13. APPLICATIONS OF LE CHÂTELIER'S PRINCIPLE

Introduction

Most chemical reactions do not go to completion; that is, giving 100% of the expected yield. In fact, most chemical reactions are reversible and when the forward rate of reaction is equal to the reverse rate, a chemical system is said to be in equilibrium. Le Châtelier's Principle states that if a constraint or stress is applied to a system in equilibrium, the equilibrium will shift so as to relieve or counteract the effect of stress. This principle is used by chemical engineers to manipulate processes and maximize the amount of product yield. In this lab, you will investigate the effect of various external stressors on systems in equilibrium.

Concepts

- Equilibrium
- Equilibrium constant, K_c
- Le Châtelier's principle
- Reaction quotient, Q
- ICE table

Background

Many chemical reactions form some product: a solid precipitate, a colored compound or a gas. These reactions are carried out under conditions that favor the creation of the product and are assumed to go to completion. However, for many chemical changes, reactions do not go to completion. Instead, these reactions remain in a state of equilibrium where amounts of products and reactants are always present in varying amounts. Any stress imposed on a system in equilibrium will cause a shift in a manner so as to minimize the stress.

One example of an equilibrium system that is constantly being stressed by changes in conditions is the process responsible for the transport of oxygen and carbon dioxide in the body. Molecular oxygen, O2, is in equilibrium with the oxygenated (HbO2) and deoxygenated (Hb) forms of hemoglobin, the iron-containing, oxygen-transport metalloprotein in the red blood cells of almost all vertebrates as well as tissues of some invertebrates. Hemoglobin the blood carries oxygen from the lungs or gills to the rest of the body. The equilibrium can be represented as:

$$\mathbf{Hb + O_2 \rightleftarrows HbO_2}$$

When one inhales, O2 pressure in the lungs is high therefore shifting the equilibrium reaction conditions to favor the formation of HbO2. Once HbO2 exits the lungs to carry oxygen to other parts of the body, the O2 pressure in the lungs decreases, and the equilibrium no longer favors formation of HbO2, but rather the reverse reaction (Hb). Thus, the result of the change in conditions is the release of O2 into cells and the equilibrium now shifts to favor the reactants.

At the same time as O2 is being released into the cell, the pressure of carbon dioxide (CO2) is building up in the cell so CO2 binds to hemoglobin (Hb) in a reaction similar to that with O2 transport. When CO2 is carried to the lungs by hemoglobin, the cellular CO2 pressure is decreased and the reactants (Hb + CO2) are again favored and free CO2 is expelled to the atmosphere.

Le Châtelier's Principle is named for Henry Louis Le Châtelier who is best known for research that showed it is possible to predict what effect a change of conditions (such as temperature, pressure or concentration of reaction components) will have on a chemical reaction. Le Châtelier began his scientific career under the direction of the French mineralogist Ernest-Francois Mallard where he conducted studies on combustion as applied to mining safety. In 1901, in his own lab, he attempted to "fix" nitrogen and create ammonia by mixing nitrogen gas with hydrogen gas. Sadly, a tragic laboratory explosion killed his associate and caused him to abandon this work. Within five years of Le Châtelier abandoning his search for the synthesis of ammonia, Fritz Haber was able to create ammonia from hydrogen and nitrogen gas. His work became the basis for making explosive bombs used in World Wars I and II. Today, the Haber process is used in industry to manufacture ammonia, a key component in fertilizer that revolutionized industrial agriculture around the world. Ammonia-based fertilizer is responsible for sustaining one-third of the earth's population. Ammonia is produced through the following catalyzed reaction:

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

Under normal conditions, the yield of ammonia is only 10–20%. This is not enough to keep up with global demand of ammonia. Haber discovered that increasing the pressure on the gas mixture pushed the reaction in the forward direction to produce more ammonia and heat. By concurrently removing product from the system, the Haber process allows maximization of ammonia production.

Le Châtelier's principle is often used to manipulate the outcomes of reversible reactions to maximize yield. If a system in dynamic equilibrium is subjected to a stress such as changes in concentration, temperature, volume, and partial pressures, the concentration of products and reactants change to reestablish the equilibrium constant, K_c. Quantitatively, the direction the reaction shifts to re-establish equilibrium can be determined by comparing the value of the reaction quotient, Q to the value of the equilibrium constant, K_c.

Pre-Lab Questions

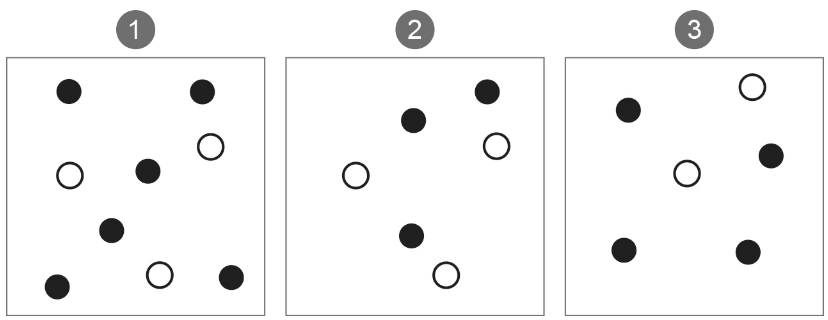
1. Consider the following equilibrium system:

$$A(aq) \rightleftharpoons B(aq)$$

   a. Write the equilibrium expression for this system.

   b. If the value of K_c is 2, what is the ratio of the [A] to the [B]?

   c. Which picture(s) represent the system at equilibrium?



   d. Is there a single set of data for [A] and [B] that satisfies the equilibrium state?

2. Consider the following system:

$$\underset{\text{Pink}}{Co(H_2O)_6^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons 6H_2O(l) + \underset{\text{Blue}}{CoCl_4^{2-}(aq)}$$

   a. Write the equilibrium expression for this system.

   b. The reaction quotient Q expresses the relative ratio of products to reactants at a given instant. Write the reaction quotient expression for this system.

3. How is an equilibrium constant different from a reaction quotient?

Materials and Equipment

Use the following materials to complete the initial investigation. For conducting an experiment of your own design, check with your teacher to see what materials and equipment are available.

- Data collection system
- Wireless temperature sensor
- Wireless colorimeter
- Cuvettes (3)
- Beakers (3), 50-mL
- Beakers (2), 250-mL
- Test tube rack
- Test tubes (2), 19 mm x 150 mm
- Distilled water, 2 mL
- Transfer pipettes, 10-mL
- Pipette bulb
- Kimwipes®
- 0.0080 M Iron(III) nitrate ($Fe(NO_3)_3$), 3.0 mL
- 0.0010 M Potassium thiocyanate (KSCN), 3.0 mL
- Cobalt(II) chloride ($CoCl_2$), 1.5 g
- 0.10 M Silver nitrate ($AgNO_3$), 2 mL
- 6.0 M Hydrochloric acid (HCl)
- Scoop
- Glass stirring rod
- Marking pen
- Water bath
- Ice
- Graduated cylinder, 10-mL
- Hot plate
-

Safety

Follow these important safety precautions in addition to your regular classroom procedures:

- Wear safety goggles and gloves at all times.
- Hydrochloric acid is corrosive. If you come in contact with it, flush the area with plenty of water. It can cause severe tissue burns.
- Cobalt solutions are moderately toxic and are body tissue irritants. If you come in contact with it, flush the area with plenty of water.
- Potassium thiocyanate is moderately toxic by ingestion. It emits toxic fumes of cyanide if heated strongly or comes in contact with concentrated acids. Handle only in well-ventilated area or fume hood.
- Silver nitrate solution will stain skin and clothing. Wear gloves when you work with it. If you do come in contact with it, flush the area with plenty of water. Compound is corrosive and causes chemical burns. Avoid contact with skin and eyes.
- Cobalt chloride is moderately toxic by ingestion. It has been classified as a *possible carcinogen* as fume or dust and a *possible reproductive hazard*.
- Wash hands thoroughly with soap and water before leaving laboratory.
- Review chemical handling and disposal instructions as directed by Material Safety Data Sheet.

Disposal

If your drain system is connected to a sanitary sewer system, the following instructions apply. Acid solutions may be rinsed down the drain with an excess of water. Excess potassium thiocyanate be disposed of with solid trash in a landfill (Flinn Suggested Disposal #26A). Silver nitrate is very expensive. It must be used with economy. Excess silver nitrate or reacted silver nitrate must be collected and submitted to your instructor for proper handling and disposal. Cobalt chloride in solid or solubilized form must also be submitted to your instructor for proper handling and disposal.

Initial Investigation

K_c as a constant

When iron(III) nitrate ($Fe(NO_3)_3$) and potassium thiocyanate (KSCN) solutions react, the following equilibrium is created:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

1. Start a new experiment from the data collection system on your Chromebook, computer or mobile device.
2. Connect the colorimeter sensor to the data collection system.
3. Obtain clean cuvettes for this experiment.
4. Fill one cuvette at least ¾ full with distilled water. This is the *blank*.
5. Wipe off the sides of the cuvette with a lint free tissue and only handle it by the top. Place the cuvette into the colorimeter and close the cover.
6. Calibrate the colorimeter with the distilled water sample (Reference Guide 013-15830A at pasco.com).
7. Place 3.0 mL of 0.0080 M iron(III) nitrate and 3 mL of 0.00100 M potassium thiocyanate into separate 50-mL beakers. Record the molarity, volume, and color of the solutions in Table 1 under "Before Reaction".
8. Pour the solutions into a third 50-mL beaker and swirl gently to mix thoroughly. Then pour the solution into a cuvette. Wipe off the sides of the cuvette with a lint free tissue and only handle it by the top. Record the color of the equilibrium mixture in Table 2 under "After Reaction".
9. Place the cuvette into the colorimeter, close the top, and start data collection.
10. Once the reading stops fluctuating, record the absorbance in the Data Table under "After Reaction".
11. Clean up all solutions and equipment according to your instructor's instructions.

Table 1: Before reaction

Parameter	Iron(III) nitrate	Potassium thiocyanate
Concentration		
Volume		
Color		

Table 2: After reaction

Parameter	Equilibrium Mixture
Color	
Absorbance	

12. Consider the equilibrium system above. When the two solutions were mixed in the beaker, which of the following calculations represent the initial concentration of Fe^{3+} ions in the mixture? Circle your answer.

$$3.00 \text{ mL} \times 0.0080 \text{ M} = 2.40 \times 10^{-5} \text{ M Fe}^{3+} \quad \text{OR} \quad \frac{3.00 \text{ mL} \times 0.0080 \text{ M}}{6.0 \text{ mL (total volume of solution)}} = 0.0040 \text{ M Fe}^{3+}$$

13. What is the initial concentration of SCN^- ions in the mixture?

14. Complete the following ICE table and equilibrium expression for this equilibrium system using the volumes and concentrations of the reactants in the Initial Investigation.

ICE table for calculating equilibrium concentrations

Condition	Fe^{3+}	+ SCN^-	$\rightleftharpoons$	$FeSCN^{2+}$
I (Initial concentration)				
C (Change)				
E (Equilibrium concentration)				

15. If K_c is not known, describe how you could use a spectrophotometer or a colorimeter to find x or $[FeSCN^{2+}]_{eq}$ in the lab. *Note: see Lab # 1.*

16. Determine the equilibrium constant. Assume (path length × molar absorptivity) for this system is 5900 M^{-1}.

17. How does the value of your equilibrium constant compare to the values of the other groups in your class?

Compare class results

Group	Equilibrium Constant
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	

❓ 18. Is your data similar to that of your classmates? What should you do if your sample deviates by a significant amount?

NOTE: Often the equilibrium constant is considered constant when it varies within a power of ten.

Advanced Investigation

Adding stress to a system in equilibrium

1. Obtain a test tube, test tube rack and marking pen.
2. Label the test tube "K" and place it in the test tube rack.
3. Add approximately 0.5 g of cobalt(II) chloride hexahydrate into the test tube. Then add 10 drops of distilled water using a pipette and mix the solution with a glass stirring rod. This solution will remain untouched during the lab and represents the original condition of the cobalt system:

$$\underset{\text{Pink}}{Co(H_2O)_6^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons 6H_2O(l) + \underset{\text{Blue}}{CoCl_4^{2-}(aq)}$$

4. Repeat the previous step for two more test tubes and label them "A" and "B". Record your initial observations for all of the solutions in Table 3 below.

   NOTE: Hold the test tubes over a white background to make your observations easier.

5. ❓ HCl will be added to test tubes A and B. Will this addition increase or decrease the concentration of chloride ions in the equilibrium system? Explain.
6. While wearing gloves, carefully add 6.0 M HCl, drop-wise, to test tube A until a noticeable change has occurred. Then add the 6.0 M HCl, drop-wise, to test tube B. Record your observations in Table 3.
7. ❓ AgNO3 will be added to test tube B and a precipitate should form. What reaction will occur to produce this precipitate? Write the net ionic reaction.
8. ❓ Should the formation of a precipitate increase or decrease the concentration of chloride ions in the equilibrium system? Explain.
9. While wearing gloves, add 0.1 M $AgNO_3$ drop-wise to test tube B until a color change is produced. You should notice a precipitate on the bottom of the test tube. Record your observations in the Table 3 below.

   NOTE: Don't discard the solutions. You will use the solution in test tube A in the following section.

Table 3: Results of adding stress

Test Tube	Color of the Solution		
	Initial Observations	After Addition of HCl	After Addition of $AgNO_3$
K			
A			

B			

10. In all test tubes, what color is the solution prior to the addition of the HCl or AgNO3?

11. Considering the appearance of the solution prior to the addition of HCl or AgNO3, are there more products or reactants present at equilibrium? Explain your reasoning.

12. After adding HCl, what observation indicated that the reaction shifted to re-establish equilibrium?

13. From the appearance of the solution in test tubes A and B after the addition of HCl, are there more products or reactants present at this re-established equilibrium position? Explain your reasoning.

14. Upon the addition of HCl, is the value of the reaction quotient Q greater than, less than or equal to value of K_c? Write the reaction quotient and use it to explain your answer.

15. Based on the observations above, does the reaction shift to the left, increasing the concentration of the reactants or to the right, increasing the concentration of products upon the addition of HCl?

16. Have the concentrations of $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$ increased or decreased after hydrochloric acid is added?

17. The addition of silver nitrate to the equilibrium system created a change to the system by removing Cl^- ions through a precipitation reaction. How does the new concentration of Cl^- in test tube B compare to the Cl^- concentration in test tube A?

    The concentration of Cl^- in test tube B after Ag^{2+} is added is _________ (<, > or =) the concentration of Cl^- in test tube A.

18. Upon the addition of $AgNO_3$, is the value of the reaction quotient greater than, less than or equal to value of K_c? Write the reaction quotient and use it to explain your answer.

19. Based on the observations above, does the reaction shift to the left (more reactants) or right (more products) upon the addition of $AgNO_3$?

20. Did the concentrations of $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$ increase or decrease after silver nitrate was added?

21. Consider the following equilibrium system:

$$\underset{\text{Pink}}{Co(H_2O)_6^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons 6H_2O(l) + \underset{\text{Blue}}{CoCl_4^{2-}(aq)}$$

Complete Table 4 to indicate how experimental stresses due to changing the amounts of substances in the solution shifted the equilibrium.

Table 4: Stress results due to changing reactant amounts

Stress	Resulting Color	Direction of Shift	Q vs K_c (<, >, =)
Removal of Cl^-			Q K_c

Addition of Cl^-			Q K_c

Predict in Table 5 how the following stresses in the amounts of substances would shift the equilibrium in the solution.

Table 5: Stress result prediction

Stresses That Could Cause This Shift	Resulting Color	Direction of Shift	Q vs K_c (<, >, =)
Removal of $Co(H_2O)_6^{2+}$			Q K_c
Addition of $Co(H_2O)_6^{2+}$			Q K_c
Removal of $CoCl_4^{2-}$			Q K_c
Addition of $CoCl_4^{2-}$			Q K_c

❓ 22. The solutions in test tube K, test tube A (after the addition of HCl) and test tube B (after the addition of AgNO3) are all at equilibrium. Which of the following must be true about the solutions in the three test tubes? Circle the correct answer.

i. They have the same amounts of reactants and products, same value of K_c, same color of equilibrium mixture.

ii. They have different amounts of reactants and products, different values of K_c, different color of equilibrium mixture.

iii. They have the same amounts of reactants and products, same value of K_c, different color of equilibrium mixture.

iv. They have different amounts of reactants and products, same value of K_c, different color of equilibrium mixture.

Endothermic or exothermic

1. Connect the wireless temperate sensor to your data collection system.

2. Set up a warm water bath using a hot plate and a 250-mL beaker, and a cold water bath using ice water and a 250-mL beaker.

❓ 3. What lab observation will confirm that the reaction studied in is endothermic? Why?

❓ 4. What lab observation will confirm that the reaction is exothermic? Why?

5. Place test tube A and the temperature probe into the hot water bath for three minutes and then into the cold water bath for 3 minutes. Record your observations for each situation in the Data Table below.

6. Clean up all solutions and equipment according to your instructor's instructions.

Results of hot and cold stress

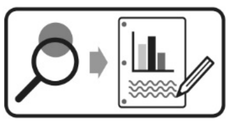
Condition	Resulting Color
After 3 minutes in hot water	Blue
After 3 minutes in ice water	Pink

7. Is the cobalt equilibrium system endothermic or exothermic? Why? Provide evidence from your lab that supports your claim.

8. Add energy to the appropriate side of the equation below.

$$\_\_\_\_\_\_\_\_\_\_ \quad Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons 6H_2O(l) + CoCl_4^{2-}(aq) \quad \_\_\_\_\_\_\_\_\_\_$$

Extended Inquiry Investigation



Determining a constant equilibrium constant

With your group, design an experiment using the iron(III) thiocyanate equilibrium system to show that K_c remains constant when temperature is constant, within experimental error, despite different stresses added to the system. Record your procedure below.

While designing your lab, keep the following items in mind:

- Change only one variable when creating a stress to the system.
- Calibrate the colorimeter prior to use and select 500 nm (blue) to measure absorbance.
- Excess SCN^- produces colored side products; keep SCN^- as the limiting reactant at 0.0010 M.
- Keep all iron solutions at low concentrations (0.0080 M or lower) so as to not overload the colorimeter.
- You may dilute solutions further as needed, using distilled water.

Synthesis Question

1. Does the absorbance you measured in the Initial Investigation come only from the $FeSCN^{2+}$ ion? Explain your answer.

2. The Fe^{3+} ion can react with three SCN^- ions according to the following equilibrium equations to form $Fe(SCN)^{2+}$ and $Fe(SCN)_3$. These products are also red.

$$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+} \qquad \text{(SQ1)}$$

$$FeSCN^{2+} + SCN^- \rightleftharpoons Fe(SCN)^{2+} \qquad \text{(SQ2)}$$

$$Fe(SCN)^{2+} + SCN^- \rightleftharpoons Fe(SCN)_3 \qquad \text{(SQ3)}$$

In light of these reactions, propose an explanation as to why this experiment uses a large excess of Fe^{3+} ions.

AP® Chemistry Review Question

Reaction	Equation	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}
X	$C(s) + H_2O \rightleftharpoons CO(g) + H_2(g)$	+131 kJ mol^{-1}	+134 J mol^{-1}K^{-1}	+91 kJ mol^{-1}
Y	$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$	+41 kJ mol-1	+42 J mol-1K-1	+29 kJ mol-1
Z	$2\ CO(g) \rightleftharpoons C(s) + CO_2(g)$	?	?	?

(a) For reaction X, write the expression for the equilibrium constant, K_p

(b) For reaction X, will the equilibrium constant, K_p, increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.