

Protocol | Measurement of K

Measurement of an Equilibrium Constant

Watch the [conceptual introduction video Links to an external site.](#) and [lab tips video Links to an external site.](#) for this experiment.

Introduction

When we mix substances in solution or in the gas phase, chemical reactions occur until the system reaches a state in which the concentrations of reactants and products appear to remain constant over time. This state of unchanging concentrations is called *chemical equilibrium*. Intuitively, chemical equilibrium represents the state that nature “wants” the system to have, in the absence of other constraints or forces on the molecules in the system. Chemical systems evolve spontaneously from non-equilibrium states toward equilibrium states. Once a system is in chemical equilibrium, chemical reactions are still occurring at the microscopic level but the *rates* of forward and reverse reactions are equal. The result is no observable macroscopic change in concentrations.

The ratio of the amounts of reactants and products in an equilibrium state is referred to as the *position of equilibrium*. Importantly, the position of equilibrium is usually *not* an equal mixture of reactants and products. More often one side or the other dominates at equilibrium, and in fact this has been the norm in reactions we have worked with in previous units. Up to this point, we have called the dominating side the “products” and the side that is consumed spontaneously the “reactants.” A core assumption of simple stoichiometry is that the reactants react as much as they can to form products based on the law of conservation of mass. Stated another way, the assumption is that the position of equilibrium is entirely on the product side. This need not be true in general. Some reactions tend to reach an equilibrium state in which significant amounts of both products and reactants are present at equilibrium.

We can quantify the tendency of a chemical reaction to proceed toward products (i.e., to reach an equilibrium state in which the products dominate) or not. For a particular reaction, the quantity that captures this information is called the *equilibrium constant (K)*. The value of the equilibrium constant is completely independent of the concentrations of reactants and products within a particular chemical system; it depends only on the identities of the reactants and products and the temperature and pressure of the system. In other words, *K* is an intrinsic property of a chemical reaction performed at a particular temperature and pressure. For a general reaction $a A + b B \rightleftharpoons c C + d D$, the equilibrium constant is defined as a specific ratio of product and reactant concentrations *at equilibrium*.

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ system at equilibrium}$$

For a general system that is not necessarily at chemical equilibrium, the right-hand side of the equation is called the reaction quotient (Q). The reaction quotient can be written for *any* system given the concentrations of its components.

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ any system}$$

For a chemical system at constant temperature and pressure, K is simply a number. The ratio on the right-hand side of these equations (the *equilibrium expression*) is equal to K for *all* chemical systems containing A, B, C, and D at equilibrium. This means that any system containing A, B, C, and D starting at any value of Q will undergo reaction spontaneously until Q is equal to K . Note that net reverse reaction may be required to achieve this if an excess of product is present initially!

A simple way to measure the value of K for a reaction involves preparing a system containing the reactants and/or products, allowing the system to evolve until macroscopic change stops, and measuring the concentrations of the reactants and products in the resulting equilibrium state. Theoretically, no matter the initial concentrations of reactants and products, the value of Q should converge to K (a number) at equilibrium. We will test this hypothesis in this experiment.

To determine K , we need a method for measuring concentrations at equilibrium. We will measure concentrations indirectly using absorbance spectroscopy along with stoichiometry and the ICE table method. The absorbance of a colored species in solution is proportional to its concentration (molarity) according to the Beer-Lambert law. Most generally $A = mC + b$, where A is the absorbance of the colored species, m is a constant that relates absorbance and concentration, and b is an error term that reflects any residual measured absorbance when $C = 0$. Absorbance A is defined as the base-10 logarithm of the ratio of the intensity of the input light beam (I_0) to the intensity of the light beam after passing through the sample (I). Absorbance is a unitless quantity.

$$A = \log_{10} \left(\frac{I_0}{I} \right)$$

Absorbance depends on the wavelength of light impinging on the sample; the wavelength at which absorbance is at a maximum (and measurement is thus most sensitive) is called λ_{max} . The constant m is the product of the path length l of the sample through which the light beam passes (1 centimeter in all of our experiments) and the *extinction coefficient* ϵ for the colored species. The extinction coefficient has units of inverse concentration times inverse length, most typically $M^{-1} \cdot \text{cm}^{-1}$. Like absorbance

itself, the extinction coefficient depends on the wavelength of light used and is largest at λ_{max} .

The reaction we will study in this experiment involves complexation of the thiocyanate anion (SCN^-) to the iron(III) cation (Fe^{3+}) in aqueous solution. Mixing aqueous solutions of the two colorless reactant ions results in the spontaneous formation of a product that appears orange in aqueous solution, iron(III) thiocyanate. In general the reaction is reversible, meaning that significant amounts of reactants and product are present at equilibrium.



Aqueous nitric acid will be added to each reaction mixture to dilute the reactant solutions and ensure that iron does not precipitate and remains in the +3 oxidation state. You can think of the nitric acid as a solvent for the reaction.

In the first part of the experiment, we will measure the precise numerical form of the Beer-Lambert law for $\text{Fe}(\text{SCN})^{2+}$, the product of the reaction of interest. Doing this will enable us to calculate the molarity of $\text{Fe}(\text{SCN})^{2+}$ in any solution from a measurement of the absorbance of the solution at λ_{max} . Substituting $[\text{Fe}(\text{SCN})^{2+}]$ for C in the general equation above and rearranging, for a general reaction mixture j with measured absorbance A_j ,

$$\left[\text{Fe}(\text{SCN})^{2+} \right]_j = \frac{(A_j - b)}{m}$$

The reactions in part A will be set up so that they proceed completely to products, eliminating the need for complicated equilibrium calculations in measurement of the Beer-Lambert law for $\text{Fe}(\text{SCN})^{2+}$. Even though the reaction is generally reversible, using a massive excess of one of the reactants will cause a strong shift of the position of equilibrium toward products and essentially complete consumption of the limiting reactant. Five reactions will be prepared to generate five data points for a graph of absorbance as a function of concentration. The table below lists the volumes of stock reactant solutions and nitric acid to use in these reactions. **Carefully note the concentrations in the table below! Make sure you use the correct concentrations in the lab.**

Table 1. Concentrations and Volumes of Reactant Solutions for Part A

Reaction	$\text{Fe}^{3+}(\text{aq}), 1.0 \times 10^{-4} \text{ M}$	$\text{SCN}^-(\text{aq}), 0.50 \text{ M}$	$\text{HNO}_3(\text{aq}), 0.10 \text{ M}$	Total Volume
1	1.0 mL	5.0 mL	4.0 mL	10.0 mL

2	2.0 mL	5.0 mL	3.0 mL	10.0 mL
3	3.0 mL	5.0 mL	2.0 mL	10.0 mL
4	4.0 mL	5.0 mL	1.0 mL	10.0 mL
5	5.0 mL	5.0 mL	–	10.0 mL

In the second part of the experiment, we will prepare a variety of solutions of aqueous Fe^{3+} and SCN^- , allow them to come to equilibrium, and measure the absorbance at λ_{max} of the solution. With knowledge of the initial concentrations of reactants from stoichiometry, a measurement of the equilibrium product concentration (via absorbance), and a balanced chemical equation for the reaction that occurs, we have sufficient information to complete an ICE table and use the concentrations of reactants and product at equilibrium to calculate K . Ten reactions will be prepared to generate ten measurements of K . The table below lists the volumes of stock reactant solutions and nitric acid to use in these reactions. **Carefully note the concentrations in the table below! Make sure you use the correct concentrations in the lab.**

Table 2. Concentrations and Volumes of Reactant Solutions for Part B

Reaction	$\text{Fe}^{3+}(\text{aq})$, 0.0025 M	$\text{SCN}^-(\text{aq})$, 0.0025 M	$\text{HNO}_3(\text{aq})$, 0.10 M	Total Volume
6	1.0 mL	1.0 mL	5.0 mL	7.0 mL
7	1.0 mL	1.5 mL	4.5 mL	7.0 mL
8	1.0 mL	2.0 mL	4.0 mL	7.0 mL
9	1.0 mL	2.5 mL	3.5 mL	7.0 mL
10	1.0 mL	3.0 mL	3.0 mL	7.0 mL

11	2.0 mL	1.0 mL	4.0 mL	7.0 mL
12	2.0 mL	1.5 mL	3.5 mL	7.0 mL
13	2.0 mL	2.0 mL	3.0 mL	7.0 mL
14	2.0 mL	2.5 mL	2.5 mL	7.0 mL
15	2.0 mL	3.0 mL	2.0 mL	7.0 mL

Safety and Materials

Watch the [video introduction to reagents, glassware, and instruments](#) [Links to an external site.](#) for this experiment.

The following reagents will be available:

- [0.0025 M iron\(III\) nitrate \(\$\text{Fe}\(\text{NO}_3\)_3\$ \) solution](#) [Links to an external site.](#)
- [0.50 M potassium thiocyanate \(KSCN\) solution](#) [Links to an external site.](#)
- [0.10 M nitric acid \(\$\text{HNO}_3\$ \) solution](#) [Links to an external site.](#)
- [0.0025 M potassium thiocyanate \(KSCN\) solution](#) [Links to an external site.](#)

Refer to the linked Safety Data Sheets above for important safety information on these materials.

Relevant Experimental Techniques

- [Pipetting Liquids](#)
- [Preparing Solutions: Dilution of a Stock Solution](#)
- [Visible Absorbance Spectroscopy](#)

Research Question

How is the iron(III) thiocyanate reaction equilibrium position shifted by relative increases in each reactant's concentration?

Procedures

A. Measuring the Beer-Lambert Law for Iron(III) Thiocyanate

1. *Prepare a diluted solution of iron(III).* Using appropriate glassware and good pipetting techniques, dilute the stock **0.0025 M iron(III) nitrate solution** from 4.0 mL to a total volume of 100.0 mL. Label this solution "Part A Fe³⁺"; it will be used only in this part of the experiment.
2. *Prepare a spectrophotometer or colorimeter.* Connect a SpectroVis spectrophotometer to a laptop with LoggerLite or LabQuest 2 device and blank the spectrometer using deionized water ("Calibrate"). If only a colorimeter is available, set it to measure at 470 nm.
3. Rinse out the pipets you used with deionized water, leaving a minimum of water inside the pipets after rinsing. Do not skip this step or your results in Part B will be inaccurate!
4. *Prepare aqueous mixtures of potassium thiocyanate and nitric acid.* Obtain about 50 mL of **0.50 M potassium thiocyanate solution** and 50 mL of **0.10 M nitric acid solution** in beakers labeled "Part A SCN⁻" and "nitric acid" respectively.
5. Using good pipetting techniques, transfer the appropriate volumes of potassium thiocyanate solution and nitric acid solution into medium test tubes labeled 1 – 5. See Table 1 in the Introduction.
6. *Add iron(III) and observe what happens.* Transfer appropriate volumes of your lab partner's diluted iron(III) solution ("Part A Fe³⁺") into the test tubes. Record your observations when the iron(III) solution is added.
7. *Measure absorbance spectra.* Obtain absorbance spectra for all five solutions and note both λ_{max} (if using a spectrophotometer) and the maximum absorbance value for each solution. If your measured absorbances are greater than 1.500 or less than 0.030 for any of the tubes, repeat solution preparation steps above (you either didn't dilute the stock iron(III) nitrate solution or used the 0.0025 M potassium thiocyanate solution instead of 0.50 M solution).
8. Make sure to record the maximum absorbance and λ_{max} for each reaction.
9. Rinse out the pipets you used with deionized water, leaving a minimum of water inside the pipets after rinsing. Do not skip this step or your results in Part B will be inaccurate!

Concept Check!

Assume that you've worked through part A and found that the Beer-Lambert law for Fe(SCN)²⁺ at λ_{max} is $A = (7600 \text{ M}^{-1})C$. (Do not use this equation in your report; it's purely for illustrative purposes. Use the relation you measured in part A.) Prepare an ICE table for reaction 6 in your lab notebook, discussing your approach to each cell of the table with your lab partner. Start by writing the balanced chemical equation and the Initial, Change, and Equilibrium rows. Then, work through calculations of each cell of the ICE table, showing enough detail that you can apply the same process to reactions 7 – 15 later. Working through the table in the order indicated in the figure below will be helpful; label your calculations with these numbers to organize them. Start with box 1, then proceed to box 2, 3, 4...etc. Note that at the end, each entry of the ICE table should be a *number* (really, a concentration in mol/L).

$$\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{Fe}(\text{SCN})^{2+}(\text{aq})$$

Initial	2	3	4
Change	5	6	7
Equilibrium	8	9	1

B. Measuring the Equilibrium Constant for the Reaction of Iron(III) and Thiocyanate

1. Add iron(III) to the Part B reactions and observe what happens. Obtain about 25 mL of 0.0025 M iron(III) nitrate solution in a beaker labeled "Part B Fe³⁺."
2. Label 10 medium test tubes with the numbers 6 – 15.
3. Prepare aqueous mixtures of potassium thiocyanate and nitric acid. Obtain about 50 mL of **0.0025 M potassium thiocyanate solution** in a beaker labeled "Part B SCN⁻." Obtain additional nitric acid solution in your previously labeled beaker so that you have about 75 mL to work with.
4. Using good pipetting techniques, transfer the appropriate volumes of potassium thiocyanate solution and nitric acid solution into tubes 6 – 15. See Table 2 in the Introduction.
5. Transfer the appropriate volumes of the "Part B Fe³⁺" solution into these tubes. See Table 2 in the Introduction. Look for a color change and record your observations.
6. *Measure absorbance spectra.* Once your lab partner has added iron(III) solution into the test tubes, obtain absorbance spectra for all ten solutions and note both λ_{max} (if using a spectrophotometer) and the maximum absorbance value for each solution. Measured absorbances should not be greater than 1.500 or less than 0.010; if they are, re-examine your solutions, clean your pipets, and repeat this part of the experiment.
7. Make sure to record the maximum absorbance and λ_{max} for each reaction.

Group Argumentation

Discuss and merge data with the other students at your bench. Without calculating anything, consider trends in the data to answer the research question. Using the white board provided, write an argument responding to the research question based on your findings. Support it with evidence from the experiment and reasoning from your knowledge of equilibrium concepts. Share your argument with other groups and discuss

alternative interpretations of the results. Revise the argument as a group and write it in your lab notebooks.

Post-lab Calculations and Data Workup

To perform these calculations, working in the data workup template spreadsheet will be helpful. Take full advantage of Excel formulas to save yourself time and effort. Use the [data workup spreadsheet Download data workup spreadsheet](#) to organize your data and results.

Part A. Tabulate your concentrations, volumes, and measured absorbances for reactions 1 – 5. Calculate the equilibrium concentration of $\text{Fe}(\text{SCN})^{2+}$ for reactions 1 – 5. Note that only stoichiometry and a bit of chemical logic is required to do this; no ICE tables are necessary! Prepare a graph with absorbance on the y-axis and $[\text{Fe}(\text{SCN})^{2+}]$ on the x-axis. Add a line of best fit with equation and correlation coefficient R^2 . This line of best fit is your measured Beer-Lambert law for $\text{Fe}(\text{SCN})^{2+}$.

Part B. Add your measured absorbance values to the template, which already includes the concentrations and volumes of solutions used in part B. Use Excel formulas in the reaction 6 row (including cell references to keep things general!) to calculate the initial concentrations of iron(III) and thiocyanate in reaction 6. Then, use your Beer-Lambert law to calculate the equilibrium concentration of the product, using a cell reference to refer to the measured absorbance of reaction 6. Finally, calculate the equilibrium concentrations of the reactants by referring to initial concentrations and the changes implied by what you have already determined. If this process is unclear, revisit the calculations from the Concept Check in your lab notebook. Calculate K for reaction 6 using references to cells containing the equilibrium concentrations of reactants and product in reaction 6.

If you use Excel formulas for all of these calculations and take care to use cell references for all quantities that vary across reactions, the formulas can be copied down to reactions 7 – 15 to make the remaining calculations a breeze. After determining equilibrium constants for the remaining reactions, calculate the mean and standard deviation of your K values.