

Experiment 6: Equilibrium and Le Châtelier's Principle

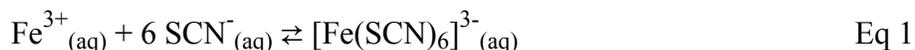
Objective: The objective of this experiment is to examine equilibrium systems and the effects of stresses placed on those systems.

Background: Not all reactions go to completion, or use up all of one of the reactants. In some chemical reactions there is always some amount of products and some reactants present. In these chemical systems two competing processes are occurring, the forward reaction and the reverse reaction of that system. Both the forward and the reverse reactions are taking place simultaneously. When the rate of the forward reaction equals the rate of the reverse reaction, the system is at **equilibrium**. The concentrations of the products and reactants remain constant. That is not to say that the system is static. Both reactions are occurring and are doing so at the same rate, so there is no net change in the concentrations of the reactants or of the products. When writing an equation for a reaction at equilibrium a double headed arrow (\leftrightarrow) or double arrows pointing in opposite directions (\rightleftharpoons) is used. These designations indicate that both the forward and reverse reactions are occurring at the same time.

Any system at equilibrium will remain at equilibrium unless the conditions of the system change. **Le Châtelier's principle** states that a system at equilibrium will respond to a stress on the system in such a way so as to relieve the stress and establish a new equilibrium. The system will have one reaction dominate until the offsetting changes allow the rates of the forward and reverse reactions to be equal again (reestablishing equilibrium). If the forward reaction dominates in order to offset the changes, we say the system "shifts to the right" or "shifts toward products" in order to reestablish equilibrium conditions. This will increase the concentration of the products and decrease the concentration of the reactants. However, if the reverse reaction dominates in order to offset the changes, we say the system "shifts to the left" or "shifts toward reactants" to reestablish equilibrium conditions. This will increase the concentrations of the reactants and decrease the concentrations of the products. The changes will not return the system to the original conditions, but to a new set of conditions that establish equilibrium.

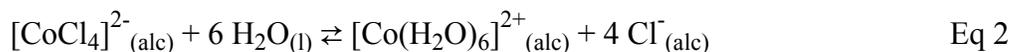
For endothermic reactions, heat can be considered a reactant, since heat is absorbed by the system from the surroundings. When heat is added to an endothermic reaction, the system will shift toward the products. For exothermic reactions, heat can be considered a product, since heat is released from the system to the surroundings. When heat is added to an exothermic reaction, the system will shift toward the reactants.

In this experiment, you will analyze two equilibrium systems. The reaction for the first system is shown below and produces one colored complex ion.



The $[\text{Fe}(\text{SCN})_6]^{3-}$ complex ion forms a blood-red solution. We can induce a shift in this equilibrium, and in so doing induce a color change in the solution, which we can monitor visually and by determining the absorbance of our system using the Spec 20.

The reaction for the second system is shown below and has two colored complex ions.



The $[\text{CoCl}_4]^{2-}$ complex ion produces a brilliant blue color while the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion produces a rose-pink color. Again by observing changes in the color and by monitoring the absorbance of the system resulting from placing a stress on the system we can monitor the equilibrium of the system. For each of the two systems you will make observations of the results from stresses placed on each system, and use the information you collect to determine whether the reaction in each system is endothermic or exothermic.

Procedure: Begin by setting up a hot water bath using a 250 mL beaker. The water does not have to reach boiling, but it should be hot. Set up an ice water bath in a 150 mL beaker by filling the beaker about 2/3 full with ice and adding about 25 mL water. *For each experiment (Part I and Part II), each group of students working together should assemble 6 clean test tubes (15 × 125 mm) and 2 clean Spec- 20 cuvettes.*

Part I: $\text{Fe}(\text{NO}_3)_3 + \text{KSCN}$ Equilibrium

- Using a 100 mL graduated cylinder, transfer 50 mL of 0.002 M KSCN into a clean 100 or 150 mL beaker. Observe any color in the solution. Using a disposable pipet, add 4 drops of 0.2 M $\text{Fe}(\text{NO}_3)_3$ to the solution in the beaker and mix well. Observe the color of the solution. This is your equilibrium solution as described by eq. 1 above.
- Prepare 6 clean, dry small to medium size test tubes. Add approximately equal amounts of the equilibrium solution prepared in step 1 above to each test tube and label them 1-6. It is important that you use all 50 mL of the equilibrium solution divided into 6 approximately equal parts so that when each is poured into a cuvette, it will cover the entire beam of light in the Spec 20. The first test tube is your control or reference test tube.
- Add two drops of 0.2 M KSCN solution, side shelf, to test tube 2 and mix well. Observe color changes.
- Add one drop of 0.2 M $\text{Fe}(\text{NO}_3)_3$ solution, side shelf, to test tube 3 and mix well. Observe color changes.
- Add a pinch of solid NaF, side shelf, to test tube 4 and mix well. Observe color changes. Fluoride reacts and coordinates with Fe^{3+} , thus removing it from participating in the equilibrium reaction.



6. Place test tube 5 in the hot water bath. Place test tube 6 in the ice water bath. After about 5 minutes observe color changes for both.

7. Next, you will use a Spec 20 to measure and record the absorbance of each solution you prepared. The Spec 20 instrument should be set to the desired wavelength (475 nm) and with the cell compartment empty the left control dial should be adjusted to read 0%T. With DI H_2O in your cuvette, place the cuvette in the cell compartment and adjust the right control dial to read 100%T. Remember to make sure the filter lever, front left bottom, is set appropriately for the wavelength you are using.

8. Record the absorbance of the solution in each of the 6 test tubes at 475 nm. Each solution was mixed in a test tube, but should be poured into a cuvette before placing in the Spec 20 for the absorbance measurement. Do not place test tubes in the sample compartment of the Spec 20 even if the tubes fit. The optical quality of the cuvettes is higher and more consistent than that of test tubes. For tubes 5 and 6, record the absorbance immediately after removing them from their respective water bath.

9. When your work is complete pour all solutions into the waste container under the fume hood.

Part II: $[\text{CoCl}_4]^{2-}_{(\text{alc})} / [\text{Co}(\text{H}_2\text{O})_6]^{2+}_{(\text{alc})}$ Equilibrium

10. Using a clean, dry 100 mL graduated cylinder, transfer 40 mL of 0.01 M $[\text{CoCl}_4]^{2-}$ in alcohol to a clean, dry 100 or 150 mL beaker. (**The beaker and the graduated cylinder must be clean and DRY!!!!**) Observe the color of the solution. Using a disposable pipet, add 30 drops DI water to the solution in the beaker and mix well. Observe the color of the solution. This is your equilibrium solution.

11. Prepare 6 clean, dry small to medium size test tubes. (**Again, the test tubes must be DRY!!**) Add approximately equal amounts of the equilibrium solution prepared in step 9 above to each test tube and label them 1-6. It is important that you use all 40 mL of the equilibrium solution divided into 6 approximately equal parts so that when each is poured into a cuvette and placed in the Spec 20, it will cover the entire beam of light in the instrument. The first test tube is your control or reference test tube.

12. Add one drop of concentrated HCl to test tube 2 and mix well. Observe color changes.

13. Add 3-4 drops DI H_2O to test tube 3 and mix well. Observe color changes. Since ethanol is the solvent, water would be considered a reactant and not a solvent.

14. Add one drop 0.02 M AgNO_3 to test tube 4 and mix well. Ag^+ in solution reacts with Cl^- to precipitate as AgCl according to the following equation:



After a couple of minutes, centrifuge for about 2 minutes and observe color changes in the supernatant.

15. Place test tube 5 in the hot water bath. Place test tube 6 in the ice water bath. After about 5 minutes observe color changes for both. Be sure to turn off the bunsen-burner flame when test tube 5 is placed in the hot water because it might ignite the escaping alcohol vapors.

16. Next, you will use a Spec 20 to measure and record the absorbance of each solution you prepared. The Spec 20 instrument should be set to the desired wavelength (655 nm) and with the cell compartment empty the left control dial should be adjusted to read 0%T. With alcohol in your cuvette, place the cuvette in the cell compartment and adjust the right control dial to read 100%T. Remember to make sure the filter lever, front left bottom, is set appropriately for the wavelength you are using.

17. Record the absorbance of the solution in each of the 6 test tubes at 655 nm. A wavelength of 655 nm is used because this wavelength gives us the greatest differences in the absorbances for the solutions you are preparing. Remember, mixing of solutions is done in test tubes: absorbance measurements are done in cuvettes. For tubes 5 and 6, record the absorbance immediately after removing them from their respective water bath.
18. When your work is complete pour all solutions into the waste container under the fume hood.
19. Fill in the information in the tables of the Data Report in preparation for your lab report and make sure you answer the questions.

Data Report:

Name: _____ Partner: _____

Part I:

Test Tube	Absorbance, 475 nm	Color observations	Shift from Equilibrium, toward reactants or toward products
1			
2			
3			
4			
5			
6			

Part II:

Test Tube	Absorbance, 655 nm	Color observations	Shift from Equilibrium, toward reactants or toward products
1			
2			
3			
4			
5			
6			

Questions:

As part of your lab report answer each question below for both Part I and Part II above:

1. Explain how each change affected the equilibrium in terms of Le Châtelier's principle.
2. Is the forward reaction endothermic or exothermic?