Using Beer's Law To Find An Equilibrium Constant For Iron(III) Thiocyanato Ion

Introduction

For the reaction

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

it has been shown in class that

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where *K*eq is the equilibrium constant for the reaction. The value of the equilibrium constant may be calculated from experimental data if the concentrations of both the reactants and products at equilibrium are known. Additionally, all equilibrium concentrations can be calculated if a single equilibrium concentration is known along with all other "initial" concentrations are known. The student will use spectrophotometry and Beer's Law to determine this single equilibrium concentration.

The equilibrium reaction studied in this experiment is formation of the iron(III) thiocyanato complex [$Fe(SCN)^{+2}$] from the iron and thiocyanate ions:

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

with the corresponding equilibrium expression:

$$K_{eq} = \frac{[Fe(SCN)^{+2}]}{[Fe^{+3}][SCN^{-}]}$$

The thiocyanate ion is colorless, the iron cation is slightly yellowish, but the iron(III) thiocyanato complex is a deep red-orange.

Remember that many colored species will follow Beer's law:

$$A = abc$$

where A is the absorbance measured by a spectrophotometer, a is the absorptivity at a given wavelength of light, b is the path length and c is the concentration of the absorbing species. Since the wavelength and path length will be held constant, the relationship between absorbance and concentration should be linear.

In order to use this method, we have a major problem that must be overcome. In order to make a Beer's Law plot, we need to know the concentration of [$Fe(SCN)^{2+}$]. But, how can this be known, since it is not known how much of the iron(III) ions will remain after mixing in the thiocyanate ion. At first it may seem like we need the equilibrium constant to calculate how much [$Fe(SCN)^{+2}$] will form and we are in an impossible circular situation. So how do we escape? We "stack the deck"! Recall Le Chatelier's principle. First, establish the equilibrium by mixing iron(III) nitrate solution with potassium thiocyanate. (What are the spectator ions????) Now let's add a "truckload" of thiocyanate ions to the beaker. What happens according to Le Chatelier's principle? **The equilibrium shifts toward the right and forms** [$Fe(SCN)^{+2}$]. By adding a large amount of thiocyanate ion, the iron(III) can be made to completely react and exist as $[Fe(SCN)^{+2}]$. By knowing how much iron(III) ions we started with, and that we have converted these completely to $[Fe(SCN)^{+2}]$, allows us to know the concentration of the $[Fe(SCN)^{+2}]$. A Beer's law plot constructed from solutions with a large amount of potassium thiocyanate gives us the key to overcoming our circular problem.

From another set of solutions in which the equilibrium has **not** been pushed so far to the right, we can now find K_{eq}. The absorbance of these solutions is measured. From the Beer's Law plot, the **equilibrium** concentration of the $[Fe(SCN)^{+2}]$ is calculated. To mathematically solve for the value of K_{eq}, it is necessary to have values for **all** the concentration species: $[Fe(SCN)^{2+}]$, $[Fe^{3+}]$, and $[SCN^-]$ <u>at equilibrium.</u> For this, a method called the 'ICE' approach will be used: **I**nitial concentration, **C**hange that occurs, and the new **E**quilibrium concentration. Let's consider the experimental design. A standard solution of SCN^- are obtained and small amounts of a standard Fe(III) are added. The system reaches equilibrium and absorbance values are obtained. The $[Fe^{3+}]$ and $[SCN^-]$ can be calculated using the standard dilution expression. These, are initial concentrations since this is what was added before the system came to equilibrium. The $[Fe(SCN)^{+2}]$, however, is an equilibrium concentration because it is calculated from the absorbance of the equilibrium state. To use ICE, a table is set up under the equilibrium expression. This topic is covered in detail in the textbook and in lecture. In this example, the table is:

	$Fe(H_2O)^{3+}$ (aq) +	SCN^- (aq)	$\rightleftharpoons$	$Fe(SCN)^{2+}$ (aq) + H_2O (l)
Initial	A	B		0
Change	-x	-x		+x
Equilibrium	A-x	B-x		x

Substituting these values into equation 1 yields:

$$K_{eq} = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{X}{(A-x)(B-x)} \qquad (1)$$

A value of K_{eq} is found for each addition of iron(III) to the flask. 'A' and 'B' are found from the stock concentrations and the dilution expression and 'x' is found from the Beer's law plot. This method has an advantage in that the precision of the K_{eq} can be found by calculating the mean and standard deviation of all the separate K_{eq} values for each solution.

Procedure

PART I: A Beer's law plot for $Fe[SCN]^{2+}$

To prepare diluted iron(III) solutions for the Beer's Law plot, obtain 35-40 mL of stock $Fe(NO_3)_3$ solution that is 0.00250 M and has been made up using 0.5 M HNO_3 as the solvent. Condition a 10 mL volumetric pipet with a couple of milliliters of the solution. Repeat the conditioning with a second and third volume. Fill the pipet to the mark and above being careful not to overfill and pull solution into the rubber bulb. Using your forefinger, seal the pipet and allow small amounts of air into the pipet by rocking your fingertip. This lowers the meniscus to the mark (**if it goes below - refill!**). Transfer the pipet tip into a 100 mL volumetric flask and allow the solution to flow into the flask. Once the transfer is completed, touch the tip of the pipet against the flask wall and give a quarter turn. The solution left in the pipet should remain there! Do not blow it out. Add 0.5 M nitric acid to the flask while periodically mixing. Fill the flask up to the base of the neck - invert and mix well. Continue filling until the meniscus is on the line. Cap, invert and shake well, then revert. Repeat the latter step a total of 15 (fifteen) times. Label this flask as 'diluted' Fe^{3+}. Calculate the final iron concentration in your notebook, and record.

Obtain about 35 mL of concentrated potassium thiocyanate that is 1.00 M.

Using your diluted' Fe^{3+}, the 1.00 M KSCN and 0.5 M HNO_3, prepare 5 solutions with pipets according to the table below in clean test tubes.

Table 1: Solutions to prepare a Beer's Law plot for thiocyanatoiron(III) ion

Soln. No.	**Diluted $Fe(NO_3)_3$, mL**	**Concentrated KSCN, mL**	**0.5 M HNO_3, mL**
1	1	5	4
2	2	5	3
3	3	5	2
4	4	5	1
5	5	5	0

Measure the absorbance of each solution in the spectrophotometer using a distilled water blank at a wavelength of 447 nm. Make a graph of absorbance vs. concentration. Perform linear regression (best straight line, or in Excel terms, the trend line) and draw the best straight line through the data. Make sure you have Excel put the equation of the line on the graph.

PART II: Determining the Equilibrium Constant

In this section we will need to use 'concentrated' iron(III) ion and 'diluted' thiocyanate ion. Be careful to use the appropriate solutions! If the diluted KSCN is not available in lab, you might need to make it as well!

Make five trial solutions for the $Fe[SCN]^{2+}$ equilibrium. Pipet 5 mL of 0.00250 M $Fe(NO_3)_3$ into five clean medium-sized test tubes. Pipet 1 mL, 2 mL, 3 mL, 4 mL, and 5 mL of 0.00250 M KSCN, respectively into test tubes 1 - 5. Pipet 4 mL, 3 mL, 2 mL, 1 mL and 0 mL 0.5 M HNO_3, respectively, into each test tube so that all solutions have a total volume of 10.0 mL. Measure the absorbance at the wavelength used in Part I and determine the $Fe[SCN]^{2+}$ concentration of each solution from the Beer's law plot drawn in Part I.

From the concentration of the complex, determine the concentrations of the iron and thiocyanate ions, and from these three concentrations determine an equilibrium constant for each trial. Report the average value of K_{eq} for this reaction.