NAME ______________________________

DATE ______________________________

Carolina ChemKits™:
Chemical Equilbrium and Le Chatelier's Principle
Overview

Reversible chemical reactions reach a state of dynamic equilibrium when the rate of the forward reaction equals the rate of the reverse reaction. You will conduct experiments to determine how this equilibrium can be shifted to favor reactants or products. By adjusting concentrations or temperature, you observe how a stress alters the dynamic equilibrium and how the ongoing reaction relieves that stress and reestablishes equilibrium.

Background

Dynamic Equilibrium

A chemical reaction that creates products until one or more of the reactants are used up is called a completion reaction, or irreversible reaction. By contrast, in a reversible reaction some of the products are converted back into reactants. Eventually, the rate of the reverse reaction equals the rate of the forward reaction, and a state of dynamic equilibrium is reached. At this point, the concentrations of the reactants and products remain fixed, but this does not mean that the forward and reverse reactions have stopped. Reactants are still being converted into products, and products into reactants. A good analogy is walking down an up escalator at the same speed as the escalator moves upward. There is no change in your position, due to the balance of the opposing motions.

Mathematically, a reaction at equilibrium can be expressed as a ratio. For example, given the generic equilibrium equation $aA + bB \rightleftharpoons cC + dD$, the equilibrium expression would be the product of the products raised to the power of their coefficients over the product of the reactants raised to the power of their coefficients.

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The expression above is called the Law of Mass Action, or the Law of Chemical Equilibrium. The symbol K is the equilibrium constant. Square brackets [ ] represent the concentration of the products and reactants in molarity (M).

The size of the equilibrium constant tells a lot about the extent of the reaction. If $K > 1$, the products are favored, meaning more products than reactants exist at equilibrium. If $K < 1$, then the reactants are favored, meaning more reactants than products exist at equilibrium.

If $K = 1$, then neither products nor reactants are favored at equilibrium.

In industry, the challenge with reversible reactions is to keep the products from decomposing back into reactants. Chemical engineers prefer 100% product yield from a reaction. In 1918, Fritz Haber, a German chemist, was awarded the Nobel Prize in chemistry for developing the "Haber process" for taking nitrogen from the atmosphere and combining it with hydrogen to produce ammonia, a vital component of inorganic fertilizers and explosives.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{heat}$

At room temperature, normal pressure, and normal concentrations of reactants, the percent yield of ammonia is quite low. However, as Henri Le Chatelier had discovered in the late 1800s, a reaction at equilibrium can be forced to make more products or reactants by placing a stress on the reaction. A stress can be a change in temperature or concentration or, if the reactants or products are gases, it can be a change in pressure. Le Chatelier's principle states that if a stress is placed upon a reaction at equilibrium, the reaction shifts to relieve that stress.

To produce ammonia, chemical engineers need a shift to the right. This is achieved by increasing the supply of N_2 and H_2 while removing the ammonia gas as soon as it forms. This forces the reaction to the right to lower the concentration of the additional N_2 and H_2 and to replace the NH_3. At the same time, heat is removed, further shifting the reaction to the right to replace the removed heat. The pressure is increased, also shifting the reaction to the right to relieve the excess pressure (because 2 moles of ammonia exert less pressure than 4 moles of reactants in the balanced equation). Simultaneous application of all three stresses (concentration, heat, pressure) brings about an optimum yield of ammonia for the reaction.

Equilibrium in Weak Acids and Bases

Weak acids and weak bases exhibit a special type of equilibrium. Because little of the molecular form of the acid or base ionizes, equilibrium is quickly established. A good example is formic acid as it slightly ionizes in water.

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$$

Because the concentration of water is almost unchanged in the reaction, it is considered a constant and is multiplied by the equilibrium constant (K) to form the ionization constant, K_a.

$$K = \frac{[H_3O^+][HCOO^-]}{[HCOOH][H_2O]}$$

$$K\,[H_2O] = K_a$$

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

The size of the K_a tells a lot about the strength of a weak acid. The smaller the K_a value, the weaker is the acid, due to less ionization. An acid is considered weak if it is less than 5% ionized.

Sample problem:

a. Calculate the K_a for 0.10 M formic acid (HCOOH) if the $[H_3O^+] = 4.2 \times 10^{-3}$ M.
b. Calculate the percent of ionization for this weak acid.

Answers:

a. At equilibrium, $[H_3O^+] = [HCOO^-]$ on the product side. $[HCOO^-] = 4.2 \times 10^{-3}$.
   The concentration of molecular HCOOH remaining after equilibrium hardly changes; after rounding, it remains at 0.10 M in the denominator of the K_a expression.

   $$0.1\text{ M} - 4.2 \times 10^{-3} = 9.58 \times 10^{-2} = 1.0 \times 10^{-1} = 0.10\text{ M}$$

   $$K_a = \frac{[4.2 \times 10^{-3}][4.2 \times 10^{-3}]}{[0.10\text{ M}]} = 1.8 \times 10^{-4}$$

b. $$\frac{4.2 \times 10^{-3}}{0.10\text{ M}} \times 100 = 4.2\%$$

The ionization constant of a weak base is K_b. As with weak acids, the size of the K_b gives an indication of the strength of the weak base. A common weak base reaction is ammonia gas with water:

$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

The expression for the ionization constant of NH_3 is $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$.

Materials

For your group:

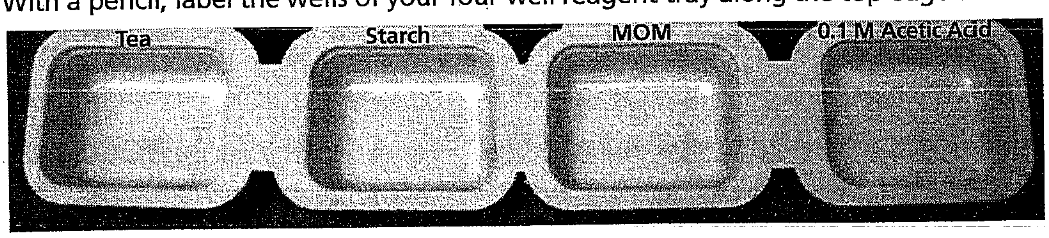
- 1 four-well reagent tray
- 1 three-well reaction tray
- 2 petri dishes
- 4 dropping pipets
- 1 wooden stirrer
- 1 wash bottle filled with water
- paper towels
- 2 250-mL beakers
- Bunsen burner (with ring stand, iron ring, and wire gauze) or hot plate
- laboratory thermometer
- graduated cylinder
- pH chart, 1–14
- pH paper strip, 2.0 cm
- ice

All groups will share the following from the materials station:

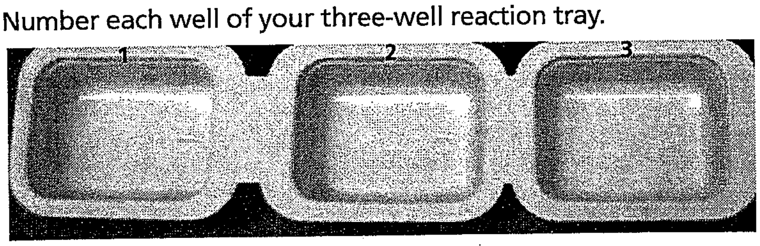
- 1 bottle of 0.04% bromthymol blue
- 2 bottles of 0.1 M sodium hydroxide
- 2 bottles of Lugol solution
- 1 bottle of white vinegar, with pipet

Pre-lab Procedure

1. With a pencil, label the wells of your four-well reagent tray along the top edge as shown.



2. Number each well of your three-well reaction tray.



3. Your teacher will assign four students to distribute the four reagents. They will half-fill each well in the four-well tray with the appropriate reagent.
4. Dedicate a pipet to each of the reagents and be sure to use only the designated pipet with each reagent during the activities to avoid any cross-contamination.

Activity A: Changing Concentration of Hydrogen Ions in a Tea Solution

Have you ever noticed what happens to tea when you add lemon juice? In this equilibrium activity, you investigate the effect of adding or removing a stress on a chemical equilibrium by changing the hydrogen ion concentration in a tea solution. The reaction is tea + $H^+ \rightleftharpoons$ teaH^+.

Procedure

1. Fill a pipet with tea and add 5 drops in the center of wells 1, 2, and 3 of the reaction tray.
2. The middle well (no. 2) will serve as a control for comparing reactions in wells 1 and 3.
3. Obtain a dropping bottle of 0.1 M NaOH from the materials station, add 2 drops to the tea in well 1, and stir with a wooden stirrer. Adding hydroxide ions removes the H^+ on the reactant side by formation of water ($H^+ + OH^- \rightarrow H_2O$). The reaction will shift to replace the H^+ that are removed. Record the direction of the shift in equilibrium (← or →) and the resulting color in Data Table 1.
4. Fill a pipet with 0.1 M acetic acid, add 2 drops to the tea in well 3, and stir with the wooden stirrer. This places a stress on the reactant side by adding more H^+. Record the direction of the shift in equilibrium (← or →) and the resulting color in Data Table 1. **Hint:** If a stress is added, such as an increase in concentration or temperature for a reaction at equilibrium, the reaction will shift in an opposite direction to relieve that stress.
5. Rinse out your reaction trays with water and dry with a paper towel.
6. **Data Table 1**

Stress	Direction of Shift (→ or ←)	Color
Control	n/a	
0.1 M acetic acid addition		
0.1 M NaOH addition		

According to your observations, fill in the blanks for the color changes in the equation below.

tea + H^+ $\rightleftharpoons$ teaH^+

__________color __________color

Activity B: Changing Temperatures for a Starch-Iodine Equilibrium Solution

A classic test for starch is to add a few drops of iodine solution. A positive test is indicated by a dramatic color change. In this activity, you investigate the effect of adding or removing temperature as a stress on a reaction at chemical equilibrium. The reaction is iodine + starch $\rightleftharpoons$ starch-iodine complex.

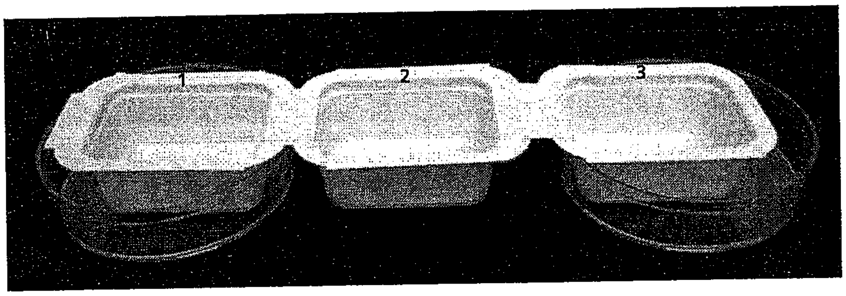
Procedure

1. Heat 100 mL of water in a 250-mL beaker to 85°C.
2. Place 100 mL of water in a second 250-mL beaker and add ice to make a cold water bath.
3. Make a dilute starch solution by filling a pipet with starch solution and placing 5 drops in each well of the reaction tray. Add 5 mL of water to each well and stir with a wooden stirrer. Record the color of the starch solution in the blank below starch in the above reaction.
4. Obtain a dropping bottle of Lugol solution from the materials station. Add 2 drops of this iodine solution into each well and record the color of the starch-iodine complex in Data Table 2 of the control row and in the blank in the equation below.

   iodine + starch $\rightleftharpoons$ starch-iodine complex

   ____________color ____________color

5. Remove the tops from the two petri dishes and place the bottoms of both dishes under reaction wells 1 and 3 as shown below.



6. To the petri dish under well 3, add 85°C water until almost full. Hold well 3 down into the warm water while stirring with a thermometer. Note the highest temperature and record the temperature and color in Data Table 2. Increasing the temperature causes a stress on this equilibrium. Based upon the colors of the original equilibrium above, what is the direction of shift for this new equilibrium? Record this in Data Table 2.
7. Now add ice water to the petri dish under well 1. Note the lowest temperature and compare the color to the control tray. Record both the temperature and color in the data table. Indicate the direction of shift for the new reaction.

Data Table 2

Stress	Direction of Shift (→ or ←)	Color
Control (at room temp.)	n/a	
Raise temperature		
Lower temperature		

8. Based upon your data table, include the word heat in one of the blanks below. Remember that if you increase heat for a heat-sensitive equilibrium, the reaction will shift to the opposite side to absorb the added heat or shift to the same side to replace heat if it is removed.

   ____________ + iodine + starch $\rightleftharpoons$ starch-iodine complex + ____________

9. Rinse out your reaction trays with water and dry with a paper towel.

C. Changing Concentration of Hydroxide Ions in a Slightly Soluble Compound

Milk of magnesia (MOM) can be used as either a laxative or in smaller dosages as an antacid. It is barely soluble in water (only 0.012 g/L dissolves). The equilibrium that is set up with the small amount dissolved is as follows:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{+2}(aq) + 2OH^-(aq)$$

The stress that you will place on the above equilibrium reaction will be to remove OH^- ions by adding vinegar, which supplies H^+ ions. The H^+ ions react with OH^- ions and form water.

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

This reaction can be monitored visually by adding drops of the acid/base indicator, bromthymol blue. The range of colors for this pH indicator is as follows:

Yellow < 6.0 ---- green ---- 7.6 > blue

Yellow, then, indicates an acid with pH below 6.0, blue indicates a base with a pH above 7.6, and green indicates a pH between 6.0 and 7.6.

Procedure

1. Add 5 mL of water to wells 1 and 2 in the reaction tray and fill well 3 half-full with white vinegar from the bottle at the materials station.
2. Stir the white MOM liquid in well 3 of the four-well reagent tray with a wooden stirrer to get it suspended before transferring.
3. Fill a pipet with the MOM suspension and place 25 drops in wells 1 and 2 of the reaction tray.
4. Stir each well with the wooden stirrer, get a bromthymol blue dropping bottle from the materials station, and add 6 drops to wells 1 and 2.
5. Record the color of both wells and record the pH range for this reaction at equilibrium in Data Table 3. Again, the pH range for bromthymol blue is: Yellow < 6.0 ---- green ---- 7.6 > blue. Well 2 will be a control for comparing colors as you add stresses to well 1.
6. Stress 1: Fill a pipet with vinegar from well 3 of the reaction tray and add it to well 1. Stir quickly with the wooden stirrer. Record in Data Table 3 the color change and range of pH for this reaction.
7. Stress 2: Repeat step 6.
8. Stress 3: Repeat step 6
9. Continue adding vinegar and stirring.
   a. What eventually happens?
   b. Looking at the equation for the solubility of $Mg(OH)_2$, explain what happens to the equilibrium each time you add vinegar?
   c. Explain why there is a limit to how much vinegar you can add until there is no further change in color.

Data Table 3

	Color	pH Range
At Equilibrium	Well 1:	
	Well 2 (control):	
Stress 1: Adding Vinegar		
Stress 2: Adding Vinegar		
Stress 3: Adding Vinegar		

10. Discard the contents of the three wells of the reaction tray, rinse with water, and dry with paper towels.

D. Determining the Acid Ionization Constant (K_a) for a Weak Acid

All weak acids only partially ionize in a water solution. An equilibrium is quickly established in which the hydronium ion concentration is considerably less than the original molecular acid. Thus the term, "weak acid" applies. The pH is usually 2 or greater. The following equation illustrates this partial ionization of a weak molecular acid, HA.

$HA(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

The expression for the acid-ionization constant, K_a, is:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Note that because the coefficients are the same for both products in the above equation, the molar concentration of $[A^-]$ ions will always equal the concentration of the hydronium ions $[H_3O^+]$. For instance, if the pH of 0.1 M HA acid is measured to be 2, then the H_3O^+ ion concentration of the solution is 1.0×10^{-2}, and the A^- ion concentration also is 1.0×10^{-2}.

Inserting these values into the K_a equation, we have

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[1 \times 10^{-2}][1 \times 10^{-2}]}{1 \times 10^{-1}} = 1 \times 10^{-3}$$

Procedure

1. Take your 2.0-cm pH strip and dip the end into the 0.1 M acetic acid well of the reagent tray.
2. Match the color of the paper to your pH chart for the whole number pH. pH = ________
3. Convert the pH to exponential notation like the example above. $[H_3O^+]$ = __________
4. Write the equation for the ionization of the 0.1 M acetic acid (CH_3COOH)

________________ + ________________ $\rightleftharpoons$ ________________ + ________________

5. Write the equilibrium expression for the ionization constant (K_a). Solve the equation by inserting the exponential notations of the hydronium ions (H_3O^+), the acetate ions (CH_3COO), and the acetic acid (CH_3COOH) into the equation, as in the example above.

K_a =

The theoretical value for the K_a of 0.1 M acetic acid is 1.8×10^{-5}.

6. Calculate the % of ionization for the 0.1 M acetic acid as shown in the formic acid example problem in the Background section.

Post-lab Questions

1. Given the equilibrium equation for a general reaction, $A + B \rightleftharpoons C + D$, explain what happens to the reactants and products from Time 0 until the reaction reaches equilibrium.

2. Consider the following reaction at equilibrium: $SO_2(g) + O_2(g) \rightleftharpoons SO_3(g)$
   a. Balance the equation.

   b. Write the equilibrium expression.

   c. If the concentrations for the above reaction are $[SO_2] = 0.00377$ M, $[O_2] = 0.00430$ M, and $[SO_3] = 0.00413$ M, calculate the equilibrium constant.

   d. Which reaction is favored (forward or reverse), based on the size of the K?

3. The formation of SO_3 in the above reaction is exothermic.
   a. Write the balanced equation with the word *heat* on the side that would indicate an exothermic reaction.

   b. Describe the shift in equilibrium that would occur (left or right) if the following changes were made.

      Adding more SO_3 ____________

      Removing heat ____________

      Increasing the pressure ____________

      Adding more SO_2 ____________

      Removing O_2 ____________

      Removing SO_3 ____________

4. Carbon monoxide poisoning displaces the oxygen in oxyhemoglobin (HbO_2) and forms carboxyhemogloblin (HbCO) that deprives cells of oxygen for respiration.

$$HbO_2(aq) + CO(g) \rightleftharpoons HbCO(aq) + O_2(g)$$

   Brainstorm with your group as to the best medical treatment for shifting the equilibrium back to the side that would restore oxyhemogloblin in a victim's blood.

5. One of the equilibrium systems in the blood for regulating pH is the bicarbonate ion (HCO_3^-).

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

   When a person hyperventilates, the rapid deep breathing causes a depletion of CO_2 in the bloodstream, which shifts the above equilibrium to the left to restore the CO_2 level. This shift reduces the H^+, causing a potentially dangerous increase in pH known as alkalosis. Brainstorm on how this pH balance can be restored and explain your suggestion in terms of the equilibrium equation given above. (There is one very simple remedy.)