

Experiment 2: Chemical Equilibrium¹

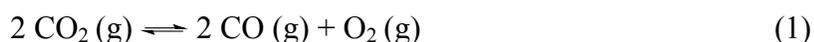
Reading: *Chemistry the Central Science*, Chapter 15 (all sections)

Purpose: The shift in equilibrium position of a chemical reaction with applied stress is determined.

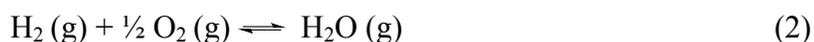
Introduction:

Chemical Equilibrium

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



as though it goes entirely to products, at 2000K only 2% of the CO₂ decomposes. A chemical reaction reaches *equilibrium* when the concentrations of the reactants and products no longer change with time. The position of equilibrium describes the relative amounts of reactants and products that remain at the end of a chemical reaction. The position of 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 H₂ and O₂ remain after the reaction reaches equilibrium. Since chemists often wish to maximize the yield of 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 CO₂, CO, and O₂, as in reaction (1). If a small amount of CO is then injected into the flask, the concentration of CO₂ increases. Here the external stress is the increase in concentration of CO. The system responds by reacting some of the added CO with O₂ to yield an increased amount of CO₂. 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.

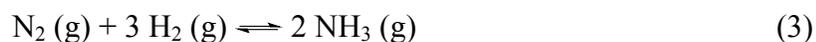
The response of a reaction at equilibrium to changes in conditions is summarized by

LeChâtelier's Principle:

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

¹ This experiment was modified from J. P. Birk, R. Bauer, and D. Sawyer, *Laboratory Inquiry in Chemistry*, Brooks/Cole, 2001.

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, which is 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 K^+ and NO_3^- ions, but these are spectator ions and do not participate in the reaction. The relative amounts of the various ions participating in the reaction can be judged from the color of the solution. In neutral or slightly acidic solutions, Fe^{+3} is light yellow, NCS^- is colorless, and FeNCS^{2+} is 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.

Use of the Standard Curve (for week 2)

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 the absorbance of each standard solution is measured. The absorbance is then plotted versus concentration to yield the standard curve, which is often a straight line with some 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 ([Beer's Law primer](#)) to relate the resulting experimentally determined values of absorbance to the known concentrations.

Absorbance of Iron Thiocyanate Chromophore versus Concentration

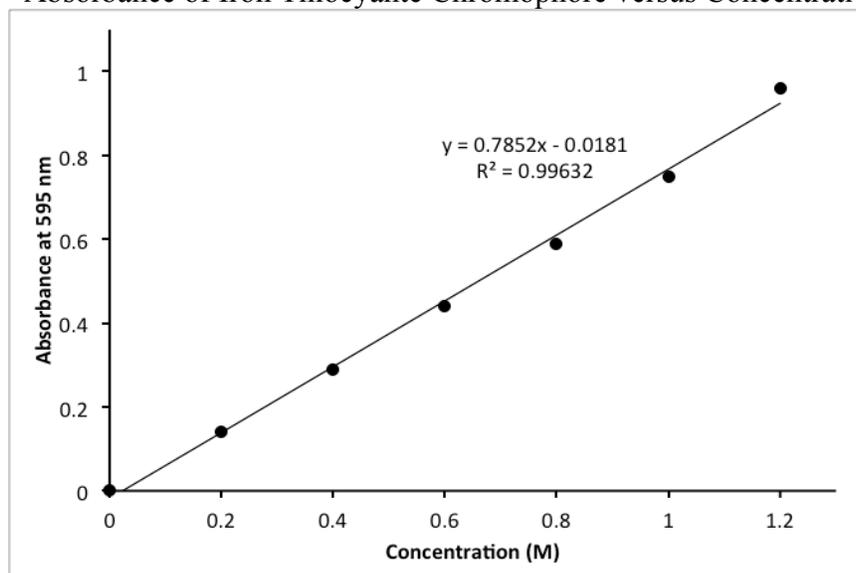


Figure 1: A typical standard curve based on Beer's Law. Beer's Law is considered to be most reliable for absorbance values between 0.1 and 1. Unknown concentrations of a given molecule can be determined using the equation of the linear trend line. Use the (0,0) point in the curve fit.

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 5:



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.

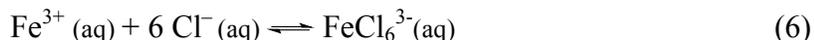
Experimental Procedure

Procedure for Week 1:

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:

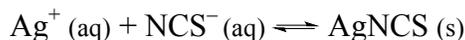
Stress	Observation	Reactions of Interest	Explanation
+1 drop HCl	sol'n turned yellow	$\text{Fe}^{3+} + 6 \text{Cl}^- \rightleftharpoons \text{FeCl}_6^{3-}$ <i>and what other reaction?</i> <i>(see Week 1 prelab)</i>	Equilibrium shifted left in response to a decrease in $[\text{Fe}^{3+}]$ caused by reaction with Cl^- .

A. Operations to Introduce an External Stress- Record your observations in your data table in the format shown above.

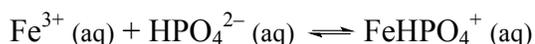
1. Add two drops each of 1 M $\text{Fe}(\text{NO}_3)_3$ and 1 M KNCS to 20 mL of distilled water. Mix well.
2. Add a few drops of this solution to each of seven wells of a spot plate. One well serves as a color standard against which to judge color changes in the other wells. The other six wells are for performing your operations to introduce an external stress.
3. Add two drops of 1 M $\text{Fe}(\text{NO}_3)_3$ to one of the wells, mix, and observe.
4. Add two drops of 1 M KNCS to a second well, mix, and observe.
5. Add two drops of 0.1M SnCl_2 to a third well, mix, and observe. Tin (II) ions reduce iron (III) ions to colorless iron(II) ions:



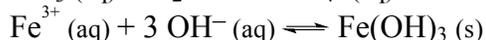
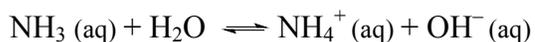
6. Add two drops of 0.1 M AgNO_3 to a fourth well, mix, and observe. Silver ions react with thiocyanate ions to give a white precipitate of silver thiocyanate:



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



8. Add two drops 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- Record your observations in the same data table as **Part A**.

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

Make sure you have all the relevant data documented before you leave lab – check with your lab instructor!

Procedure for Week 2:

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 etched/white line to achieve a very accurate final volume. Use automatic micropipettors to deliver the reagents (other than water) into the volumetric flask.

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. The SpectroVis Plus instructions will be available in the laboratory.

1. Calibrate the spectrophotometer using 0.200 M $\text{Fe}(\text{NO}_3)_3$ alone as the reference solution in its own cuvette. For each subsequent determination, the spectrum of the reference solution is subtracted from the sample spectrum. Through this calibration process, the reference spectrum accounts for any background absorption that is not related to the chromophore that is being determined.
2. 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 4.00 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 and solution droplets.
3. Measure this iron-thiocyanate solution to 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 1.5, 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 the 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 1.5. 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.
2. Take the absorbance at the wavelength determined in **Part A** of 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 0.1 – 1.5 absorbance range.
3. Construct a standard curve as described in the **Data Analysis** section.

C. Determination of the K_f

You will now make 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 new combinations of Fe^{3+} and NCS^- each in a total final volume of 10.00 mL. For each trial, use 5.00 mL of **0.00200 M** $\text{Fe}(\text{NO}_3)_3$ with varied amounts of 0.00200 M KNCS, making up the total volume with water. Record the laboratory temperature; equilibrium constants are temperature dependent.
2. Recalibrate the spectrophotometer. What should the reference solution be now? Determine the absorbance of the five new FeNCS^{2+} complex ion solutions. Use the standard curve generated in **Part B** to convert the just measured absorbance values into concentrations, $[\text{FeNCS}^{2+}]_{\text{eq}}$. Remember that measured 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 new solutions until you have five trials with each being within the standard curve limits.

Data Analysis

1. In Excel, construct a standard curve of absorbance versus $[\text{FeNCS}^{2+}]$ (mol/L) for the standard solutions from **Part B**. Remember for plots in Excel the first data column corresponds to X and the second corresponds to Y; thus, the 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. Determine LINEST for the slope and intercept (**Error Analysis Handout**). Make sure to save a copy of this standard curve and Excel tables for your report.
2. From the standard curve, calculate the $[\text{FeNCS}^{2+}]_{\text{eq}}$ for each of your trials of **Part C**.

3. Use the stoichiometry of the FeNCS^{2+} complex ion formation to determine how much of each reactant was consumed and what were the corresponding equilibrium concentrations of Fe^{+3} and NCS^- for the five trials of **Part C**.
4. 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 2 for each of your solutions. For the five trials calculate an AVG, STDEV, SDOM, %error, and %precision of K_f . Use SDOM to determine the number of significant figures in the final equilibrium constant.

Make sure you have all the relevant data documented before you leave lab – check with your lab instructor!

Laboratory Report: Use the provided Report Form for this experiment.