DETERMINATION OF AN EQUILIBRIUM CONSTANT
A STUDY OF THE IRON-THIOCYANATE REACTION

OBJECTIVES:

When this experiment is completed you should be able to:

- ✓ Calculate the Molarity of all prepared solutions using the formula for dilutions.
- ✓ Use the visible spectrometer to produce the calibration curve for the Iron (III) Thiocyanate complex.
- ✓ Measure equilibrium concentrations of the Iron (III) Thiocyanate complex using the visible spectrometer and calibration curve determined above.
- ✓ Determine the equilibrium constant, K_c, for this reaction.

PRE-LAB PREPARATION:

1. Read the lab discussion and procedures to decide (and write down) your learning objective.

2. Summarize the discussion in bullet format.

3. Pre-lab math exercises:

   a) A silver nitrate ($AgNO_3$) solution is 0.150 M. 100.0 mL of a diluted silver nitrate solution is prepared using 10.0 mL of the more concentrated solution (which is then diluted with distilled water to 100.0 mL). Use the dilution equation to find the molarity of silver nitrate in the diluted solution.

   b) Silver ion (Ag^+) forms a complex with ammonia (NH_3); the formula of the silver ammine complex is $[AgNH_3]^+$. Write the equilibrium reaction for the formation of the complex from the ions.

   c) Silver ammine ($[AgNH_3]^+$) has an equilibrium constant value of 1.7×10^3. If 0.015 M silver ion is mixed with 0.100 M ammonia, what are the concentrations of reactants and products at equilibrium? (Hint: use an ICE table)

4. Flowchart the procedures (on new pages). Don't forget to watch for places to take data and make observations.

5. Prepare data and observations tables (on a new page) to record observations. Leave space for "unexpected" observations (in addition to the ones you're looking for).

6. Prepare data tables for each equilibrium experiment (follow the suggestions, on a new page). There are other tables needed besides the example tables.

Example table for Data Collection and Analysis for Procedure A., 7.

Calibration Curve		
Flask	**$[FeSCN]^{+2} = [SCN]^{-1}$**	**Absorbance**
2		
Continue for remaining flasks!		

Example table for Data Collection and Analysis for Procedure B.4.:

Equilibrium Mixture		
Beaker	**Absorbance**	**$[FeSCN]^{+2}$ from calibration curve**
2		
Continue for remaining beakers!		

DISCUSSION:

Tro (textbook) references: Chapter 4, Section 4-4, Chapter 14, Sections 14-2 to 14-3, 14-6 and 14-9, Chapter 16, 16-8, Chapter 24, Section 24-6.

Chemical equilibrium is defined as that *dynamic* state that exists in a chemical reaction, when the rates of the forward and reverse reactions are equal. When a reaction has reached the state of equilibrium, the concentrations of all species become constant.....not equal..... but constant. It is a legitimate question to ask how one knows when this occurs. The answer is dependent on the type of reaction and the nature of the reactants and products. In this experiment, we take advantage of the fact that the product is a colored compound and that the concentration of this compound can be determined by measuring its absorbance using spectrophotometric methods. This procedure requires a calibration curve using samples of known concentration. At this point you should review the experiment titled “Beer’s Law”.

The system studied is the reaction between aqueous solutions of iron (III) nitrate and potassium thiocyanate. Since the potassium and nitrate ions are spectators in this reaction, the net ionic equation is:

$$[Fe(H_2O)_6]^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons [Fe(H_2O)_5SCN]^{2+}_{(aq)} + H_2O(\ell) \qquad [1]$$

Because the concentration of water, in dilute solution, is essentially constant, we omit the water from the above equation.

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons \underset{\text{(red)}}{[FeSCN]^{2+}_{(aq)}} \qquad [2]$$

The equilibrium constant expression for this reaction is:

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

where the concentrations are expressed at equilibrium and in moles/Liter (M).

When studying equilibrium reactions it is often necessary to consider the effect of changes in such variables as concentration, temperature, or pressure. Le Châtelier's Principle states: "*Whenever a stress is applied to a reaction in equilibrium, the reaction shifts in a direction to relieve that stress*." We will take advantage of this principle to drive the reaction toward the colored complex ion.

In the first part of the experiment, we use 0.200 M Fe^{+3} solution and 0.00200 M SCN^{-} solution. The high concentration of the iron(III) ion, relative to that of the thiocyanate ion, drives the reaction to the right; essentially to completion. It is assumed that this large excess of the iron(III) ion completely consumes the thiocyanate ion resulting in the concentration of the $FeSCN^{+2}$ being equal to the concentration of the SCN^{-1} ion. Concentrations can be determined using volume and molarity of the reacting species in conjunction with the dilution formula:

$$M_i x V_i = M_f x V_f \quad [4]$$

V_f is the total volume of all the reagents, including the solvent and HNO_3, after they are mixed, V_i is the volume and M_i is the concentration of the specific reagent before mixing. M_f is the concentration of the specific reagent after mixing. i.e., If you take 10 mL of a 0.2 M solution of $Fe(NO_3)_2$ and mix it with 8 mL of KSCN and 2 mL of HNO_3, then $V_f = (8+10+2) = 20$ mL,
$V_i = 10$ mL, $M_i = 0.2$ M, and so M_f can be found by simple algebra.

Finally, we develop the calibration curve by plotting the absorbance of the resulting red-solution vs. the concentration. The wavelength setting on the Spec-20 spectrophotometer is
447 nm.

The second part of this experiment is used to calculate the equilibrium constant. For each set of solutions we will need an ICE table, an example of which is shown in the Data Analysis section.

The **initial concentrations of reactants are** determined using the volumes and molarities of these solutions. While the calculations mimic those in done in the first part of the experiment, you must remember that the starting concentrations may be different. The **equilibrium concentration of the red complex** is determined by measuring its absorbance and using the calibration curve developed in the first part of the experiment. The **changes in concentration** as well as the **equilibrium concentration of the reactant ions** are determined by noting the stoichiometry of the reaction and using simple addition and subtraction.

DETERMINATION OF AN EQUILIBRIUM CONSTANT
A STUDY OF THE IRON-THIOCYANATE REACTION

PROCEDURE:

A. The Calibration Curve

1. Obtain six (6), clean, dry 25 mL volumetric flasks. Label the flasks 1-6.

2. Into each flask, pipet 6.00 mL of **0.200 M** iron (III) nitrate, then pipet the quantity of 0.00200 M potassium thiocyanate specified in **Table 1** (record the actual volume delivered in a data table). Both reagent bottles will be fitted with pump pipetters, set to the appropriate volume. You will adjust the KSCN pipetter to the volume needed. Fill each flask to the mark with 0.100 M nitric acid, mixing as you fill (making the final volume 25.00 mL in each flask).

Table 1.Volume requirements for Calibration Curve. Don't fill the table in when you prepare it; you'll record ACTUAL volumes when you make the solutions.

Flask	**0.200 M $Fe(NO_3)_3$ in 0.100 M HNO_3, mL**	**0.00200 M KSCN in 0.100 M HNO_3, mL**
#1 (blank)	6.00	~0.00
#2	6.00	~0.25
#3	6.00	~1.00
#4	6.00	~1.75
#5	6.00	~2.25
#6	6.00	~3.00

3. Allow the solution to sit in their flasks for a minimum of 10 minutes.
4. Directions for using the SpectraVis spectrophotometer are found on the laminated card by the computer. Set the wavelength to 447 nm.
5. Clean 6 cuvettes with soap and water, and rinse thoroughly with distilled water.
6. Rinse the first cuvette with a few mL of the blank solution. Discard the rinse in a waste beaker and repeat with a fresh portion of the blank. Discard this second rinse in the waste beaker. Fill the cuvette ¾ full with the blank. Wipe the outside with a Kimwipe to remove any finger prints and handle only by the top lip.
7. Repeat this process with clean cuvettes and solutions 2-6. Make sure the cuvettes are labeled.
8. Calculate the molarity of the $[FeSCN]^{+2}$ solutions and complete the concentration/ absorbance data table. The colored iron(III) complex ion concentration is approximately equal to the diluted concentration of the of SCN^{-1} in each volumetric flask.
9. Measure the absorbance of the solutions, recording the values in a data table.
10. Save your flasks until the calibration curve is prepared in Data Analysis. After the calibration curve is prepared, discard all solutions into the BLUE (Inorganic) waste. Clean the flasks with soap and rinse with water.

DETERMINATION OF AN EQUILIBRIUM CONSTANT
A STUDY OF THE IRON-THIOCYANATE REACTION

B. Determination of the Equilibrium Constant

1. Clean and rinse (with distilled water) six (6) 50.00 mL beakers (or Erlenmeyer flasks) and all the cuvettes used in the previous section (discard the solution in the cuvettes into the waste beaker). Drain as much water from the cuvettes as possible by inverting them on a paper towel as you gather your reagents.
2. Prepare the solutions shown in **Table 2** in your beakers, stir well and label. You will be using manual pipettes to measure these volumes so it's important to record your ACTUAL volume delivered of $Fe(NO_3)_3$, KSCN, and HNO_3 in a data table. Add your solution additions to find actual total volume.

Table 2. Volume requirements for Equilibrium Constant Determination. Don't fill the table in when you prepare it; you'll record ACTUAL volumes when you make the solutions.

Beaker	0.00200 M $Fe(NO_3)_3$ in 0.100 M HNO_3, mL	0.00200 M KSCN in 0.100 M HNO_3, mL	Additional 0.100 M HNO_3, mL	Total volume, mL
#1 (blank)	~5.00	0.00	~5.00	~10.00
#2	~5.00	~1.00	~4.00	~10.00
#3	~5.00	~2.00	~3.00	~10.00
#4	~5.00	~3.00	~2.00	~10.00
#5	~5.00	~4.00	~1.00	~10.00
#6	~5.00	~5.00	0.00	~10.00

3. Allow the solutions to sit in their beakers for a minimum of 10 minutes.
4. Rinse a cuvette twice with the solution from beaker 1. Discard each rinse into the waste beaker. Fill the cuvette until it is ¾ full. Dry the outside of the cuvette. Repeat this procedure with each of the other solutions in beakers 2 – 6.
5. Measure and record the absorbance values of the solutions from the beakers.
6. After the absorbance values are recorded, discard all solutions, including the waste beaker, in the BLUE (Inorganic) waste. Clean the flasks with soap and rinse with water.

Turn in your Data and Observations tables before leaving the lab.

DATA ANALYSIS/LABORATORY REPORT:

Procedure A:

In an Excel spreadsheet, plot absorbance (on the y-axis) vs. the Molarity of $[FeSCN]^{+2}$. Don't forget a title, axis labels, a trendline, and the equation for the line with R^2 value. Print a copy of the graph for each group member.

Procedure B:

1. Prepare ICE tables for beakers 2 – 6 (you will have 5 different ICE tables).

Table 3. Sample "ICE" table.

	$Fe_{(aq)}^{+3}$	+	$SCN_{(aq)}^{-1}$	$\rightleftharpoons$	$[FeSCN]^{+2}$
Initial:	** $M_{f,\,Fe^{3+}}$ calculated using your Table 2 volumes		** $M_{f,\,SCN^{-}}$, calculated using your Table 2 volumes		**0**
Change:	**–1x**		**–1x**		**+1x**
Equilibrium:	$M_{f,\,Fe^{3+}}$ **– 1x**		$M_{f,\,SCN^{-}}$ **– 1x**		**1x** = concentration calculated from Procedure A slope-intercept equation

2. Use the values of concentration and volume in from your data table (from **Table 2;** you know M_i, V_i, and V_f) and the dilution formula to calculate the initial, diluted molarity of Fe^{+3} and SCN^{-} in beakers 2 – 6. Fill in the “Initial” row in your ICE tables with this data.

3. Use the absorbance values from the Procedure B data table and the slope-intercept equation from Procedure A graph to find the Molarity of $[FeSCN]^{+2}$ at equilibrium for each ICE table; this value is “x” in the ICE table. Calculate the equilibrium concentrations of the Fe^{+3} and SCN^{-} (by subtraction of x from initial Molarity).

4. Use the equilibrium Molarity values to calculate an equilibrium constant for each of the beakers, and then determine the average of these values.

5. What is the significance of the value of the equilibrium constant with respect to the equilibrium reaction you studied? Does it indicate a reactant-favored or product-favored equilibrium? Explain!

Assemble your post-lab report with data analysis sheet; no title page is required. Post-lab report includes your graph and worksheet, data analysis with laboratory report questions answered (from above), and conclusion (what did you learn, what were your results, did you accomplish your objective, etc.).