

1. Determining an Equilibrium Constant

Introduction

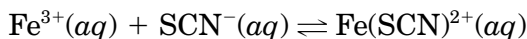
Equilibria in gaseous reactions, homogeneous equilibria for substances in solution, and heterogeneous equilibria between solids and substances in solution occur frequently. All forms of homogeneous and heterogeneous equilibria are important in the laboratory and in industrial, geological, agricultural, and biological chemistries. Examples of some of these equilibria appear in your textbook. You will find that the principles of equilibria (Ebbing/Gammon, Chapter 15) are applicable to all homogeneous and heterogeneous equilibria.

Purpose

This experiment will give you an opportunity to determine the equilibrium constant for the formation of $\text{Fe}(\text{SCN})^{2+}$. Moreover, the experiment will require you to use Le Chatelier's principle.

Concept of the experiment

When the reaction between Fe^{3+} and SCN^- (thiocyanate) ions in aqueous solution comes to equilibrium, the system consists of the reactants and $\text{Fe}(\text{SCN})^{2+}$. The chemical equation for this reaction is



The product is a complex ion (Ebbing/Gammon, Section 23.3) that has a coordinate covalent bond between the iron atom and an atom (probably the S atom) from the thiocyanate anion. The color of this complex ion is so intense that thiocyanate ions can be used to detect very small quantities of Fe^{3+} . Interestingly, $\text{Fe}(\text{SCN})^{2+}$ appears to exist solely in solution. Solid compounds containing this ion have never been isolated.

The objective of this experiment is to determine the equilibrium constant for this reaction. The equilibrium constant is given by the expression

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

where the concentrations of the substances are those at equilibrium. If these concentrations are measured or inferred, K can be calculated easily.

Because the reactants are essentially colorless, whereas the complex ion is deeply colored, you will use a spectrophotometer (Appendix: The Absorption of Light) to monitor the absorbance due to the complex ion without interference from the reactants. The absorbance (A) is proportional to the concentration (c) of the species that absorbs the light—in this case, $\text{Fe}(\text{SCN})^{2+}$ —according to Beer's law, $A = kc$. Beer's law and the usual method for the determination of k (not to be confused with the equilibrium constant K) are discussed in Appendix: The Absorption of Light. If you did the experiment "The Absorption Spectrum of Cobalt(II) Chloride," you already know a great deal about using

this law. After the concentration of $\text{Fe}(\text{SCN})^{2+}$ has been measured by way of the absorbance, the concentrations of the reactants can be inferred from their starting concentrations and the concentration of the complex ion.

There is a problem, however. To determine k , we must measure the absorbances of a series of solutions with known amounts of the complex ion. How can known amounts of $\text{Fe}(\text{SCN})^{2+}$ be obtained? After all, this substance is an active participant in the equilibrium with Fe^{3+} and SCN^- ions. Stoichiometric quantities of the reactants will not yield a known amount of the product.

This difficulty can be avoided. Le Chatelier's principle (Ebbing/Gammon, Section 15.7) indicates that a net reaction from left to right (that is, in the forward direction) can be achieved when more of a reactant is added. As more and more of the same reactant is added, more and more of the product forms. It is possible to add so much of this reactant that essentially all of the other reactant is converted to the product. You will use limiting quantities of Fe^{3+} and overwhelming amounts of SCN^- to achieve this result. The amount of $\text{Fe}(\text{SCN})^{2+}$ that is formed will then be essentially identical to the starting amount of the limiting reactant.

In this manner, you will prepare a series of solutions with known concentrations of $\text{Fe}(\text{SCN})^{2+}$. You will measure the absorbances of these solutions at 450 nm, the wavelength of maximum absorbance. When these absorbances are plotted against the concentrations of $\text{Fe}(\text{SCN})^{2+}$ on a graph, k can be determined from the slope of the straight line (see Appendix: The Absorption of Light) using linear regression. You may do this calculation by hand or, if your laboratory instructor wishes, you may use a computer and the Internet. Once k has been determined, working under these conditions will no longer be advantageous. In fact, you will determine the equilibrium constant K under conditions in which substantial amounts of both of the reactants and the product are present.

Doing the calculations

You will have to account for every dilution in order to do the calculations in this experiment. Consider, for example, the dilutions of the solution of $\text{Fe}(\text{NO}_3)_3$ that occur during the determination of k . First, 4.0 mL of a 0.0025 M solution of this substance is diluted to 100 mL. Portions of this solution (1.0 mL to 5.0 mL) are then diluted to 10.0 mL. The concentrations of Fe^{3+} that result are the ones to use in determining k . Do not use the original concentration.

In the determination of k , you will need to construct a graph in which absorbance appears on the vertical axis and the concentration of $\text{Fe}(\text{SCN})^{2+}$, in moles per liter, appears on the horizontal axis. Use the second figure in Appendix: The Absorption of Light as an exact model.

Procedure

Getting started

1. Your laboratory instructor may ask you to work in a group rather than alone.
2. Obtain 5 large test tubes and 5 matching rubber stoppers. Wash, rinse, and dry the test tubes and the stoppers.

3. Mark each of the test tubes with an identification number (1 through 5).
4. Obtain directions for discarding the solutions you will use in this experiment.
5. If necessary, obtain instructions for using your spectrophotometer.
6. You will use 1 *M* and 0.0025 *M* solutions of KSCN in this experiment. Do not confuse them!

Determining k in Beer's law

1. Use a Mohr pipet to transfer exactly 4 mL of a 0.0025 *M* solution of $\text{Fe}(\text{NO}_3)_3$ (in 0.1 *M* HNO_3) to a 100-mL volumetric flask. If such a flask is not available, use a 100-mL graduated cylinder. Add distilled water until the bottom of the meniscus coincides with the 100-mL mark on the flask or graduated cylinder. (See Figure I.2 in the Introduction to this manual.) Add the last 0.5 mL from a medicine dropper to make sure that you do not add too much water. Mix the solution thoroughly.
2. Rinse the Mohr pipet several times with this solution. Discard each of these portions.
3. Using this pipet, the solution you have just prepared, and Table 1.1, add the specified amount of this solution to each of the numbered test tubes.

Table 1.1 Composition of Solutions for Determining k

Test Tube No.	Diluted $\text{Fe}(\text{NO}_3)_3$ (mL)	1 <i>M</i> KSCN (mL)	0.1 <i>M</i> HNO_3 (mL)
1	1.0	5.0	4.0
2	2.0	5.0	3.0
3	3.0	5.0	2.0
4	4.0	5.0	1.0
5	5.0	5.0	0

4. Rinse the pipet with 1 *M* KSCN solution. Do not put the pipet directly into the stock bottle.
5. Add the correct amount of this solution, as shown in the table, to each test tube.
6. Rinse the pipet with 0.1 *M* HNO_3 solution. Do not put the pipet directly into the stock bottle.
7. Add the correct amount of this solution, as shown in the table, to each test tube. The volumes of the solutions in the test tubes should now be identical.
8. Insert the rubber stoppers. Mix each test tube thoroughly.
9. Measure and record the absorbance of each solution at 450 nm.

Determining the equilibrium constant

1. Wash and dry the test tubes and rubber stoppers. Renumber the test tubes (6 through 10).
2. Do not use the diluted solution of $\text{Fe}(\text{NO}_3)_3$ in this part of the experiment. Use the 0.0025 *M* solution of this substance instead.

3. Do not use the 1 *M* KSCN solution in this part of the experiment. Use the 0.0025 *M* solution of this substance instead.
4. Prepare the first five solutions shown in Table 1.2. Use a properly rinsed Mohr pipet for each addition. After you mix these solutions thoroughly, measure their absorbances at 450 nm and record your results.

Table 1.2 Composition of Solutions for Determining *K*

Test Tube No.	0.0025 <i>M</i> Fe(NO₃)₃ (mL)	0.0025 <i>M</i> KSCN (mL)	0.1 <i>M</i> HNO₃ (mL)
6	1.0	1.0	5.0
7	1.0	1.5	4.5
8	1.0	2.0	4.0
9	1.0	2.5	3.5
10	1.0	3.0	3.0
11	2.0	1.0	4.0
12	2.0	1.5	3.5
13	2.0	2.0	3.0
14	2.0	2.5	2.5
15	2.0	3.0	2.0

5. Wash and dry the test tubes. Renumber them (11 through 15), and prepare the remaining solutions. Measure the absorbances of these solutions at the same wavelength, and record your results.

f. Beer's law

2. a. What reaction are you studying in this experiment?

b. Give the mathematical expression for the equilibrium constant that pertains to this reaction.

c. What is the difference between k and K ?

d. How will Le Chatelier's principle be used to obtain k ?

Determining an Equilibrium Constant

Date: Student name:
Course: Team members:
Section:
Instructor:

Results

1. Obtaining data for determining k

Test Tube No.	A
1
2
3
4
5

2. Obtaining data for determining K

Test Tube No.	A	Test Tube No.	A
6	11
7	12
8	13
9	14
10	15

Questions

1. a. Complete the following table by calculating $[\text{Fe}(\text{SCN})^{2+}]$ for each test tube and inserting the absorbance as a first step in determining k . All concentrations are to be given in M .

Test Tube No.	$[\text{Fe}(\text{SCN})^{2+}]$	A
1
2
3
4
5

Representative calculation:

- b. Use the available piece of graph paper to plot these absorbances and values of $[\text{Fe}(\text{SCN})^{2+}]$.

Student name: Course/Section: Date:

- c. Calculate the slope of the best straight line, using linear regression (see Appendix: The Absorption of Light). Either do the calculation by hand or, if your laboratory instructor wishes, use a computer and the Internet. If you wish, draw a straight line with this slope on your graph. The line should pass through the origin ($A = 0$, $[\text{Fe}(\text{SCN})^{2+}] = 0$).

$k =$ (give units)

2. a. Complete the following table (with all concentrations in M).

Test Tube No.	Starting $[Fe^{3+}]$	Starting $[SCN^-]$	$[Fe(SCN)^{2+}]$	Equilibrium $[Fe^{3+}]$	Equilibrium $[SCN^-]$	K
6
7
8
9
10
11
12
13
14
15

Mean:

Representative calculation:

