Name: _____

# Chemistry 142 Exam #2 Preparation KEY

## Part I

**Directions.** You will work out the problems on this page then enter them on the computer. Once you enter them into the computer you can submit your work for grading. You can re-enter (and re-score) the problems as many times as you wish.

**Question 1.** A weak acid, HA, has a pKa of 4.05. What is the pH of a 0.149 $M$ solution of HA?

$$K_a = \frac{[A^-][H^+]}{[HA]} = 10^{-4.05} = \frac{x^2}{(0.149-x)}$$

$$x = 3.64 \times 10^{-3}$$

$$pH = 2.44$$

**Question 2.** A weak base, B⁻, has a $pK_b$ of 5.52. A 25.00 mL aliquot of 0.137M B⁻ is titrated with 0.082$M$ HCl. Calculate the pH after 18.05 mL of acid are added.
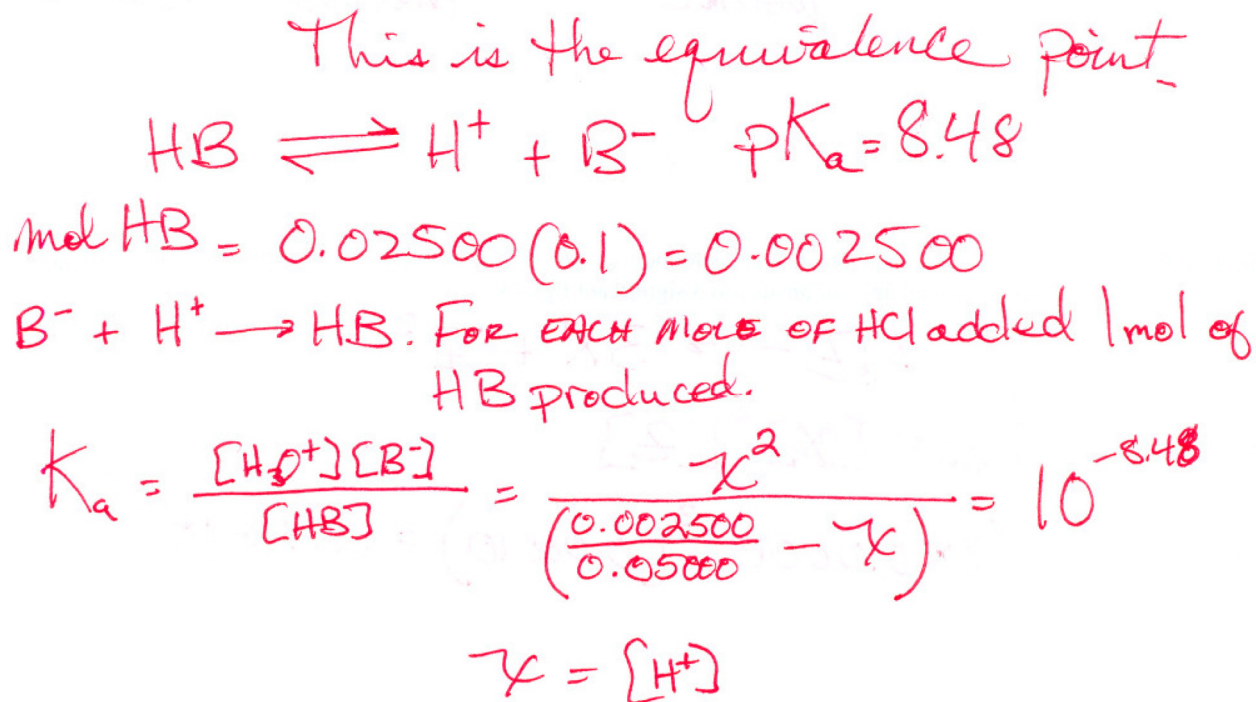
moles B⁻ before HCl added: $0.02500(0.137) = 3.425 \times 10^{-3}$

moles HCl added: $0.01805(0.082) = 1.480 \times 10^{-3}$

moles B⁻ after acid: $3.425 \times 10^{-3} - 1.480 \times 10^{-3} = 1.94 \times 10^{-3}$

moles HB after acid: $1.48 \times 10^{-3}$

$$10^{-5.52} = \frac{\left(\frac{1.48 \times 10^{-3}}{0.04305} + x\right) x}{\left(\frac{1.94 \times 10^{-3}}{0.04305} - x\right)}$$
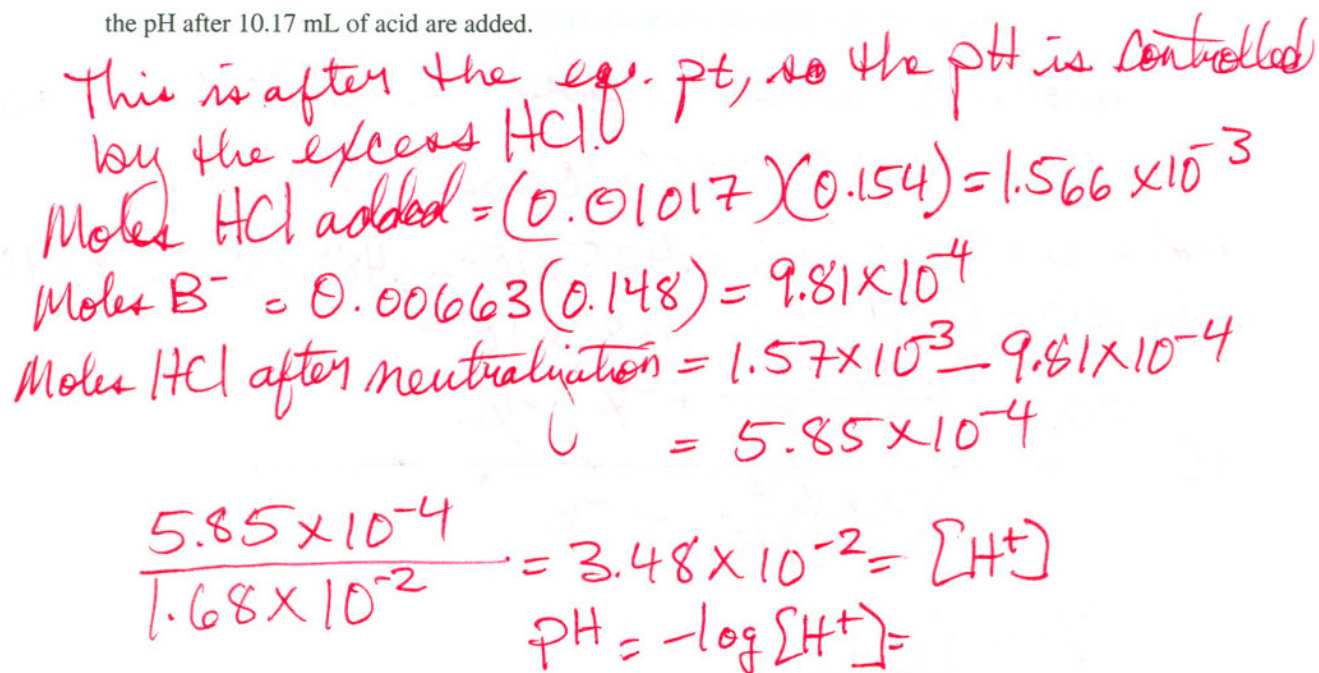
$$x = [OH^-]$$

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**Question 3.**    A weak base, B⁻, has a $pK_b$ of 5.52. A 25.00 mL aliquot of 0.100M B⁻ is titrated with 0.100$M$ HCl. Calculate the pH after 25.00 mL of acid are added.
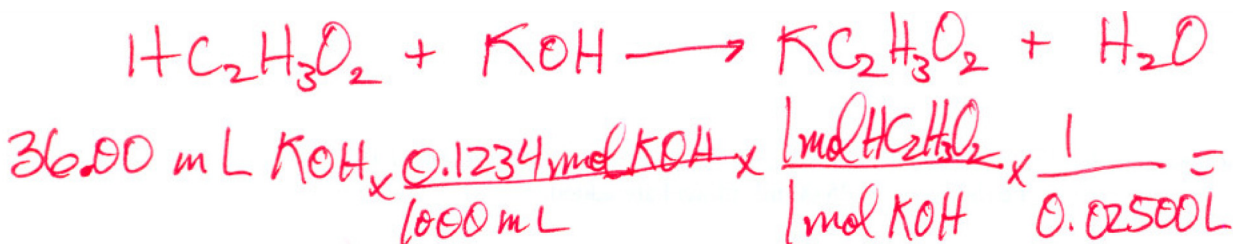
This is the equivalence point.

$$HB \rightleftharpoons H^+ + B^- \quad pK_a = 8.48$$

$$mol\ HB = 0.02500(0.1) = 0.0025000$$

$B^- + H^+ \longrightarrow HB$. For EACH MOLE OF HCl added 1 mol of HB produced.

$$K_a = \frac{[H_3O^+][B^-]}{[HB]} = \frac{x^2}{\left(\frac{0.002500}{0.05000} - x\right)} = 10^{-8.48}$$

$$x = [H^+]$$

**Question 4.**    A weak base, B⁻, has a $pK_b$ of 5.52. A 6.63 mL aliquot of 0.148$M$ B⁻ is titrated with 0.154$M$ HCl. Calculate the pH after 10.17 mL of acid are added.

the pH after 10.17 mL of acid are added.

This is after the eq. pt, so the pH is controlled by the excess HCl.

$$Moles\ HCl\ added = (0.01017)(0.154) = 1.566 \times 10^{-3}$$

$$Moles\ B^- = 0.00663(0.148) = 9.81 \times 10^{-4}$$

$$Moles\ HCl\ after\ neutralization = 1.57 \times 10^{-3} - 9.81 \times 10^{-4}$$

$$= 5.85 \times 10^{-4}$$

$$\frac{5.85 \times 10^{-4}}{1.68 \times 10^{-2}} = 3.48 \times 10^{-2} = [H^+]$$
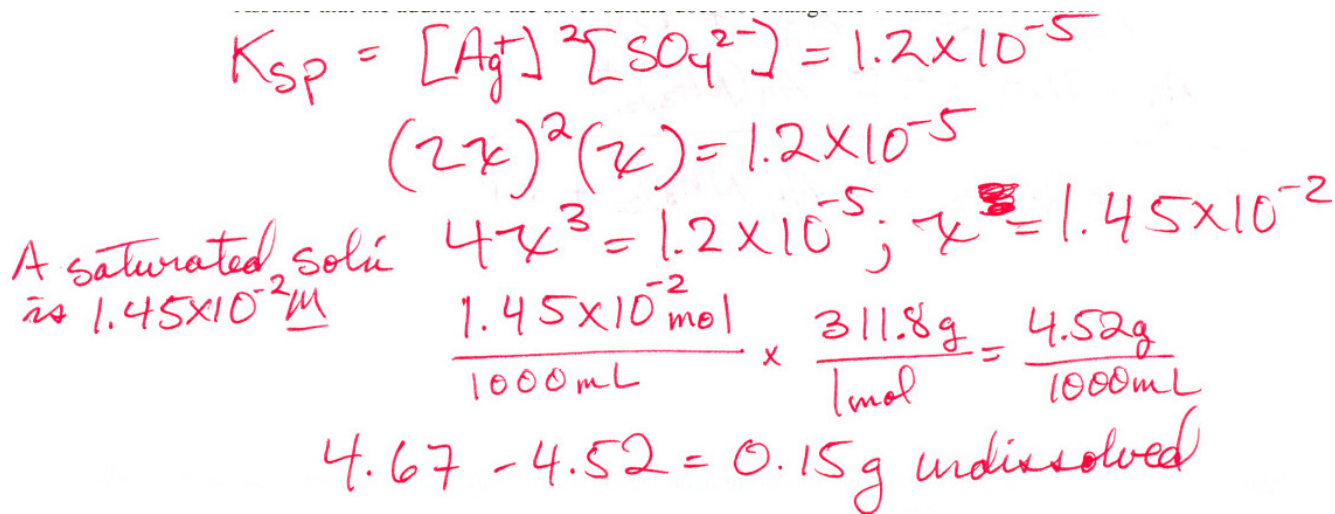
$$pH = -\log[H^+] =$$

**Question 5.** 25.00 mL of an acetic acid solution are titrated to the endpoint with 36.00 mL of 0.1234 *M* KOH solution. The $K_a$ for acetic acid is 1.8 x 10$^{-5}$. What is the molarity of the acetic acid solution?

$$HC_2H_3O_2 + KOH \longrightarrow KC_2H_3O_2 + H_2O$$

$$36.00 \text{ mL KOH} \times \frac{0.1234 \text{ mol KOH}}{1000 \text{ mL}} \times \frac{1 \text{ mol } HC_2H_3O_2}{1 \text{ mol KOH}} \times \frac{1}{0.02500 L} =$$

**Question 6.** A solution of the compound, $X_3Z$, is found to have a $Z^{3-}$ concentration of 0.00010$M$. Calculate $K_{sp}$ for this compound. Calculate your answer to 3 significant figures.
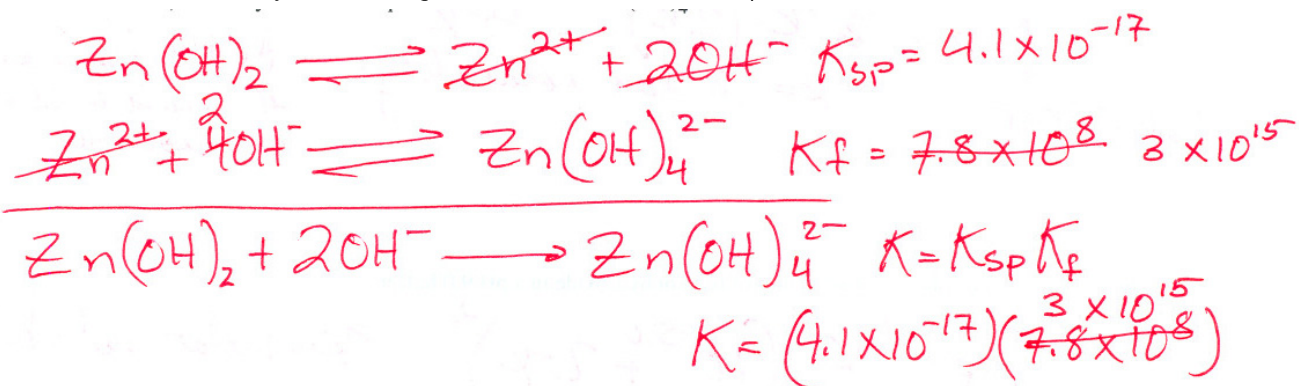
$$X_3Z \longrightarrow 3X^+ + Z^{3-}$$

$$K_{sp} = [X]^3[Z]$$

$$(3 \times 0.00010)^3 (0.00010) = 2.7 \times 10^{-15}$$
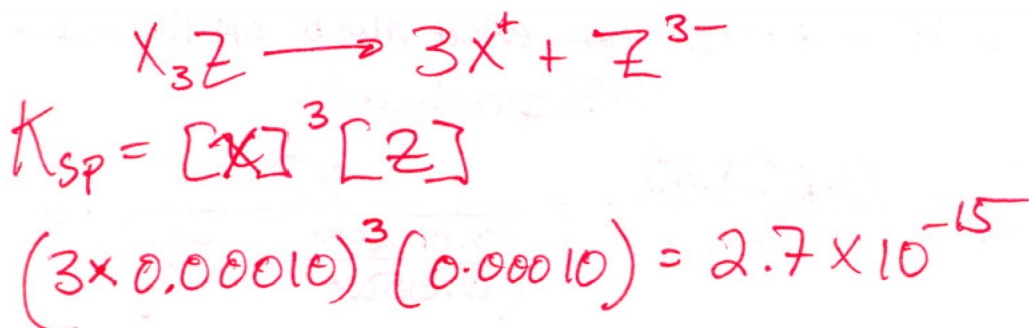
**Question 7.** 4.67 g of $Ag_2SO_4$ are placed in 1000 mL of distilled water in a 2 L beaker. After sufficient time is allowed, how many g of solid, undissolved silver sulfate remain in the beaker? $K_{sp}$ for silver sulfate is 1.2x10$^{-5}$. Assume that the addition of the silver sulfate does not change the volume of the solution.

$$K_{sp} = [Ag^+]^2[SO_4^{2-}] = 1.2 \times 10^{-5}$$

$$(2x)^2(x) = 1.2 \times 10^{-5}$$

A saturated soln
is $1.45 \times 10^{-2}M$

$$4x^3 = 1.2 \times 10^{-5}; \quad x = 1.45 \times 10^{-2}$$

$$\frac{1.45 \times 10^{-2} \text{ mol}}{1000 \text{ mL}} \times \frac{311.8 g}{1 \text{ mol}} = \frac{4.52 g}{1000 \text{ mL}}$$

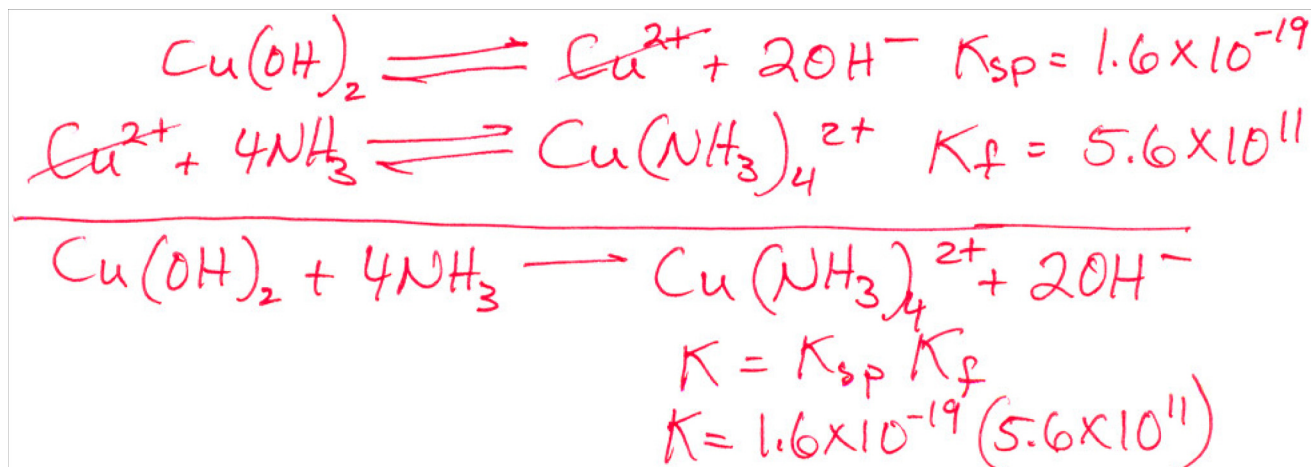$$4.67 - 4.52 = 0.15 g \text{ undissolved}$$

**Question 8.**   Write a balanced net ionic reaction for each of the following dissolution reactions, and use the appropriate $K_{sp}$ and $K_f$ values in the appendix of your text to calculate the equilibrium constant for each.

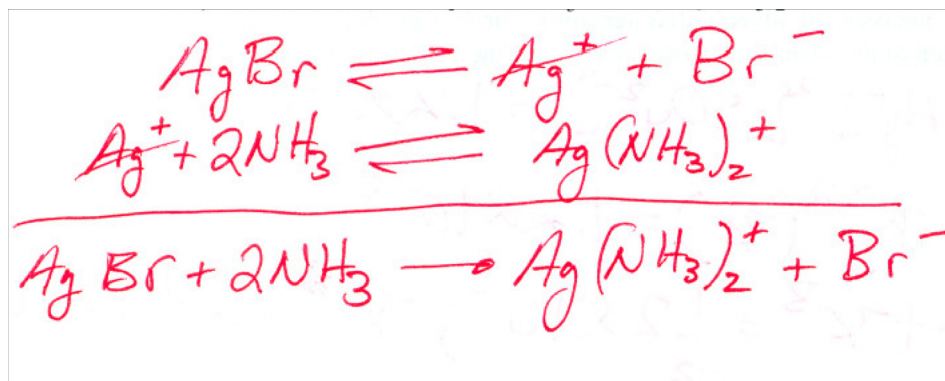*a)* Zinc hydroxide in aqueous NaOH to form $Zn(OH)_4^{2-}$

$$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^- \quad K_{sp} = 4.1 \times 10^{-17}$$

$$Zn^{2+} + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} \quad K_f = 7.8 \times 10^8 \quad 3 \times 10^{15}$$

$$Zn(OH)_2 + 2OH^- \longrightarrow Zn(OH)_4^{2-} \quad K = K_{sp}K_f$$

$$K = (4.1 \times 10^{-17})\left(\frac{3 \times 10^{15}}{7.8 \times 10^8}\right)$$

*b)* Copper(II) hydroxide in aqueous ammonia to form $Cu(NH_3)_4^{2+}$

$$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^- \quad K_{sp} = 1.6 \times 10^{-19}$$

$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+} \quad K_f = 5.6 \times 10^{11}$$

$$Cu(OH)_2 + 4NH_3 \longrightarrow Cu(NH_3)_4^{2+} + 2OH^-$$

$$K = K_{sp}K_f$$

$$K = 1.6 \times 10^{-19}(5.6 \times 10^{11})$$

c) Silver bromide in aqueous $NH_3$ to form $Ag(NH_3)_2^+$

$$AgBr \rightleftharpoons Ag^+ + Br^-$$
$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$$
$$\overline{AgBr + 2NH_3 \longrightarrow Ag(NH_3)_2^+ + Br^-}$$

**Question 9.** What is the molar solubility of barium hydroxide in water? Would you characterize barium hydroxide as being "soluble"? Why?

$$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$$
$$K_{SP} = [Ba^{2+}][OH^-]^2$$
$$K_{SP} = x(2x)^2 = 4x^3$$
$$x = molar\ solubility$$

look up $K_{SP}$

If the $K_{sp}$ is small it would be classified as insoluble
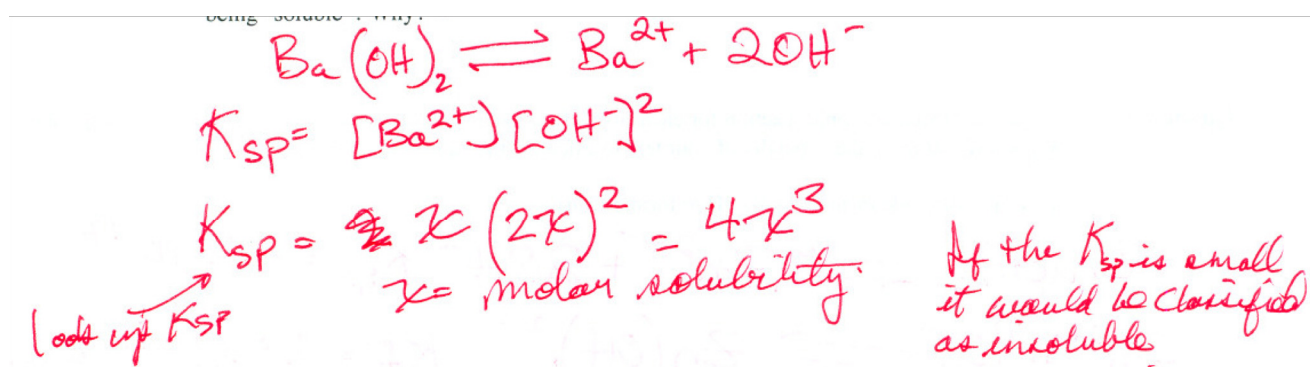
**Question 10.** What is the molar solubility of barium hydroxide in a pH 9.0 buffer?

$$K_{SP} = (x)(10^{-5.0} + 2x)^2 \qquad x = molar\ solubility$$
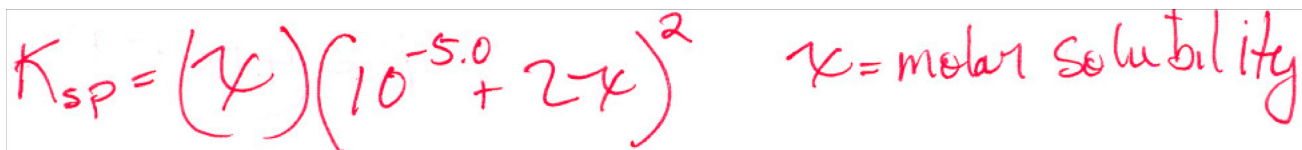
**Question 11.** For the vaporization of benzene, $\Delta H_{vap}$ = 30.7 kJ/mol, and $\Delta S_{vap}$ = 87.0 J/molK. Calculate $\Delta S_{total}$ at 70 °C.

$$\Delta S_{surr} = -\frac{\Delta H_{vap}}{T}; \quad \Delta S_{sys} = \Delta S_{vap}$$

$$\Delta S_{TOT} = \Delta S_{surr} + \Delta S_{sys}; \quad \Delta S_{surr} = \frac{-30,700 \text{ J/mol}}{343 \text{ K}}$$

$$\Delta S_{surr} = -89.5 \text{ J/K mole}$$

$$\Delta S_{TOT} = 87.0 \text{ J/mol K} + \left(-89.5 \text{ J/mol K}\right) = -2.5 \text{ J/K mol}$$

**Question 12.** Will benzene boil at 70 °C? Why?

No, the benzene will not boil because $\Delta S_{TOT}$ is negative at that temperature.

**Question 13.** Calculate, to three significant figures, the normal boiling point for benzene in °C.

At normal B.P. $\Delta S_{TOT} = 0$

$$\Delta S_{TOT} = -\frac{30,700 \text{ J/mol K}}{X} + 87.0 \text{ J/mol K} = 0$$

$$X = 353 \text{ K}; \ 80°C$$

**Question 14.** For melting of NaCl, $\Delta H_{fusion}$ = 30.2 kJ/mol, and $\Delta S_{fusion}$ = 28.1 J/molK. Calculate $\Delta S_{total}$ at 1050 K. Watch your significant figures.

$$\Delta S_{surr} = \frac{-\Delta H_{fus}}{T} = \frac{-30,200 \, J/mol}{1050 K} = -28.8 \, J/Kmol$$

$$\Delta S_{TOT} = 28.1 \, J/Kmol + 28.8 \, J/Kmol = -0.7 \, J/Kmol$$

**Question 15.** Does NaCl melt at 1050 K? Why?

No, because $\Delta S_{TOT}$ is negative.

**Question 16.** Calculate the melting point of NaCl. Report your answer in °C. Report your answer to three signficant figures.

$$\Delta S_{TOT} = \frac{-30,200 \, J/mol \, K}{X} + \left( -28.1 \, J/mol K \right) = 0$$

$$X = 1075 K$$

**Question 17.**   What ratio of acid to conjugate base ($[HA]/[A^-]$) is required to prepare a buffer with a pH of 3.6 using lactic acid. $K_a$ for lactic acid, $HC_3H_5O_3$ is $1.4 \times 10^{-4}$. Give two methods by which this buffer can be prepared.

**Answer.** $K_a = [H_3O^+][A^-]/[HA] = 1.4 \times 10^{-4} = 10^{-3.6}$ $[A^-]/[HA]$; $[A^-]/[HA] = 0.557$; $[HA] / [A^-] = 1.79$

One method that this buffer can be made is with a solution of lactic acid and a solution of sodium lactate. Mix the two solutions in the ratio calculated above for the correct pH. Another method involves the mixing of lactic acid and sodium hydroxide. A solution of lactic acid of sufficient titration is titrated with a solution of NaOH until the lactic acid / lactate ion concentrations are that calculated in the first part of this question.

# Part II

**Question 1.**   Discuss chemical spontaneity in terms of movement towards or away from equilibrium.

**Answer.** A spontaneous process in one where the process is moving towards equilibrium. A process moving away from equilibrium is a non-spontaneous process.

**Question 2.**   Discuss thermodynamic stability and kinetic stability.

**Answer.** A stable substance is one that does not readily undergo reaction under a certain set of conditions. This stability can be the result of a slow kinetic process where a reaction is too slow to occur in a timely manner. A substance can also be thermodynamically stable where a reaction is non-spontaneous.

**Question 3.**     How can a reaction be endothermic, yet spontaneous? Offer an example with an explanation.

**Answer.** To be spontaneous $\Delta S_{total}$ needs to be positive. Since $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$, there are two changes in entropy that must be considered. $\Delta S_{surr}$ is dependent on the enthalpy change change of the reaction. For an endothermic reaction $\Delta S_{surr}$ is negative. Thus, $\Delta S_{sys}$ must be suffciently positive to counter-act the negative $\Delta S_{surr}$. An example of this is the dissolution of $NH_4NO_3$. This is an endothermic process, yet it is spontaneous due to the entropy-favorable provcess of dissociation.

**Question 4.**     Explain the statement, "A disordered state is more probable than an ordered state." Be sure to offer examples.

**Answer.** The greater the number of ways that a particular state can be arranged, the higher the probability of any single state occuring. Consider two flasksconnected by a stopcock. One flask is evacuated and the other is filled with $N_2$. If the stopcock is opened the $N_2$ will spontaneously flow into the evacuated container until the pressure is the same in both containers. While possible, it is *highly* improbable that the $N_2$ would collect preferentially in a single flask. Therefore, the state with the $N_2$ equally distributed is more probable and more disordered.

**Question 5.**     Explain the statement, "In any spontaneous process at constant temperature and pressure, the free energy of the system always decreases."

**Answer.** $\Delta G$ for a spontaneous process is negative and $\Delta G$ for all processes is 0 at equilibrium. Since a spontaneous process is heading toward equilibrium, the $\Delta G$ for this process is approaching zero, thus decreasing.

**Question 6.**     Discuss the notion that free energy is the maximum useful work that can be produced by a system.

**Answer.** In all spontaneous processes there is energy that can be used to do useful work. Some energy, however, goes to heating the surroundings and increasing the entropy of the surroundings. Since $\Delta G = \Delta H - T\Delta S$, $\Delta G$ represents the total energy produced minus that used to warm the surroundings.

**Question 7.**     Discuss the relationship between free energy and the equilibrium constant.

**Answer.** $\Delta G° = -RT\ln K$. A negative $\Delta G$ indicates a K value larger than 1. This indicates a reaction that, when complete, is mostly products. A small value of K is typical for a non-spontaneous process.

# Thermodynamics

1. How the tendency of a process to occur by itself is distinct from how long it takes to occur
2. The distinction between a spontaneous and a non-spontaneous change.
3. Why the first law of thermodynamics and the sign of $\Delta H°$ cannot predict the direction of a spontaneous reaction
4. The natural tendency of a system to become disordered over time and why a disordered system is more probable than an ordered one
5. How disorder is expressed quantitatively by entropy ($S$)
6. How the second law of thermodynamics expresses the criterion of spontaneity, that a change increases $S_{univ}$
7. How absolute entropies ($S°$) can be obtained because the third law of thermodynamics provides a "zero point"
8. How temperature, physical state, dissolution, molar mass, and molecular complexity influence $S°$ values
9. How $\Delta S°_{rxn}$ is based on the difference between the $S°$ values of the reactants and the products
10. How the surroundings add heat to or remove heat from the system and how $\Delta S°_{surr}$ influences the overall $\Delta S°_{rxn}$.
11. The relationship between $\Delta S°_{surr}$ and $\Delta H°_{sys}$
12. How reactions proceed spontaneously toward equilibrium ($\Delta S°_{univ} > 0$) and then proceed no further at equilibrium ($\Delta S°_{univ}= 0$)
13. How the free energy change combines the system's entropy and enthalpy changes
14. How the expression for the free energy change is derived from the second law
15. The relationship between $\Delta G$ and the maximum work a system can perform and why this quantity of work is never performed in a real process
16. How temperature determines spontaneity for reactions in which $\Delta S°$ and $\Delta H°$ have the same sign
17. Why the temperature at which a reaction becomes spontaneous occurs when $\Delta G° = 0$
18. How $\Delta G°$ is the free energy change from the start of a reaction (expressed by $Q$) to its end (expressed by $K$)
19. The meaning of $\Delta G°$ and its relation to $K$
20. The relation of $\Delta G$ to $\Delta G°$ and $Q$
21. How $\Delta G$ decreases, no matter what the starting concentrations, as the reacting system moves spontaneously toward equilibrium

## *Required Skills*

1. Predicting relative $S°$ values of substances and mixtures
2. Calculating $\Delta S°_{rxn}$ for a chemical or physical change
3. Determining reaction spontaneity from $\Delta S°_{surr}$, and $\Delta H°_{sys}$
4. Calculating $\Delta G°_{rxn}$ from $\Delta H°_f$ and $S°$ values
5. Calculating $\Delta G°_{rxn}$ from $\Delta G°_f$ values
6. Calculating the effect of temperature on $\Delta G°_{rxn}$
7. Calculating the temperature at which a reaction becomes spontaneous
8. Calculating $K$ from $\Delta G°$
9. Using $\Delta G°$ and $Q$ to calculate $\Delta G$ at any temperature

## *Equations*

1. $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

2. $\Delta S°_{rxn} = \Sigma mS°_{products} - \Sigma mS°_{reactants}$

3. $\Delta S_{surr} - \dfrac{\Delta H}{T}$

4. $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$

5. $\Delta G°_{sys} = \Delta H°_{sys} - T\Delta S°_{sys}$

6. $\Delta G°_{rxn} = \Sigma mG°_{products} - \Sigma mG°_{reactants}$

7. $T = \dfrac{\Delta H°}{\Delta S°}$

8. $\Delta G = RT\ln\dfrac{Q}{K} = RT\ln Q - RT\ln K$

9. $\Delta G = \Delta G° + RT\ln Q$