

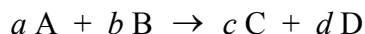
Determination of Reaction Stoichiometry and Chemical Equilibrium

Be sure to turn in your completed ASA (on the last two pages of this handout) by noon on Wednesday, November 13!

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

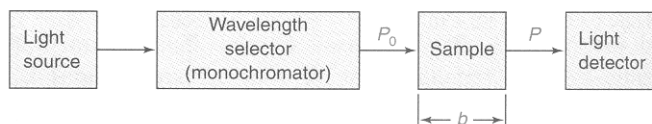
$$K = \frac{[\text{Fe}(\text{SCN})_x^{(3-x)}]}{[\text{Fe}^{3+}][\text{SCN}^-]^x} \quad (3)$$

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, $2.00 \times 10^{-3} \text{ M Fe}(\text{NO}_3)_3(\text{aq})$ in $1 \text{ M HNO}_3(\text{aq})$ and $2.00 \times 10^{-3} \text{ M KSCN}(\text{aq})$. 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; else $\text{Fe}(\text{OH})_3(\text{s})$ 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 this 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

$$T \equiv \frac{P}{P_0} \quad (4)$$

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 unitless.

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 $\lambda = 447$ 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 pipetting 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 volume mixtures and at least one exact duplicate to test your ability to reproduce 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 equilibrium number of moles of Fe^{3+} and SCN^- 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.

You and your partner will turn in a short report on your work. It should include raw data (volumes of stock solutions used in each trial and absorbance measurements), sample calculations and results for each of the formulas assumed for the complex (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), conclusion about the correct formula for the complex and evidence supporting the conclusion, and a discussion of errors. Your raw data and results must be presented as a printed spreadsheet in your report.

[originally written by ATS]

Advance Study Assignment

The following questions illustrate the sorts of calculations you will be making in this experiment.

1. Assume that the formula of the iron thiocyanate complex is $\text{Fe}(\text{SCN})_2^+$. Write a balanced chemical equation for its formation 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.
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.

(continued on the next page!)

