NAME ________________________________

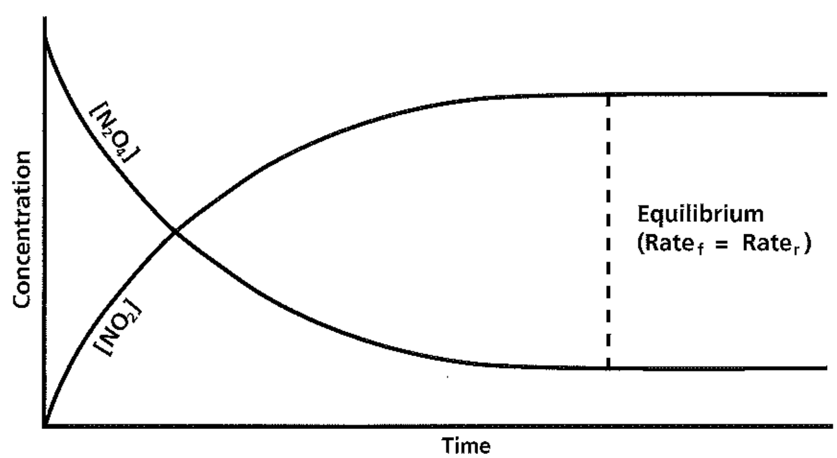
DATE ________________________________

Carolina Investigations® for AP Chemistry
Le Châtelier's Principle and Equilibrium Shifts
Guided Activity

Have you ever drunk from a bottle of soda only to discover that it tastes flat? The chemical reaction for making carbonated soda is $CO_2(g) + H_2O(g) \rightleftharpoons H_2CO_3(aq)$. Notice the double arrows between reactants and products. This is one of many chemical reactions that are reversible. When you leave a bottle of soda uncapped for a period of time, the carbonic acid, $H_2CO_3(aq)$, decomposes back into carbon dioxide gas, which escapes into the atmosphere, leaving only water and dissolved drink mix. Without the carbonic acid, the drink tastes flat. This reverse reaction can be slowed by tightly replacing the cap on the bottle, causing the pressure to increase as some of the CO_2 escapes from the liquid. This results in both the forward and reverse reactions reaching a state of equilibrium which helps to preserve the carbonic acid in the drink. You will conduct experiments to determine how this equilibrium can be shifted to favor reactants or products.

Background

A chemical reaction that creates products until one or more of the reactants are used up is called a **completion** or **irreversible reaction**. Another type of reaction is a **reversible reaction**. At the beginning of the reaction, time 0, there are no products. When the reactants collide, the forward reaction proceeds, forming products. As the product concentration increases, a reverse reaction occurs in which 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 are still being converted into reactants. However, the rates of conversion for the forward and reverse reactions are the same after a given period of time, resulting in no net change in concentration. The following graph shows the equilibrium that is established for colorless N_2O_4 and amber-colored NO_2 after a brief period of time.



How is equilibrium for nitrogen dioxide established? Initially, only the forward reaction occurs, as colorless dinitrogen tetroxide (N_2O_4) changes into amber-colored nitrogen dioxide (NO_2), as shown by the following equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

However, in a short period of time, a reverse reaction takes place as some of the NO_2 decomposes into N_2O_4 until dynamic equilibrium exists between the two compounds. After that, the concentrations remain at fixed values because the rate of the forward reaction equals the rate of the reverse reaction ($R_f = R_r$).

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. Such is the case for ammonia production. Fritz Haber, a German chemist, won the 1918 Nobel prize in chemistry for developing the "Haber process" for taking nitrogen directly 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 due to its decomposition. However, as Henri Le Châtelier 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, concentration, or, if the reactants or products are gases, it can be a change in pressure for the whole reaction system (as in an enclosed tank). Le Châtelier's principle states that if a stress is placed upon a reaction at equilibrium, the reaction will shift to relieve that stress.

To produce ammonia efficiently, chemical engineers need to shift the equilibrium to the right side of the equation (the product side). This is achieved by increasing the concentrations of N_2 and H_2 while at the same time removing the ammonia gas as soon as it is formed. 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 NH_3 exert less pressure than 4 moles of reactants in this reaction). Simultaneous application of all three stresses (concentration, heat, and pressure) brings about an optimum yield of ammonia for the reaction.

Increase concentration	N_2	H_2			
	⇩	⇩			
Increase pressure	$N_2(g)$ +	$3H_2(g)$ ⇌	$2NH_3(g)$ +	heat	
			⇩	⇩	
		Remove	NH_3	heat	

Pre-laboratory Questions

1. Using Le Châtelier's principle, determine whether reactants or products are favored as you add or remove the following stresses that shift equilibrium for the following reaction.
   $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) + \text{heat}$

   a. Remove O_2.

   b. Lower the temperature.

   c. Add CO.

d. Remove CO_2.

e. Decrease pressure.

2. Consider the following equilibrium reaction for the production of sulfur trioxide:
   $SO_2(g) + O_2(g) \rightleftharpoons SO_3(g)$ The standard enthalpy change: ($\Delta H° = -196.6$ kJ)
   a. Write a balanced equation with the heat value on the proper side of the equation.

   b. Describe the shift in equilibrium that would occur (left or right) by the following changes and how the concentrations of the reactants and products would be affected:
   Adding more SO_3

   Removing heat

   Increasing pressure by decreasing the volume (because reactants and products are gases)

   Adding more SO_2

   Removing O_2

   Removing SO_3

3. Read through the laboratory procedures. Diagram the procedure using illustrations and/or a flow chart to describe the steps. Ensure that your diagrams are labeled with quantities and descriptions.

Materials

For your group:

- 4-well reagent tray
- 3-well reaction tray
- 2 petri dishes
- 4 dropping pipets
- wooden stirrer
- 3 weigh boats
- 10-mL syringe
- syringe end cap
- 2 250-mL beakers
- 50-mL beaker or small cup
- 4 standard test tubes
- test tube rack
- permanent marker or wax pencil
- wash bottle with distilled water
- Bunsen burner (with ring stand, iron ring, and wire gauze) or hot plate
- laboratory thermometer
- graduated cylinder
- ice
- paper towels

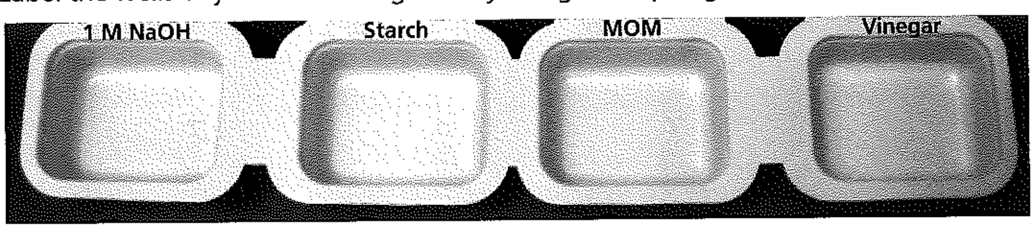
All groups will share the following from the Materials Station:

- 0.04% bromthymol blue
- iodine–potassium iodide with pipet
- 0.5 M copper(II) chloride
- 0.1 M silver nitrate with pipet
- Bogen universal indicator
- Bogen universal indicator color chart
- seltzer water
- sodium chloride
- balance(s)

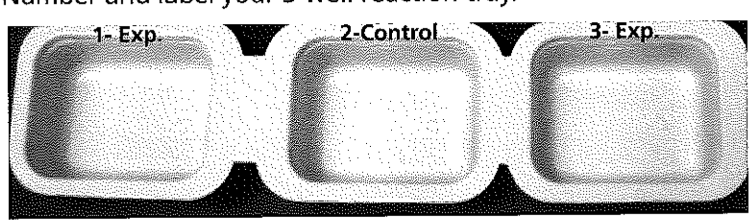
Procedure

Pre-lab Procedure

1. Label the wells of your 4-well reagent tray along the top edge as shown. (A pencil will work.)



2. Number and label your 3-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 reagent tray with the appropriate reagent.
4. Dedicate a pipet to each of the reagents wells and be sure to use only the designated pipet with each reagent during the activities to avoid any cross contamination.

Activity A: Changing Temperature on an Equilibrium Reaction (Starch–Iodine)

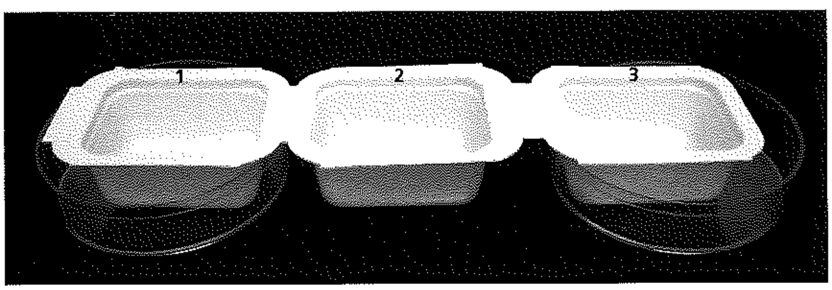
A classic test for starch is to add a few drops of iodine solution. A positive test is indicated by a dramatic color change. In this activity, you will investigate the effect of adding or removing temperature as a stress on a reaction at chemical equilibrium. The equilibrium reaction you will investigate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

Procedure

1. Heat 100 mL water in a 250-mL beaker to 85°C.
2. Place 100 mL 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 10 mL water to each well and stir with a wooden stirrer. Record the color of the starch solution on the reactant side of the equation in step 5 below.
4. Obtain a bottle of iodine–potassium iodide solution from the Materials Station. Add 1 drop of this solution into each well. The middle well will serve as the control well, while wells 1 and 3 will be experimental wells for temperature changes. Measure the temperature of the control well in degrees and record in Data Table 1.
5. Record the color of the starch–iodine complex in the equation below and in the Control well row of Data Table 1.

   iodine + starch $\rightleftharpoons$ starch–iodine complex

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



7. To the petri dish under well 3, add 85°C water until it is almost full. Have one partner hold well 3 down into the warm water while the other partner stirs with a thermometer. Note the highest temperature and compare the color to the control tray. Record the temperature and color in Data Table 1. Increasing the temperature causes a stress on this equilibrium. Based upon the colors of the original equilibrium equation above, what is the direction of shift for this new equilibrium? Record this in Data Table 1.
8. Now add ice water to the petri dish under tray 1. Note the lowest temperature and compare the color to that of the control tray. Record both the temperature and color in the data table. Indicate the direction of equilibrium shift for the new reaction.
9. On the basis of your data, include the word "heat" in the correct blank below. (Remember that if you increase heat for a heat-sensitive equilibrium, the reaction shifts to the opposite side to absorb the added heat.)

   ________ + iodine + starch $\rightleftharpoons$ starch–iodine complex + ________
10. Rinse your three-well reaction tray with water and dry with a paper towel.

Activity B: Changing Concentration on an Equilibrium Reaction (Milk of Magnesia)

Milk of magnesia (MOM) is used as a laxative or an antacid. It is barely soluble in water (only 0.012 g/L). The following equilibrium is established with the small amount that does dissolve:

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

The stress that you will place on the above equilibrium reaction will be to remove OH^{-} ions by adding vinegar. The H^{+} ions from the vinegar react with the aqueous OH^{-} ions to form water (This is how milk of magnesia acts as an antacid.)

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

This reaction can be monitored visually by adding drops of the acid–base indicator, bromthymol blue. The pH range of colors for this 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 3 mL of water to wells 1 and 2 in the reaction tray.
2. Stir the milk of magnesia in well 3 of the reagent tray with a wooden stirrer before transferring.
3. Use a pipet to place 15 drops of the MOM suspension in wells 1and 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 1and 2.
5. Record the color of both wells and record the pH for this reaction at equilibrium in Data Table 2. Again, the pH range for bromthymol blue is as follows: Yellow < 6.0 ---- green ---- 7.6 > blue. Well 2 will be a control for comparing colors as you add stresses to well 1. Well 3 will remain empty.
6. Fill a pipet with vinegar from well 4 of the reagent tray.
7. Stress 1: Add 10 drops of vinegar to well 1. Stir quickly with the wooden stirrer. Record in Data Table 2 the color change and range of pH for this reaction.
8. Stress 2: Repeat step 7.
9. Stress 3: Repeat step 7.
10. Continue adding additional increments of 10 drops of vinegar and stirring. What eventually happens?
11. In terms of the equation for the solubility of $Mg(OH)_2$, explain what happens to the equilibrium each time you add vinegar?
12. Explain why there is a limit to how much vinegar you can add until there is no further change in color.
13. Add 10 drops of 1 M NaOH to well 1. Record the color and pH in Data Table 2.
14. Add another 10 drops of 1 M NaOH to well 1. Record the color and pH in Data Table 2.
15. In terms of the $Mg(OH)_2$ equilibrium equation, explain what happened to the equilibrium as you added 1 M NaOH?
16. Rinse the 4-well reagent tray, the 3-well reaction tray, and the 4 dropping pipets with water.

Activity C: Changing Pressure on an Equilibrium Reaction (Carbonic Acid)

Carbonated water is made by dissolving carbon dioxide gas into water, forming a weak acid, carbonic acid. Carbonic acid then ionizes into H^+ ions and HCO_3^- ions. The equilibrium reactions involved in making carbonated water are as follows:

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ carbonic acid

$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

The stress that you will manipulate on this reaction is lowering the pressure and observing the shift in the equilibrium as the reaction changes inside a syringe.

Procedure

1. Pour 10 mL of seltzer water into a 50-mL beaker or a small cup.
2. Place 5 drops of Bogen universal indicator into the 10 mL of seltzer water.
3. Take a 10-mL syringe and push the plunger down to 0.0 mL to remove all the air.
4. Place the tip of the syringe into the solution and draw up 3 mL of the solution. Compare the solution color to the Bogen universal indicator chart and record the color and pH of the solution in the Control row of Data Table 3.
5. The pressure on this equilibrium solution is the same as the room atmospheric pressure.
6. Screw the syringe end-cap tightly onto the syringe tip.
7. Pull the plunger up to the 10-mL mark. As you increase the volume, you are decreasing the pressure on your solution. Observe any changes in the solution.
8. Release the plunger. Does the plunger go back to its original starting position of 3 mL?
9. Repeat pulling back to 10 mL and releasing numerous times. Note the changes occurring in the solution. Compare the color of the solution at the end of several pulls to the Bogen color chart and record color and pH in Data Table 3. Also record the direction of the equilibrium shift that occurs.
10. How does decreasing the pressure affect the initial equilibrium of this reaction?

Activity D: Common Ion Effect

You have a reaction at equilibrium containing 0.5 M copper(II) chloride dissolved in water.

$Cu(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CuCl_4^{2-}(aq) + 6H_2O(l)$

blue green

You will shift the equilibrium by adding a "common ion" (a compound that has an ion common to the reaction). A blue color indicates a shift left due to an excess of the $Cu(H_2O)_6^{2+}$ complex. A green color indicates a shift right due to an excess of the $CuCl_4^{2-}$ complex.

Procedure

Common Ion Effect

1. Place four test tubes in a test tube rack. Use a marker to label the test tubes 1, 2, 3, and 4.
2. Measure 8 mL of copper(II) chloride from the 120-mL bottle. Add 2 mL (40 drops) to each of the 4 test tubes.
3. Keep test tube 1 as a control and reference for color. Record this color in Data Table 4.

4. Weigh 0.3 g of NaCl into one weigh boat, weigh 0.6 g of NaCl into the second boat, and weigh 0.9 g of NaCl into the third boat.
5. Bend one corner of the 0.3 g NaCl boat in half to make a pouring spout. Carefully pour the 0.3 g of NaCl into test tube 2. Gently stir by swirling the test tube.
6. Likewise pour the 0.6 g into test tube 3 and gently swirl to mix.
7. Now pour the 0.9 g into test tube 4 and gently swirl to mix.
8. Compare the colors of test tubes 2, 3, and 4 to that of test tube 1. Record the colors in Data Table 4.
9. Record your answers in Data Table 4
   a. What is the "common ion" that you added to test tubes 2, 3, and 4?
      Common ion:________
   b. How is the common ion affecting the equilibrium reaction, as the amount of NaCl increases?

Addition of $AgNO_3$

1. Obtain a bottle of silver nitrate ($AgNO_3$) from the materials station. Add 20 drops of silver nitrate to test tube 3 and observe what happens. Record the color in Data Table 4. Based upon color, in which direction does the equilibrium shift? Record in Data Table 4.
2. Write an equation showing what happened when you added the $AgNO_3$ and explain why the equilibrium shifted. Record in Data table 4.

Addition of H_2O

1. Use a dropper pipet to add 80–100 drops of water to test tube 4. Gently stir by swirling the test tube. What happens to the color? Record this color in Data Table 4.
2. Explain this equilibrium shift in terms of the original equilibrium equation:
   $Cu(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CuCl_4^{2-}(aq) + 6H_2O(l)$
   blue green
3. Keep all four test tube solutions for Activity E.

Activity E: Altering Equilibrium to Achieve Optimum Yield

Assume your lab group is a team of chemical engineers. Your company has a customer that wants to purchase large quantities of two aqueous complexes that can be produced from the 0.5 M copper(II) chloride equilibrium reaction investigated in part D.

$Cu(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CuCl_4^{2-}(aq) + 6H_2O(l)$
blue green

The customer wants Solution 1 to have a maximum concentration of $Cu(H_2O)_6^{2+}(aq)$ and Solution 2 to have a maximum concentration of $CuCl_4^{2-}(aq)$.

You must design two experimental procedures that would determine the addition or removal of concentration and temperature stresses for shifting the equilibrium to produce the maximum amount of each complex in solution. There are no gases in this reaction, so pressure will not be a factor. Have your teacher approve both procedures. Then, experiment to demonstrate that your procedures will work. Use control test tube 1 as a reference for color comparisons. Your trial in the test tubes will help your company decide how to scale the reaction to an industrial level.

Follow your teacher's instructions for proper disposal of all four solutions.

Data: Observations and Analysis

Data Table 1: Changing Temperature on an Equilibrium Reaction (Starch-Iodine)

Stress	Direction of Shift ← or →	Temp. °C	Color
Control well 2 (room temp.)	n/a		
Higher temperature (well 3)			
Lower temperature (well 1)			

Data Table 2: Changing Concentration on an Equilibrium Reaction (Milk of Magnesia)

Well 1	Color	pH Range
At initial equilibrium	Well 1:	
	Well 2 (control)	
Stress 1: Adding vinegar		
Stress 2: Adding vinegar		
Stress 3: Adding vinegar		
Stress 4: Adding 1 M NaOH		
Stress 5: Adding 1 M NaOH		

Data Table 3: Changing Pressure on an Equilibrium Reaction (Carbonic Acid)

Stress	Changes Observed in Solution	Color	pH	Direction of Shift (← or →)
Control (3 mL at atmospheric pressure)	n/a			n/a
(10 mL < atmospheric pressure) after several pulls				

Data Table 4: Addition of Common Ion, Silver Nitrate, and Water

Reagent	Test Tube 1, Control	Test Tube 2	Test Tube 3	Test Tube 4
Copper(II) chloride	40 drops	40 drops	40 drops	40 drops
Common ion from NaCl	0.0 g NaCl Color: ___________	0.3 g NaCl Color: ___________	0.6 g NaCl Color: ___________	0.9 g NaCl Color: ___________
0.10 M $AgNO_3$	N/A	N/A	Color: ___________	N/A
Water	N/A	N/A	N/A	Color: ___________

Laboratory Questions

1. Consider 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:
   $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$. $\Delta H° = 119$ kJ
   Explain the changes that would occur as the following stresses are applied or removed for this reaction.
   a. CO is removed.

   b. Heat is added.

   c. CO_2 is added.

   d. Heat is removed.

3. Carbon monoxide poisoning occurs when the oxygen in oxyhemoglobin (HbO_2) is displaced by carbon monoxide and forms carboxyhemoglobin (HbCO). This deprives the cells of the oxygen needed for respiration: $HbO_2(aq) + CO(g) \rightleftharpoons HbCO(aq) + O_2(g)$

   Identify the best medical treatment for shifting the equilibrium in a direction that would restore the proper levels of oxyhemoglobin in a victim's blood.