

Applications of LeChâtelier's Principle AP* Chemistry Big Idea 6, Investigation 13 An Advanced Inquiry Lab

Introduction

Not all chemical reactions proceed to completion, that is, to give 100% yield of products. In fact, most chemical reactions are reversible, meaning they can go both ways. When the forward rate and reverse rate are equal, the system is at equilibrium. What happens when the equilibrium system is disturbed? Is there a way to predict and explain the effects of the disturbances?

• Exothermic and endothermic reactions

· Acid-base reactions

Concepts

- Chemical equilibrium
- LeChâtelier's principle
- Complex-ion reactions

Background

In a closed system, any reversible reaction will eventually reach a point where the amounts of reactants and products do not change. This occurs when the rate of the forward reaction equals the rate of the reverse reaction. At this point, the system is said to be in a dynamic balance or dynamic equilibrium—the reactions are occurring but no observable changes can be measured. *Chemical equilibrium* can therefore be defined as the state where the concentrations of reactants and products remain constant with time. This does not mean the concentrations of reactants and products are equal. The forward and reverse reactions create an equal balance of opposing rates.

These ideas can be expressed mathematically in the form of the equilibrium constant. Consider the following general equation for a reversible chemical reaction:

$$aA + bB \rightarrow cC + dD$$
 Equation 1

The *equilibrium constant*, K_{eq} , for this general reaction is given by Equation 2, where the square brackets refer to the molar concentrations of the reactants and products at equilibrium.

$$K_{\rm eq} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \qquad Equation 2$$

The equilibrium constant gets its name from the fact that for any reversible chemical reaction, the value of K_{eq} is a constant at a particular temperature. The concentrations of reactants and products at equilibrium vary, depending on the initial amounts of materials present. The special ratio of reactants and products described by K_{eq} is always the same, however, as long as the system has reached equilibrium and the temperature does not change.

Any change that is made to a system at equilibrium may be considered a stress—this includes adding or removing reagents, or changing the temperature or pressure. The rates of the forward and reverse reactions will change as a result until equilibrium is again extablished. Henri LeChâtelier published many studies of equilibrium systems. *LeChâtelier's principle* predicts how equilibrium can be restored:

"If an equilibrium system is subjected to a stress, the system will react in such a way as to reduce the stress."

LeChâtelier's principle is a qualitative approach to predicting and interpreting shifts in equilibrium systems. A quantitative approach utilizes the K_{eq} of the reaction and the reaction quotient, Q. The reaction quotient is a snapshot of the concentrations of reactants and products at a particular time. Q is calculated using the same formula as K_{eq} (Equation 2). Depending on the instanta-

- Precipitation reactions
- Gas solubility

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neous concentrations of reactants and products, Q and K_{eq} may differ or be the same. If Q and K_{eq} differ, the system is not at equilibrium and the rates of the forward and reverse reactions will change until $Q = K_{eq}$.

The effect of concentration on a system at equilibrium depends on whether the change in concentration is affecting a reactant or product species. In general when the concentration of a species is increased, the system will shift and increase the rate of the reaction that decreases the concentration of that species. If the concentration of a species is decreased, the system will shift and increase the rate of the reaction that increases the concentration of the species. For example, if the concentration of a reactant is increased, the rate of the forward reaction will increase because the forward reaction decreases the concentration of reactants.

The equilibrium constant for a reaction depends on or changes with temperature. The observable effect of temperature on a system at equilibrium depends on whether the reaction is endothermic (absorbs heat) or exothermic (produces heat). If a reaction is endothermic, heat appears on the reactant side in the chemical equation. Increasing the temperature of an endothermic reaction shifts the equilibrium in the forward direction, absorbing some of the excess energy and making more products. The opposite effect is observed for exothermic reactions. In the case of an exothermic reaction, heat appears on the product side in the chemical equation. Increasing the temperature of an exothermic reaction shifts the equilibrium in the reverse directions.

The effect of pressure on a gaseous system at equilibrium depends on the partial pressures of the gases and the stoichiometry of the reaction. A change in pressure of a gaseous system has the effect of altering the partial pressures of the gases, and is typically accomplished through changes in volume. An increase in volume results in an overall decrease in pressure. The system will respond in a way as to produce more gas molecules to fill the space. Thus, the reaction will shift towards the side with the greater number of moles of gas. If the volume of the container is decreased, the overall pressure will increase and the system will shift in the direction of the side with fewer number of moles of gas in order to decrease the pressure.

Experiment Overview

In this advanced inquiry kit, six equilibrium systems will be investigated to gain a deeper understanding of equilibrium and LeChâtelier's principle. An introductory activity guides you through the equilibrium achieved between iron(III) nitrate and potassium thiocyanate. Deliberate stresses are added to the system to cause the equilibrium to shift and the color to change. The procedure provides a model for guided-inquiry investigation of five additional equilibrium systems, which are set up as lab stations. The inquiry activities include an acid–base indicator, copper complex ion, cobalt complex ion, solubility of carbon dioxide, and the solubility of magnesium hydroxide. The key to success in this lab is detailed notes and observations. The activity may be extended to create a rainbow-colored display using the equilibrium systems—see the *Opportunities for Inquiry* section.

Pre-Lab Questions

Iodine (I₂) is only sparingly soluble in water (Equation 3). In the presence of potassium iodide, a source of iodide (I[−]) ions, iodine reacts to form triiodide (I₃[−]) ions (Equation 4).

$$I_2(s) \rightleftharpoons I_2(aq)$$
 Equation 3

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$
 Equation 4

Use LeChâtelier's principle to explain why the solubility of iodine in water increases as the concentration of potassium iodide increases.

2. Although both N_2 and O_2 are naturally present in the air we breathe, high levels of NO and NO₂ in the atmosphere occur mainly in regions with large automobile or power plant emissions. The equilibrium constant for the reaction of N_2 and O_2 to give NO is very small. The reaction is, however, highly endothermic, with a heat of reaction equal to +180 kJ (Equation 5).

$$N_2(g) + O_2(g) + 180 \text{ kJ} \rightleftharpoons 2NO(g)$$
 Equation 5

- *a.* Use LeChâtelier's principle to explain why the concentration of NO at equilibrium increases when the reaction takes place at higher temperatures.
- *b.* Use LeChâtelier's principle to predict whether the concentration of NO at equilibrium should increase when the reaction takes place at high pressures.

Materials*

Iron(III) nitrate solution, Fe(NO ₃) ₃ , 0.2 M, 5 drops	Ice		
Potassium nitrate, KNO ₃ , 0.5 g	Labeling or marking pen		
Potassium thiocyanate, KSCN, 0.5 g	Petri dish, disposable		
Potassium thiocyanate solution, KSCN, 0.002 M, 20 mL	Pipet, Beral-type, graduated		
Sodium phosphate, monobasic, NaH ₂ PO ₄ ·H ₂ O, 0.5 g	Spatulas, 2		
Water, distilled or deionized	Test tubes, 2		
Water, tap	Test tube holder		
Beakers, 250-mL, 3	Test tube rack		
Graduated cylinder, 50-mL	Thermometer, digital		
Hot plate	Wash bottle		

*Materials are shown only for the Introductory Activity. See the individual activities in the Guided-Inquiry Design and Procedure for the materials required for each lab station activity.

Safety Precautions

Cobalt chloride solution is a flammable liquid and moderately toxic by ingestion. Iron(III) nitrate solution may be a skin and body tissue irritant. Concentrated ammonia (ammonium hydroxide) solution is severely corrosive and toxic by inhalation and ingestion. Work with concentrated ammonium hydroxide only in a fume hood. Hydrochloric acid solution is toxic by ingestion and inhalation and is corrosive to skin and eyes. Dilute hydrochloric acid and sodium hydroxide solutions are skin and eye irritants. Potassium thiocyanate is toxic by ingestion and emits a toxic gas if strongly heated—do not heat this solution and do not add acid. Sodium phosphate monobasic is moderately toxic by ingestion. Avoid contact of all chemicals with eyes and skin. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the laboratory. Please follow all laboratory safety guidelines.

Introductory Activity

Complex-Ion Equilibrium Reaction between Iron(III) Nitrate and Potassium Thiocyanate

Part A. Effect of Concentration

- 1. Prepare hot-water and ice-water baths: Fill a 250-mL beaker half full with tap water. Place it on a hot plate and heat to 65–70 °C for use in Part B. In a second 250-mL beaker, add water and ice to prepare an ice-water bath for use in Part B.
- 2. Using a 50-mL graduated cylinder, measure 20 mL of potassium thiocyanate solution and pour the solution into a Petri dish. Record the initial color and all color changes that occur throughout the investigation (Parts A and B).
- 3. Add 3 drops of iron(III) nitrate solution to different spots in the Petri dish.
- 4. Swirl the solution until the color is uniform throughout.
- 5. Add ½ pea-size amount of potassium thiocyanate crystals in one spot. Wait 30 seconds and record any further changes to the solution. Swirl the solution to dissolve the crystals until the solution color becomes uniform throughout.
- 6. Add ½ pea-size amount of potassium nitrate crystals in one spot. Wait 30 seconds and record any further changes to the solution. Swirl the solution to dissolve the crystals until the solution color becomes uniform throughout.
- 7. Add ¹/₄ pea-size amount of sodium phosphate monobasic crystals in one spot. Wait about 60 seconds and observe any changes to the solution.
- 8. Swirl the solution to dissolve the crystals. Record the solution color.
- 9. Add one drop of iron(III) nitrate solution in one spot off to the side. Do not stir. Record any color change.
- 10. Add a pea-size amount of potassium thiocyanate crystals in a different spot. Wait about 30 seconds and record any changes to the solution around the crystals.
- 11. Swirl the solution until it is uniform and keep the solution for use in Part B-Effect of Temperature.

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Part B. Effect of Temperature

- 12. Label two clean, dry test tubes A and B, and place them in a test tube rack.
- 13. Using a graduated Beral-type pipet, add about 10 mL of the complex-ion solution from Part A to each test tube.
- 14. Test tube A will be the control for the experiment.
- 15. Place test tube B in the ice-water bath. After 3–5 minutes, remove the test tube from the ice bath using a test tube holder and compare the color of the solution to the control in test tube A. Record the color comparison.
- 16. Using a test tube holder, place test tube B in a hot-water bath at 65–70 °C. After 2–3 minutes, remove the test tube from the hot-water bath and compare the color of the solution to the control in test tube A. Record the color comparison.
- 17. Empty the contents of both test tubes and the Petri dish into the wash beaker provided. Rinse the glassware with distilled water.

Analyze the Results

Form a working group with other students and discuss the following questions.

- 1. Write the chemical equation for the reversible reaction of iron(III) ions with thiocyanate ions. Use the information in your data table to write the color of each reactant and product underneath its formula.
- 2. How did the color of the solution change when additional reactant—either $Fe(NO_3)_3$ or KSCN—was added? Explain the observed color changes by discussing the rates of the forward and reverse reactions, as well as the concentrations of products and reactants.
- 3. In step 6, KNO₃ was added to the solution. How did the color of the solution change in Part A when KNO₃ was added? Explain this observation.
- 4. In step 7, $H_2PO_4^-$ ions combined with iron(III) ions and removed them from solution. How did the color of the solution change in Part A when NaH₂PO₄ was added? Explain the observed color change by discussing the rates of the forward and reverse reactions, as well as the concentrations of the products and reactants.
- 5. How did the color of the solution change when Fe³⁺ ions were added in step 9 and SCN⁻ ions were added in step 10? How do these observations demonstrate that both reactant ions are present at equilibrium?
- 6. How did the color of the solution change in Part B when it was cooled (step 15) or heated (step 16)? How do these results demonstrate that the reaction does indeed occur in both the forward and reverse directions?
- 7. Based on the color changes observed when the solution was cooled and heated, is the reaction between iron(III) ions and thiocyanate ions exothermic or endothermic? Write the *Heat* term on the correct side of the equation from Question 1.

Guided-Inquiry Design and Procedure

Using the procedure in the *Introductory Activity* as a guide, investigate the following chemical equilibrium systems A–E. Materials will be provided for each activity—investigations are limited to those materials. A short procedure is provided to set up the initial conditions for each equilibrium system. For each activity, design a testing procedure to determine the color and appearance of both reactants and products and to investigate the effects of concentration, temperature and pressure as warranted.

Activity A. Acid–Base Indicator Equilibrium

An indicator is a dye that can gain or lose hydrogen ions to form substances that have different colors. For simplicity, the uncharged indicator molecule may be represented as HIn, and the anionic indicator molecule after the loss of a hydrogen ion may be written as In^- . Bromthymol blue will be used as the indicator in this activity.

Materials

Bromthymol blue indicator solution, 0.04%, 1 mL	Graduated cylinder, 10-mL
Hydrochloric acid solution, 0.1 M, HCl, 2 mL	Stirring rod
Sodium hydroxide solution, NaOH, 0.1 M, 2 mL	Test tubes and test tube rack
Water, distilled or deionized	Wash bottle

Initial Conditions

Measure approximately 2 mL of distilled water and add to a test tube. Add 5 drops of 0.04% bromthymol blue. Swirl gently.

Activity B. Formation of a Copper Complex Ion

An equilibrium system can be formed in a solution of copper(II) ions and ammonia. A copper–ammonia complex ion forms when the amount of ammonia in solution reaches a high enough concentration. Please note that ammonia (NH_3) is provided in the form of a concentrated solution in water, which is usually referred to as ammonium hydroxide (NH_4OH). These two names are interchangeable. The reaction of copper(II) ions with this solution should be written for convenience as $Cu^{2+} + NH_3$.

Materials

Ammonium hydroxide solution (conc.), NH_4OH , 14.8 M, 2 mL	Pipets, Beral-type, graduated, 2
Copper(II) sulfate solution, CuSO ₄ , 0.2 M, 5 mL	Stirring rod
Hydrochloric acid solution, HCl, 1 M, 1 mL	Test tube
Water, distilled or deionized	Test tube rack
Graduated cylinder, 10-mL	Wash bottle

Labeling or marking pen

Initial Conditions

Add approximately 5 mL of 0.2 M CuSO_4 to a test tube. In a fume hood, add the concentrated ammonium hydroxide solution dropwise.

Activity C. Formation of Cobalt Complex Ions

When cobalt(II) chloride hexahydrate (CoCl₂·6H₂O) is dissolved in ethyl alcohol, three different solute species are present: Co^{2+} cations, Cl^- anions, and water molecules. These can react to form two different complex ions: $Co(H_2O)_6^{2+}$, where the cobalt ion is surrounded by six water molecules, and $CoCl_4^{2-}$, in which the metal ion is surrounded by four chloride ions.

Materials

Calcium chloride, CaCl ₂ , 2–3 grains	Pipets, Beral-type, graduated, 3
Cobalt chloride solution, CoCl ₂ , 1% in alcohol, 6 mL	Spatula
Hydrochloric acid solution, HCl, 6 M, 1 mL	Stirring rod
Silver nitrate solution, AgNO ₃ , 0.1 M, 1 mL	Test tubes, 3
Water, distilled or deionized	Test tube holder
Beakers, 250-mL, 2	Test tube rack
Hot plate	Thermometer
Ice	Wash bottle
Labeling or marking pen	

Initial Conditions

Label three test tubes A–C and place them in a test tube rack. Using a graduated, Beral-type pipet, add about 2 mL of the cobalt chloride solution to each test tube A–C. *Note:* The exact volume is not important, but try to keep the volume of the solution approximately equal in each test tube.

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Activity D. Solubility of Carbon Dioxide

When carbon dioxide dissolves in water, it forms a weakly acidic solution due to the following reversible reaction:

$$2CO_2(g) + H_2O(l) \rightleftharpoons CO_2(aq) + H^+(aq) + HCO_3^-(aq) \qquad Equation 6$$

The hydrogen ion concentration in solution depends on the amount of dissolved carbon dioxide. According to Henry's law, the amount of gas dissolved in solution is proportional to the pressure of the gas above the solution.

Materials

Bromcresol green indicator solution, 0.04%, 2 mL	Graduated cylinder, 10-mL
Seltzer water, 10 mL	Syringe, 30-mL
Beaker, 50-mL	Syringe tip cap (septum)
Color chart for bromcresol green	Wash bottle

Initial Conditions

Obtain approximately 10 mL of fresh seltzer water in a 50-mL beaker. Add about 20 drops of 0.04% bromcresol green indicator. Swirl to mix the solution. Draw up about 10 mL of the seltzer/indicator solution into a 30-mL syringe. Seal the syringe by pushing a tip cap firmly onto its open end.

Activity E. Solubility of Magnesium Hydroxide

The active ingredient in milk of magnesia, an over-the-counter antacid remedy, is magnesium hydroxide. Magnesium hydroxide forms a suspension in water due to its low solubility—0.0009 g/100 mL in cold water and 0.004 g/100 mL in hot water.

Materials

Hydrochloric acid solution, HCl, 3 M, 20 mL	Graduated cylinder, 10-mL
Milk of magnesia, 10 mL	Magnetic stir bar
Universal indicator solution, 5-10 drops	Magnetic stir plate (or stirring rod)
Water, distilled or deionized	Pipet, Beral-type, graduated
Beaker, 250-mL	Wash bottle

Initial Conditions

Obtain 10 mL of the milk of magnesia solution. Add this to a 250-mL beaker. Add approximately 50 mL of distilled water. Add 5–10 drops of universal indicator solution. Swirl to mix the solution.

Analyze the Results for Activities A-E

Form a working group with other students to review and summarize each equilibrium system studied. Devise a way to clearly display the chemical reaction(s), procedural steps, observations and explanations for any and all color changes for each equilibrium system. The results for all indicators should include the pH range and color for each form of the indicator (HIn and In⁻).

Opportunities for Inquiry

Equilibrium Rainbow Display

The equilibrium systems studied in this activity lend themselves toward use in colorful displays. In small groups or as a cooperative class activity, plan how a rainbow-colored display can be made using the equilibrium systems studied in this activity. Develop procedures to incorporate each system into the display.

AP Chemistry Review Questions

Integrating Content, Inquiry and Reasoning

When a chemical is manufactured, chemists and chemical engineers choose conditions that will favor the production of the desired product as much as possible. In the early 20th century, Fritz Haber developed a process for the large-scale production of ammonia from its constituent elements. Some of his results are summarized in the chart below.



Percentage Ammonia at Equilibrium*

*Each experiment began with a stoichiometric mixture of H_2 and N_2 .

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1. Write the balanced chemical equation, including the heat term, for the synthesis of ammonia from its constituent elements.

2. Based on the results above, explain the effect of temperature on the equilibrium position of the reaction.

3. Explain the effect of pressure on the equilibrium position of the reaction.

4. The optimal conditions to synthesize ammonia are high pressures and low temperatures. However, each factor comes with a drawback: high pressures require strong pipework and hardware, and at low temperatures the reaction is slow. In order to get high yields of ammonia at lower pressures and higher temperatures, ammonia is removed from the system as it is formed. Use LeChâtelier's principle to explain why this is effective.

Teacher's Notes

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Part III. Sample Data, Results, and Analysis

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•	Sample Data and Results for Guided-Inquiry Activities A–E
•	Answers to AP Chemistry Review Questions

Safety Precautions

Cobalt chloride solution is a flammable liquid and moderately toxic by ingestion. Iron(III) nitrate solution may be a skin and body tissue irritant. Concentrated ammonia (ammonium hydroxide) solution is severely corrosive and toxic by inhalation and ingestion. Work with concentrated ammonium hydroxide only in a fume hood. Hydrochloric acid solution is toxic by ingestion and inhalation and is corrosive to skin and eyes. Keep sodium carbonate and citric acid on hand to neutralize any acid or base spills, respectively, in the lab. Dilute hydrochloric acid and sodium hydroxide solutions are skin and eye irritants. Potassium thiocyanate is toxic by ingestion and emits a toxic gas if strongly heated—do not heat this solution and do not add acid. Sodium phosphate monobasic is moderately toxic by ingestion. Avoid contact of all chemicals with eyes and skin. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Remind students to wash their hands thoroughly with soap and water before leaving the laboratory. Please review current Material Safety Data Sheets for additional safety, handling, and disposal information.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures, and review all federal, state and local regulations that may apply, before proceeding. Cobalt-containing solutions from Activity C may be combined and handled according to Flinn Suggested Disposal Method #27f. The end solution of Activity E may be slightly acidic and may be neutralized according to Flinn Suggested Disposal Method #24b. The copper–ammonia solutions from Activity B may be combined and handled according to Flinn Suggested Disposal Method #10. Solutions from the *Introductory Activity* and Activities A and D may be rinsed down the drain with excess water according to Flinn Suggested Disposal Method #26b.

Part I. Lab Preparation

	Introductory Activity‡	Guided-Inquiry Lab Stations*				
Master Materials List (for 24 students working in pairs)	Iron(III) Complex Ion	Acid–Base Indicator Equilibrium	Formation of a Copper Complex Ion	Formation of Cobalt Complex Ions	Solubility of Carbon Dioxide	Solubility of Magnesium Hydroxide
Chemicals Included in Kit						
Ammonium hydroxide solution, concentrated, NH_4OH , 14.8 M			30 mL			
Bromcresol green indicator solution, 0.04%					35 mL	
Bromthymol blue indicator solution, 0.04%		20 mL				
Calcium chloride, anhydrous, CaCl ₂				5 g		
Cobalt chloride solution, CoCl ₂ , 1% in alcohol				100 mL		
Copper(II) sulfate solution, CuSO ₄ , 0.2 M			100 mL			
Hydrochloric acid solution, HCl, 0.1 M		25 mL				
Hydrochloric acid solution, HCl, 1 M			15 mL			
Hydrochloric acid solution, HCl, 3 M						250 mL
Hydrochloric acid solution, HCl, 6 M				20 mL		
Iron(III) nitrate solution, Fe(NO ₃) ₃ , 0.2 M	125 mL					
Milk of magnesia solution						150 mL
Potassium nitrate, KNO ₃	15 g					
Potassium thiocyanate, KSCN	10 g					
Potassium thiocyanate solution, KSCN, 0.10 M**	30 mL					
Seltzer water					240 mL	
Silver nitrate solution, AgNO ₃ , 0.1 M				30 mL		
Sodium hydroxide solution, NaOH, 0.1 M		30 mL				
Sodium phosphate, monobasic, NaH ₂ PO ₄ ·H ₂ O	15 g					
Universal indicator solution						20 mL
Materials Included in Kit	Introductory Activity‡					
Bromcresol green color chart					1	
Petri dishes, disposable	12					
Pipets, Beral-type, graduated	12		4	6		2
Syringes, 35 mL					2	
Syringe tip caps (septum)					2	

‡Includes enough materials for 12 groups of students.
*Based on two workstations for each activity.
**Dilute for use in the *Introductory Activity*. See *Pre-Lab Preparation*.

Continued on next page.

Additional Materials Required	Introductory Activity‡	Guided-Inquiry Lab Stations*				
Beakers, 250-mL	24			4		2
Beakers, 50-mL					2	
Graduated cylinders, 10-mL		2	2		2	2
Graduated cylinders, 25- or 50-mL	12					
Hot plates	6			2		
Ice	Yes			Yes		
Labeling or marking pens			2	2		
Magnetic stir plates (or stirring rods)						2
Magnetic stir bars						2
Spatula	24			2		
Stirring rods		2	2	2		2
Test tubes	24	2	2	6		
Test tube holders	12			2		
Test tube racks	12	2	2	2		
Thermometers, digital	Yes			Yes		
Wash bottles	Yes	Yes	Yes	Yes	Yes	Yes
Water, distilled or deionized	Yes	Yes	Yes	Yes		Yes

‡Includes enough materials for 12 groups of students.

*Based on two workstations for each activity.

Additional Materials Required (for *Pre-Lab Preparation*)

Water, distilled or deionized Graduated cylinder, 10-mL Volumetric flask, 500-mL Wash bottle

Time Required

This laboratory activity can be completed in two 50-minute class periods. It is important to allow time between the *Introductory Activity* and the *Guided-Inquiry Activity* for students to discuss and design the guided-inquiry procedures. Also, all student-designed procedures must be approved for safety before students are allowed to implement them in the lab. *Pre-Lab Questions* may be completed before lab begins the first day.

Pre-Lab Preparation

To prepare potassium thiocyanate, KSCN, 0.002 M, 500 mL for the Introductory Activity:

- 1. Measure 10.0 mL of 0.10 M KSCN solution in a 10-mL graduated cylinder.
- 2. Fill a 500-mL volumetric flask one-third to one-half full with distilled or deionized water.
- 3. Pour the 10.0 mL of KSCN into the flask. Swirl to mix.
- 4. Fill the flask to the mark with distilled water.
- 5. Stopper the flask and mix well by inverting several times prior to dispensing.

Part II. Teacher Guidance

Alignment to AP Chemistry Curriculum Framework

Enduring Understandings and Essential Knowledge

Chemical and physical transformations may be observed in several ways and typically involve a change in energy. (3C)

3C2: Net changes in energy for a chemical reaction can be endothermic or exothermic.

Chemical equilibrium is a dynamic, reversible state in which rates of opposing processes are equal. (6A)

- 6A1: In many classes of reaction, it is important to consider both the forward and reverse reactions.
- 6A3: When a system is at equilibrium, all macroscopic variables, such as concentrations, partial pressures, and temperature, do not change over time. Equilibrium results from an equality between the rates of the forward and reverse reactions, at which point Q = K.

Systems at equilibrium are responsive to external perturbations, with the response leading to a change in the composition of the system. (6B)

- 6B1: Systems at equilibrium respond to disturbances by partially countering the effect of the disturbance (LeChâtelier's principle).
- 6B2: A disturbance to a system at equilibrium causes Q to differ from K, thereby taking the system out of the original equilibrium state. The system responds by bringing Q back into agreement with K, thereby establishing a new equilibrium state.

Chemical equilibrium plays an important role in acid-base chemistry and in solubility. (6C)

- 6C1: Chemical equilibrium reasoning can be used to describe the proton-transfer reactions of acid-base chemistry.
- 6C3: The solubility of a substance can be understood in terms of chemical equilibrium.

Learning Objectives

- 3.11 The student is able to interpret observations regarding macroscopic energy changes associated with a reaction or process to generate a relevant symbolic and/or graphical representation of the energy changes.
- 6.3 The student can connect kinetics to equilibrium by using reasoning about equilibrium, such as LeChâtelier's principle, to infer the relative rates of the forward and reverse reactions.
- 6.8 The student is able to use LeChâtelier's principle to predict the direction of the shift resulting from various possible stresses on a system at chemical equilibrium.
- 6.9 The student is able to use LeChâtelier's principle to design a set of conditions that will optimize a desired outcome, such as product yield.

Science Practices

- 1.4 The student can use representations and models to analyze situations or solve problems qualitatively and quantitatively.
- 1.5 The student can re-express key elements of natural phenomena across multiple representations in the domain.
- 4.2 The student can design a plan for collecting data to answer a particular scientific question.
- 4.4 The student can evaluate sources of data to answer a particular scientific question.
- 5.1 The student can analyze data to identify patterns or relationships.
- 5.2 The student can refine observations and measurements based on data analysis.
- 5.3 The student can evaluate evidence provided by data sets in relation to a particular scientific question.
- 6.4 The student can make claims and predictions about natural phenomena based on scientific theories and models.
- 7.2 The student can connect concepts in and across domain(s) to generalize or extrapolate in and/or across enduring understandings and/or big ideas.

Lab Hints

- The Introductory Activity contains enough materials for 12 groups of students to work at the same time.
- The guided-inquiry activities contain enough materials for two lab stations to be set up throughout the lab. For best results, set up two stations for each activity at the same lab table. This will allow two groups of students to work on each activity. An optional sixth activity can be set up following the instructions in the *Teaching Tips*. The activities may be completed in any order and students should only need 10 minutes per station.
- Activity B must be completed in a fume hood. Concentrated ammonia vapors are extremely irritating, especially to the eyes.

Teaching Tips

- An optional sixth activity station may be used to model equilibrium using small objects such as pennies, paper clips or plastic discs. Student groups may be given 60 objects with which to start. In the reaction, one-third of the total reactants are converted into products; one-fourth of all products are converted into reactants. After each round of reaction, students should count the total number of reactants and products. These amounts can be graphed to model equilibrium amounts of reactants and products. Students can investigate how the amounts of reactants and products change if reactants or products are added at equilibrium, if the starting amount(s) is different, and if reactants or products are removed from equilibrium.
- In Activity B, the solid formed initially in the reaction between copper(II) ions and ammonia is copper(II) hydroxide. The concentrated ammonia solution produces hydroxide ions that bond with the Cu²⁺ ions as shown in the following equation: Cu²⁺(aq) + 2OH⁻(aq) → Cu(OH)₂(s). Copper(II) hydroxide is insoluble. Adding excess ammonia is necessary to displace the OH⁻ ions to create the dark blue complex ion, [Cu(NH₃)₄]²⁺.
- In Activity C, the most common misconception students make regarding the shift in equilibrium when water is added is that the concentration of water increases. The concentration of water is constant around 55 M, so the addition of more water does not affect its concentration. However, the addition of water dilutes the other species in the solution. The concentrations of the chloride ion (Cl⁻), $[CoCl_4]^{2-}$ ion, and $[Co(H_2O)_6]^{2+}$ ion all decrease. The rates of the forward and reverse reactions are affected, but not equally. The best way to explain the shift in equilibrium is through a comparison between Q, the reaction quotient, and K_{eq} , the equilibrium constant.
- The activity of hemoglobin, the main oxygen-binding protein in red blood cells, illustrates an application of complex-ion equilibrium. Hemoglobin (Hb) contains four iron(II) ions that bind to oxygen molecules. This is a reversible reaction, since the hemoglobin must be able to release the oxygen molecules in cells and body tissues (Equation 7).

$$Hb(aq) + O_2(g) \rightleftharpoons HbO_2(aq)$$
 Equation 7

At high altitudes, where the concentration of oxygen is lower, the equilibrium shown in Equation 7 is shifted in the reverse direction. Less bound oxygen is therefore available in the bloodstream to be transported to the cells. The physical symptoms of the reduced oxygen availability are fatigue and dizziness. The human body, however, is marvelous in its adaptability. People who live or train at high altitudes compensate for the reduced oxygen supply by synthesizing more red blood cells. Increasing the concentration of hemoglobin increases the rate of the forward reaction and thus increases the amount of available oxygen.

- Most textbooks use LeChâtelier's Principle to predict and explain the effects of both concentration and temperature. Strictly speaking, however, the two effects are different, in that changes in concentration affect the position of equilibrium, while changes in temperature affect the value of the equilibrium constant. At a given temperature, there are an infinite number of possible equilibrium positions, but only a single equilibrium constant value.
- The effect of acid on the solubility equilibrium of magnesium hydroxide can be used to illustrate the action and effectiveness of Milk of Magnesia, a popular antacid. Milk of Magnesia is a suspension of solid magnesium hydroxide in water. The suspension dissolves as required in the stomach to combat excess acidity.
- The equilibrium constant, K_{eq} , of the iron(III) thiocyanate complex ion (FeSCN²⁺) can be determined through colorimetric or spectrophotometric analysis. The Flinn Scientific student laboratory kit, *Determination of* K_{eq} for FeSCN²⁺ (Catalog No. AP6352), may be used to reinforce LeChâtelier's principle as well as show the change in equilibrium position based on the concentration of the products and reactants.

Part III. Sample Data, Results, and Analysis

Answers to Pre-Lab Questions (Student answers will vary.)

Iodine (I₂) is only sparingly soluble in water (Equation 3). In the presence of potassium iodide, a source of iodide (I⁻) ions, iodine reacts to form triiodide (I₃⁻) ions (Equation 4).

$$I_2(s) \rightleftharpoons I_2(aq)$$
 Equation 3

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$
 Equation 4

Use LeChâtelier's principle to explain why the solubility of iodine in water increases as the concentration of potassium iodide increases.

Increasing the concentration of the iodide ions creates a "stress." According to LeChâtelier's principle, the system will react in a way that tends to reduce the stress. The reaction shown in Equation 4 will shift in the forward direction, to make more triiodide ions and consume some of the added iodide with aqueous iodine. This, in turn, also causes more solid iodine to dissolve in the solution. **Note to teachers:** Not all of the excess reagent is consumed when the equilibrium shifts. This is a common misconception. The equilibrium is re-established with higher concentrations of all substances in solution.

2. Although both N_2 and O_2 are naturally present in the air we breathe, high levels of NO and NO_2 in the atmosphere occur mainly in regions with large automobile or power plant emissions. The equilibrium constant for the reaction of N_2 and O_2 to give NO is very small. The reaction is, however, highly endothermic, with a heat of reaction equal to +180 kJ (Equation 5).

$$N_2(g) + O_2(g) + 180 \text{ kJ} \rightleftharpoons 2NO(g)$$
 Equation 5

a. Use LeChâtelier's principle to explain why the concentration of NO at equilibrium increases when the reaction takes place at higher temperatures.

According to LeChâtelier's principle, increasing the temperature shifts the equilibrium in the direction of the reaction in which heat is absorbed. Therefore, the reaction shifts to increase the forward reaction, in favor of the production of NO.

b. Use LeChâtelier's principle to predict whether the concentration of NO at equilibrium should increase when the reaction takes place at high pressures.

According to LeChâtelier's principle, increasing the pressure should not affect the position of the equilibrium for the reaction. Since there are an equal number of gas molecules on each side of the equation, an increase in pressure will not favor the forward or reverse reactions. Note to teachers: There is also a kinetic argument that can be made. Reactions of gases generally occur much faster at elevated temperatures and pressures.

Sample Data for Introductory Activity

Part A. Observations

Add 3 drops of Fe(NO ₃) ₃ to KSCN solution	Produces dark orange spots
Add KSCN crystals	Produces dark orange spots; color diffuses through solution over time
Add KNO ₃ crystals	No color change observed
Add NaH ₂ PO ₄ crystals	Orange color lightens around crystals; solution eventually turned colorless over time
Add 1 drop of Fe(NO ₃) ₃	Produces blood-red spot
Add KSCN crystals	Produces orange spots around crystals.

Part B. Observations

Test tube B placed in ice-water bath	Orange color becomes darker
Test tube B placed in hot-water bath	Dark orange color becomes lighter

Answers to Introductory Activity Discussion Questions

1. Write the chemical equation for the reversible reaction of iron(III) ions with thiocyanate ions. Use the information in data table to write the color of each reactant and product underneath its formula.

$Fe^{3+}(aq)$	+	$SCN^{-}(aq)$	⋛	$FeSCN^{2+}(aq)$
Yellow		Colorless		Red-orange

2. How did the color of the solution change when additional reactant—either $Fe(NO_3)_3$ or KSCN—was added? Explain the observed color changes by discussing the rates of the forward and reverse reactions, as well as the concentrations of products and reactants.

Adding $Fe(NO_3)_3$ or KSCN produced the same effect. The color of the solution changed from orange to dark red. The dark red color indicates that the amount of product, $FeSCN^{2+}$, increased. Adding more reactant(s) to an equilibrium system increases the concentration of the reactant(s). This increases the rate of the forward reaction to produce more product and increases the concentration of the product.

3. In step 6, KNO₃ was added to the solution. How did the color of the solution change in Part A when KNO₃ was added? Explain this observation.

Adding KNO_3 to the solution had no effect on the observed color. This indicates that neither the potassium nor nitrate ions are involved in the equilibrium reaction. This supports the net ionic equation for the equilibrium reaction that involves only the iron(III) and thiocyanate ions.

4. In step 7, $H_2PO_4^-$ ions combined with iron(III) ions and removed them from solution. How did the color of the solution change in Part A when NaH₂PO₄ was added? Explain the observed color change by discussing the rates of the forward and reverse reactions, as well as the concentrations of the products and reactants.

Adding sodium phosphate decolorized the solution—the red color disappeared and the solution turned light yellow and cloudy. The amount of product, $FeSCN^{2+}$, decreased because of the loss of the red color. This indicates that one of the reactant concentrations decreased due to the addition of the $H_2PO_4^-$ ion. Therefore, the rate of the reverse reaction was increased to form more reactants. **Note to teachers:** The reaction that occurs in step 7 is the formation of another iron(III) complex ion. The Fe^{3+} reacts with $H_2PO_4^-$ to produce $FeH_2PO_4^{2+}$, a colorless ion. When the reverse reaction is favored, the $H_3PO_4^-$ ion reacts with the newly formed Fe^{3+} ions, continuing the cycle until there are very few Fe^{3+} ions left in solution.

5. How did the color of the solution change when Fe³⁺ ions were added in step 9 and SCN⁻ ions were added in step 10? How do these observations demonstrate that both reactant ions are present at equilibrium?

Adding either reactant caused the solution to change color to red (Fe^{3+}) or orange (SCN^{-}), indicating an increase in the amount of product. Since additional product formed when both reactants were added independently, the other reactant must be present in the solution.

6. How did the color of the solution change in Part B when it was cooled (step 15) or heated (step 16)? How do these results demonstrate that the reaction does indeed occur in both the forward and reverse directions?

Opposite color changes were observed when the solution was cooled or heated. The solution changed from an orange color to a red-orange color when it was cooled. The solution then changed to a lighter orange color when it was heated. These results indicate that the reaction can "go both ways." The solution must contain equilibrium concentrations of both reactants and products. When the solution was cooled, the concentration of the red product increased, indicating the rate of the forward reaction was increased. When the solution was heated, the concentration of red product decreased, indicating the rate of the reverse reaction was increased.

7. Based on the color changes observed when the solution was cooled and heated, is the reaction between iron(III) ions and thiocyanate ions exothermic or endothermic? Write the *Heat* term on the correct side of the equation from Question 1.

Based on the observations from steps 15 and 16, the reaction between iron(III) ions and thiocyanate ions is exothermic.

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

Sample Data and Analysis for Guided-Inquiry Activities A–E

Activity A. Acid–Base Indicator Equilibrium

Reactions	$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$
	$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Procedure	Observations	Explanation
Initial color of water and bromthymol blue solution	Solution is green	The green color shows that the pH of distilled water is between 6.0 and 7.6, and the indicator is a mix of HIn and I ⁻ .
Add 0.1 M HCl dropwise	Solution turned yellow, pH ≤6.0	The addition of HCl increased the $[H^+]$, which caused the reverse reaction to increase and form a greater concentration of the yellow HIn.
Add 0.1 M NaOH dropwise	Solution turned green then finally ended on blue, $pH \ge 7.6$	The addition of NaOH decreased the $[H^+]$ because of the neutralization reaction between H^+ ions and OH^- ions. The decrease in $[H^+]$ caused the forward reaction to increase to form more of the blue In^- ion.
Additional drops of HCl and NaOH	Solution changes consistently from yellow (with HCl) and blue (with NaOH)	The additions of HCl and NaOH confirm that the reaction is indeed reversible. The forward and reverse reactions can both be increased by the addition of either the HCl or NaOH.

Activity B. Formation of a Copper Complex Ion

Reactions $\operatorname{Cu}^{2+}(\operatorname{aq}) + 4\operatorname{NH}_3(\operatorname{aq}) \rightleftharpoons [\operatorname{Cu}(\operatorname{NH}_3)_4]^{2+}(\operatorname{aq})$ $\operatorname{H}^+(\operatorname{aq}) + \operatorname{NH}_3(\operatorname{aq}) \twoheadrightarrow \operatorname{NH}^{4+}(\operatorname{aq})$

Procedure	Observations	Explanation
Initial color of copper solution	Solution is blue	
Add concentrated NH ₃ solution dropwise	Solution turned light blue with a solid forming; with additional NH_3 the solid dissolved and turned to a deep blue color	The addition of NH_3 increased the concentra- tion of NH_3 on the reactant side of equilibrium. This causes the rate of the forward reaction to increase, producing more of the $[Cu(NH_3)_4]^{2+}$ ion, which is dark blue.
Add 1.0 M HCl dropwise	Deep blue color faded to lighter blue and solid formed again	The addition of HCl causes the concentration of NH_3 to decrease. H^+ ions react with NH_3 to produce ammonium ions, NH_4^+ . The decrease in NH_3 causes the rate of the reverse reaction to increase to produce more NH_3 and Cu^{2+} ions, which is a lighter blue color.
Additional drops of NH ₃	Solid dissolved again and solution turned to a deep blue	The addition of NH_3 confirms the reaction is reversible. The reverse reaction can be increased by the addition of HCl and the forward reaction can be increased by the addition of NH_3 .

Activity C. Formation of Cobalt Complex Ions

Reactions	$[Co(H_2O)_6]^{2+}(aq) + 4Cl^{-}(aq) + Heat \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$
	$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$

Procedure	Observations	Explanation
Color of cobalt chloride solution	Solution is violet	
Add 6.0 M HCl dropwise to test tube B	Solution turned blue	The addition of HCl increased the concentra- tion of the Cl ⁻ ion on the reactant side of equi- librium. This causes the rate of the forward reaction to increase producing more of the $[CoCl_4]^{2-}$ ion, which is blue.
Add 0.1 M AgNO ₃ dropwise to test tube B	White solid precipitated and solu- tion changed color to pink	Silver ions react with chloride ions to pro- duce an insoluble white solid. This reaction decreases the $[Cl^-]$ thereby increasing the rate of the reverse reaction to produce Cl^- ions and the pink $[Co(H_2O)_6]^{2+}$ ion.
Add distilled water dropwise to test tube C	Solution turned pink	Adding water reduces each concentration term in the K_{eq} expression by a factor of about one- third (due to dilution). This causes the reaction quotient Q to become greater than K_{eq} , which causes the concentration of Cl^- ions and the pink $[Co(H_2O)_6]^{2+}$ ion to increase.
Add 5–6 grains of CaCl ₂ to test tube C	Crystals dissolved and solution turned blue	The addition of $CaCl_2$ increases the concentra- tion of the chloride ion, Cl^- . This increases the rate of the forward reaction to produce a greater concentration of $[CoCl_4]^{2-}$ ion, which is blue.
Test tube C placed in ice-water bath for 2–3 minutes	Solution turned pink	The loss of heat by cooling caused the reac- tion to increase the concentration of Cl^- ions and the pink $[Co(H_2O)]_6]^{2+}$ ion to increase. This means the rate of the reverse reaction was increased. Heat can be thought of as a reactant and in order to increase the amount of heat, the reverse reaction was increased. This confirms that the equilibrium reaction is endothermic.
Test tube C placed in hot-water bath for 2–3 minutes	Solution turned to royal blue color	The addition of heat to the system caused the reaction to increase the concentration of the blue $[CoCl_4]^{2-}$ ion. This means the rate of the forward reaction was increased to use the excess heat. Therefore, the equilibrium reaction is endothermic.

*Please see the *Teaching Tips* for a more thorough explanation.

Activity D. Solubility of Carbon Dioxide

Procedure	Observations	Explanation
Initial color of seltzer water and bromcresol green solution	<i>Green color, approximate</i> pH = 4.4	Some $CO_2(g)$ has already dissolved in the seltzer water to create carbonic acid.
Pull back on syringe to create a decrease in pressure (larger overall volume); hold plunger steady and shake until bubbles stop forming	Solution turned teal, approximate pH = 4.8	An increase in the pH indicates that the rate of the reverse reaction increased to produce more $CO_2(g)$. This aligns with Henry's law because with a smaller pressure above the solution the amount of CO_2 dissolved in solution will decrease.
Push syringe in to increase pressure (smaller overall volume); hold plunger steady	Solution turned green, approximate pH = 4.4	Color change shows an increase in the concentration of the carbonic acid. This aligns with Henry's law: the amount of CO_2 dissolved in solution will increase with a greater pressure above the solution.

Reactions $2CO_2(g) + H_2O(l) \rightleftharpoons CO_2(aq) + H^+(aq) + HCO_3^-(aq)$

Activity E. Solubility of Magnesium Hydroxide

Reactions $Mg(OH)2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^{-}(aq)$ $H^{+}(aq) + OH^{-}(aq) \rightarrow H_{2}O(l)$

Procedure	Observations	Explanation
Initial color of milk of magnesia and universal indicator solution	Purple solution with white solid suspended in liquid	The white solid is undissolved magnesium hydroxide. The purple color is from the uni- versal indicator and shows that there are some OH^- ions present in the solution because the purple is associated with higher pH values >10.
Add one drop of 3 M HCl with constant stirring	Solution immediately turned pink; with more stirring pink color turned to orange, green, and then blue	The addition of 3 M HCl caused the indicator to turn pink, which means the pH was lowered significantly. The H ⁺ ions reacted with the OH^- ions to form water. With stirring, the indi- cator changed colors to indicate more basic conditions. This is due to more Mg(OH) ₂ solid dissolving into solution. With the initial reduc- tion of the [OH ⁻] ions, the rate of the forward reaction increased until more Mg(OH) ₂ (s) dissolved, all of the H ⁺ were reacted with OH ⁻ ions, and equilibrium is reestablished.
Additional drops of 3 M HCl with constant stirring	Solution immediately turned pink; slower change to the blue-green end color	The longer time for the solution to turn back to the basic end of the indicator spectrum shows that there was less $Mg(OH)_2$ solid to react with the acid. The end color is also showing that there are less OH^- ions in solution because it did not return to the same degree of alkalinity. There are less OH^- ions in solution due to more of the $Mg(OH)_2$ reacting with the HCl.
Additional drops of 3 M HCl with constant stirring	Solution immediately turned pink; color remained pink and the solu- tion was not cloudy	The solution remained pink and was clear because all of the solid $Mg(OH)_2$ had reacted with the HCl. With no source for OH^- ions, the solution is slightly acidic, which is pink on the indicator spectrum.

Answers to AP Chemistry Review Questions

When a chemical is manufactured, chemists and chemical engineers choose conditions that will favor the production of the desired product as much as possible. They want the forward reaction to occur more quickly than the reverse reaction. In the early 20th century, Fritz Haber developed a process for the large-scale production of of ammonia from its constituent elements. Some of his results are summarized in the chart below.



Percentage Ammonia at Equilibrium*

- 1. Write the balanced chemical equation, including the heat term, for the synthesis of ammonia from its constituent elements.

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + Heat$

2. Based on the results above, explain the effect of temperature on the equilibrium position of the reaction.

When the pressure of the reaction was held constant, an increase in the temperature decreased the amount of ammonia at equilibrium. The reaction is exothermic. With an increase in the amount of heat, the rate of the reverse reaction increased to absorb the excess heat. Note that the value of K_{ea} depends on temperature.

3. Explain the effect of pressure on the equilibrium position of the reaction.

When the temperature of the reaction is held constant, an increase in pressure increases the amount of ammonia formed at equilibrium. An increase in pressure on a gaseous equilibrium system will increase the rate of the reaction in the direction of the side with fewer moles of gases. In this case, the rate of the forward reaction is increased because the product side has two moles of gas (ammonia) while the reactant side has four moles of gas (hydrogen and nitrogen).

4. The optimal conditions to synthesize ammonia are high pressures and low temperatures. However, each factor comes with a drawback: high pressures require strong pipework and hardware, and at low temperatures the reaction is slow. In order to get high yields of ammonia at lower pressures and higher temperatures, ammonia is removed from the system as it is formed. Use LeChâtelier's principle to explain why this is effective.

Although the percent yield of ammonia is less at lower pressures and high temperatures, the amount of ammonia collected can be increased by constantly removing ammonia from the system as it is produced. This will increase the rate of the forward reaction because the concentration of ammonia will be reduced.

References

AP* Chemistry Guided-Inquiry Experiments: Applying the Science Practices; The College Board: New York, NY, 2013. Zumdahl, S. et al. Chemistry, 5th ed; Massachusetts: Houghton Mifflin Company, 2000. Print.

Applications of LeChâtelier's Principle—Advanced Inquiry Laboratory Kit and supporting materials are available from Flinn Scientific, Inc.

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