Equilibrium and Le Châtelier's Principle

The $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$ equilibrium will be investigated. Predictions made regarding the effects of stressed applied to the system will be compared to experimental outcomes, and explanations will be developed based on Le Châtelier's principle.

Objectives and Science Skills

Prepare solutions and mixtures that can be interpreted as systems at equilibrium.
Describe dynamic equilibrium, including how it differs from static equilibrium and what conditions are required.
Construct representations to describe equilibrium systems, including the development of balanced chemical equations.
Explain Le Châtelier's principle and give examples of "stresses" that can disturb an equilibrium system.
Predict the effect of a disturbance such as a change in temperature or a change in concentration of one of the species in solution and compare observations to predictions.
Identify and discuss factors or effects that may contribute to deviations between theoretical and experimental results and formulate optimization strategies.

Suggested Review and External Reading

Reference materials and textbook sections on equilibrium systems, the equilibrium constant K, the reaction quotient Q, and Le Châtelier's principle

Introduction

Many physical and chemical systems involve changes or reactions that are considered reversible. Assuming all components in the system remain in contact, such a system can attain an equilibrium state.

The forward reaction, converting reactants to products, and the reverse reaction, converting products to reactants, can occur simultaneously. When these rates are equal, the macroscopic concentrations of the reactants and products appear constant, and the system is in a state of equilibrium.

Some conventions apply when considering reversible reactions:

– Products are the chemical species to the right of the arrow in the reaction equation as written. Reactants are the species to the left of the arrow.

– The forward reaction is the process occurring left to right as written in the equation; the reverse, from right to left.

In 1884, a French chemist, Henri-Louis Le Châtelier, expressed a principle that predicts the response of an equilibrium system when it is subjected to a change in conditions. Any change to a variable associated with the equilibrium is considered a "stress" or "disturbance". The system will respond by shifting in the direction that reduces the applied stress and allows the re-establishment of a new state of equilibrium.

In this experiment, you will investigate the equilibrium established when aqueous solutions containing the iron (III) and thiocyanate ions are mixed, resulting in the formation of the red-orange complex ion, iron (III) thiocyanate. Because the intensity or depth of the orange-red color reflects the relative concentration of $FeSCN^{2+}$ in solution, it is possible to visually track changes in the system.

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq) \qquad K = \frac{[FeSCN^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^{-}]_{eq}}$$

Causing a change in the relative amount of a reactant or product is an example of a stress on a system at equilibrium. For example, if one of the system's components was added to the equilibrium mixture, the system would shift in order to reduce that component's concentration (or partial pressure if a gas) until equilibrium is re-established. Reducing the amount of one of the components in the system can be caused in a number of ways, including by changing the pH of the solution or by causing the precipitation of one of the ions in the equilibrium system. As long as the temperature of the system remains unchanged, the value of the equilibrium constant K is unaffected.

Heating or cooling the system represents another stress. The value of K is affected by this change. If the forward reaction is exothermic (releases heat energy), heating the system will cause a shift to the left, which indicates that the value of K decreases with increasing temperature. Cooling such a system causes a shift to the right, reflecting an increase in the value of K. An endothermic forward reaction would show the opposite trends.

The disturbances you will apply to this system will include those that change the concentration of a reactant or product. Additionally, you will examine the effect of temperature on the equilibrium position of the system. This will also allow you to determine whether the forward reaction is endo- or exothermic.

Further information (you may not need all of this for your analysis):

$$AgSCN(s) \rightleftharpoons Ag^{+}(aq) + SCN^{-}(aq) \qquad K_{sp} = 1.0 \times 10^{-12}$$

$HSCN(aq) \rightleftharpoons H^+(aq) + SCN^-(aq)$ $\quad K_a = 0.12$

$FePO_4(s) \rightleftharpoons Fe^{3+}(aq) + PO_4^{3-}(aq)$ $\quad K_{sp} = 2.3 \times 10^{-18}$

Note:
$Fe^{3+}(aq)$ forms a number of complex ions in the presence of aqueous phosphate species (*e.g.*, $H_2PO_4^-(aq)$ and $HPO_4^{2-}(aq)$), particularly under acidic conditions like those present in the iron (III) nitrate solutions. Examples include $FeH_2PO_4^{2+}(aq)$ and $FeHPO_4^+(aq)$.

$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$ $\quad K_{a1} = 7.5 \times 10^{-3}$
$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$ $\quad K_{a2} = 6.2 \times 10^{-8}$
$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$ $\quad K_{a3} = 4.8 \times 10^{-13}$

$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\ OH^-(aq)$ $\quad K_{sp} = 4.0 \times 10^{-38}$

Equipment List

Volumetric pipets and flasks, disposable pipets
Thermometer, ice and water baths
Labeled test tubes, test tube rack
Miscellaneous labeled glassware (beakers, pipets, etc.)
Labeled deionized water wash bottle

Caution

Please be careful. Wear goggles and a lab coat; make sure clothing and shoes cover skin (aside from your hands and face). Wash your hands frequently.
Read the labels on the reagent bottles carefully. Label all glassware.
There are two $Fe(NO_3)_3$ solutions. One is 500 times more concentrated than the other.
Using the wrong $Fe(NO_3)_3$ solution will not lead to good data.
$Fe(NO_3)_3$ solutions are acidic, and the Fe^{3+} ion is an oxidizing agent. In the event of skin contact, wash the area and then flush it with water for 5 – 10 minutes. Inform your TA and fill out any required forms.
Ag^+ solutions can stain skin and clothing.
Inform your TA in the event of any spill.

Procedure

Lab bench organization: it is strongly recommended that you organize and label your glassware and other equipment before starting the experiment.

Please wait to do any calculations until after you have finished the experimental procedure and have cleaned up your lab bench.

Part 1 Preparation of the aqueous $Fe^{3+}/SCN^{-}/FeSCN^{2+}$ solution

1. Obtain ~40 mL of 2.0×10^{-3} M NaSCN and ~20 mL of 2.0×10^{-3} M $Fe(NO_3)_3$, in small, labeled beakers.

Caution

Incorrect use of the pipet and pipetter can result in **serious injury**.
Please **do NOT force or jam the pipet** into the pipetter.
If you push too hard, the pipet can break and **cut your hand**.
Use **just enough force** to create a seal. The pipet does not "click" into place.
Hold both the pipet and pipetter at all times.
If you pull any solution into the pipetter, please give it to your TA so that it can be cleaned.

If you have trouble, **ask your TA for help**.

2. Volumetrically pipet 40.00 mL of the 2.0×10^{-3} M NaSCN solution into a labeled beaker. Volumetrically pipet 20.00 mL of the 2.0×10^{-3} M $Fe(NO_3)_3$ into the beaker. The resulting solution should be pale orange-red.

3. Split the solution among 6 large test tubes labeled with numbers 1 through 6, pouring ~7 – 8 mL of the solution in each. Reserve the remaining solution in the beaker in case you need to repeat any step.

Part 2 Temperature: Stressing the System by Heating or Cooling

4. Place test tube #1 in an ice bath and #3 in the warm water bath for **at least** 10 minutes (the time does not have to be exact but it should be no less than 10 minutes). Leave test tube #2 at room temperature.

5. After temperatures have equilibrated, compare the relative depths of the orange-red color of the equilibrium solutions in test tubes #1 – 3 (ice, room, and warm temperatures). Which solution is the deepest orange-red? What do your observations mean in terms of the relative equilibrium concentrations of Fe^{3+}, SCN^{-}, and $FeSCN^{2+}$ in each equilibrium mixture? What does this imply about the effect of temperature on the value of K? Is the forward reaction endo- or exothermic? Explain your reasoning.

Part 3 Concentration: Stressing the System by Increasing or Decreasing the Concentration of One Component in the System

For each of the following (test tubes #4 – 6), record your observations regarding the depth of the orange-red color, the appearance of any precipitate, and any other changes you see. How did each "concentration stress" affect the system at equilibrium? How did the system respond? Why? In each case, did the value of *K* change?

6. Obtain a dropper bottle of 0.10 M $Fe(NO_3)_3$ solution from the reagent bench (note that 0.10 M is 50 times greater than 2.0×10^{-3} M). Add ~7-8 drops of the 0.10 M Fe^{3+} solution to test tube #4 and return the dropper bottle to the reagent bench. Record your observations.

7. Obtain a dropper bottle of 0.10 M $AgNO_3$ solution from the reagent bench. Add ~7-8 drops of the 0.10 M Ag^+ solution to test tube #5 and return the dropper bottle to the reagent bench. Record your observations.

8. Obtain a dropper bottle of 0.10 M Na_3PO_4 from the reagent bench. Add ~7-8 drops of the 0.10 M PO_4^{3-} solution to test tube #6 and return the dropper bottle to the reagent bench. Record your observations. Recall that the solution is somewhat acidic, so the phosphate ion may be in a partially protonated form (*e.g.*, $H_2PO_4^-(aq)$ and $HPO_4^{2-}(aq)$).

9. Please follow your TA's instructions for cleanup and waste disposal.

Make sure that you have thoroughly washed all of your glassware, have returned any equipment/glassware that you borrowed, and have wiped down your lab station. To correctly wash glassware and other equipment, use the dilute liquid soap and tap water. Remove all traces of soap with plenty of tap water. Perform a final rinse with a small volume of deionized water.

10. Compare and discuss your observations with your lab colleagues, using Le Châtelier's principle to guide your analysis and conversation.

Results / Sample Calculations

Depths of color of the equilibrium mixtures at different temperatures (ice, room, and warm temperatures), plus explanation and analysis
Depth of color of the solution and/or other observed changes after a stress is applied and equilibrium is re-established: temperature (ice, room, and warm) and concentration (increasing or decreasing the concentration a component of the system), plus explanation and analysis

Discussion Questions and Review Topics

What did you find and how?
How does this experiment illustrate Le Châtelier’s principle?