. Which answer below best describes the behavior of a sparingly soluble amphoteric hydroxide in water?
   a. With conc. aqueous NaOH, its suspension dissolves.
   b. With conc. aqueous HCl, its suspension dissolves.
   c. With conc. aqueous NaOH, its clear solution forms a precipitate.
   d. With both conc. aqueous NaOH and conc. aqueous HCl, its suspension dissolves.

7. Aluminum ion, Al\(^{3+}\), in water is acidic. Write a balanced reaction to show how Al\(^{3+}\) is acidic in solution.

\[
\text{Al(H}_2\text{O)}_6^{3+} \rightleftharpoons \text{Al(H}_2\text{O)}_5(\text{OH})^{2+} + \text{H}^+
\]

Part 2. Answer 4 of the following 5 questions. If you answer more than 4 questions, cross out the one you wish not to be graded. Otherwise only the first 4 will be graded. 10 points each.

8. A buffer is made from 0.200 mol of acetic acid and 0.200 mol of sodium acetate in 1.00 L total volume. The \(K_a = 1.8 \times 10^{-5}\) for acetic acid. Calculate the pH after the addition of 1.00 mL of 1.00 M HCl.

\[
\begin{align*}
\text{OAc}^- & \quad \text{H}^+ & \quad \rightarrow & \quad \text{HOAc} & \quad \text{assume goes to completion} \\
\text{initial} & \quad 0.200 \text{ mol} & \quad 1.00 \times 10^{-3} \text{ mol} & \quad 0.200 \text{ mol} \\
\text{completion} & \quad 0.199 \text{ mol} & \quad 0 \text{ mol} & \quad 0.201 \text{ mol}
\end{align*}
\]

\[
[\text{H}^+] = K_a \frac{[\text{HOAc}]}{[\text{OAc}^-]} = 1.8 \times 10^{-5} \frac{0.201/V}{0.199/V} = 1.82 \times 10^{-5} \text{ M} \quad \text{pH} = 4.74
\]

9. Give the name for the following compounds:
   a. KClO\(_3\) ___potassium chlorite_______ perchloric acid is HClO\(_4\)
   b. H\(_3\)PO\(_3\) ___phosphorous acid_______ phosphoric acid is H\(_3\)PO\(_4\)
   c. (NH\(_4\))\(_2\)SO\(_3\) ___ammonium sulfite_______ sulfuric acid is H\(_2\)SO\(_4\)

10. Calculate the solubility of PbI\(_2\) in pure water if \(K_{sp} = 8.7 \times 10^{-9}\).

\[
\begin{align*}
\text{K}_{sp} &= [\text{Pb}^{2+}][\Gamma]^2 \quad \text{and} \quad s = [\text{Pb}^{2+}] \\
\text{PbI}_2 (s) & \rightleftharpoons \text{Pb}^{2+} + 2 \Gamma \\
& \quad s = 2s \quad \text{K}_{sp} = (s)(2s)^2 = 4s^3 \\
s &= \sqrt[3]{K_{sp}/4} = \sqrt[3]{8.7 \times 10^{-9}/4} = 1.30 \times 10^{-3} \text{ M}
\end{align*}
\]
11. The $K_{sp}$ for HgI$_2$ is $3.0 \times 10^{-26}$. The formation constant for HgI$_4^{2-}$ is $1.6 \times 10^{30}$. Calculate the I$^-$/concentration in a solution that has a molar solubility for HgI$_2$ of 0.100 M.

\[
K_{sp} = [Hg^{2+}][I^-]^2
\]

\[
K_f = [HgI_4^{2-}]/[Hg^{2+}][I^-]^2
\]

Add reactions and multiply the equilibrium constants

\[
K = K_{sp}K_f = (3.0 \times 10^{-26})(1.6 \times 10^{30}) = 4.8 \times 10^4
\]

K is so large we can assume all dissolved Hg$^{2+}$ is in the form HgI$_4^{2-}$, giving [HgI$_4^{2-}$] = 0.100 M:

\[
K = K_{sp}K_f = 4.8 \times 10^4 = [HgI_4^{2-}]/[I^-]^2
\]

\[
[I^-] = \sqrt{[HgI_4^{2-}]/K} = \sqrt{0.100/4.8 \times 10^4} = 1.44 \times 10^{-3} M
\]

12. How would you dissolve the following precipitates? Assume you have available dilute aqueous solutions of HCl, H$_2$SO$_4$, NaOH, and NH$_3$.

a. Fe(OH)$_3$ (s): add _HCl or H$_2$SO$_4_ all hydroxides dissolve in acid
b. AgI (s): add ___NH$_3_ Ag^+$ forms complexes with NH$_3$
c. CaF$_2$ (s): add _HCl or H$_2$SO$_4_ F$ is the conjugate base of a weak acid

Part 3. Answer the following questions. 15 points each.

13. Calculate the pH at the equivalence point of a titration of 25.0 mL of 0.100 M HCN with 0.100 M NaOH. $K_a$ for HCN is $4.00 \times 10^{-8}$. Show the reaction that determines the pH.

At equivalence: moles CN$^-$ = initial moles HCN and $V_{tot}$ = 25 + 25 mL

\[
[CN^-] = (0.0250 \text{ L})(0.100 \text{ M})/0.0500 \text{ L} = 0.0500 \text{ M}
\]

b. Calculate the pH at the equivalence point:

\[
K_b = \frac{[HCN][OH^-]}{[CN^-]} = \frac{x^2}{0.0500-x} \approx \frac{x^2}{0.0500}
\]

The equilibrium constant is small

\[
x = [OH^-] = \sqrt{c_bK_b} = \sqrt{(0.0500)(2.5 \times 10^{-7})} = 1.11 \times 10^{-4} \text{ M}
\]

pOH = 3.95 pH = 10.05
14. What is the solubility of FeS at pH = 8.00? \( K_{sp} = 4.2 \times 10^{-17} \), and for H\(_2\)S the acid dissociation constants are \( K_{a1} = 9.5 \times 10^{-8} \) and \( K_{a2} = 3.0 \times 10^{-13} \).

\[
\text{FeS} (s) \leftrightharpoons \text{Fe}^{2+} + \text{S}^{2-} \quad K_{sp} = 4.2 \times 10^{-17}
\]

with

\[
\text{HS}^- \leftrightharpoons \text{H}^+ + \text{S}^{2-} \quad K_2 = 3.0 \times 10^{-13}
\]

At pH = 8, \([H^+] = 1.00 \times 10^{-8} \text{ M}\)

\[
S = [\text{Fe}^{2+}] = \sqrt{\frac{4.2 \times 10^{-17}}{1 + \frac{1.0 \times 10^{-8}}{3.0 \times 10^{-13}}}} = 1.2 \times 10^{-6} \text{ M}
\]

*Neglecting hydrolysis we would have gotten* \( S = [\text{Fe}^{2+}] = \sqrt{K_{sp}} = 6 \times 10^{-9} \text{ M or a factor of 200 less.}*

15. Calculate the free Cu\(^{2+}\) concentration in a solution that is initially contains 1.00 \times 10^{-3} \text{ M Cu(NH}_3)_4^{2+}\) and 0.0100 M NH\(_3\). The formation constant is \( K_f = 5 \times 10^{12} \).

\[
\text{Cu}^{2+} + 4 \text{NH}_3 \leftrightharpoons \text{Cu(NH}_3)_4^{2+}
\]

\[
K_f = \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}
\]

*This problem is easier if we look at the dissociation:*

\[
\text{Cu(NH}_3)_4^{2+} \leftrightharpoons \text{Cu}^{2+} + 4 \text{NH}_3
\]

The equilibrium constant is so small we can assume \([\text{Cu(NH}_3)_4^{2+}] = [\text{Cu(NH}_3)_4^{2+}]_o = 1.00 \times 10^{-3} \text{ M}\)

\[
K_d = \frac{1}{K_f} = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu(NH}_3)_4^{2+}]} \quad K_d = 1/K_f = 2 \times 10^{-13}
\]

\[
[Cu^{2+}] = K_d \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{NH}_3]^4} = 2 \times 10^{-13} \frac{1.00 \times 10^{-3}}{(0.0100)^4} = 2.00 \times 10^{-8} \text{ M}
\]