# Determining the Value of the Equilibrium Constant for the Reaction of Iron(III) with Thiocyanate

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Summary: Equilibrium constants are introduced. The equilibrium constant for the reaction of Fe(III) ion with thiocyanate ion is determined. The concentration of FeNCS2+ is determined from a Beer’s Law plot, constructed from solutions of known concentrations of FeNCS2+.

## Introduction

Chemical reactions are often treated as if they go to completion, which means that reactants are completely converted to products (or, more properly, the limiting reactant is completely converted to product). However, all chemical reactions are actually equilibrium systems, so there is always some reactant still present at equilibrium. (For some reactions, the amount of reactant remaining at equilibrium is negligible, so the reaction can be treated as if it went to completion.)

Equilibrium is represented by a double arrow.

 2HI(g) ⇌ H2(g) + I2(g) Eq (1)

If mainly reactant is present at equilibrium, the system is said to lie close to the reactants’ side of the reaction; likewise the system may lie close to the products’ side. The position of the equilibrium is characterized by an equilibrium constant, *K*c, where the subscript “c” is for concentration. **An equilibrium constant is the product of product concentrations divided by the product of reactant concentrations, with each species’ concentration is raised to the power of the coefficient of that species.** For equation (1) the equilibrium constant expression would be

 $K\_{c}=\frac{\left[H\_{2}\right]\left[I\_{2}\right]}{\left[HI\right]^{2}}$. Eq ()

The square brackets, [ ], are used to indicate concentration in mol/liter, i.e., molarity, *M*.

In this experiment the value of the equilibrium constant will be determined for the reaction between iron(III) ion and thiocyanate ion:

 Fe3+(aq)+SCN−(aq) ⇌ FeNCS2+(aq) Eq ()

(Task: write an equilibrium expression for this chemical reaction and insert it in the equilibrium constant expression row on the first data sheet page.)

**About the name thiocyanate**: Cyanide is CN–. It can be oxidized to form cyanate, OCN–. The oxygen can be replaced with sulfur, giving SCN–. The presence of sulfur in a compound is indicated by “thio”, so SCN– is called the thiocyanate ion. Its Lewis structure is :S−C≡N:–. It has a lone pair on each end. When it combines with iron ion, it donates the lone pair on the nitrogen to the iron, which is why the iron compound is shown as FeNCS2+, instead of FeSCN2+.

When a solution containing Fe3+ ion (pale yellow) is mixed with a solution containing thiocyanate ion (colorless), the deep red thiocyanatoiron(III) ion, FeNCS2+, forms. As FeNCS2+ forms, the concentrations of free Fe3+ and SCN− decrease, because every mole of FeNCS2+ that forms consumes one mole of Fe3+ and one mole of SCN−.

The value of *K*c is constant (at a given temperature). So, mixtures can be prepared that have various concentrations of Fe3+ and SCN− (and FeNCS2+), but the ratio of these concentrations, as given by the equilibrium constant expression, should be a constant. In this experiment mixtures of various concentrations of Fe3+ and SCN– will be prepared, and the value of *K*c will be determined for each mixture to see if it really does seem to be a constant. The equilibrium concentration of the red FeNCS2+ ion will be determined using a spectrometer. The concentrations of Fe3+ and SCN– at equilibrium can be determined from their initial concentrations, and by knowing how much their initial concentrations decrease due to the formation of FeNCS2+.

**Example:** Equilibrium concentrations are calculated using an ICE table, which stands for initial, change, and equilibrium. First, initial concentrations of reactants are needed. Suppose a solution is made up by adding 10.0 mL of 0.500 *M* of Fe3+ and 3.00 mL of 0.200 *M* SCN– to a 100 mL volumetric flask, which is then filled to the mark with water (the numbers are just made up for this example). The initial concentration of Fe3+ is calculated using the dilution equation, *M*d*V*d = *M*c*V*c. The 10.0 mL was the volume concentrated; the 0.500 *M* was the molarity concentrated, the 100 mL is the volume dilute, and what is desired is the molarity dilute. Plugging those into the dilution equation gives 0.0500 *M* for the iron ion concentration in the volumetric flask. Likewise, the molarity of SCN– in the flask is 0.00600 *M*. No FeNCS2+ was present initially. These initial concentrations are entered on the first line of the ICE table. The concentration of FeNCS2+ at equilibrium is determined spectroscopically and is found to be 0.00100 *M*. That is entered on the third line. The change in concentration of FeNCS2+ is the same value (since no FeNCS2+ was present initially), which is entered on the “Change” row. Now, if [FeNCS2+] increase by 0.00100 *M*, then [Fe3+] must have decrease by the same amount, because the Fe3+ in FeNCS2+ had to come from somewhere. That is, the change in [Fe3+] is –0.00100 *M*. Likewise, the change for [SCN–] is –0.00100 *M*. The equilibrium concentrations of Fe3+ and SCN– are the sum of the initial values and the change. So the equilibrium concentrations of free Fe3+ and SCN– are 0.0490 *M* and 0.00500 *M*, respectively. Those values are entered in the last row of the table.

Table 1. An ICE Table

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Fe3+(aq) | + | SCN−(aq) | ⇌ | FeNCS2+(aq) |
| Initial conc./ *M*: | 0.0500 |  | 0.00600 |  | 0 |
| Change in conc. at equilibrium/ *M*: | –0.00100 |  | –0.00100 |  | +0.00100 |
| Equilibrium conc./ *M*: | 0.0490 |  | 0.00500 |  | 0.00100 |

Finally, the value of the equilibrium constant is calculated from the last row of the table.

 $K\_{c}=\frac{\left[FeNCS^{2+}(aq)\right]}{\left[Fe^{3+}\left(aq\right)\right]\left[SCN^{-}(aq)\right]}=\frac{0.00100}{\left(0.0490\right)\left(0.00500\right)}=4.08$. Eq(4)

The concentration of FeNCS2+ present in solutions will be determined using a spectrometer, which measures how much light is absorbed at particular wavelength. The amount of light absorbed is displayed as absorbance, *A*, which is related to the compound’s molar concentration, *c*, by Beer’s Law:

 *A* = ε*bc* Eq(5)

In this equation *b* is the light path length (1 cm for the equipment in this lab) and ε is the molar absorptivity. This indicates that absorbance is proportional to concentration. A plot of absorbance *vs*. concentration, which is called a Beer’s Law plot, should be linear. In this lab, five solutions of known concentrations of FeNCS2+ will be prepared. Solutions of known concentrations are called *standards*. The absorbance of these standards will be measured, and a Beer’s Law plot will be prepared, and used to determine the concentration of FeNCS2+ in equilibrium mixtures.

Figure . **Using a Beer’s Law plot. The absorbance of five different standards is measure and plotted. The best-fit straight line through the data is determined. The absorbance of an unknown is measured. Using that best-fit straight line, the concentration corresponding to that absorbance is determined. (The numbers are made up.)**

To construct a Beer’s Law plot requires having solutions of known concentrations of FeNCS2+. This is tricky, because FeNCS2+ tends to dissociate into Fe3+ and SCN– ions. The trick is to have a high concentration of Fe3+; this causes essentially all of the SCN– to be converted to FeNCS2+.

To see this, look at the equilibrium constant expression you put on the first data sheet page . If [Fe3+] is made large, then, for the equilibrium constant expression to be a constant, [SCN–] would have to become very small. And, the way [SCN–] becomes low is by being converted into FeNCS2+. Nearly all of the SCN– is converted into FeNCS2+, so the equilibrium concentration of FeNCS2+ is essentially the same as the starting concentration of SCN–, but only because of the high concentration of Fe3+.

Iron3+(aq) tends to precipitate as iron oxide. The precipitation does not occur in acidic solutions. Therefore, all of the solutions used in this lab are also 0.1 *M* in the acid HNO3.

## Procedure

### Hazard: As always, wear Safety glasses while performing this experiment. The nitric acid solutions can cause chemical burns.

#### Chemical locations

0.20 *M* Fe(NO3)3–KCl–HNO3 mixture: An “orangish” **stock** solution of iron stored in a carboy on the side of the lab.

0.10 *M* HNO3: A colorless solution stored in a carboy on the side of the lab.

0.002 *M* Fe3+: in a bottle on each lab bench.

0.002 *M* SCN–: in a bottle on each lab bench.

Contamination Notes: If your flask is wet before you prepare your standard/sample solutions, it may be contaminated. To remove any contaminants, rinse the flask with a little of the 0.1 *M* HNO3.

### Part I, Prepare Standard Solutions for the Beer’s Law Plot

A *standard solution* is a solution of known concentration. Because these standard solutions have high concentrations of iron, the concentration of FeNCS2+ in them is the same as the initial concentration of SCN-.

1. **Label six containers.** Label a 125 mL Erlenmeyer flask as “Blank”. Label five 50 mL volumetric flasks as “S1” through “S5”. (In industry, lab technicians have been fired for making up solutions, but not labeling the containers.)

*A blank contains everything but the compound of interest* (in this case FeSCN2+). Blanks are used to correct for interfering contaminants.

Several standard solutions will be prepared. The contents of the tubes are shown in the following table. The next three steps give directions for preparing these solutions.

Table 2. Components of Standard Solutions for Beer’s Law plot (As Prepared Below)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | S1 | S2 | S3 | S4 | S5 |
| 0.2 *M* Fe(NO3)3 / mL | 10.00 | 10.00 | 10.00 | 10.00 | 10.00 |
| 0.002 *M* NaSCN / mL | 1.00 | 2.00 | 3.00 | 4.00 | 5.00 |
| 0.10 *M* HNO3 / mL | Fill to the mark on the neck of the 50-mL volumetric flask |
| Total volume of solution / mL | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |

1. **Add Fe3+ to the containers.** Label a 150 mL beaker “Fe3+”. Dispense about 80 mL of **0.2 *M*** Fe(NO3)3(aq) from a carboy into that beaker, so that the solution is conveniently available. Record the actual Fe(NO3)3 concentration, which is written on that carboy, on Data Sheet 1. Rinse the pipet before first using it, and before switching to a different solution. Pipet 10.00 mL of that solution into each of the six containers labeled in step 1. Note: if **0.002 *M*** Fe(NO3)3 solution is used by mistake, the calibration curve will not work.
2. **Add SCN– to the containers.** Label a 150 mL beaker “NaSCN”. Dispense about 50 mL of 0.002 *M* NaSCN (in 0.1 *M* HNO3) into that beaker from a carboy, so that the solution is conveniently available. Record the actual NaSCN solution concentrations, which is written on the carboy, on Data Sheet 1. Pipet 1.00, 2.00, 3.00, 4.00, and 5.00 mL of that solution into volumetric flasks “S1” through “S5”, respectively. If the solutions do not turn dark when the SCN– is added, then something is wrong. Record the volumes of NaSCN solution added to the volumetric flasks on Data Sheet 1. (These should be given with three significant figures, because pipettes can be quite accurate.)
3. **Use HNO3 to make total volume of containers 50 mL.** Label a 400 mL beaker “0.1 *M* HNO3”. Place about 275 mL of 0.10 *M* HNO3 into that beaker. Using a graduated cylinder, transfer about 40 mL of that acid solution to the “Blank” flask (so the blank will have everything except the SCN– in it). Dilute the solutions in the volumetric flasks to 50 mL with the 0.10 *M* HNO3 by filling each to the mark with the acid solution. To prevent overfilling the flasks, transfer the last few drops of solution with a plastic dropper pipet (or, if it is available, a squirt bottle labeled “0.1 *M* HNO3”). Stopper the flask and mix it. *The standard way to mix the contents of a volumetric flask is to invert the container, swirl it, turn it right side up and repeat for a total of three times* to ensure that the flask is well-mixed. (Not mixing the solutions will cause the experiment to fail.)
4. **Calculations.** Calculate the “initial SCN– concentration”, and the “equilibrium FeNCS2+ ion concentration” for each flask. These values are needed for the next step.

Initial SCN– concentration: use the dilution equation: *M*d*V*d = *M*c*V*c, where the “c” and “d” refer to concentrated and dilute molarities and volumes (see the example calculation for help on this).

Equilibrium FeNCS2+ concentration: the concentration of iron is so large that all of the initial SCN- is converted to FeNCS2+ at equilibrium, so this value is the same as the initial SCN- concentration.

### Part II, Prepare the Beer’s Law Plot

1. **Set up spectrometer with blank.** Plug the USB cable from the SpectroVis Plus spectrometer into the computer. Start the Logger Pro 3 software by double-clicking on the icon on the desktop. (If the software doesn’t work, try plugging the spectrometer in after the software is running.) Calibrate the spectrometer: the menu path is: Experiment/Calibrate/Spectrometer 1. The instrument will wait 90 seconds for the lamp to warm up. Obtain a cuvette. Fill it two-thirds full with your **blank solution**; this is the “blank cuvette”. Wipe the clear windows with a KimWipe. When the spectrometer has warmed up, the software will say “Place a blank cuvette in the device:”. Do so, ensuring that the clear windows are on the sides of the spectrometer with the white marks. Then click on the “Finish Calibration” button and, when enabled, click the “OK” button to exit that dialog box.
2. **Configure the spectrometer** using the solution from the flask containing the highest concentration of SCN–. Rinse the cuvette with that solution. Place the washings in a waste beaker on your table. (At the end of the lab, empty this into the “Discarded Equilibrium Mixtures” waste container.) Fill the cuvette (always about two-thirds full) with this sample solution. Place the cuvette in the spectrometer.

Configure button

Collect button

Linear fit button

Click the “Configure” button. Change “Collection Mode” to “absorbance vs. concentration”. A mark should appear above the highest peak between 400 and 600 nm. (If it doesn’t, click on that maximum on the spectrum; the corresponding wavelength should now have a check mark in the displayed table.) The wavelength of highest absorption is referred to as λmax (it should be around 447 nm). Click “OK”. The software asks “Do you want to store the latest run before switching Collection Mode?” “Yes” keeps the data, which looks nice, but isn’t essential.

1. **Create calibration plot.** Click the “Collect” button. **Don’t** press “Stop”! Instead, press the “Keep” button, which has appeared to the right of the “Stop” button. Enter the concentration of this sample (“S5”), and press “OK”. (The concentration can be entered as, e.g., 1.23e-4.) A point will appear in the absorbance vs. concentration plot. Don’t press “Stop”! Rinse the cuvette with solution “S4”, then fill the cuvette with that solution, wipe the cuvette (as always), insert the cuvette in the spectrometer, and wait for the reading to stabilize. Then press “Keep” again. (To spread the data out, press the “Autoscale Graph” icon, .) Repeat for the remaining samples. When finished, click “Stop” to end data collection.
2. **Check your data.** Look at the data: it should be on a straight line. If it isn’t, the concentrations may have been entered incorrectly. The concentrations can be edited to correct the values. The straight line should go through the origin, or close to it.

If the line does not pass close to the origin, the blank may have been done incorrectly. The blank can be reset by going back to the menu item, Experiment/Calibrate/Spectrometer 1; warm-up can be skipped.

Another possible cause of error is if the cuvette was inserted into the spectrometer with light going through the ribbed sides instead of the clear sides.

1. **Add a straight line.** Click the “Linear Fit” button to see the best fit line equation for the standard solutions. On the Data Sheet, enter the parameters for this equation (that is, the slope, y-intercept, and correlation coefficient squared).
2. **Have the instructor look** at the graph before continuing.
3. **Do not shut down the software**, because the calibration plot just created will be used to determine the concentration of FeNCS2+ in equilibrium mixtures in the following steps.

### Part III, Prepare and Measure the Equilibrium Mixtures

Several equilibrium mixtures will be prepared in test tubes. The contents of the tubes are shown in the following table. Directions for preparing these solutions are given in the following steps.

|  |
| --- |
| **Table 2.**  Composition of the equilibrium mixtures |
|  | E1 | E2 | E3 | E4 | E5 |
| 0.002 *M* Fe(NO3)3/mL | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| 0.002 *M* NaSCN/mL | 1.00 | 2.00 | 3.00 | 4.00 | 5.00 |
| 0.10 *M* HNO3/mL | 4.00 | 3.00 | 2.00 | 1.00 | 0.00 |
| Total volume of solution/mL | 10.00 | 10.00 | 10.00 | 10.00 | 10.00 |

1. **Label test tubes.** Obtain 5 clean, dry test tubes that can hold 10 mL of solution (18 mm × 150 mm tubes work). Label these tubes “E1” through “E5” (the “E” is for equilibrium).
2. **Add Fe3+ to the test tubes.** Label a 50 mL beaker “0.002 *M* Fe3+”. Place about 40 mL of **0.002 *M* Fe(NO3)3**(aq) into that beaker. Using a pipet, transfer 5.00 mL of the 0.002 *M* Fe(NO3)3 solution into each tube. Note: this is the dilute iron solution; if the concentrated solution is used the experiment will fail. In Data Sheet II, record the concentration of Fe(NO3)3 written on the carboys, and also the volume of Fe(NO3)3 added to each tube.
3. **Add SCN– to the test tubes.** Pipet 1.00, 2.00, 3.00, 4.00, and 5.00 mL of the 0.002 *M* NaSCN solution into tubes “E1” through “E5”, respectively. In Data Sheet II, record the concentration of SCN– written on the carboys, and also the volume of SCN–added to each tube.
4. **Use HNO3 to make total volume of containers 10 mL.**To make the total volume of each tube be 10.00 mL, 0.10 *M* HNO3 is added. Do this by pipetting 4.00, 3.00, 2.00, 1.00, and 0 mL of 0.10 *M* HNO3 solution into tubes “E1” through “E5”, respectively. Cover the tubes with Parafilm and invert them several times to mix. Check that these equilibrium solutions are lighter orange than the calibration solutions were. (If they are darker, then the wrong iron solution was used.)
5. **Measure container concentrations with spectrometer.** Place sample “E1” in the spectrometer and, in the “Analyze” menu select “Interpolation Calculator”. A helper box will appear, displaying the absorbance and concentration of FeNCS2+ of the unknown. This is the equilibrium concentration of FeNCS2+ in this sample. Record that concentration in the ICE table for this sample in Data Sheet II. Click “OK”. Repeat for the other samples. Print this graph, and turn it in with the two data sheets (the previous graph does not need to be turned in).
6. **Calculate** the initial Fe3+ and initial SCN– concentrations using the dilution equation, as before. Record these in the ICE tables.
7. Calculate the change in FeNCS2+ by subtracting its initial concentration (zero) from its equilibrium concentration; enter this in the “Change” row of the ICE table; give the number a plus sign.
8. Enter the change in Fe3+ concentration in the ICE table. Since the FeSCN2+ concentration increased, the Fe3+ concentration must have decreased by the same amount, since there is just one “Fe” in FeSCN2+. So, this value is the negative of the change of FeSCN2+.
9. Likewise, enter the change in concentration of SCN–.
10. Calculate the equilibrium Fe3+ concentration by adding the initial concentration to the change in concentration. Record this in the ICE table.
11. Likewise, calculate the equilibrium SCN– concentration.
12. Write the equilibrium expression for equation Fe3+(aq)+SCN−(aq) ⇌ FeNCS2+(aq) Eq (3) in the Data Sheet II (just before the ICE tables).
13. Calculate the value of the equilibrium constant expression, *K*c, using your equilibrium concentrations.
14. Calculate the average value of *K*c.
15. Discard all solutions into the “Discarded Equilibrium Mixtures” container.
16. If this is the last lab section of the day, disconnect the spectrometer from the computer (after closing the “Logger Pro” software).