Name______________________________ Section________________

Partner(s)__________________________ Date___________________

SPECTROPHOTOMETRIC DETERMINATION OF THE EQUILIBRIUM CONSTANT FOR THE FORMATION OF A COMPLEX ION

PRE-LAB QUERIES

1. What is the oxidation number of iron in $FeSCN^{+2}$?

2. Consider the equilibrium for this activity given in the introduction below. How could you shift the reaction to change the concentration of the complex ion?

OBJECT

In this activity you will determine the equilibrium constant for the formation of the thiocyanatoiron (III) ion, $FeSCN^{+2}$. Since this ion has a reddish-orange color, its concentration can be determined by spectrophotometry.

INTRODUCTION

An orange colored complex ion is formed by the addition of iron (III) ion and thiocyanate ion as long as the iron (III) ion concentration is well above the thiocyanate concentration.

$$Fe^{+3}(aq) + SCN^{-}(aq) \rightarrow FeSCN^{+2}(aq) \quad (1)$$

Since the thiocyanatoiron (III) ion, $FeSCN^{+2}$, is the only colored ion in the reaction above, its concentration can be determined by spectrophotometry. If excess SCN^- is present the following reaction occurs forming a blood-red complex, $Fe(SCN)_2^+$ (dithiocyantoiron (III)), an old movie method of making blood.

$$FeSCN^{+2}(aq) + SCN^{-}(aq) \rightarrow Fe(SCN)_2^{+}(aq) \quad (2)$$

In this activity we will maintain the SCN^- at low values compared to the iron (III) ion to avoid reaction (2) from occurring.

The equilibrium constant for reaction (1) is given below:

$$K = \frac{[FeSCN^{+2}]}{[Fe^{+3}]\,[SCN^{-}]}$$

If we start out with a very large iron (III) concentration, reaction (1) will be shifted to the products such that the $[SCN^-]_o = [FeSCN^{+2}]$ and the absorbance of the complex ion can be measured. This will serve as the standard since both concentration and absorbance are known. We will assume that Beer's Law holds and that we can determine the concentration of the complex by measuring absorbances of the complex ion while lowering the concentration of Fe^{+3} in solution. The complex ion concentration in various equilibrium mixtures can be found from the following equation.

$$c_{unkn} = (A_{unkn}/A_{std})c_{std}$$

PROCEDURE

1. Working in pairs, each group will need to clean and dry six test tubes and label them 1 to 6. Obtain seven spectrophotometer tubes and two 5 mL pipets.

2. Pipet 5 mL of 2.0×10^{-4} M NaSCN into each of the six test tubes. Pipet 5 mL of 0.20 M $Fe(NO_3)_3$ into test tube #1. This is your standard for the analysis. The concentration of Fe^{+3} is so large as to shift essentially all the SCN^- into the complex.

The remaining solutions will be made by diluting the Fe^{+3} in a graduated cylinder, allowing the reaction to shift to the left and be at equilibrium. **Mix all the solutions thoroughly.**

3. Place 10 mL of 0.20 M $Fe(NO_3)_3$ into a 25 mL graduated cylinder and add distilled water to bring the volume to 25 mL. You have 25 mL of 0.080 M $Fe(NO_3)_3$. Pipet 5 mL of this solution into test tube #2.

4. Place 10 mL of 0.080 M $Fe(NO_3)_3$ into another 25 mL graduated cylinder and add distilled water to bring the volume to 25 mL. You now have 25 mL of 0.032 M $Fe(NO_3)_3$. Pipet 5 mL into test tube #3.

5. Place 10 mL of 0.032 M $Fe(NO_3)_3$ into another 25 mL graduated cylinder and add distilled water to bring the volume to 25 mL. You have 25 mL of 0.0128 M $Fe(NO_3)_3$. Pipet 5 mL into test tube #4.

6. Place 10 mL of 0.0128 M $Fe(NO_3)_3$ into another 25 mL graduated cylinder and add distilled water to bring the volume to 25 mL. You have 25 mL of 0.00512 M $Fe(NO_3)_3$. Pipet 5 mL into test tube #5.

7. Place 10 mL of 0.00512 M $Fe(NO_3)_3$ into another 25 mL graduated cylinder and add distilled water to bring the volume to 25 mL. You have 25 mL of 0.002048 M $Fe(NO_3)_3$. Pipet 5 mL

into test tube #6.

8. Using the standard (test tube #1), perform a wavelength scan from 400 to 650 nm at 20 nm intervals to determine λ_{max}. Record in the table and generate/print an absorbance vs. wavelength graph (absorption spectrum). If you use Excel, select a smooth, connected scatter plot format.

9. Set the spectrophotometer to λ_{max}. Measure the absorbances of the solutions in all six test tubes after setting the spectrophotometer using distilled water as a blank. Record the data.

DATA/RESULTS

Absorption Spectrum

Wavelength	Absorbance	Wavelength	Absorbance
400 nm		540	
420		560	
440		580	
460		600	
480		620	
500		640	
520		650	

λ_{max} = ___________

Attach the absorption spectrum of $Fe(SCN)^{+2}$. Label λ_{max} on the graph.

Tube Number	$[Fe^{3+}]_o$	Absorbance
1 (standard)		
2		
3		
4		
5		
6		

For all tubes: $[SCN^-]_o$ = ______________________

Open the following file from the CHM 103 Folder: Fe(SCN)++_equil_const.xls. Record the absorbance and Fe^{3+} concentration data in the Excel spreadsheet. The spreadsheet will calculate the equilibrium values for all reactants and products and the equilibrium constant (K) using the following equations:

$$[FeSCN^{+2}]_{eq} = [Fe^{+3}]_{reacted} = [SCN^-]_{reacted}$$

$$[SCN^-]_{eq} = [SCN^-]_o - [FeSCN^{+2}]_{eq}$$

$$[Fe^{+3}]_{eq} = [Fe^{+3}]_o - [FeSCN^{+2}]_{eq}$$

$$K = \frac{[FeSCN^{+2}]}{[Fe^{+3}]\,[SCN^-]}$$

The spreadsheet will compute the average K, %CV, and % error. Be sure that you complete the spreadsheet with the group member names and save the file on the desktop with a different file name. Print a copy of the spreadsheet for the instructor and submit this before you leave the lab. The instructor will post an address where you will be able to obtain the class data. Use these to analyze results and make conclusions.

ANALYSIS/CONCLUSIONS

Be sure to attach a copy of the spreadsheet and any graphs to this activity if it is being submitted for credit.

1. The literature value of the equilibrium constant is 140. How does your average value compare to this value? Rank the groups based on the degree of error.

   Discuss factors that might contribute to a larger % error and how they affect the value.

2. How does your precision compare to other groups of students? Which group was most precise? Least precise? Support your statements!

POST-LAB QUESTIONS

1. Using a mathematical equation, show how the equilibrium concentration of the complex ion, $[Fe(SCN)^{2+}]_{eq}$, is determined? Define all known and unknown variables.

2. Complete the table below using **ONLY** the quantities already given in the table or the number zero if appropriate.

Reaction	Fe^{3+} +	SCN^- →	$Fe(SCN)^{++}$
initial	$[Fe^{3+}]_o$	$[SCN^-]_o$	
equilibrium			$[Fe(SCN)^{2+}]_{eq}$

3. Write the equilibrium constant for the reaction.

4. The calculation of the equilibrium constant will be done by supplying your data for the six test tubes into an "active" Excel spreadsheet. The Excel spreadsheet is set up with all the necessary calculations stored and protected in the appropriate cells, you just type in your data and the calculations will be done for you. **You must still understand how the calculations are done!** Attach the printout of the Excel spreadsheet results.

5. For test tube #1, which is the *standard* due to its very high (Fe^{3+}), how is the reaction influenced by the following additions? Consider both how the reaction shifts and how the absorbance might change.

Addition	Fe^{3+} +	SCN^- →	$Fe(SCN)^{2+}$	Shift	Absorbance
case 1	add more				
case 2		add more			