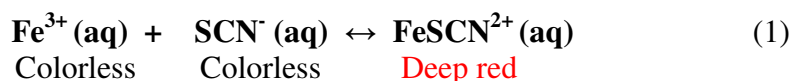


Determination of the Equilibrium Constant for a Chemical Reaction

Background

When chemical substances react, the reaction typically does not go to completion. Rather, the system goes to some intermediate state in which both the reactants and products have concentrations that do not change with time. Such a system is said to be in chemical equilibrium. When in equilibrium at a particular temperature, a reaction mixture obeys the Law of Chemical Equilibrium, which imposes a condition on the concentrations of reactants and products. This condition is expressed in the equilibrium constant K_c for the reaction.

In this experiment we will study the equilibrium properties of the reaction between iron (III) ion, Fe^{3+} , and thiocyanate ion, SCN^- :



When solutions containing Fe^{3+} ion and SCN^- ion are mixed, Reaction 1 occurs to some extent, forming the iron (III) thiocyanate complex ion, FeSCN^{2+} , which has a deep red color. As a result of the reaction, the equilibrium amounts of Fe^{3+} and SCN^- will be less than they would have been if no reaction occurred; *for every mole of FeSCN^{2+} that is formed, one mole of Fe^{3+} and one mole of SCN^- will react.* According to the Law of Chemical Equilibrium, the equilibrium constant expression K_c for Reaction 1 is formulated as follows:

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

The value of K_c in Equation 2 is constant at a given temperature. This means that mixtures containing Fe^{3+} and SCN^- will react until Equation 2 is satisfied, so that the same value of the K_c will be obtained no matter what initial amounts of Fe^{3+} and SCN^- were used.

The objectives of this experiment are: (1) to find K_c for Reaction 2 for several mixtures of Fe^{3+} and SCN^- made up in varying proportions; and (2) to show that K_c indeed has the same value in each of the mixtures. The reaction is a particularly good one to study because K_c is of a convenient magnitude and the color of the FeSCN^{2+} ion makes for an easy analysis of the equilibrium mixture.

The mixtures will be prepared by mixing solutions containing known concentrations of iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$, as a source of Fe^{3+} ions and potassium thiocyanate, KSCN , as a source of SCN^- ions. The color of the FeSCN^{2+} ions formed will allow us to determine its equilibrium concentration using a spectrophotometer (discussed later). Knowing the initial concentrations of reactants in a mixture and the equilibrium concentration of FeSCN^{2+} , we can calculate the equilibrium concentrations of the rest of the pertinent species and then determine K_c .

Since the calculations required in this experiment may not be apparent, we will go through a step-by-step procedure by which they can be made. As a specific example, let us assume that we prepared a

mixture by mixing 10.0 mL of 2.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3$ with 10.0 mL of 2.00×10^{-3} M KSCN . As a result of Reaction 1, some red FeSCN^{2+} ion is formed. By the method of analysis described later, its concentration at equilibrium is found to be 1.50×10^{-4} M. Our problem is to find K_c for the reaction from this information. To do this we follow the five steps below:

1. Calculate the initial number of moles of each reactant in the mixture.
2. Determine the number of moles of product that were formed at equilibrium. Since the product was formed at the expense of reactants, we can calculate the amount of each reactant that was used up.
3. Calculate the number of moles of each reactant remaining in the equilibrium mixture.
4. Determine the concentration of each reactant.
5. Calculate K_c for each reaction using Equation 2.

Step 1: Finding the Initial Number of Moles of Each Reactant. This requires relating the volumes and concentrations of the reagent solutions that were mixed to the numbers of moles of each reactant species in those solutions. By definition, the molarity of species A, M_A , is:

$$M_A = \frac{\text{Moles of A}}{\text{total volume of solution, } V_{\text{soln}} \text{ (in L)}} \quad (3a)$$

Or

$$\text{Moles of A} = M_A \times V_{\text{soln}} \quad (3b)$$

Using Equation 3b, it is easy to find the initial number of moles of Fe^{3+} and SCN^- . For each solution the volume used was 10.0 mL, or 0.0100 L. The molarity of each of the solutions was 2.00×10^{-3} mol/L, so $M_{\text{Fe}^{3+}} = 2.00 \times 10^{-3}$ mol/L and $M_{\text{SCN}^-} = 2.00 \times 10^{-3}$ mol/L. Therefore, in the reagent solutions, we find that

$$\text{Initial moles } \text{Fe}^{3+} = M_{\text{Fe}^{3+}} \times V_{\text{Fe}^{3+}} = 2.00 \times 10^{-3} \text{ mol/L} \times 0.0100 \text{ L} = 2.00 \times 10^{-5} \text{ mol}$$

$$\text{Initial moles } \text{SCN}^- = M_{\text{SCN}^-} \times V_{\text{SCN}^-} = 2.00 \times 10^{-3} \text{ mol/L} \times 0.0100 \text{ L} = 2.00 \times 10^{-5} \text{ mol}$$

Step 2: Finding the Number of Moles of Product Formed. Here again we can use Equation 3b.

Let's say that the molarity of FeSCN^{2+} was found to be 1.50×10^{-4} mol/L at equilibrium using the spectrophotometer (described later). The total volume of solution or the mixture at equilibrium is the *sum* of the two volumes that were mixed, and is 20.0 mL, or 0.0200 L. So,

$$\begin{aligned} \text{Moles } \text{FeSCN}^{2+} \text{ formed} &= M_{\text{FeSCN}^{2+}} \times V_{\text{soln}} = 1.50 \times 10^{-4} \text{ mol/L} \times 0.0200 \text{ L} \\ &= 3.00 \times 10^{-6} \text{ mol} \end{aligned}$$

The number of moles of Fe^{3+} and SCN^- that reacted, or were *used up*, in producing the FeSCN^{2+} must also be both equal to 3.00×10^{-6} moles since, by Equation 1, it takes *one mole* Fe^{3+} and *one mole* SCN^- to make each mole of FeSCN^{2+} . Thus:

$$\begin{aligned} \text{Number of moles } \text{Fe}^{3+} \text{ reacted} &= \text{Number of moles } \text{FeSCN}^{2+} \text{ formed} = 3.00 \times 10^{-6} \text{ mol} \\ \text{Number of moles } \text{SCN}^- \text{ reacted} &= \text{Number of moles } \text{FeSCN}^{2+} \text{ formed} = 3.00 \times 10^{-6} \text{ mol} \end{aligned}$$

Step 3: Finding the Number of Moles of Each Reactant Present at Equilibrium. In Step 1 we determined that initially we had 2.00×10^{-5} moles Fe^{3+} and 2.00×10^{-5} moles SCN^- present. In Step

2 we found that in the reaction 3.00×10^{-6} moles Fe^{3+} and 3.00×10^{-6} moles SCN^- reacted. The number of moles present at equilibrium must equal the initial moles minus the number of moles that reacted. Therefore, at *equilibrium*,

Number of moles at equilibrium = initial no. moles - no. moles reacted

$$\text{Equil. moles } \text{Fe}^{3+} = 2.00 \times 10^{-5} - 3.00 \times 10^{-6} = 1.70 \times 10^{-5} \text{ mol} \quad (4)$$

$$\text{Equil. moles } \text{SCN}^- = 2.00 \times 10^{-5} - 3.00 \times 10^{-6} = 1.70 \times 10^{-5} \text{ mol}$$

Step 4 Finding the Concentrations of All Species at Equilibrium. Experimentally, say we obtained the concentration of FeSCN^{2+} to be 1.50×10^{-4} M (as given in step 2). The number of moles of each of Fe^{3+} and SCN^- at equilibrium was obtained in Step 3. The volume of the mixture being studied was 20.0 mL, or 0.0200 L. So, at *equilibrium*, the concentrations of Fe^{3+} and SCN^- equal:

$$\begin{aligned} [\text{Fe}^{3+}]_{\text{eq}} &= M_{\text{Fe}^{3+}, \text{eq}} = (\text{Equil. moles } \text{Fe}^{3+} / V_{\text{soln}}) = (1.70 \times 10^{-5} \text{ moles} / 0.0200 \text{ L}) \\ &= 8.50 \times 10^{-4} \text{ mol/L} \end{aligned}$$

$$\begin{aligned} [\text{SCN}^-]_{\text{eq}} &= M_{\text{SCN}^-, \text{eq}} = (\text{Equil. moles } \text{SCN}^- / V_{\text{soln}}) = (1.70 \times 10^{-5} \text{ moles} / 0.0200 \text{ L}) \\ &= 8.50 \times 10^{-4} \text{ mol/L} \end{aligned}$$

Step 5: Finding the Value of K_c for the Reaction. Once the equilibrium concentrations of all the reactants and products are known, one needs merely to substitute into Equation 2 to determine K_c :

$$\begin{aligned} K_c &= \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} \\ K_c &= \frac{1.50 \times 10^{-4}}{(8.50 \times 10^{-4})(8.50 \times 10^{-4})} = 204 \end{aligned}$$

In this experiment you will obtain data similar to that shown in this example. The calculations involved in processing your data are completely analogous to those we have made. (However, your results will differ from the ones we obtained, since the data in our example were obtained at a different temperature and so relate to a different value of K_c .)

In carrying out this analysis we made the assumption that the reaction which occurred was given by Equation 1. There is no inherent reason why the reaction might not have been:



Notice that in Reaction 5 2 moles of SCN^- reacted with one mole of Fe^{3+} , so the reaction stoichiometry is 1:2. If you are interested in matters of this sort, you might ask how we know whether we are actually observing Reaction 1 or Reaction 5. The line of reasoning is the following. If Reaction 1 is occurring, K_c for that reaction as we calculate it should remain constant with different reagent mixtures. If, however, Reaction 5 is going on, K_c as calculated for that reaction should remain constant. In part B of the Data and Calculations section, we will assume that Reaction 5 occurs and make the analysis of K_c

on that basis. The results of the two sets of calculations should make it clear that Reaction 1 is the one that we are studying.

Two analytical methods can be used to determine $[\text{FeSCN}^{2+}]$ in the equilibrium mixtures. The more precise method uses a spectrophotometer, which measures the amount of light absorbed by the red complex at 447 nm, the wavelength at which the complex most strongly absorbs. The absorbance, A , of the complex is proportional to its concentration, M , and can be measured directly on the spectrophotometer:

$$A = kM \quad (6)$$

Your instructor will show you how to operate the spectrophotometer, if available to your laboratory, and will provide you with a **calibration curve or equation** from which you can find $[\text{FeSCN}^{2+}]$ once you have determined the absorbance of your solutions.

In preparing the mixtures in this experiment we will maintain the concentration of H^+ ion at 0.5 M. The hydrogen ion does not participate directly in the reaction, but its presence is necessary to avoid the formation of brown-colored species such as FeOH^{2+} , which would interfere with the analysis of $[\text{FeSCN}^{2+}]$.

Procedure

In the hoods you'll find the solutions of 2.00×10^{-3} M KSCN and 2.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3$ in 1 M HNO_3 . The volumes of reagents to be added to each test tube are summarized in Table 1. Note that the total volume in each test tube is 10.00 ml. Deliver the required amount of each chemical by means of a graduated or volumetric pipette, but do not mix the Fe^+ solution and SCN^- solution until you are ready to use the spectrophotometer. Do one trial at a time.

The moment $\text{Fe}(\text{NO}_3)_3$ solution is in contact with KSCN solution the reaction starts.

Table 1. Volumes of reagents needed

	Test Tube No.				
	1	2	3	4	5
Volume $\text{Fe}(\text{NO}_3)_3$ solution (mL)	5.00	5.00	5.00	5.00	5.00
Volume KSCN solution (mL)	1.00	2.00	3.00	4.00	5.00
Volume H_2O (mL)	4.00	3.00	2.00	1.00	0.00

Mix each solution thoroughly with the Vortexer or a glass stirring rod. Be sure to dry the stirring rod after mixing each solution.

Determination of concentration of FeSCN^{2+} by spectrophotometry

Place a portion of the mixture from test tube 1 in a spectrophotometer cuvette, as demonstrated by your instructor, and measure the absorbance of the solution at 447 nm. Determine the concentration of FeSCN^{2+} from the calibration curve provided for each instrument or from the equation furnished to

you. Record the value on the Data page. Repeat the measurement using the mixtures in each of the other 4 test tubes.

DISPOSAL OF REACTION PRODUCTS

In this experiment, reactant concentrations are very low. In most localities you can pour the contents of the test tubes down the sink when you have completed your measurements. However, consult your instructor for alternate disposal procedures.

Processing the Data

Part A: Calculation of K_c assuming the reaction: $\text{Fe}^{3+}_{(aq)} + \text{SCN}^{-}_{(aq)} \leftrightarrow \text{FeSCN}^{2+}_{(aq)}$

This calculation is easily done by following Steps 1 through 5 in the procedure. Results are to be entered in the table either by hand or using Excel. If you are familiar with Excel, you may enter in the formulas directly and have the spreadsheet perform your calculations. Please keep all values to 3 significant figures.

Step 1. Find the initial number of moles of Fe^{3+} and SCN^{-} in the 5 mixtures. The initial number of moles is determined by the following: **initial moles = $M \times V$ (in L)**
Enter these values into Columns 1 and 2 of the table.

Step 2. Determine the equilibrium concentration of FeSCN^{2+} from the measured absorbance and the calibration curve. Since the light absorbed is proportional to the concentration (**$A = k \times M$**):
 $M_{\text{FeSCN}^{2+}} = [\text{FeSCN}^{2+}]_{\text{eq}} = A/k$ where k is the slope of the line of the calibration curve. Enter this value into column 8 of the data table.

Next calculate the Equilibrium # of moles for FeSCN^{2+} in a similar fashion as Step 1:

Equil. moles $\text{FeSCN}^{2+} = [\text{FeSCN}^{2+}]_{\text{eq}} \times V_{\text{soln}}$ (in L)

Enter the value into column 5 of the data table. Please note that the equilibrium number of moles of FeSCN^{2+} equals the number of moles of Fe^{3+} and the number of moles SCN^{-} that reacted.

Step 3. Determine the equilibrium moles of Fe^{3+} and SCN^{-} by subtracting the moles that reacted for Fe^{3+} or SCN^{-} (from step 2) from the initial moles present: **Equil. moles = Initial moles – Moles reacted.** Enter these values into Columns 3 and 4 respectively.

Step 4. Determine the equilibrium concentrations of Fe^{3+} and SCN^{-} , $[\text{Fe}^{3+}]_{\text{eq}}$ and $[\text{SCN}^{-}]_{\text{eq}}$, by dividing the equil. moles for each species by the total volume of the reaction mixture (total volume = 10.0 mL or 0.010 L): **$[\]_{\text{eq}} = \text{equil. moles}/V$ (in L).** Enter these values into Columns 6 and 7.

Step 5 Calculate K_c for the reaction for each of the mixtures by substituting values for the equilibrium concentrations of Fe^{3+} , SCN^{-} and FeSCN^{2+} into the equilibrium expression for the reaction. Enter these values into the last column and find the average value of K_c .

Part B: Calculations Assuming the formation of $\text{Fe}(\text{SCN})_2^+$

In calculating K_c in Part A, we assume, correctly, that the formula of the complex ion is $\text{Fe}(\text{SCN})_2^{2+}$. It is by no means obvious that this is the case and one might have assumed that $\text{Fe}(\text{SCN})_2^+$ was the species formed. The reaction would then be:



We can use the fact that the equilibrium constant must remain constant no matter what the initial concentrations of reactants or products are to help identify the correct equilibrium present. If we analyze the equilibrium system we have studied, assuming that 2 equivalents of SCN^- bond to the Fe rather than 1 as suggested in equation (5) above, we should obtain non-constant values of K_c .

Using the same kind of procedure as in Part A, **calculate K_c for Mixtures 1, 3 and 5** on the basis that $\text{Fe}(\text{SCN})_2^+$ is the formula of the complex ion formed by the reaction between Fe^{3+} and SCN^- .

The assumption of two SCN^- reacting requires **three changes in the calculation:**

(i) Equilibrium $[\text{Fe}(\text{SCN})_2^+]$ will equal **one-half** the $[\text{FeSCN}^{2+}]$ obtained for each solution in Part A.

(ii) The reaction requires that 2 moles of SCN^- react. As a result, the change in # of moles will be $2 * \text{Eq. moles Fe}(\text{SCN})_2^+$. Therefore in calculating the equilibrium number of moles SCN^- you will need to **subtract ($2 * \text{number of moles Fe}(\text{SCN})_2^+$) from the initial number of moles SCN^- .**

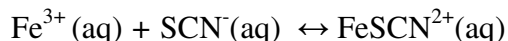
(iii) Since two moles of SCN^- are required to react, this changes the equilibrium expression as well. **The $[\text{SCN}^-]$ will need to be squared in the equilibrium expression.**

Name _____

Section _____

Advance Study Assignment: Determination of the Equilibrium Constant for a Chemical Reaction

1. A student mixes 5.0 mL 2.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3$ with 5.0 mL 2.00×10^{-3} M KSCN. She finds that in the equilibrium mixture the concentration of FeSCN^{2+} is 1.2×10^{-4} M. Find K_c for the reaction



Step 1 Find the number of moles Fe^{3+} and SCN^- initially present. (Use Eq. 3.)

_____ moles Fe^{3+} _____ moles SCN^-

Sample calculation:

Step 2 How many moles of FeSCN^{2+} are in the mixture at equilibrium? What is the volume of the equilibrium mixture? (Use Eq. 3.)

_____ mL; _____ moles FeSCN^{2+}

Sample calculation:

How many moles of Fe^{3+} and SCN^- reacted to form FeSCN^{2+} ?

_____ moles Fe^{3+} reacted _____ moles SCN^- reacted

Sample calculation:

Step 3 How many moles of Fe^{3+} and SCN^- remain in the solution at equilibrium? (Use Eq. 4 and the results of Steps 1 and 2.)

_____ equilibrium moles Fe^{3+} _____ equilibrium moles SCN^-

Step 3 *Sample calculation:*

Step 4 What are the concentrations of Fe^{3+} , SCN^- , and FeSCN^{2+} at equilibrium? What is the volume of the equilibrium mixture? (Use Eq. 3 and the results of Step 3.)

$$[\text{Fe}^{3+}] = \text{_____ M}; [\text{SCN}^-] = \text{_____ M}; [\text{FeSCN}^{2+}] = \text{_____ M}$$

Sample calculation:

$$\text{_____ mL} = \text{_____ L}$$

Step 5 What is the value of K_c for the reaction? (Use Eq. 2 and the results of Step 4.)

$$K_c = \text{_____}$$

Sample calculation:

2. Assume that the reaction studied in Problem 1 is $\text{Fe}^{3+}(\text{aq}) + 2 \text{SCN}^-(\text{aq}) \leftrightarrow \text{Fe}(\text{SCN})_2^+(\text{aq})$. Find K_c for this reaction, given the data in Problem 1, except that the equilibrium concentration of $\text{Fe}(\text{SCN})_2^+$ is equal to 0.6×10^{-4} M.
- a. Formulate the expression for K_c for the alternate reaction just cited.

b. Find K_c as you did in Problem 1; take due account of the fact that two moles SCN^- reacted per mole $\text{Fe}(\text{SCN})_2^+$ that formed.

Step 1 Results are as in Problem 1.

Step 2 How many moles of $\text{Fe}(\text{SCN})_2^+$ are in the mixture at equilibrium (Use Eq. 3b)?

Sample calculation: _____ moles $\text{Fe}(\text{SCN})_2^+$

How many moles of Fe^{3+} and SCN^- reacted to form $\text{Fe}(\text{SCN})_2^+$?

Sample calculation: _____ moles Fe^{3+} reacted _____ moles SCN^- reacted

Step 3 How many moles of Fe^{3+} and SCN^- remain in solution at equilibrium? Use the results of Steps 1 and 2, noting that no. moles SCN^- at equilibrium = original no. moles SCN^- - (2 x no. moles $\text{Fe}(\text{SCN})_2^+$).

Sample calculation: _____ equil. moles Fe^{3+} _____ equil. moles SCN^-

Step 4 What are the concentrations of Fe^{3+} , SCN^- , and $\text{Fe}(\text{SCN})_2^+$ at equilibrium? (Use Eq. 3 and the results of Step 3.)

Sample calculation: $[\text{Fe}^{3+}] =$ _____ M; $[\text{SCN}^-] =$ _____ M; $[\text{Fe}(\text{SCN})_2^+] =$ _____ M

Step 5 Calculate K_c on the basis that the alternate reaction occurs. (Use the answer to Part 2a.)

Sample calculation: $K_c =$ _____