INTRODUCTION

Every chemical reaction has a characteristic condition of equilibrium at a given temperature. If two reactants are mixed, they will tend to react to form products until a state is reached where the amounts of reactants and products no longer change. Under such conditions the reactants and products are in chemical equilibrium and will remain so until the system is altered in some way.   Associated with the equilibrium state there is a number called the *equilibrium constant*, K_{eq}, that expresses the necessary condition on the concentrations of reactants and products for the reaction. Consider the following idealized reaction, where a, b, c and d represent coefficients and A, B, C and D represent reactants and products.

$$aA + bB \longleftrightarrow cC + dD \qquad (1)$$

The expression for the equilibrium constant is as follows.

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (2)$$

Concentrations of solutes in solution are expressed in terms of molarity. The equilibrium constant will have a fixed value for the reaction at any given temperature. If A, B, C and D are mixed in arbitrary amounts in a container they will tend to react until their concentrations satisfy equation 2. Depending upon the magnitude of K_{eq} and the amounts of species used initially, reaction 1 will proceed to the right or to the left until equilibrium in attained.

In this experiment we will study the equilibrium properties of the reaction between the iron(III) ion and thiocyanic acid (HSCN):

$$Fe^{3+}_{(aq)} + HSCN_{(aq)} \longleftrightarrow FeSCN^{2+}_{(aq)} + H^+_{(aq)} \qquad (3)$$

When solutions containing Fe^{3+} ion and thiocyanic acid are mixed, reaction 3 occurs to some extent, forming the $FeSCN^{2+}$ complex ion, which has a deep blood red color, and H^+ ion. As a result of the reaction, the equilibrium amounts of Fe^{3+} and HSCN will be less than they would have been if no reaction had occurred; for every mole of $FeSCN^{2+}$ that is formed, one mole of Fe^{3+} and one mole of HSCN will react. According to the general law, K_{eq} for reaction 3 takes the following form.

$$K_{eq} = \frac{[FeSCN^{2+}][H^+]}{[Fe^{3+}][HSCN]} \qquad (4)$$

Our purpose in the experiment will be to evaluate K_{eq} for the reaction by determining the equilibrium concentrations of the four species in equation 4 in several solutions made up in different ways. The equilibrium constant for the reaction has a convenient magnitude and the color of the $FeSCN^{2+}$ ion makes for an easy analysis of the equilibrium mixture.

       The solutions will be prepared by mixing solutions containing known concentrations of iron(III) nitrate and thiocyanic acid. The color of the $FeSCN^{2+}$ ion formed will allow us to determine its equilibrium concentration by spectroscopy. Knowing the initial composition of the solution and the equilibrium concentration of $FeSCN^{2+}$, we can calculate the equilibrium concentrations of the rest of the pertinent species and then calculate K_{eq}.

       Since the calculations that are necessary to find K_{eq} may not be apparent, let us consider a specific example. Assume that we prepare our solution by mixing 10.0 mL of 2.00×10^{-3} M $Fe(NO_3)_3$ with 10.0 mL of 2.00×10^{-3} M HSCN under conditions which keep $[H^+]$ equal to 0.500 M. The Fe^{3+} in the iron(III) nitrate reacts with the HSCN to produce some red $FeSCN^{2+}$ complex ion. By spectroscopy and Beer's Law, it is found that $[FeSCN^{2+}]$ at equilibrium is 1.50×10^{-4} M.

       To find K_{eq} for the reaction from these data, it is convenient first to determine how many moles of reactant species were initially present before a reaction occurred. By the definition of the molarity of a species A,

$$M_A = \frac{\text{moles A}}{\text{Liters A}} \text{ or moles A} = M_A V$$

where V is the volume of the solution in liters. (Remember that 1000 mL = 1 L.)

       initial moles $Fe^{3+} = (M_{Fe}{}^{3+})(V_{Fe}{}^{3+}) = 2.00 \times 10^{-3}$ mol/L (0.0100 L)
            $= 2.00 \times 10^{-5}$ mol Fe^{3+}

       initial moles HSCN $= (M_{HSCN})(V_{HSCN}) = 2.00 \times 10^{-3}$ mol/L (0.0100 L)
            $= 2.00 \times 10^{-5}$ mol HSCN

The number of moles of $FeSCN^{2+}$ present at equilibrium is found from the molarity and the volume of the solution (10.0 mL + 10.0 mL = 20.0 mL).

       equilibrium moles $FeSCN^{2+} = (M_{FeSCN}{}^{2+})(V_{FeSCN}{}^{2+}) = 1.50 \times 10^{-4}$ M (0.0200 L)
            $= 3.00 \times 10^{-6}$ mol $FeSCN^{2+}$

The $FeSCN^{2+}$ ion is produced by reaction 3.

$$Fe^{3+}{}_{(aq)} + HSCN_{(aq)} \longleftrightarrow FeSCN^{2+}{}_{(aq)} + H^+{}_{(aq)} \quad\quad (3)$$

Therefore, for every mole of $FeSCN^{2+}$ present in the equilibrium mixture, one mole Fe^{3+} and one mole HSCN are reacted. We can see then that

equilibrium moles Fe^{3+} = initial moles Fe^{3+} – equilibrium moles $FeSCN^{2+}$
equilibrium moles Fe^{3+} = 2.00 x 10^{-5} mol – 3.00 x 10^{-6} mol = 1.70 x 10^{-5} mol Fe^{3+}

Similarly for HSCN,

equilibrium moles HSCN = 2.00 x 10^{-5} mol – 3.00 x 10^{-6} mol = 1.70 x 10^{-5} mol HSCN

Knowing the number of moles of Fe^{3+} and HSCN present in the equilibrium mixture and the volume of the mixture, we can easily find the concentrations of those two species.

$$[Fe^{3+}] = \frac{mol\ Fe^{3+}}{L\ solution} = \frac{1.70\ x\ 10^{-5}\ mol}{0.0200\ L} = 8.50\ x\ 10^{-4}\ M$$

$$[HSCN] = \frac{mol\ HSCN}{L\ solution} = \frac{1.70\ x\ 10^{-5}\ mol}{0.0200\ L} = 8.50\ x\ 10^{-4}\ M$$

To organize all the initial and final numbers of moles and the final (equilibrium) molarities,

	$Fe^{3+}_{(aq)}$	+	$HSCN_{(aq)}$	$\leftrightarrow$	$FeSCN^{2+}_{(aq)}$	+	$H^{+}_{(aq)}$
Initial moles	2.00 x 10^{-5}		2.00 x 10^{-5}		0		
Change	-3.00 x 10^{-6}		-3.00 x 10^{-6}		+3.00 x 10^{-6}		Concentration kept constant at 0.500 M
Final moles	1.70 x 10^{-5}		1.70 x 10^{-5}		3.00 x 10^{-6}		
Final volume	0.0200 L		0.0200 L		0.0200 L		
Final M	8.50 x 10^{-4}		8.50 x 10^{-4}		1.50 x 10^{-4}		

We can now substitute into equation 4 to find the equilibrium constant for this reaction:

$$K_{eq} = \frac{[FeSCN^{2+}][H^{+}]}{[Fe^{3+}][HSCN]} = \frac{(1.50\ x\ 10^{-4}\ M)(0.500\ M)}{(8.50\ x\ 10^{-4}\ M)(8.50\ x\ 10^{-4}\ M)} = 104$$

(The data in this calculation correspond to a different temperature than the one at which you will be working, so the actual value of K_{eq} you will obtain will not be the one found above.)

Methods of analysis have been developed to determine the [FeSCN^{2+}] in the equilibrium mixtures. A very precise method makes use of a spectrophotometer, which measures the amount of light absorbed (or transmitted) by the red complex at 447 nm, the wavelength at which the complex most strongly absorbs. The absorbance, A, of the complex is proportional to its concentration, c, according to Beer's Law. (Check the Beer's Law lab if you need more information.)

$$A = abc \quad (5)$$

In order to use Beer's Law to determine the equilibrium concentration of FeSCN^{2+} you will have to prepare a calibration curve using known concentrations of FeSCN^{2+}. You will measure percent transmittance and then convert it to absorbance using equations 6 and 7, which can be combined into equation 8. Use either equations 6 <u>and</u> 7 or equation 8 alone.

$$T = \%T/100 \quad (6) \qquad A = -\log(T) \quad (7) \qquad A = -\log(\%T/100) \quad (8)$$

PROCEDURE

<u>Preparation of Calibration Curve</u>

Pipet 0.50 mL, 1.00 mL and 1.50 mL aliquots of 2.00×10^{-3} M HSCN in 0.5 M HNO$_3$ into three 10 mL volumetric flasks. Fill to the mark with 0.200 M Fe(NO$_3$)$_3$ in 0.5 M HNO$_3$. Stopper and mix well. Measure the percent transmittance of each of these three solutions at 447 nm, using distilled water as the blank to calibrate the spectrophotometer.

<u>Equilibrium Reaction</u>

Label five 10 mL volumetric flasks 1 through 5. Pipet 5.00 mL of 2.00×10^{-3} M Fe(NO$_3$)$_3$ in 0.500 M HNO$_3$ into each volumetric flask. Into each of the five flasks labeled 1 through 5, pipet the corresponding number of mL (1 through 5) of 2.00×10^{-3} M HSCN in 0.500 M HNO$_3$. To each flask except the one labeled 5, fill to the mark with 0.500 M HNO$_3$. Each flask will now contain 10.0 mL of total solution. Stopper each flask and mix well.

Measure the percent transmittance of a portion of each solution in the spectrophotometer at 447 nm.

General Chemistry II Lab　　　　　　**#7 – Determination of the Equilibrium Constant**

DATA AND CALCULATIONS

Calibration Curve

Volume HSCN (mL)	[HSCN] (M)	% Transmittance	Absorbance
0.50			
1.00			
1.50			

Equilibrium Reaction

#	Volume (mL)			% Transmittance	Absorbance	[FeSCN^{2+}] (M)
	Fe(NO$_3$)$_3$	HSCN	HNO$_3$			
1	5.00	1.00	4.00			
2	5.00	2.00	3.00			
3	5.00	3.00	2.00			
4	5.00	4.00	1.00			
5	5.00	5.00	0.00			

Instructor's Stamp_____

CALCULATIONS

Calibration Curve

Calculate the concentrations of your three reference solutions. Since the $[Fe^{3+}]$ is so much greater than the [HSCN], one can safely assume that all the HSCN has been changed to $FeSCN^{2+}$. (That is, HSCN is the limiting reactant and will determine the amount of $FeSCN^{2+}$.)

Using a computer graphing program such as Excel or Graphical Analysis, plot Absorbance vs. Concentration. Have the computer put the best straight line and the equation of the line on the graph. Include the graph with the report.

Equilibrium Reaction

Calculate K_{eq} assuming the reaction: $Fe^{3+}_{(aq)} + HSCN_{(aq)} \leftrightarrow FeSCN^{2+}_{(aq)} + H^{+}_{(aq)}$. This calculation is most readily carried out by completing the following tables as follows.

1. Knowing the initial concentrations and volumes of Fe^{3+} and HSCN, calculate the initial number of moles of these species.

2. Calculate $[FeSCN^{2+}]$ using A = abc. From your calibration curve, the slope of the line, m, equals the product ab. Therefore, A = mc. You measured %T and can calculate A. From A and m, calculate c, which is $[FeSCN^{2+}]$.

3. Realizing that 1 mole of $FeSCN^{2+}$ is formed at the expense of 1 mole of Fe^{3+} and 1 mole of HSCN, calculate the number of moles of Fe^{3+} and HSCN at equilibrium.

4. Knowing the number of moles of Fe^{3+} and HSCN at equilibrium and the volume (10.0 mL), calculate $[Fe^{3+}]$ and [HSCN].

5. Use equation 4 to calculate K_{eq}.

General Chemistry II Lab   **#7 – Determination of the Equilibrium Constant**
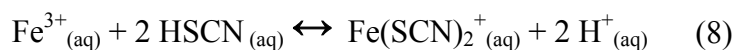
CALCULATIONS

#	Initial Moles		Equilibrium Moles		
	Fe^{3+}	HSCN	$FeSCN^{2+}$	Fe^{3+}	HSCN
1					
2					
3					
4					
5					

#	$[Fe^{3+}]$ (M)	[HSCN] (M)	$[FeSCN^{2+}]$ (M)	$[H^+]$ (M)	K_{eq}
1				0.500	
2				0.500	
3				0.500	
4				0.500	
5				0.500	

General Chemistry II Lab   **#7 – Determination of the Equilibrium Constant**

QUESTIONS

In calculating K_{eq} above, we assumed that the formula of the complex ion was $FeSCN^{2+}$. It is by no means obvious that this is the case, and one might have assumed, for instance, that $Fe(SCN)_2^+$ was the species formed. The reaction would then have been:

$$Fe^{3+}_{(aq)} + 2\ HSCN_{(aq)} \longleftrightarrow Fe(SCN)_2^+{}_{(aq)} + 2\ H^+{}_{(aq)} \quad (8)$$

If we analyzed the equilibrium reaction assuming that reaction 8 occurred rather than reaction 3, we would probably obtain nonconstant values of K_{eq}. Using the same kind of procedure as above, calculate K_{eq} for solutions 1, 3 and 5 on the basis that $Fe(SCN)_2^+$ formed by reaction between Fe^{3+} and HSCN. Because of the procedure used for calibrating the system by this method, $[Fe(SCN)_2^+]$ will equal one-half the $[FeSCN^{2+}]$ obtained for each solution above. Note that 2 moles of HSCN are needed to form one mole $Fe(SCN)_2^+$ according to reaction 8. This changes not only the relative numbers of moles from the previous case but also the expression for K_{eq}. (See the prestudy, question 3b and fill in the expression below)

$$K_{eq} = \underline{\hspace{4cm}}$$

#	Initial Moles		Equilibrium Moles		
	Fe^{3+}	HSCN	$Fe(SCN)_2^+$	Fe^{3+}	HSCN
1					
3					
5					

#	$[Fe^{3+}]$ (M)	[HSCN] (M)	$[Fe(SCN)_2^+]$ (M)	$[H^+]$ (M)	K_{eq}
1				0.500	
3				0.500	
5				0.500	

The correct reaction should have K_{eq} values that are truly constants (within experimental error). An incorrect K_{eq} expression from an incorrect equation will lead to nonconstant K_{eq} values.

1. Based on your results, which equation, 3 or 8, leads to constant K_{eq} values? Justify your answer.

$$Fe^{3+}_{(aq)} + HSCN_{(aq)} \longleftrightarrow FeSCN^{2+}_{(aq)} + H^+_{(aq)} \qquad (3)$$
$$Fe^{3+}_{(aq)} + 2\,HSCN_{(aq)} \longleftrightarrow Fe(SCN)_2^+{}_{(aq)} + 2\,H^+_{(aq)} \qquad (8)$$
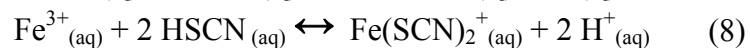
2. What is the correct formula of the iron(III)-thiocyanate complex ion?

NAME _____

PRESTUDY

Include a separate piece of paper showing your calculations.

1. (2) a.   When Fe^{3+} and HSCN react to form an equilibrium with $FeSCN^{2+}$ and H^+, what happens to the concentration of Fe^{3+}?

b. How are the numbers of moles of $FeSCN^{2+}$ produced and the number of moles of Fe^{3+} used up related to each other?

2. (6)   In an experiment similar to the one you will be doing, the $FeSCN^{2+}$ equilibrium concentration was found to be 3.20×10^{-5} M in a solution made by mixing 5.00 mL of 1.00×10^{-3} M $Fe(NO_3)_3$ with 5.00 mL of 1.00×10^{-3} M HSCN. The H^+ concentration was maintained at 0.500 M.

a. How many moles $FeSCN^{2+}$ are present at equilibrium?   _____

b. How many moles each of Fe^{3+} and HSCN were initially present?   _____

c. How many moles Fe^{3+} remained unreacted in the equilibrium mixture?   _____

d. How many moles of HSCN remained unreacted?   _____

e. What are $[Fe^{3+}]$ and [HSCN] in the equilibrium solution?   _____

f. Calculate K_{eq} for the reaction.   _____

3. (2) In this experiment, we assume that the complex ion formed is $FeSCN^{2+}$. It would be possible, however, to form $Fe(SCN)_2^+$ under certain conditions.

a. Write the equation for the reaction between Fe^{3+} and HSCN in which $Fe(SCN)_2^+$ is produced. (Hint: Look in the previous pages!)

b.   Formulate the expression, analogous to equation 4, for the equilibrium constant, K_{eq}, associated with the reaction in part a.