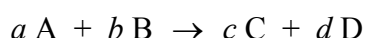


Chemistry 112 Laboratory
Experiment 7:
Determination of Reaction Stoichiometry and Chemical Equilibrium

Introduction

The word equilibrium suggests balance or stability. The fact that a chemical reaction occurs means that the system is not in equilibrium. The process will continue until the system reaches equilibrium. At this point, there is no observable change in the concentrations of reactants and products. While the reaction appears to stop, the reality is that reactants are being converted to products at the same rate that products are being converted to reactants.

These principles can be illustrated with a generic reaction:



If only A and B are present, the reaction will proceed to the right; if only C and D are present, the reaction will proceed to the left. In both cases, the reaction will apparently stop when equilibrium is reached. This state is characterized by a specific value for the equilibrium constant K , defined for this reaction by the following expression.

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (1)$$

Here the brackets signify the equilibrium concentrations (in M) of the various species. Note that the coefficients in the balanced equation appear as exponents in the equilibrium constant and that the products always appear in the numerator and the reactants in the denominator.

The value of the equilibrium constant depends on the chemical reaction and on temperature. However, the value of K will not depend on the initial concentrations of reactants and products. Furthermore, the specific mathematical form of the equilibrium constant must correspond to the correct chemical equation for the reaction. If the equation is not correct – for example, if the formula of one or more of the species is wrong – the value of K , even if calculated using accurate concentrations and making no numerical errors, will not be constant.

In this experiment you will investigate the reaction of the Fe^{3+} [iron(III), or “ferric”] ion with the SCN^- (thiocyanate) ion. The product of this reaction is a complex ion that imparts a red color to aqueous solutions. You are asked to experimentally determine the formula for the complex ion and a numerical value for the equilibrium constant for the reaction in which it is formed.

Let us represent the reaction under investigation with this chemical equation:



Note that we are not certain of the formula for the complex ion. [Note also that Fe(III) complexes are usually octahedral, so there are $6 - x$ water ligands coordinated to the metal as well. We will neglect H_2O for the remainder of this discussion.] We assume that, like most complexes, this species contains a single metallic cation, but we represent the unknown integer

number of ligands with an x . For this reaction, the corresponding equilibrium constant expression is as follows:

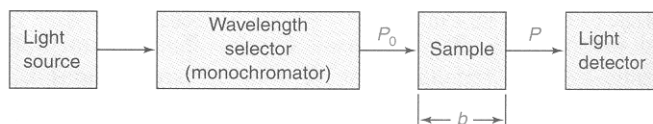
$$K = \frac{[\text{Fe}(\text{SCN})_x^{(3-x)}]}{[\text{Fe}^{3+}][\text{SCN}^-]^x} \quad (3)$$

Note that for any reaction mixture, the equilibrium concentrations of these three species can be different, but if the system is truly at equilibrium, the ratio of concentrations we call the equilibrium constant will be, as the name suggests, constant.

Experimental Procedure

The laboratory contains two stock solutions, 2.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3(\text{aq})$ in 1 M $\text{HNO}_3(\text{aq})$ and 2.00×10^{-3} M $\text{KSCN}(\text{aq})$. The former is a source of Fe^{3+} , and the latter a source of SCN^- . (We put strong acid in the first stock solution to lower the pH; otherwise $\text{Fe}(\text{OH})_3(\text{s})$ would precipitate.) In addition to your usual laboratory equipment, you are also supplied with measuring pipettes. The general strategy is to prepare mixtures containing various initial concentrations of the two reactive species. The above reaction will occur very rapidly, achieving equilibrium and producing the colored complex.

The equilibrium concentration of the complex can be determined with a spectrometer. A schematic of the instrument you will use (a Spectronic 20) is shown below:



(from *Quantitative Chemical Analysis*, 5th ed., D. C. Harris, New York, Freeman, 1999)

The light source in the Spectronic 20 is a tungsten filament light bulb that supplies all wavelengths of visible light. You (or your instructor) will set the wavelength, λ , to 447 nm. It turns out that the complex absorbs some of this light; the light power P_0 entering the sample is therefore higher than the light power P leaving the sample. We can define two experimental variables to quantify the loss of light. The transmittance (T) is given by

$$T = P/P_0 \quad (4)$$

Since T can vary between 0 and 1, it is also common to record percent transmittance, where T is multiplied by 100%. The absorbance A is defined as

$$A \equiv -\log T \quad (5)$$

The negative sign makes sense because the more light a sample transmits, the less light it absorbs. Note that both T and A are dimensionless (they do not have units).

Chemists are usually interested in absorbance because, according to Beer's Law, A is linearly proportional to the concentration C of the species doing the absorbing:

$$A = \epsilon b C \quad (6)$$

The absorbance is also linearly proportional to the distance b that light travels through the sample. The special test tubes you will use in lab have $b = 1.00$ cm. Finally, there is a constant of proportionality, ϵ , called the molar absorptivity. Its value depends on the particular substance

you are measuring and on the wavelength of light you have selected. For the $\text{Fe}(\text{SCN})_x^{(3-x)}$ complex at $\lambda = 447 \text{ nm}$, $\epsilon = 5.03 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Solving for concentration, we get

$$[\text{Fe}(\text{SCN})_x^{(3-x)}] = (1.99 \times 10^{-4} \text{ M}) A \quad (7)$$

In order to calculate a numerical value for the equilibrium constant, you need to know the equilibrium concentrations of all three species participating in the reaction. Equation (7) enables you to determine the equilibrium concentration of the complex ion, but you cannot measure the concentrations of the other species directly. You can, however, determine them with a little computation, as described below.

In carrying out your experiment, try mixing various volumes of the $\text{Fe}(\text{NO}_3)_3$ and KSCN solutions, using pipettes and a pipette bulb to accurately measure the volumes. You may find it helpful to add known volumes of water to your reaction mixtures so that all your trials involve the same total volume. In any case, a total volume of 10.00 mL should be sufficient. It is important to be able to know, as accurately as possible, the initial number of moles of Fe^{3+} and SCN^- in the reaction mixture. Therefore, you will want to avoid contamination of the solutions. You should try at least five different mixtures, as well as at least one exact duplicate (a replicate) to test your ability to reproduce your results. After you have mixed and stirred the reactant solutions, measure and record the absorbance of each of the equilibrium solutions, following the procedure described by your laboratory instructor.

You will find that the experimental part of this laboratory exercise can be done quickly. The calculations will take a good deal longer. (We will go to the department computer lab and use Excel to do these calculations.) From the known concentrations of the $\text{Fe}(\text{NO}_3)_3$ and KSCN stock solutions, and the volumes used, you should be able to calculate the initial number of moles of Fe^{3+} and SCN^- in each reaction mixture. With your absorbance data and equation (7), you can calculate the equilibrium concentration of the complex for each trial, and using the total volume, the number of moles of the complex present in the equilibrium mixture. From these pieces of information, the formula you assume for the complex, and the corresponding reaction stoichiometry, you should be able to calculate the number of moles of Fe^{3+} and SCN^- present at equilibrium for each reaction mixture. These values are easily converted to equilibrium concentrations. Once you have these concentrations, it is a simple procedure to plug their values into the appropriate equilibrium constant expression and solve for K .

Repeat the calculation for at least three reasonable values for x , using Excel to simplify the process. For one of these values of x , all your trials should yield reasonably constant values for K . You should calculate both the absolute and relative standard deviations for each set of K values. The smaller these statistical parameters are, the more constant we can judge K to be. Note, however, that in order to get constant values for K the following conditions must all be met: the formula for the complex ion and the chemical equation representing its formation must both correspond to what in fact occurs; the expression for K must correspond to the correct chemical equation; the equilibrium concentrations of the three species must be correctly calculated; the absorbance of the equilibrium mixtures must be accurately measured; the volumes of the reagent solutions must be accurately measured; and the system must truly be at chemical equilibrium. If none of your assumed formulas yields a reasonably constant K_{eq} , something is amiss and you should double-check your work!

Report

This experiment will be the subject of your third (and final) formal lab report. In addition to your formal report, you and your partner will turn in your lab books, as well as a spreadsheet that numerically analyzes your results. Your lab book should include:

- A clear description of the procedure you followed and what you observed
- A logical tabulation of your raw data (volumes of the stock solutions used in each trial, and the absorbance measurements obtained for each, including replicates)
- Detailed sample calculations for ONE of your trials, which you can use the ASA to help you get right

Your spreadsheet should carry out the calculations for *all* of your trials, including replicates. It should clearly depict your numerical results (K_{eq} , as well as values calculated in order to get it) for each of the formulas assumed for the complex. (Include initial moles of reactants, equilibrium moles of all reactive species, equilibrium concentrations of all reactive species, values for K , absolute standard deviation in K , and relative standard deviation in K) Please submit your spreadsheet electronically, by putting it into the Chem 112L course folder dropbox. To do so, please do the following: (If you can't do this, emailing it to Rob is okayfine too.)

1. Name your spreadsheet as follows: 112L7-YourName-1, where you replace YourName with, um, your name. For example, for Rob it would be 112L7-RobRossi-1.
2. Start up your very favorite web browser.
3. Go to LESTER, <http://lester.macalester.edu>.
4. Log into LESTER, then click on the COURSES tab.
5. Click on the box at the right edge of the **CHEM112L-02 - General Chem II Lab** tab.
6. Put your password into the Course Folder login box and click the button.
7. Click on "Dropbox" in the window that opens up.
8. Click "Browse" under File Options and find your finished spreadsheet file.
9. Click the "Upload File" button, and be sure that your file appears in the dropbox.
10. If you need to submit a corrected spreadsheet, you will find you can't delete the first one you sent. So just submit another, incrementing the number at the end, like this: 112L7-RobRossi-2, then 112L7-RobRossi-3, and so on. I'll grade the one with the highest number at the end, and ignore (delete) all the others.

Your formal report will be similar in form and content to those you have done previously. For this lab, it is particularly important that it include the following:

- A clear and concise overview of the chemical reaction being investigated
- A clear indication of what you conclude the correct formula for the complex to be, and a clear statement of the evidence justifying or supporting this conclusion
- A discussion of what you consider to be the *main* (one or two) sources of error in this experiment. Don't be vague – be specific! Are the errors you propose random, or systematic? How might they be reduced or eliminated?
- A comparison of your results against what the chemical literature has to say about this reaction, the complex, and/or its spectroscopic properties. Try to find and cite an independent value for at least one of the following:
 - The formula of the Fe(III) thiocyanate complex
 - The extinction coefficient of the complex and/or its λ_{max}
 - The equilibrium constant for the reaction

Name _____

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Advance Study Assignment

Provide a 1-2 sentence synopsis of the objectives and procedures of the experiment below. Copy this into your lab book, to serve as an introduction to this experiment.

The following questions illustrate the sorts of calculations you will be making in this experiment. Please answer these questions on this sheet. Attach additional pages if necessary.

1. Assume that the formula of the iron thiocyanate complex is $\text{Fe}(\text{SCN})_2^+$. (That is, assume $x = 2$.) Write a balanced chemical equation for the formation of this complex, and an expression for the corresponding equilibrium constant.

2. In a version of this experiment, a pair of students mix 5.00 mL of 2.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3$, 3.00 mL of 2.00×10^{-3} M KSCN, and 2.00 mL of H_2O . Calculate the number of moles of Fe^{3+} and SCN^- initially present in this mixture.

3. Reaction occurs in the mixture described in Question 2, forming a red complex assumed to have the formula $\text{Fe}(\text{SCN})_2^+$. The absorbance of the equilibrium mixture is 0.35 at 447 nm. Calculate the equilibrium concentration of the complex ion in this solution. (Read the lab!!!)

4. Using your results from Questions 2 and 3, calculate the number of moles of Fe^{3+} , SCN^- , and $\text{Fe}(\text{SCN})_2^+$ present in this equilibrium mixture.

5. Calculate the equilibrium concentrations of the two reactant species and evaluate the equilibrium constant consistent with these assumptions.

6. What additional information would you need in order to determine whether or not the correct formula of the complex is $\text{Fe}(\text{SCN})_2^+$?