Chemical Equilibrium and Le Chatelier’s Principle

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch16/lechat.php

OBJECTIVES

The objective of this lab is to observe the effect of an applied stress on chemical systems at equilibrium.

BACKGROUND

Le Chatelier’s Principle

In 1884 the French chemist and engineer Henry-Louis Le Chatelier proposed one of the central concepts of chemical equilibria. Le Chatelier's principle can be stated as follows: A change in one of the variables that describe a system at equilibrium produces a shift in the position of the equilibrium that counteracts the effect of this change.

Le Chatelier's principle describes what happens to a system when something momentarily takes it away from equilibrium. This section focuses on three ways in which we can change the conditions of a chemical reaction at equilibrium:

(1) changing the concentration of one of the components of the reaction
(2) changing the pressure on the system
(3) changing the temperature at which the reaction is run.

A reversible reaction is a reaction in which both the conversion of reactants to products (forward reaction) and the re-conversion of products to reactants (backward reaction) occur simultaneously:

Forward reaction: \[ A + B \rightarrow C + D \]

Backward reaction: \[ C + D \rightarrow A + B \]

Reversible reaction: \[ A + B \rightleftharpoons C + D \]

Consider the case of a reversible reaction in which a concentrated mixture of only A and B is supplied. Initially the forward reaction rate (A + B \rightarrow C + D) is fast since the reactant concentration is high. However as the reaction proceeds, the concentrations of A and B will decrease. Thus over time the forward reaction slows down. On the other hand, as the reaction proceeds, the concentrations of C and D are increasing. Thus, although initially slow, the backward reaction rate (C + D \rightarrow A + B) will speed up over time. Eventually a point will be reached where the rate of the forward reaction will be equal to the rate of the backward reaction. When this occurs, a state of chemical equilibrium is said to exist.
Chemical equilibrium is a dynamic state. At equilibrium both the forward and backward reactions are still occurring, but the concentrations of A, B, C and D remain constant.

A reversible reaction at equilibrium can be disturbed if a stress is applied to it. Examples of stresses include increasing or decreasing chemical concentrations, or temperature changes. If such a stress is applied, the reversible reaction will undergo a shift in order to re-establish its equilibrium. This is known as Le Chatelier’s Principle.

Consider a hypothetical reversible reaction already at equilibrium: \( A + B \rightleftharpoons C + D \). If, for example, the concentration of A is increased, the system would no longer be at equilibrium. The rate of the forward reaction \( A + B \rightarrow C + D \) would briefly increase in order to reduce the amount of A present and would cause the system to undergo a net shift to the right. Eventually the forward reaction would slow down and the forward and backward reaction rates become equal again as the system returns to a state of equilibrium. Using similar logic, the following changes in concentration are expected to cause the following shifts:

- Increasing the concentration of A or B causes a shift to the right.
- Increasing the concentration of C or D causes a shift to the left.
- Decreasing the concentration of A or B causes a shift to the left.
- Decreasing the concentration of C or D causes a shift to the right.

In other words, if a chemical is added to a reversible reaction at equilibrium, a shift away from the added chemical occurs. When a chemical is removed from a reversible reaction at equilibrium, a shift towards the removed chemical occurs.

A change in temperature will also cause a reversible reaction at equilibrium to undergo a shift. The direction of the shift largely depends on whether the reaction is exothermic or endothermic. In exothermic reactions, heat energy is released and can thus be considered a product. In endothermic reactions, heat energy is absorbed and thus can be considered a reactant:

- Exothermic: \( A + B \rightleftharpoons C + D + \text{heat} \)
- Endothermic: \( A + B + \text{heat} \rightleftharpoons C + D \)

As a general rule, if the temperature is increased, a shift away from the side of the equation with “heat” occurs. If the temperature is decreased, a shift towards the side of the equation with “heat” occurs. In this lab, the effect of applying stresses to a variety of chemical systems at equilibrium will be explored. The equilibrium systems to be studied are given below:

- Calcium Hydroxide (with phenolphthalein)
  \[
  \text{Ca}^{2+} (aq) + 2 \text{OH}^- (aq) \rightleftharpoons \text{Ca(OH)}_2 (s)
  \]
- Acetic Acid with Sodium Hydroxide and Hydrochloric Acid (with methyl orange)
  \[
  \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+
  \]
Aqueous Ammonia Solution (with phenolphthalein)
\[
\text{NH}_3 (aq) + \text{H}_2\text{O (l)} \rightleftharpoons \text{NH}_4^+ (aq) + \text{OH}^- (aq)
\]
Clear \hspace{1cm} \text{pink}

Cobalt(II) Chloride Solution
\[
\text{Co(H}_2\text{O)}_{6}^{2+} (aq) + 4 \text{Cl}^- (aq) \rightleftharpoons \text{CoCl}_4^{2-} (aq) + 6 \text{H}_2\text{O (l)}
\]
pink \hspace{1cm} \text{blue}

**PROCEDURES**

**Part 1. \( \text{Ca}^{2+} (aq) + 2 \text{OH}^- (aq) \rightleftharpoons \text{Ca(OH)}_2 (s) \)**

1. Label a test tube #1, and add a few mL of NaOH to it.

2. Then add CaCl\(_2\) dropwise until a noticeable precipitate of Ca(OH\(_2\)) is present.
   
   a. What happens to the OH\(^-\) ions? Are they all “in” the precipitate, or do some remain in solution? How can we prove where they are?
   
   **HINT:** A test is to use the indicator phenolphthalein, which can be used to detect hydroxide ions (OH\(^-\)) in solution. To learn how the indicator works do the following:
   
   - Add a few mL of deionized water to a separate test tube.
   - Add a few drops of phenolphthalein.
   - Then add a few drops of NaOH (aq) to the test tube.
   
   **RECORD ALL OBSERVATIONS, ANSWER IN-LAB QUESTIONS IN YOUR LAB NOTEBOOK!**

3. Now add a few drops of the indicator to the test tube #1 with the Ca(OH\(_2\)).
   
   b. What happened? What does this demonstrate?
   
   c. What is the role of the Na\(^+\) ions in this experiment? The Cl\(^-\) ions?

4. Add 6 \( M \) HCl (NOT 12 \( M \)!!!) dropwise to the test tube #1 with the Ca(OH\(_2\)) until a change is observed. Record your results.
   
   d. How does the equilibrium respond to the addition of HCl? What happens to the precipitate?
   
   e. What happens to the OH\(^-\) ions?
   
   f. Which OH\(^-\) ions are reacting in this test, the ones in the precipitate, the ones in the solution or both? How do you know? What is the evidence?
   
   g. What happens at the molecular/ionic level as the HCl is added? What is the role of the H\(^+\) and the Cl\(^-\)? List all species that are present in the test tube at the end of the test.
**Part 2.** \( \text{CH}_3\text{COOH} \Leftrightarrow \text{CH}_3\text{COO}^- + \text{H}^+ \)

1. Label a test tube #2, and add 5 mL of 1.0 M acetic acid to it. Add 1 or 2 drops of methyl orange. RECORD ALL OBSERVATIONS IN YOUR LAB NOTEBOOK.
2. Add a few drops of 6 M NaOH and record your observations.
3. Add HCl dropwise until a noticeable change in color has taken place.

What happens at the molecular/ionic level as the HCl is added? What is the role of the \( \text{H}^+ \)? The \( \text{OH}^- \)? List all species that are present in the test tube at the end of the experiment.

**PART 3.** \( \text{NH}_3 (aq) + \text{H}_2\text{O} (l) \Leftrightarrow \text{NH}_4^+ (aq) + \text{OH}^- (aq) \)

1. Label a test tube #3, and add 5 mL of 1.0 M ammonia to it. Add 1 or 2 drops of phenolphthalein. RECORD ALL OBSERVATIONS IN YOUR LAB NOTEBOOK!
2. Add a few drops of 6 M HCl and record your observations. What is the primary species that is present after the HCl has been added?
3. Add NaOH dropwise until a noticeable change in color has taken place.

What happens at the molecular/ionic level as the NaOH is added? What is the role of the \( \text{H}^+ \)? The \( \text{OH}^- \)? List all species that are present in the test tube at the end of the experiment.

**PART 4.** \( \text{Co(H}_2\text{O})_6^2+ + 4 \text{Cl}^- (aq) \Leftrightarrow \text{CoCl}_4^{2-} (aq) + 6 \text{H}_2\text{O} (l) \)

1. Place a few crystals of CoCl\(_2\)-6H\(_2\)O into each of three test tubes. Label your test tubes #4, #5 and #6.

2. Add 2 mL of water to Tube #4. Stir the crystals to dissolve them into solution.
   
   Record these observations:
   
   What is the color of this solution?
   
   What is the dominant species of cobalt in this solution?
   
   Explain your observations with a chemical equation.

3. Add 2 mL of 12 M HCl to Tube #5. This tube will be used for steps 3-6. Stir the crystals to dissolve them into solution.
   
   Record these observations:
   
   What is the color of this solution?
   
   What is the dominant species of cobalt in this solution?

4. Slowly add distilled or deionized water drop by drop with stirring, until no further color change occurs.
   
   Record these observations:
   
   What is the color of the solution?
What is the dominant species of cobalt in this solution?
Explain your observations using a chemical equation.

5. Now put Tube #5 into a hot-water bath and observe the color of the solution.
   Record these observations:
   What is the color of the solution at room temperature?
   What is the color of the solution in the hot-water bath?
   What is the dominant species of cobalt in the hot water bath?

6. Take Tube #5 out of the hot-water bath and place it in an ice bath. Observe the color of the solution.
   Record these observations:
   What is the color of the solution in the ice bath?
   What is the dominant species of cobalt in this solution?
   Explain your observations using the ideas presented in the Discussion section.

7. Add a few drops of distilled or deionized water to the contents of Tube #6. This tube will be used for steps 7-9. Add just enough water to wet the contents. Don't try to dissolve the salt.
   Record these observations:
   What is the color of the solution?
   What is the dominant species of cobalt in this solution?

8. Using a test tube holder, heat the contents of the test tube using a Bunsen burner until you are satisfied that all of the water has been driven off.
   Record these observations:
   What is the color of the solution in the test tube?
   What is the dominant species of cobalt in this solution?
   Explain your observation using a chemical equation.

9. Add a drop of distilled or deionized water to the contents of the test tube.
   Record these observations:
   What is the color of the solution in the test tube?
   What is the dominant species of cobalt in this solution?
   Explain your observation using a chemical equation.

Cobalt complexes

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<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Color</th>
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<tbody>
<tr>
<td>cobalt(II) chloride</td>
<td>CoCl₂ (s)</td>
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<tr>
<td>cobalt(II) chloride hexahydrate</td>
<td>CoCl₂·6H₂O (s)</td>
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<tr>
<td>cobalt(II) ion</td>
<td>Co²⁺ (aq)</td>
<td>redish</td>
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<tr>
<td>cobalt(II) chloride ion</td>
<td>CoCl₄²⁻ (aq)</td>
<td>dark blue</td>
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