 **Determination of $K_{eq}$ (aka $K_c$) for $FeSCN^{2+}$** Name_____Per___

## Introduction

Many reactions that occur in solution are equilibrium reactions. In this Lab we will examine the formation of a "complex ion" as an equilibrium system. A complex ion is an assembly of a central metal ion surrounded by a group of ligands, negative ions (or sometimes neutral molecules). The complex that forms in this lab is formed when a solution of iron(III) ions, $Fe^{3+}_{(aq)}$, are combined with a solution of negative thiocyanate ions, $SCN^{-}_{(aq)}$ to produce the colored iron thiocyanate complex ion. This reaction is easily reversible and will establish an equilibrium position.

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$$

pale purple colorless red

- iron(III) nitrate nonahydrate is used as the $Fe^{3+}$ ion source
- potassium thiocyanate is used as the $SCN^{-}$ ion source

The potassium and nitrate ions are spectator ions and need not be considered in the reaction. The equilibrium constant can be calculated when the concentration of each component in the reaction is known at a particular temperature. So just exactly how will we determine the concentration of each ion? We will use the color of the red complex to tell us how much of the $FeSCN^{2+}$ is present in the solution at equilibrium, and the concentration of the other two ions at equilibriumcan be determined using typical RICE-box calculations.

Compounds that are colored absorb a part of the visible spectrum of light. If a compound is orange color, that compound will absorb purple light, the complementary color to orange. A spectrophotometer is an instrument that measures the amount of light absorbed by a solution. To use the spectrophotometer, an appropriate wavelength must be selected to maximize the absorption possible.

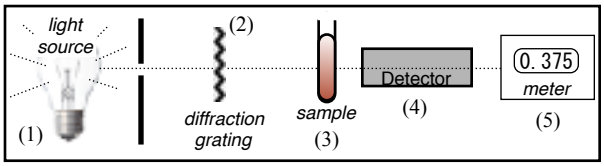
## Beers Law

Beer's Law is a mathematical relationship that is stated: $A = abc$

- In this law the term "A" is the absorption of the sample. This is a value that indicates how much light of a given wavelength is absorbed by the given substance in the cuvette. If a substance has a very intense color, it will have a high absorption.
- The term "b" is the cell path. This is the width of the test tube (aka cuvette) and will be held constant throughout the experiment.
- The term "c" is the molarity of the substance absorbing the light.

When a substance is analyzed, the absorptivity (a) of the chemical is constant, and the width of the cell path (b) is also constant (since we use the same cuvettes every time), therefore the absorbance (A) measured by the spectrophotometer is directly proportional to the concentration of the $FeSCN^{2+}$ ions present in the solution. A graph of absorbance versus concentration at concentration values that produce absorbances values between 0.1-ish to 1-ish will be a straight line. You learned this linear relationship in Lab B1 - Analysis of Copper in Brass.

A general schematic diagram for a spectrophotometer is shown to the right. A description of the spectrophotometer is outlined in the paragraph below.




It begins (1) with a light source or a light bulb. For the instrument that is used in this lab, the light bulb emits visible light of wavelengths ranging from 340 nm to 700 nm. The light then travels through a diffraction grating (2). This device as the name indicates, separates the light into its individual wavelengths so that light of a single particular wavelength shines towards the sample. Next the light of a particular wavelength and intensity, is passed through the sample (3). As the light passes through the sample, part of the light may be absorbed. This absorption lowers the intensity of the light proceeding on to the detector. The detector (4) measures this decreased intensity. The spectrophotometer expresses the amount of light as related to the concentration of the colored molecule in the solution in one of two ways at the meter (5). The instrument actually measures the percent transmittance, which is a measure of how much of the light gets through. But, the relationship between transmittance and concentration is not a linear relationship, it is curved and would be difficult to use to quantify the relationship to concentration. Thus the instrument converts transmittances to absorbance which is simply

$$Absorbance = -logTransmittance$$

Logging the transmittance will linearize the data. This linear relationship between absorbance and concentration will allow us easy comparison of the data.

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## Procedure Overview

There are two parts to this experiment. First we will prepare and then measure absorbance of a Reference Solution for which we will know [$FeSCN^{2+}$].

Then you will prepare a Test solution and measure its absorbance. By comparing the measured absorbance of your test solution to the Reference Solution you can set up a ratio to calculate the equilibrium concentration of the [$FeSCN^{2+}$]. Knowing the initial concentration of your test solution you can use a RICE box-type calculation from the equilibrium [$FeSCN^{2+}$] which will allow you to calculate the equilibrium concentration of the reactant ions in the Test Solution. Using all of the equilibrium concentrations, a $K_{eq}$ ($K_c$) can be calculated.

### Wait… How can we know the [$FeSCN^{2+}$] in the Reference Solution?

LeChatelier's Principle at Work : In the Reference solution we combined a concentration of the $Fe^{3+}$ ions that was SO MUCH in excess relative to the concentration of the $SCN^-$. The "stress" on the reactant side due to this thousand-fold greater concentration of iron(III) should be enough to consume nearly all of the small amount of thiocyanate ions and convert "essentially all" of it to product. This allows us to assume that the concentration of the equilibrium $FeSCN^{2+}$ in the Reference solution is equal to the initial $SCN^-$ in the Reference solution. This gives us the [$FeSCN^{2+}$] in the Reference solution. That allows you to set up a ratio with Reference measurements of [$FeSCN^{2+}$] and Absorbance to calculate the [$FeSCN^{2+}$] from the measured absorbance of the test solution.

## PreLAD:

1. Write the equilibrium constant expression for the reaction shown in the introduction. Put the expression next to your RICE Box in the Process the Data Section.

2. Using the "dilution equation" ($M_cV_c = M_dV_d$) calculate the "initial" concentration of the thiocyanate ion and ion ion ("initial" means: after being mixed, but before any reaction takes place) in the **Reference** Solution.

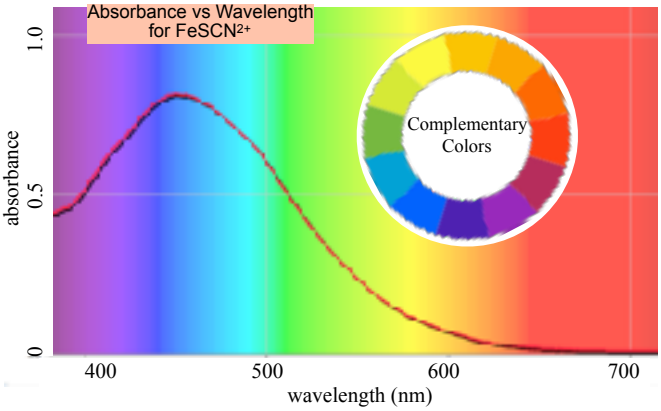
   Because of the "stress" discussion in the LeChatelier's Principle at work as discussed in the previous section, and the 1:1 stoichiometric relationship between reactants and products, we can **assume** that the initial [$SCN^-$] is *nearly* all used up and will be nearly **equal** to the equilibrium [$FeSCN^{2+}$].
   *Put your calculated concentration [$FeSCN^{2+}$] in the Data/Results Table #1 in the table in Process the Data #2.*

| Table #1 **Reference** | 0.200 $M_s$ $Fe^{3+}$ | 0.00020 $M_s$ $SCN^-$ |
|---|---|---|
| Volume (ml) | 5.0 | 5.0 |
| "Initial" Concentration | $M_i$ | $M_i$ |

$$M_cV_c = M_dV_d$$

3. The wavelength setting we used in this lab will not chosen arbitrarily. This graph is the result of running a trial for which absorbance vs wavelength was measured. The graph of the data is shown below.

   a. Explain how the color of the solution and the maximum absorbance wavelengths are related to each other.


   b. Why is 450 nm a better wavelength at which to measure absorbance than at 550 nm?

## Procedure *Goggles should be worn at all times. No exceptions. Aprons are optional.*

A. **STOP and look carefully at your pipette.**
Take note of the increments near the tip of the pipette. Recall that you are meant to push out ALL of the fluid for some pipettes, and for other pipettes you should only allow fluid to drain down to the last mark and NOT push out all of the fluid. LOOK carefully and make sure you know how to use your pipette correctly. ASK for help before you begin if you are not sure.

B. **ASK the teacher if you need to "season your pipettes."**
At the start of the lab session, it is a good idea to prepare the pipettes by rinsing each with its own appropriate solution that you will be using (the same way we prepare burettes). Draw 3 to 4 ml of the new solution up into the pipette, then twirl and rinse to coat the tube with the new solution, and then squirt the solution out into the sink. BE MINDFUL and do NOT allow the solutions to be drawn up into the pipet bulb or pipet pump. This leads to contamination and to "nasties" collecting inside the bulb or pump.

C. Prepare your Test Solutions in the small 30 ml beaker.

### *Measuring Absorbance*

D. **Preparing the cuvettes:** Remember to touch the cuvettes with your fingers only on the ridged sides to avoid putting scratches or finger prints on the portion of the cuvette through which the light from the spectrophotometer will pass. You should prepare your cuvette by rinsing it with a tiny amount of the solution you will be putting into it, then pour that rinsing solution down the drain. Fill the cuvette three quarters full.

E. **Calibrating the spectrophotometer:** The spectrophotometer will be warmed up and calibrated.

F. **Making the measurements:** When your cuvets are prepared, bring the cuvets to the front of the room to test your solutions with the spectrophotometer.

## Disposal

All solutions may be poured down the sink with plenty of water. Rinse out any beakers you used, and hang them to dry.

## Processing the Data - *Show all calculations clearly in the space below.*

1. Using the "dilution equation" ($M_cV_c = M_dV_d$) calculate the initial concentration of your iron(III) ion [$Fe^{3+}$] ("initial" means: after being mixed, but before any reaction takes place) for your selected **Test** solution combination. Repeat the ($M_cV_c = M_dV_d$) calculation to determine the initial concentration of your thiocyanate ion [$SCN^-$].
*Record your results in the RICE Box below*

| Table #2 | Reference | Test |
|---|---|---|
| [$FeSCN^{2+}$] | | |
| Absorbance | | |

2. Using the information (concentration and absorbance) for the Reference solution, and Table #2 above, calculate the equilibrium [$FeSCN^{2+}$] of your Test solution.
*Record the value in the "E" row of the RICE box below.*

3. Now you can use the logic of the RICE box to calculate the equilibrium concentrations of [$Fe^{3+}$] and [$SCN^-$].
*Enter your results in the RICE-box below.*

4. Use the equilibrium expression and the equilibrium concentrations to calculate the equilibrium constant, $K_{eq}$

$$M_cV_c = M_dV_d$$

| | Stock [$Fe^{3+}$] _____ml of 0.002 M | Stock [$SCN^-$] _____ml of 0.002 M | |
|---|---|---|---|
| **R** | [$Fe^{3+}$] | [$SCN^-$] | [$FeSCN^{2+}$] |
| **I** | | | |
| **C** | | | |
| **E** | | | |

$$K_c =$$

## Post LAD Questions

1. In the Reference Solution which reactant was the limiting reactant?
   a. Why was it important that the concentrations of the two reactants were different by three orders of magnitude.
   b. What did this allow us to conclude (assume) that would have otherwise been impossible to know?
   c. What did this allow you to calculate in your test solution?

2. Why was it important not to touch the cuvette with your fingers? Would this problem make the measured absorbance values too high or too low? Justify.

3. If the cuvette were not filled full enough would the recorded absorbance be too high or too low? Justify.

4. Beers Law is on your formula sheet. Find it, and write it here.
   a. In which section of your formula sheets did you find this formula?
   b. Label what each of the four symbols in the formula above represents.
   c. Calculate the absorptivity constant for the Reference Solution knowing that the cuvette is 0.75 cm wide.
   d. Absorbance does not equal concentration. Explain why you needed to make a ratio to determine the concentration of in your test solution.
   e. …and why do we make a ratio? and not use a formula similar to our dilution equation like I have shown below?

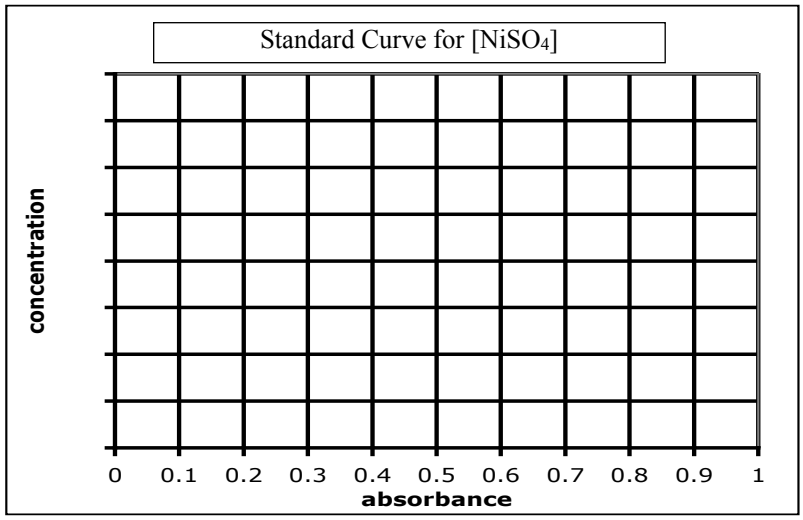
$$\left[FeSCN^{2+}\right]_{\text{Re}\,ference} \times Abs_{\text{Re}\,ference} = \left[FeSCN^{2+}\right]_{Test} \times Abs_{Test}$$

5. The spectrophotometer actually *measures* transmittance but the instrument can *report* transmittance or absorbance. Why did we graph set the instrument to absorbance vs concentration and not transmittance vs concentration?

6. A student is given the task of determining the molar concentration for a sample of nickel(II) sulfate solution of "unknown" concentration. In order to establish a standard or calibration curve, the student prepares a set of five standard solutions of nickel(II) sulfate. The student collects the data shown in the following table. Use the set of axes provided to the right to sketch a graph of the data. The student then measures the absorbance for the unknown sample and determines it to be 0.669.

   a. Determine the concentration of the unknown $NiSO_4$ solution from the graph and record it on the line below. **Mark the graph to indicate how you determined the concentration.**

| # | Concentration (mol/L) | Absorbance |
|---|---|---|
| 1 | 0.0008 | 0.205 |
| 2 | 0.0016 | 0.404 |
| 3 | 0.0024 | 0.599 |
| 4 | 0.0032 | 0.789 |
| 5 | 0.004 | 0.982 |




   b. Alternatively instead of using the graph, you could use a simple ratio (as we did in the lab calculations) to determine the concentration of the unknown sample. Show a ratio below to confirm that this method would produce the same result as in (a)

7. Explain why this method of using a spectrophotometer to determine concentration of a nickel(II) sulfate solution is effective, yet this method would not be appropriate for a zinc chloride solution.

8. How would the procedure of this lab need to be changed, if the equilibrium substance was yellow instead of red? (Refer back to the graph and color wheel in PreLAD #5 for help.)

9. One lab group's Reference absorbance value was high compared to the rest of the groups. In trying to figure out what may have happened, one lab group noticed that their solutions were left on the window sill and the window was left ajar, making their solutions very cold. Could this be the source of error? One team member suggested that this may be enough information to determine if the reaction is exothermic or endothermic. Explain their reasoning.