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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?

Concepts

- Chemical equilibrium
- LeChâtelier's principle
- Complex-ion reactions
- Exothermic and endothermic reactions
- Acid–base reactions
- Precipitation reactions
- Gas solubility

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:

$$aA + bB \rightarrow cC + dD \qquad \textit{Equation 1}$$

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.

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

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 is considered a stress—this includes adding or removing reagents, or changing the temperature or pressure. The system will adjust the rates of the forward and reverse reactions to achieve equilibrium again. 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-

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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 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, to consume some of the excess energy and make more products. The opposite effect is observed for exothermic reactions. In the case of exothermic reactions, heat appears on the product side in the chemical equation. Increasing the temperature of an exothermic reaction shifts the equilibrium in the reverse direction.

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, you will investigate six equilibrium systems 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. You may also be tasked to create a rainbow-colored display using the equilibrium systems as an optional extension or cooperative class activity.

Pre-Lab Questions

1. Iodine (I_2) 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 (I_3^-) ions (Equation 4).

   $$I_2(s) \rightleftarrows I_2(aq) \qquad \textit{Equation 3}$$

   $$I_2(aq) + I^-(aq) \rightleftarrows I_3^-(aq) \qquad \textit{Equation 4}$$

   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 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).

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

   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
Potassium thiocyanate, KSCN, 0.5 g
Potassium thiocyanate solution, KSCN, 0.002 M, 20 mL
Sodium phosphate, monobasic, $NaH_2PO_4{\cdot}H_2O$, 0.5 g
Water, distilled or deionized
Beakers, 250-mL, 2
Graduated cylinder, 50-mL
Hot plate
Ice
Labeling or marking pen
Petri dish, disposable
Pipet, Beral-type, graduated
Spatulas, 2
Test tubes, 2
Test tube holder
Test tube rack
Wash bottle

Safety Precautions

Cobalt chloride solution is 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 ¼ 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. Keep this solution for use in *Part B—Effect of Temperature*.

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 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. Wash the contents of both test tubes and Petri dish in the wash beaker provided. Rinse the test tubes with distilled water.

Analyze the Results

Form a working group with other students to discuss and answer 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, KNO_3 was added to the solution. How did the color of the solution change in Part A when KNO_3 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 NaH_2PO_4 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 Fe^{3+} 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 (step 15) and heated (step 16), is the reaction between iron(III) ions and thiocyanate ions exothermic or endothermic? Write the *Heat* term into the equation from Question 1 on the correct side.

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

Initial Conditions

Measure approximately 2 mL of distilled water in 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.

Materials

Ammonium hydroxide solution (conc.), NH_3, 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

Measure approximately 5 mL of 0.2 M $CuSO_4$ in 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 ($CoCl_2{\cdot}6H_2O$) 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	Labeling or marking pen
Cobalt chloride hexahydrate, $CoCl_2{\cdot}6H_2O$, 1% alcohol, 6 mL	Pipets, Beral-type, graduated, 3
Hydrochloric acid, HCl, 6 M, 1 mL	Stirring rod
Silver nitrate, $AgNO_3$, 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

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.

Activity D. Solubility of Carbon Dioxide

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

$$2CO_2(g) + H_2O(l) \rightleftarrows CO_2(aq) + H^+(aq) + HCO_3^-(aq) \qquad \textit{Equation 6}$$

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 solution, 0.04%, 2 mL	Graduated cylinder, 10- or 25-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 is magnesium hydroxide crystals, used as an over-the-counter antacid remedy. 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
- Milk of magnesia, 10 mL
- Universal indicator solution, 5–10 drops
- Water, distilled or deionized
- Beaker, 250-mL
- Graduated cylinder, 10-mL
- Magnetic stir bar
- Magnetic stir plate (or stirring rod)
- Pipet, Beral-type, graduated
- 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

Form a working group with other students to review and summarize the equilibrium systems 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

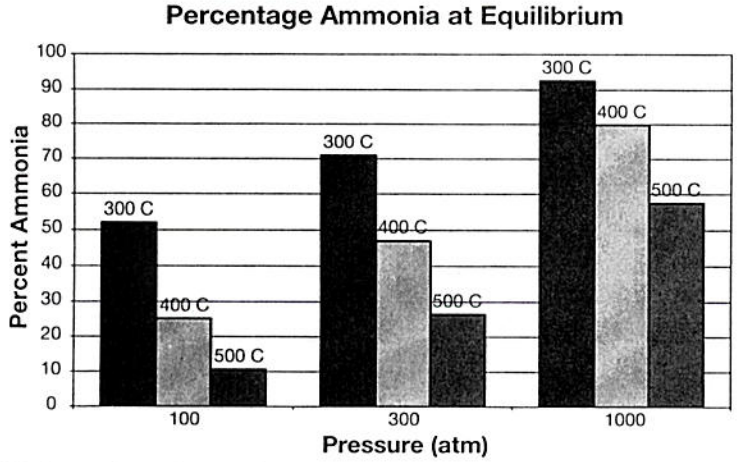
Equilibrium Rainbow Display

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. 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 ammonia from its constituent elements. Some of his results are summarized in the chart below.



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

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.