Ye Olde Measurement of a Chemical Equilibrium Constant for the Formation of an Iron(III)/Thiocyanate Complex

I. Introduction

The chemist spends a great deal of time, effort, and money turning Molecule A into Molecule B or combining Molecule C with Molecule D in order to get E:

$$1A \rightarrow 1B$$

$$2C + 3D \rightarrow 2E$$

The motivations are multiple, such as Molecules B and E demonstrate a useful, beneficial purpose. Sometimes the reaction stoichiometry is dirt simple such as in the A/B reaction. Other times, the stoichiometry is more complex as in the C/D/E chemistry. In Chem 101 and 111, one learns a lot about stoichiometry by way of reaction balancing, simplest formula, and limiting reagent problems. Reaction stoichiometry really is on the short list of important chem 101 and 111 ideas. It is grounded on landmark science ideas: the conservation of mass, charge, and energy.

But chemical reactions turn out to be a lot messier than conveyed by the above statements. This is because chemical reactions can invariably switch both ways. The chemist can transform Molecule A into Molecule B in the lab, and can combine C and D in the proper combination to obtain Molecule E. But the reverse reactions can also take place! It is thus more accurate to represent chemical reaction statements using **double arrows or an equal sign**:

$$1A = 1B$$

$$2C + 3D = 2E$$

This is not a small point. At company meetings, the chemist speaks breezily of Molecules A and B as the "reactant" and "product", respectively, in the first of the above reactions. But the chemist knows full well that Molecules A and B play more than one role in the game: in the reverse reaction that takes place, Molecule A functions as the product and B behaves as the reactant. It is always important for the chemist to understand both the forward and backward nature of a reaction. Only then can he/she begin to explore the conditions which enhance the formation of useful, beneficial Molecule B.

Important: Even if the conditions are discovered, the chemist is always cognizant that a reaction of Molecule A will result in a mixture of A and B. For the second of the above reactions, the chemistry leads to a mixture of three components. A great deal of time and effort is spent in real-life chemistry labs separating the components of reaction mixtures

from one another.

Now there is an important feature demonstrated by all chemical reactions. In ye olde days, this feature was referred to as the **Law of Mass Action**. In ye new days, the feature is identified as the **Law of Chemical Equilibrium**. Either way, the law is credited primarily to Mr. Van't Hoff and is stated as follows:

If the product of the concentrations of all the products is divided by the product of the concentrations of all the reactants, the ratio so formed is a constant under all changes except that of temperature.

So we see how this law applies the A/B reaction. In an **equilibrium mixture** of A and B, the following ratio remains constant with all changes applied to the system except heat removal or addition:

$$\frac{[B]}{[A]}$$

For the C/D/E chemistry, the key ratio is:

$$\frac{[E] \bullet [E]}{[C] \bullet [C] \bullet [D] \bullet [D] \bullet [D]}$$

Note how we are piecing together the above ratios. In the C/D/E case, the reaction stoichiometry tells us that

$$2C + 3D = 2E$$

which is really the same as

$$C + C + D + D + D = E + E$$

Mr. Van't Hoff taught colleagues the importance of the ratio of the products of the concentrations of **all** the products: $[E] \bullet [E]$, divided by the products of concentrations of **all** the reactants: $[C] \bullet [C] \bullet [D] \bullet [D] \bullet [D]$. Of course, when the reaction stoichiometry features multipliers other than 1, the ratios can be written in a more compact way:

$$\frac{[E]^2}{[C]^2 \bullet [D]^3}$$

Compact or expanded, the ratios are referred to as the **Mass Action Constant K** for a reaction, or simply as the **Equilibrium Constant**. Importantly, Mr. Van't Hoff taught us that **K is really not a constant, but rather a function of temperature--an exponential function at that.**

It would take a book-length handout to describe the importance--and limitations--of K, the Mass Action constant. Needless to say, MACs are ideas central to Chem 102. Please refer to Kotz, Treichel, and Weaver for an extended discussion that begins in Chapter Sixteen. For now, please be aware of the following:

(1) K quantitatively measures which side of a chemical reaction is favored at equilibrium. The larger the value of K, the more favorable the conditions are to the right-hand-side reaction players. Along the same lines, the smaller the value of K, the more favorable the conditions are to the left-hand-side players.

(2) The value of K is tied to the stoichiometry of a reaction. If the reaction stoichiometry is multiplied by n, this has the effect of raising the value of K to the nth power. Thus if the chemist quotes a value of K, the chemist must also specify the reaction stoichiometry pertinent to K.

(3) K connects with the thermodynamics of chemical reactions. It quantitatively measures the amount of work available from a chemical reaction given certain, standard conditions. The larger the value of K, the more work obtainable from allowing reactants to come to equilibrium with products. When seeking to harness chemical reactions for their work content, the chemist invariably chooses reactions with very large K-values.

(4) The value of K is positive--no exceptions. K also depends exponentially on temperature. This means that small changes in T effect substantial changes in K. If the chemist quotes a value of K, the chemist must include the temperature at which K was measured.

(5) Strangely but truly, the MAC offers no information about the **rate** of a chemical reaction. K tells the chemist a great deal about a reaction--who is favored at equilibrium, work content, etc., but not everything! Most notably, K offers no clues about how fast or slowly a reaction occurs.

II. The Reaction Between Iron(III) and Thiocyanate Ion

Long ago and far away, the chemist discovered that Iron(III) in the aqueous phase (Fe^{3+}(aq)) combines very quickly--in only a few seconds or less--with thiocyanate ion (SCN^-(aq)). Moreover, the product--an iron-thiocyanate complex-- has a deep and rather beautiful red color. The chemistry is written as follows:

$$Fe^{3+}(aq) + n\ SCN^-(aq) = Fe(SCN)_n^{(3-n)+}$$

To carry out such a reaction, the chemist needs only to mix aqueous solutions of Iron(III)-Nitrate with Sodium Thiocyanate at not too cold of a temperature. Under these conditions, the nitrate and sodium ions play the role of spectators. The importance of the reaction to the chemist is that thiocyanate ion provides a very effective indicator of the presence of Iron(III).

Now the multiplier "n" attached to the $SCN^{-}(aq)$ has not been specified. It can be 1, 2, or 3. At some point in the early days, ye olde chemist had to figure out the value of n.

Important: identifying the value of n is one goal of this Chem 112 experiment. In achieving that goal, we will follow in the footsteps of an early days chemist.

Yet how can one figure out experimentally the value of "n"? In this Chem 112 experiment, there will basically be a dual strategy applied to the problem.

First, we will make use of one singular feature of iron-thiocyanate complexes, namely their beautiful red color. We will measure their concentration via the amount of visible light they absorb.

Important: the concentration and visible light absorbance are linearly proportional to one another. This statement is sometimes referred to as Beer's Law.

Second, we will take advantage of the fact that the MAC is really only sensitive to temperature changes. (Full disclosure: this last statement is not strictly true. But it will be true enough for this chem 112 lab). We will perform light absorption measurements under several different concentration conditions--but all at constant temperature. These measurements will point to the correct value of n.

Identifying an average mass action constant value at room temperature is the second goal of this experiment.

III. Experimental and Calculations

A. Getting Started

Please put on both safety glasses and latex gloves. Every team should then organize the following equipment:

5 clean, drained, and dried test tubes
small graduated cylinder
large graduated cylinder
few beakers with volume $\geq$ 50 milliliters
few watch glasses

5 milliliter volumetric pipette

pipette pump
test tube cuvettes
a few labels for the test tubes

The first set of items should be found in one's lab drawer. The second set of items will be available from the center area of the lab.

As per usual, each team member should apportion five to seven pages of the lab notebook to record all data for the experiment.

Now use two clean small beakers to collect:

30 milliliters of 2.00 x 10^{-3} molar Iron(III) Nitrate
20 milliliters of 2.00 x 10^{-3} molar Sodium Thiocyanate

Please do not take more than the above chemicals. A little goes a long way; the above are all that are really necessary. The chemicals are fairly benign, but please wear gloves at all times nonetheless.

Please measure the temperatures of the solutions. Store the solutions with watch glasses on top of the beakers in order to retard evaporation.

B. Moving the Ball Forward

Now use the volumetric pipette to transfer 5.00 milliliters of the Iron(III) Nitrate aqueous solution to each of the five test tubes.

!!!!!Very Important: The pipette has a thin glass stem that snaps off very readily. When this accident happens--and it unfortunately does--the sharp edge of the broken stem causes terrible cuts to one's hands that require multiple stitches at a hospital emergency room. Please use every and all caution in handling these fragile glass devices. Do not use unnecessary force when connecting the pipette to the pump. Please seek assistance if there are any doubts or questions!!!!!

Now label the test tubes #1 - 5.

Now to **test tube #1**, add 1.00 milliliter of the 2.00 x 10^{-3} molar Sodium Thiocyanate solution. Also add 4.00 milliliters of distilled water.

Then add 2.00 milliliters of the 2.00 x 10^{-3} molar Sodium Thiocyanate solution to **test tube #2**. Also add 3.00 milliliters of distilled water.

Then add 3.00 milliliters of the 2.00 x 10^{-3} molar Sodium Thiocyanate solution to **test tube #3**. Also add 2.00 milliliters of distilled water.

Then add 4.00 milliliters of the 2.00 x 10^{-3} molar Sodium Thiocyanate solution to **test tube**

#4. Also add 1.00 milliliter of distilled water.

Finally, add 5.00 milliliters of the 2.00×10^{-3} molar Sodium Thiocyanate solution to **test tube #5.** Do not add any distilled water to this sample tube.

Important: At this point, one has prepared five mixtures of Iron(III) Nitrate and Sodium Thiocyanate at (hopefully!) the same temperature. Each of these mixtures enables the reaction which results in the formation of an Iron(III)-Thiocyanate Complex. For each mixture, calculate in moles per liter the initial concentrations of $Fe^{3+}(aq)$ and $SCN^{-}(aq)$. Each group is on the right track if the solutions in the test tubes appear red in color.

It would be helpful to apply parafilm to the test tubes to retard evaporation of the water.

C. More Forward Motion

We are now ready for light absorption measurements. Begin by filling one of the test tube cuvettes with 5.00 milliliters of the Iron(III) Nitrate solution. Close enough is good enough here. Needless to say, the solution in this cuvette does not offer any chances for iron/thiocyanate chemistry. It is important, however, because it will provide baseline values of the visible light absorption.

The lab assistant will demonstrate the workings of the spectrometer. Use the reference cuvette to set the baseline absorbance to zero at wavelength 447 nanometers.

Then use the spectrometer to measure the absorbance of *each* of the solutions in the five test tubes. Make sure that the reaction cuvette is clean and dry prior to each measurement. Please check the baseline prior to each measurement. Only the Iron-Thiocyanate complex is absorbing light because the reactant ions are both colorless.

Now please use the attached calibration graph to relate the light absorption to the concentration of Iron-Thiocyanate complex. Please identify the concentration of solution for each of the five test tubes.

We are now near the moment of truth. Let us focus attention on both the correct value of n and a *reasonably accurate* value of the Mass Action Constant K.

OK, so *assume* that n = 1. If this was correct, then the reaction stoichiometry would be

$$Fe^{3+}(aq) + 1 \ \ SCN^{-}(aq) \ = \ Fe(SCN)_1^{(3-1)+}$$

And the MAC would be given by

$$K = \frac{[Fe(SCN)_1^{(3-1)+}]}{[Fe^{3+}(aq)] \bullet [SCN^-(aq)]}$$

And if the measured concentration of $[Fe(SCN)_1^{(3-1)+}]$ is represented by the variable x, then with n = 1, the MAC becomes

$$K = \frac{x}{([Fe^{3+}(aq)]_o - x)^1 \bullet ([SCN^-(aq)]_o - x)^1}$$

where the subscript "o" indicates the initial concentrations of $Fe^{3+}(aq)$ and $SCN^-(aq)$ in the denominator.

Use the above equation and the results of five absorption measurements **to compute five values for K**. Barring acts of God, the five values will be different from one another. Please compute the average and standard deviation. **This will be the average K and standard deviation associated with n = 1.**

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Now assume for the moment that n = 2. If this were the correct value, then the reaction stoichiometry would be

$$Fe^{3+}(aq) + 2\ SCN^-(aq) = Fe(SCN)_2^{(3-2)+}$$

And the MAC would be given by

$$K = \frac{[Fe(SCN)_2^{(3-2)+}]}{[Fe^{3+}(aq)] \bullet [SCN^-(aq)]^2}$$

If the measured concentration of $[Fe(SCN)_2^{(3-2)+}]$ = x, then with n = 2, the MAC becomes

$$K = \frac{x}{([Fe^{3+}(aq)]_o - x)^1 \bullet ([SCN^-(aq)]_o - 2x)^2}$$

where the subscript "o" again indicates the initial concentrations of the reactants $Fe^{3+}(aq)$ and $SCN^-(aq)$.

Use the above equation and the results of five absorption measurements to compute another five values for K. Compute the average and standard deviation. **This will provide the average K and standard deviation associated with n = 2.**

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Finally, assume that n = 3. With this assumption in place, the reaction stoichiometry would be

$$Fe^{3+}(aq) + 3\ SCN^{-}(aq) \ = \ Fe(SCN)_3^{(3-3)+}$$

And the MAC would be given by

$$K = \frac{[Fe(SCN)_3^{(3-3)+}]}{[Fe^{3+}(aq)] \bullet [SCN^{-}(aq)]^3}$$

If the measured concentration of $[Fe(SCN)_3^{(3-3)+}] = x$, then with n = 3, the MAC becomes

$$K = \frac{x}{([Fe^{3+}(aq)]_o - x)^1 \bullet ([SCN^{-}(aq)]_o - 3x)^3}$$

where the subscript "o" indicates the initial concentrations of Fe^{3+}(aq) and SCN^{-}(aq).

Use the above equation and the results of five absorption measurements to compute yet another five values for K. Compute the average and standard deviation. **This will be the average K and standard deviation associated with n = 3.**

IV. Preliminary Report

Please complete the preliminary report sheet found on the last page of this handout. Each lab partner should complete his/her own sheet based on the team data. Please turn in the preliminary report to the lab assistant before leaving.

V. Final Report

Please write a final report based on data recorded for this experiment. Each partner of a team must write and submit their own lab report. Each report must be typewritten and should adhere to the following outline.

A. Introduction: Please describe the purpose of the experiment in your own words. Please explain the concept of Mass Action Constant. Describe the type of chemical reaction that is central to this experiment and the method by which it is studied.

B. Experimental: Please summarize the experimental method. Please note any deviations from the procedure described in the handout.

C. Results: Please clearly present the results of **five visible light absorption experiments**. A table will be helpful when organizing the following interrelated quantities:

initial concentration of Iron(III)
initial concentration of Thiocyanate Ion
absorption of Iron(III)-Thiocyanate Complex
MAC-value based on $n = 1$ stoichiometry
MAC-value based on $n = 2$ stoichiometry
MAC-value based on $n = 3$ stoichiometry

Please detail how the MACs were computed based on the trial stoichiometry.

Please report the average and standard deviation of K for all three cases.

For all three cases, please report the following ratio: the standard deviation of K divided by the average K.

Please describe the basis for which the correct reaction stoichiometry was identified.

D. Discussion: Please discuss the significance of experimental results in your own words. What happened in the experiment that was expected? What--if anything--happened that was not anticipated?

The correct stoichiometry was identified on the basis of consistent MAC measurements. Please note ambiguities in the experimental results. Please discuss the source of such ambiguities?

The mass action constant is temperature dependent. Is it likely or unlikely that the MAC of this experiment increases with temperature? Please discuss.

Please describe the next experiment that you would undertake in an investigation of the Iron(III)-Thiocyanate reaction.

Ye Olde Pre-Lab Assignment

1. A chemist mixes 7.50 milliliters of 2.00 x 10^{-3} molar Iron(III) Nitrate with 7.50 milliliters of 2.00 x 10^{-3} molar Sodium Thiocyanate and 5.00 milliliters of distilled water. A red color soon appears in the test tube. The chemist finds the product complex to have concentration of 2.25 x 10^{-4} moles per liter.

(a) What is the initial concentration of $Fe^{3+}(aq)$?

(b) What is the initial concentration of $SCN^{-}(aq)$?

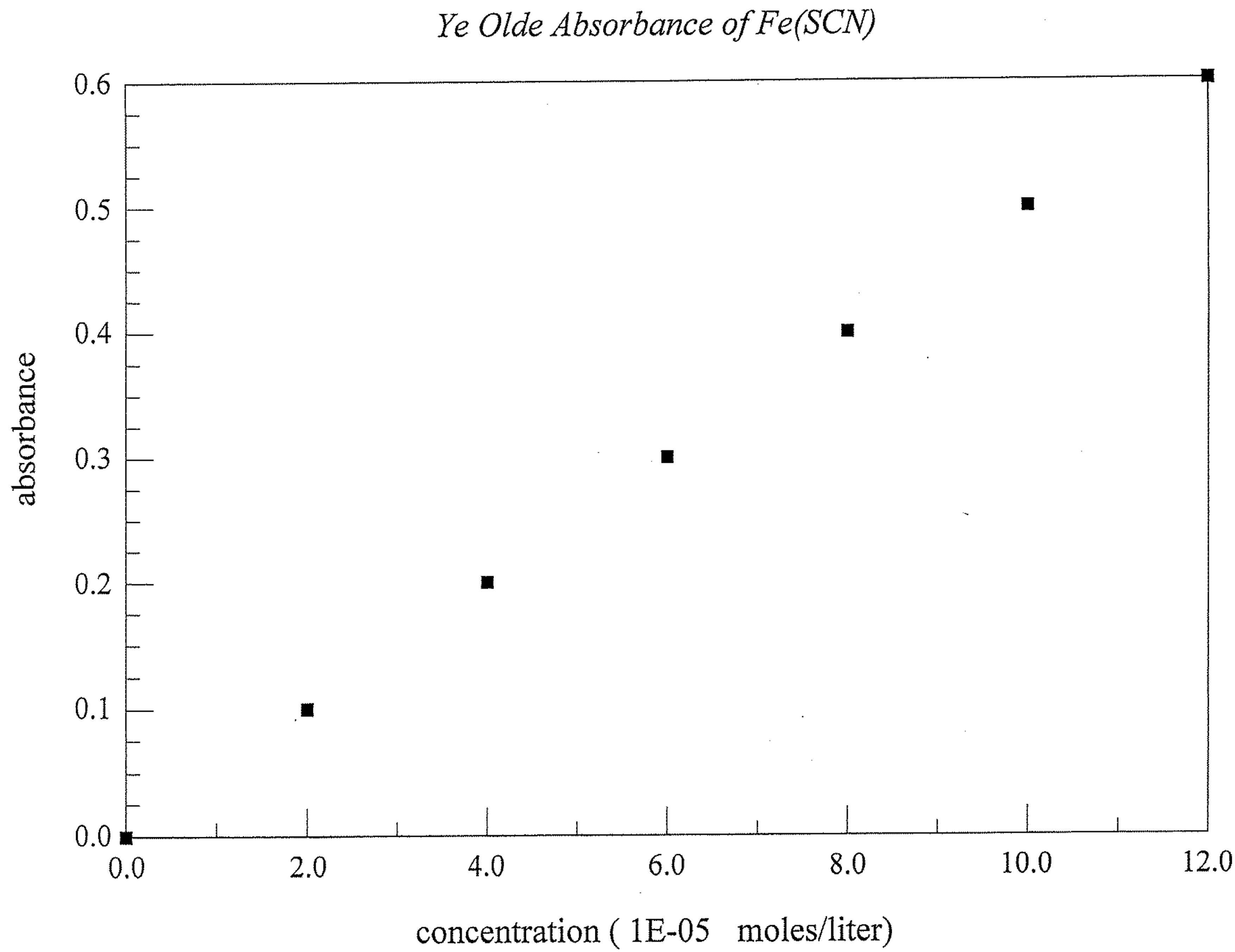
(c) If the correct value of "n" in the reaction stoichiometry is 1, what is the value of K?

(d) Given the results in (c), what would be the value of K for the reaction

$$Fe(SCN)_1^{(3-1)+} = Fe^{3+}(aq) + 1\ SCN^{-}(aq)$$

(e) Given the results in (c), what is the value of K for the following reaction if the initial concentrations of $Fe^{3+}(aq)$ and $SCN^{-}(aq)$ are cut in half:

$$Fe^{3+}(aq) + 1\ SCN^{-}(aq) = Fe(SCN)_1^{(3-1)+}$$



Ye Olde Absorbance of Fe(SCN)
absorbance
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
concentration (1E-05 moles/liter)

Preliminary Report

Name:

Lab Partner's Name:

Lab Assistant's Name

1. initial concentrations of Iron(III) and Thiocyanate in Test Tube #1:

2. Measured Concentration of Iron-Thiocyanate complex for Test Tube #1:

3. initial concentrations of Iron(III) and Thiocyanate in Test Tube #2:

4. Measured Concentration of Iron-Thiocyanate complex for Test Tube #2:

5. Using data for Test Tubes #1 and #2, the MAC values based on $n = 1$.

6. Using data for Test Tubes #1 and #2, the MAC values based on $n = 2$.