

Laboratory 7: Chemical Equilibrium¹

Reading: Olmstead and Williams, *Chemistry*, Chapter 14 (all sections)

Purpose: The shift in equilibrium position of a chemical reaction with applied stress and the equilibrium constant for the reaction are determined.

Introduction

Chemical Equilibrium

No chemical reaction goes to completion. When a reaction stops, some amount of reactants remain. For example, although we write



as though it goes entirely to products, at 2000K only 2% of the CO_2 decomposes. A chemical reaction reaches *equilibrium* when the concentrations of the reactants and products no longer change over time. The position of the equilibrium describes the relative amounts of reactants and products that remain at the end of a chemical reaction. The position of the equilibrium for reaction (1) is said to lie with the reactants, or to the left, because at equilibrium very little of the carbon dioxide has reacted. On the other hand, in the reaction



the equilibrium position lies very far to the right since only very small amounts of H_2 and O_2 remain after the reaction reaches equilibrium. Since chemists often wish to maximize the yield from a reaction, it is vital to determine how to control the position of the equilibrium.

The equilibrium position of a reaction may shift if an external stress is applied. The stress may be in the form of a change in temperature, pressure, or the concentration of one of the reactants or products. For example, consider a flask with an equilibrium mixture of CO_2 , CO , and O_2 , as in reaction (1). If a small amount of CO is then injected into the flask, the concentration of CO_2 increases. Here the external stress is the increase in concentration of CO . The system responds by reacting some of the added CO with O_2 to yield an increased amount of CO_2 . That is, the position of equilibrium shifts to the left, yielding more reactant and less CO .

Reaction (1) also shifts with changes in pressure. Starting with reaction (1) at equilibrium, an increase in pressure causes the position of equilibrium to shift to the side of the reaction with the smaller number of moles of gas. That is, by shifting the equilibrium position to the left, the reaction decreases the number of moles of gas, thereby decreasing the pressure in the flask. In so doing, some of the applied stress is relieved. On the other hand, an increase in pressure for reaction (2) shifts the equilibrium position to the right to decrease the number of moles of gas.

The response of a reaction at equilibrium to changes in conditions is summarized by

LeChâtelier's Principle:

A system perturbed from equilibrium shifts its equilibrium position to relieve the applied stress.

For an increase in temperature, the reaction shifts in the endothermic direction to relieve the stress. The decomposition of CO_2 , reaction 1, is endothermic in the forward direction. Upon an increase in temperature, the equilibrium position shifts in the forward direction to minimize the temperature increase. The formation of ammonia is exothermic:



Upon an increase in temperature, the equilibrium position shifts to the left, the endothermic direction.

The Iron-Thiocyanate Equilibrium

When potassium thiocyanate, KNCS, is mixed with iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$, in solution, an equilibrium mixture of Fe^{3+} , NCS^- , and the complex ion FeNCS^{2+} is formed:



The solution also contains the ions K^+ and NO_3^- , but these are merely spectator ions and do not participate in this reaction. The relative amounts of the various ions participating in the reaction can be judged from the color of the solution since in neutral or slightly acidic solutions, Fe^{3+} is light yellow, NCS^- is colorless, and FeNCS^{2+} is blood red. If the solution is initially reddish, and the equilibrium shifts to the right (more FeNCS^{2+}), the solution becomes darker red, while if the equilibrium shifts to the left (less FeNCS^{2+}), the solution becomes lighter red or perhaps straw-yellow.

Quantitatively, the relative amounts of the two reactants and the product are related by the equilibrium constant of the reaction; in this case, the formation constant K_f :

$$K_f = \frac{[\text{FeNCS}^{2+}]_{\text{eq}}}{[\text{Fe}^{3+}]_{\text{eq}} [\text{NCS}^-]_{\text{eq}}} \quad (5)$$

To completely characterize this reaction, it is necessary to know the value for K_f . K_f can be calculated through an experimental determination of the equilibrium concentration of the complex, $[\text{FeNCS}^{2+}]_{\text{eq}}$, in equilibrium with $[\text{Fe}^{3+}]_{\text{eq}}$ and $[\text{NCS}^-]_{\text{eq}}$. You will use a *standard curve* to determine the $[\text{FeNCS}^{2+}]_{\text{eq}}$. The equilibrium concentrations of the other two ions is determined using the 1:1 stoichiometry of the reaction:

$$[\text{Fe}^{3+}] = [\text{Fe}^{3+}]_o - [\text{FeNCS}^{2+}]_{\text{eq}} \quad (6)$$

$$[\text{NCS}^-] = [\text{NCS}^-]_o - [\text{FeNCS}^{2+}]_{\text{eq}} \quad (7)$$

Where $[\text{Fe}^{3+}]_o$ and $[\text{NCS}^-]_o$ are the initial, analytical, concentrations.

Use of the Standard Curve

Use of a standard curve is a common experimental strategy in chemistry to determine the concentration of an unknown solution. In this technique, a series of solutions with known concentrations is prepared and then a parameter such as absorbance is measured. This parameter is then plotted versus concentration to yield the standard curve, which is often a straight line, with some degree of scatter caused by experimental error. Regression analysis of the data using the method of least squares allows determination of the best fit line. Curve fitting is easily accomplished with Excel, which not only provides the equation of the best-fit line but also provides information as to the quality of the straight line with a regression coefficient, R^2 . The R^2 value ranges from 0 to 1.0, with 1.0 indicating a perfect fit. Subsequent measurement of the absorbance in an unknown sample allows determination of the unknown concentration through the equation of the standard curve.

The standard curve that you will generate is based on the red color of the FeNCS^{2+} ion. You will make up a series of solutions containing known amounts of this chromophore (a substance

that absorbs light) and use Beer's Law to relate the resulting experimentally determined values of absorbance to the known concentrations. Beer's law has many forms, the most common of which is $A = \epsilon lc$, where A is the absorbance, ϵ is the molar absorption coefficient in $\text{mol}^{-1}\text{L cm}^{-1}$, l is the path length of the cuvette in cm, and c is the concentration in mol L^{-1} . The slope of the plot of absorbance vs. concentration is the molar absorption coefficient.

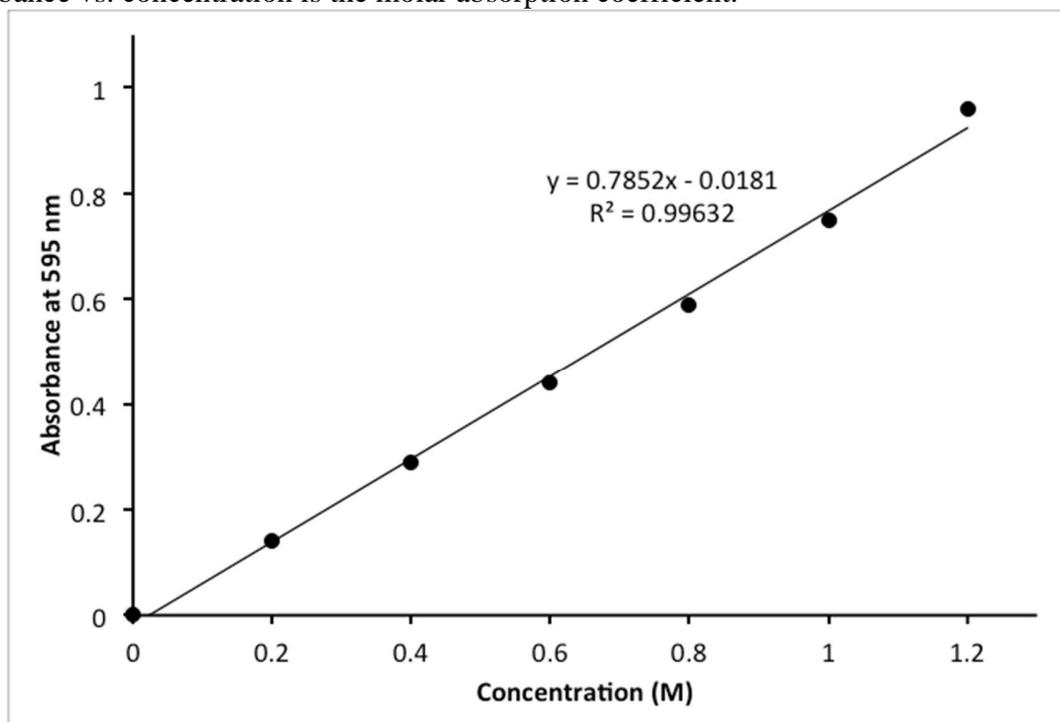


Figure 1: A typical standard curve based on Beer's Law. Beer's Law is considered to be most reliable for absorbance values between 0.1 and 1. Unknown concentrations of a given molecule can be determined using the equation of the linear trend line.

To determine the standard curve the concentration of FeNCS^{2+} in a series of solutions must be accurately known. The concentration of FeNCS^{2+} in a solution can be calculated using the formation constant, K_f . However, the formation constant is not known. Rather, the purpose of this experiment is to calculate the formation constant, which leaves us in a bit of a quandary. How can we create a series of solutions of known FeNCS^{2+} concentrations without knowing the equilibrium constant? We can use our knowledge of LeChatelier's principle to determine how to force the equilibrium position essentially to completion, so that the stoichiometry of the reaction alone can be used to find the concentrations of FeNCS^{2+} . Consider the equilibrium, reaction 4:



What stress can we apply to force the equilibrium very far to the right, while maintaining either Fe^{3+} or NCS^{-} as the limiting reagent? For example, assume NCS^{-} is the limiting reagent with initial concentration $[\text{NCS}^{-}]_0$. If the equilibrium lies very far to the right, then $[\text{FeNCS}^{2+}]_{\text{eq}} = [\text{NCS}^{-}]_0$, because of the 1:1 stoichiometry.

Experimental Procedure

Part I:

For each of the external stresses described below, necessary information is provided regarding the manner in which one or more of the chemical species is affected. You will use a spot plate containing multiple wells and use a different well for each of the operations described, recording your observations of the color change of the solution.

In a table, summarize your observations for each of the reactions that you perform on the iron-thiocyanate equilibrium. As an example, if you added a drop of concentrated HCl to the standard solution, the blood-red color lightens or perhaps disappears altogether. This change in color indicates that the FeNCS^{2+} concentration decreases. To explain this result, it is necessary to know that in the presence of a large excess of Cl^- , Fe^{3+} forms complex ions:

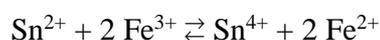


The increase in Cl^- reduces the Fe^{3+} concentration, so in accord with Le Chatelier's Principle, some FeNCS^{2+} dissociates to replace some of the Fe^{3+} removed by reaction with Cl^- . This result is summarized in the table as follows:

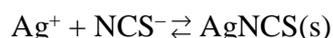
Stress	Observation	Reactions of Interest	Explanation
+1 drop HCl	sol'n turned yellow	$\text{Fe}^{3+} + 6 \text{Cl}^- \rightleftharpoons \text{FeCl}_6^{3-}$ $\text{Fe}^{3+} + \text{NCS}^- \rightleftharpoons \text{FeNCS}^{2+}$	Equilibrium shifted left in response to a decrease in $[\text{Fe}^{3+}]$ caused by reaction with Cl^- .

A. Operations to Introduce an External Stress- Record your observations in your data table.

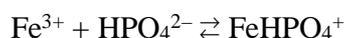
1. Add one drop each of 1 M $\text{Fe}(\text{NO}_3)_3$ and 1 M KNCS to 25 mL of distilled water. Mix well.
2. Add a few drops of this solution to each of seven wells of a spot plate. One well will serve as a color standard against which to judge color changes in the other wells. The other six wells are for performing your operations to introduce an external stress.
3. Add one drop of 1 M $\text{Fe}(\text{NO}_3)_3$ to one of the wells, mix, and observe.
4. Add one drop of 1 M KNCS to a second well, mix, and observe.
5. Add one drop of 0.1M SnCl_2 to a third well, mix, and observe. Tin(II) ions reduce iron(III) ions to iron(II) ions:



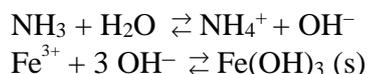
6. Add one drop of 0.1 M AgNO_3 to a fourth well, mix, and observe. Silver ions react with thiocyanate ions to give a white precipitate of silver thiocyanate:



7. Add one drop of 0.1 M Na_2HPO_4 to a fifth well, mix, and observe. Hydrogen phosphate ions form a complex ion with iron(III) ions:



8. Add one drop of 1 M NH_3 to a sixth well, mix, and observe. Any base will form a precipitate or a colloidal suspension of iron(III) hydroxide when mixed with iron(III) ions:



B. Effect of Temperature on the Equilibrium- Also record your observations in the data table.

1. Pour about 4-5 mL of the iron-thiocyanate solution made above into two test tubes. Set one tube aside as a color standard against which to judge color changes in the other tube.
2. Gently warm the other tube in a hot water bath on a hot plate. Do not boil the solution. Observe.
3. After you have determined which way the reaction shifts, cool the tube in a beaker of ice water. Do these results indicate that the forward reaction is exothermic or endothermic? Is the reaction reversible?

Part II:

You will be measuring the absorbance of the thiocyanate equilibrium with a spectrophotometer. For this type of quantitative analysis, you need to be as exact as possible about the volumes that you measure. You will use 10.00 mL volumetric flasks to make up your solutions; with a volumetric flask you bring the total volume up to the white line to achieve a very accurate final volume. You will use automatic micropipettors to deliver the reagents into the volumetric flask. Leave the micropipettors set to 500 μL for this experiment and just make multiple additions to reach 1 mL, 1.5 mL, etc. **If you have any questions about the micropipettors, please ask your instructor or student assistant before use.** Micropipettors can be severely damaged if they are incorrectly used.

A. Determination of the Wavelength of Maximum Absorbance of the FeNCS^{2+} Ion

You will establish a standard curve to calibrate the absorbance-concentration dependence of the FeNCS^{2+} complex ion, but first you will need to determine the wavelength of maximum absorbance of the chromophore using the SpectroVis Plus diode-array spectrophotometers. Refer to the SpectroVis Plus instructions hand-outs found on the lab webpage for detailed instructions on the use of these instruments.

1. Using a 10-mL volumetric flask, prepare 10.00 mL of an iron-thiocyanate solution containing 1.00 mL of 0.200 M $\text{Fe}(\text{NO}_3)_3$ and 2.00 mL of 0.00200 M KNCS. Use the micropipettes to measure these volumes. Then carefully add enough deionized H_2O to bring the final volume to the calibration line on the flask. Fill a cuvette three-quarters full with this solution. Be sure to wipe the cuvette with a Kimwipe to remove fingerprints.
2. Calibrate the spectrophotometer using 0.200 M $\text{Fe}(\text{NO}_3)_3$ alone as your reference solution in its own cuvette.
3. Replace the reference cuvette with the cuvette containing the iron-thiocyanate solution. Determine the wavelength of maximum absorbance, λ_{max} , and use this wavelength in subsequent absorbance measurements. If the peak has an absorbance that is greater than about 2, the peak may be somewhat flattened or “off-scale.” In this case, it is difficult to

determine λ_{max} exactly. You should therefore dilute the solution with water until the absorbance reading is on scale. Record the absorbance reading; you can use this value as one of the data points for your standard curve.

B. Generation of the Standard Curve

For a good standard curve, the absorbance readings should be in the range of about 0.1 to 1.7 (an absorbance of 2 corresponds to 99% of the light being absorbed, which is at the upper limit of what can be measured accurately). You will select an appropriate range of FeNCS^{2+} concentrations based on your observations from the previous section. You will use a large excess of Fe^{3+} ion, which will drive the reaction to completion, with NCS^- as the limiting reagent. (Note that the $\text{Fe}(\text{NO}_3)_3$ solution is made up to include HNO_3 at a final concentration of 0.0100 M to prevent the formation of other iron complexes that may exist in the presence of base, but you do not have to account for this addition in any of your calculations.)

1. Prepare *five more* solutions in 10-mL volumetric flasks containing varying concentrations of FeNCS^{2+} in a total final volume of 10.00 mL. Each solution should contain 1.00 mL of 0.200 M $\text{Fe}(\text{NO}_3)_3$ and known, varying amounts of 0.00200 M KNCS. Add water to bring the final volume to 10.00 mL in each case. We recommend that in all cases your final concentration of KNCS is no higher than 0.8×10^{-3} M, or the sample is likely to have an absorbance reading greater than 1.7. (*You should calculate the volume of added 0.00200 M KNCS that gives a final concentration of 0.8×10^{-3} M in your laboratory notebook.*)
2. Take the absorbance at the wavelength determined in **Part A** for each of the solutions. If the absorbance readings are not within appropriate limits, make up more solutions until you have at least six concentrations that are within the 0.01 – 1.2 absorbance range.
3. Construct a standard curve as described in the **Data Analysis** section.

C. Determination of the K_f

You will now make up solutions containing constant amounts of Fe^{3+} and varying amounts of NCS^- and use the standard curve to determine the equilibrium FeNCS^{2+} concentrations based on the measured absorbance. The equilibrium concentrations are used to calculate K_f .

1. Mix five combinations of Fe^{3+} and NCS^- each in a total final volume of 10.00 mL. For each, use 5.00 mL of **0.00200 M** $\text{Fe}(\text{NO}_3)_3$ [this is a different solution than the one used above!], and known, varying amounts of the 0.00200 M KNCS, making up the total volume with water.
2. Determine the absorbance of the FeNCS^{2+} complex ion for each solution after recalibrating appropriately (Caution: what should your reagent blank be this time? Think carefully!). Use the standard curve generated in **Part B** to convert the absorbance values into concentrations, $[\text{FeNCS}^{2+}]_{\text{eq}}$. Remember that your absorbance values should fall between the minimum and maximum absorbance values on the standard curve for best accuracy. (If some of your trials are off the standard curve, make up new solutions until you have at least five good trials.)

Data Analysis

1. In Excel, construct a standard curve of absorbance versus $[\text{FeNCS}^{2+}]$ (mol/L) for your standard solutions of **Part B**. Remember that in Excel the first data column corresponds to X and

the second corresponds to Y; thus, your first column should be concentration, not absorbance. Note that [0, 0] should be included as a data point. Determine the equation of the best-fit line and the R^2 value. Use the linest function to determine the standard deviation of the slope and intercept. An example of the output of the linest function is shown below:

slope	12443.7	42.483	intercept
\pm	123.38	0.389	\pm
R^2	0.9997	0.0387	st.dev.y
F	10171.6	3.00	df
SS _{reg}	15.2657	0.0045	SS _{resid}

In this example, the slope is $12443. \pm 123$ and the intercept is 42.48 ± 0.39 . In this example, the slope is known to 3 significant figures and the intercept is known to 2 significant figures. Make sure that you include a copy of your standard curve both in your report and your notebook.

- From the standard curve, calculate the $[\text{FeNCS}^{2+}]_{\text{eq}}$ for each of your trials of **Part C**.
- Use the stoichiometry of the FeNCS^{2+} complex ion formation to determine how much of each reactant was consumed and what the corresponding equilibrium concentrations of Fe^{3+} and NCS^- for your five trials of **Part C**.
- Use the equilibrium values, $[\text{Fe}^{3+}]_{\text{eq}}$, $[\text{NCS}^-]_{\text{eq}}$, and $[\text{FeNCS}^{2+}]_{\text{eq}}$ to calculate K_f using equation (5) above for each of your solutions. Calculate an average K_f , and the standard deviation for your trials of **Part C**. You may wish to refer to the Error Analysis hand out and the Error Analysis Example On the lab Web page for information on standard deviation, and random and systematic error.

LABORATORY REPORT: Use the Report form for this experiment.

Use complete sentences, the proper number of significant figures, and include units. Equations, reactions, tables, and diagrams can be written by hand. The sections of your report are:

Introduction (2-sentence maximum): State the scientific purpose of the experiment. Describe the method you will use, in a general sense. Do not discuss the experimental procedure details or data analysis steps. Don't include pedagogical goals (e.g to teach us how to use.....).

Procedure: Give a one sentence description of the general procedure used to study the effect of applied stresses to the position of equilibrium. Give a one sentence description of the method that you used to determine the shift in equilibrium position. Give a one to two sentence description of the general procedure used to determine the equilibrium constant. Reference the lab write-up on the CH145 On-line Laboratory Manual and list any changes. Give the cell material and path length and the manufacturer and model of the spectrophotometer.

Results: The experimental stresses listed below are from Part I. Use your table from part I to discuss the observed impact on the position of equilibrium and include a description of the underlying principle that explains the shift of the iron-thiocyanate reaction in terms of a response to the particular stress. For each case did the addition increase or decrease the amount of Fe^{3+} or NCS^- ? Make sure to give the reactions that changed the Fe^{3+} concentration for the addition of SnCl_2 , AgNO_3 , Na_2HPO_4 , and NH_3 . Determine if the complex formation reaction is endothermic or exothermic, as written.

Addition of extra $\text{Fe}(\text{NO}_3)_3$
 Addition of extra KNCS
 Addition of SnCl_2
 Addition of AgNO_3
 Addition of Na_2HPO_4
 Addition of NH_3
 Increase and decrease in temperature

For Part II, give the temperature of the equilibrium constant determination. Give the concentration of NCS^- that you used for the standard curve. Give your results in tabular form for the concentrations and absorbances used to construct the standard curve. Report the slope and intercept of the curve fit, including the uncertainty of the slope and intercept. Determine the number of significant figures in the slope and intercept. Report the molar absorption coefficient. Attach the standard curve plot. Make sure the axes are labeled. Give the initial concentration, absorbance, equilibrium concentrations and corresponding formation constant for each equilibrium constant determination:

Table 2: *add a caption.*

$[\text{NCS}^-]_0$ (M)	Absorbance	$[\text{FeNCS}^{2+}]_{\text{eq}}$ (M)	$[\text{Fe}^{3+}]_{\text{eq}}$ (M)	$[\text{NCS}^-]_{\text{eq}}$ (M)	K_f
------------------------	------------	---------------------------------------	------------------------------------	----------------------------------	-------

Report the average and standard deviation of the formation constants. Mention any student errors that may have caused problems in the determinations. All tables and plots should have a table or figure number and a caption. Refer to this Table or Figure with an explicit reference (e.g. see Figure 3) in the text of this section.

Discussion:

- (a). Purpose accomplished: Restate the purpose of the experiment, but as completed goal.
- (b). Write the reaction that you are studying.
- (c). Give a general summary statement about the observed shifts of the position of equilibrium and the predictions based on LeChatelier's principle.
- (d). For the determination of the standard curve, discuss how the position of equilibrium was shifted to allow the concentration of the FeNCS^{2+} ion to be calculated from the reaction stoichiometry.
- (e). Give the average and standard deviation for the formation equilibrium constant. Call this standard deviation the observed standard deviation.
- (f). Consider the effect of random and systematic errors.
 - (i). Use the number of significant figures in the molar absorption coefficient to predict the expected number of significant figures in the formation constant. Compare this expected number of significant figures to the observed standard deviation. There are two possibilities for this comparison (choose one):

- (1). If the expected number of significant figures, as predicted from the uncertainty in the molar absorption coefficient, is consistent with the observed standard deviation then draw a conclusion about the predominant source of random error.
 - (2). If the expected number of significant figures is not consistent with the observed standard deviation, give a likely additional source of random error.
- (ii). Suggest a source of systematic error. Remember that student mistakes are neither random nor systematic errors; student mistakes are just student mistakes. What effect does the source of systematic error have on the final results? (For example, does the systematic error cause curvature in the standard curve or increase or decrease the value determined for the formation constant?)
- (g). To summarize the experiment answer the following questions:
- (i). Note that the initial conditions for the different equilibrium measurements vary significantly in your report Table 2. Observe the values for the individual formation constants. Use the data in Table 2 to explain, in words in a general sense, the relationship between the initial conditions and the formation constant. In other words, what is the meaning of an equilibrium constant?
 - (ii). How can we control the outcome of chemical reactions at equilibrium?

Literature Cited: Give all literature cited, numbered according to the references in the body of your report.

Attach the standard curve. Attach your data tables if they are not included in the bulk of the Report.

Literature Cited:

1. This experiment was modified from *Laboratory Inquiry in Chemistry* by Bauer, Birk, and Sawyer.