Chemical Equilibrium and Le Chatelier's Principle

Objectives

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

Background

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 Reactants	$\rightarrow$	C + D Products
backward reaction	C + D Products	$\rightarrow$	A + B Reactants
reversible reaction	A + B	$\leftrightarrows$	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 $\leftrightarrows$ 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 $A + B \leftrightarrows C + D + \text{heat}$

endothermic $A + B + \text{heat} \leftrightarrows C + D$

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:

1) Saturated Sodium Chloride Solution

   $NaCl\ (s) \leftrightarrows Na^{+1}\ (aq) + Cl^{-1}\ (aq)$

2) Acidified Chromate Solution

   $2\ CrO_4^{-2}\ (aq) + 2\ H^{+1}\ (aq) \leftrightarrows Cr_2O_7^{-2}\ (aq) + H_2O\ (l)$

3) Aqueous Ammonia Solution (with phenolphthalein)

   $NH_3\ (aq) + H_2O\ (l) \leftrightarrows NH_4^{+1}\ (aq) + OH^{-1}\ (aq)$

4) Cobalt(II) Chloride Solution

   $Co(H_2O)_6^{+2}\ (aq) + 4\ Cl^{-1}\ (aq) \leftrightarrows CoCl_4^{-2}\ (aq) + 6\ H_2O\ (l)$

5) Iron(III) Thiocyanate Solution

   $Fe^{+3}\ (aq) + SCN^{-1}\ (aq) \leftrightarrows Fe(SCN)^{+2}\ (aq)$

6) BTB in Acid / Base Solution

   $HIn\ (aq) \leftrightarrows H^{+1}\ (aq) + In^{-1}\ (aq)$

By observing the changes that occur (color changes, precipitate formation, etc.) the direction of a particular shift may be determined. Such shifts may then be explained by carefully examining the effect of the applied stress as dictated by Le Chatelier's Principle.

The Central Challenge is to investigate this Principle by testing the systems at equilibrium and then selecting specific ones to produce seven colors of the rainbow - ROYGBIV. An additional challenge involves selecting which reaction system to use for which color in producing the rainbow while trying to only use a given "stress" once.

Procedure

Safety

All of the acids and bases used in this experiment (NH_3, HCl, HNO_3 and NaOH) can cause chemical burns. In particular, concentrated 12M HCl is extremely dangerous! If any of these chemicals spill on you, immediately rinse the affected area under running water and notify your instructor. Also note that direct contact with silver nitrate ($AgNO_3$) will cause dark discolorations to appear on your skin. These spots will eventually fade after repeated rinses in water. Finally, in Part 4 you will be heating a solution in a test tube directly in a Bunsen burner flame. If the solution is overheated it will splatter out of the tube, so be careful not to point the tube towards anyone while heating.

Materials and Equipment

Equipment: Several small test tubes, test tube rack, test tube holder, Bunsen burner, 2 medium-sized beakers (for stock solutions), 10-mL graduated cylinder, wash bottle, stirring rod, and scoopula.

Chemicals: solid NH_4Cl (s), saturated NaCl (*aq*), concentrated 12M HCl (*aq*), 0.1M $FeCl_3$ (*aq*), 0.1M KSCN (*aq*), 0.1M $AgNO_3$ (*aq*), 0.1M $CoCl_2$ (*aq*), concentrated 15M NH_3 (*aq*), phenolphthalein, 0.1M K_2CrO_4 (*aq*), 6M HNO_3 (*aq*), 10% NaOH (*aq*), 0.1M HCl (*aq*), 0.1M NaOH (*aq*), and 0.1M NaCl (*aq*).

Experimental Procedure

Record all observations on your report form. These should include, but not be limited to, color changes and precipitates. Note that solution volumes are approximate for all reactions below. Dispose of all chemical waste in the plastic container in the hood.

<u>Part 1: Saturated Sodium Chloride Solution</u>

a. Place 3-mL of saturated NaCl (*aq*) into a small test tube.
b. ***Carefully*** add concentrated 12M HCl (*aq*) drop-wise to the solution in the test tube until a distinct change occurs. Record your observations.

<u>Part 2: Acidified Chromate Solution</u>

a. Place 3-mL of 0.1M K_2CrO_4 (*aq*) into a small test tube.
b. Add an equal amount of 6M HNO_3 (*aq*) to this solution. Record your observations.
c. Now add 10% NaOH (*aq*) drop-wise until the original color is returned. Record your observations. Here the added sodium hydroxide is effectively removing acidic hydrogen ions from the equilibrium system via a neutralization reaction: $H^{+1}\,(aq) + OH^{-1}\,(aq) \rightarrow H_2O\,(l)$.

<u>Part 3: Aqueous Ammonia Solution</u>

Instructor Prep: At the beginning of lab prepare a stock solution of aqueous ammonia. Add 4 drops of concentrated 15M NH_3 (*aq*) and 3 drops of phenolphthalein to a 150-mL (medium) beaker, top it up with 100-mL of distilled water, and mix with a stirring rod. Label the beaker and place it on the front desk. The entire class will then use this stock solution in Part 3.

a. Place 3-mL of the prepared stock solution into a small test tube.
b. Add a medium scoop of NH_4Cl powder to the solution in this test tube. Record your observations.

Part 4: Cobalt(II) Chloride Solution

a. Place 3-mL of 0.1M $CoCl_2$ (*aq*) into 3 small test tubes. Label these test tubes 1-3.
b. The solution in test tube #1 remains untouched. It is a control for comparison with other tubes.
c. To the solution in test tube #2, carefully add concentrated 12M HCl (*aq*) drop-wise until a distinct color change occurs. Record your observations.
d. To the solution in test tube #3, first add a medium scoop of solid NH_4Cl. Then heat this solution directly in your Bunsen burner flame (moderate temperature). Firmly hold test tube #3 with your test tube holder, and waft it back and forth through the flame (to prevent overheating and "bumping") for about 30 seconds, or, until a distinct change occurs. Record your observations. Then cool the solution in test tube #3 back to room temperature by holding it under running tap water, and again record your observations.

Part 5: Iron(III) Thiocyanate Solution

Instructor Prep: At the beginning of lab prepare a stock solution of iron(III) thiocyanate. Add 1-mL of 0.1M $FeCl_3$ (*aq*) and 1-mL of 0.1M KSCN (*aq*) to a 150-mL (medium) beaker, top it up with 100-mL of distilled water, and mix with a stirring rod. Label the beaker and place it on the front desk. The entire class will then use this stock solution in Part 5.

a. Place 3-mL of the prepared stock solution into 4 small test tubes. Label these test tubes 1-4.
b. The solution in test tube #1 remains untouched. It is a control for comparison with other tubes.
c. To the solution in test tube #2, add 1-mL of 0.1M $FeCl_3$ (*aq*). Record your observations.
d. To the solution in test tube #3, add 1-mL of 0.1M KSCN (*aq*). Record your observations.
e. To the solution in test tube #4, add 0.1M $AgNO_3$ (*aq*) drop-wise until all the color disappears. A light precipitate may also appear. Record your observations. Here the added silver nitrate is effectively removing thiocyanate ions from the equilibrium system via a precipitation reaction:
   $Ag^{+1}\,(aq) + SCN^{-1}\,(aq) \rightarrow AgSCN\,(s)$.

Part 6: BTB in Acid / Base

a. Add about 5-mL of tap water and 3 drops of the BTB solution into 4 small test tubes. Label these test tubes 1-4.
b. To the solution in test tube #1 add 10 drops tap water. It is a control for comparison with other tubes.
c. To the solution in test tube #2, add 10 drops of 0.1M HCl (*aq*). Record your observations.
d. To the solution in test tube #3, add 10 drops of 0.1M NaOH (*aq*). Record your observations.
e. To the solution in test tube #4, add 10 drops of 0.1M NaCl (*aq*). Record your observations.
f. To the solution in test tube #2, add 0.1M NaCl drop by drop. Record your observations.
g. To the solution in test tube #3, add 0.1M NaCl drop by drop. Record your observations.