# UNIT 9

# Equilibrium and Advanced Thermodynamics

## The Delicate Balance of Chemical Reactions

## Unit Overview

Unit 9 introduces the concept of entropy and its role as the driving force for chemical reactions. Students will learn the Second Law of Thermodynamics in terms of entropy rather than energy and work as it had been previously presented in Unit 7. The middle sections of the unit explain spontaneity and Gibb's free energy, explaining why some chemical reactions occur spontaneously while others do not. Even nonspontaneous reactions can still occur when coupled to spontaneous reactions. The final sections introduce chemical equilibrium, the equilibrium constant, and equilibrium shifts (Le Chatelier's Principle).

### Learning Objectives and Applicable Standards

Participants should be able to:

1. Define microstate, macrostate, and entropy.
2. Explain how spontaneous processes increase the entropy of the universe.
3. Perform calculations with the Gibbs free energy equation to determine if a reaction is spontaneous.
4. Explain how nonspontaneous reactions can still happen when they are coupled with a spontaneous reaction.
5. Define the equilibrium state as the one where the Gibbs free energy is at a minimum.
6. Write the equilibrium constant expression for a chemical reaction.
7. Predict the direction a reaction will shift when: reactants/products are added/removed, the reaction vessel is compressed, or the temperature changes.

### Key Concepts and People

1. **Microstates, Macrostates, and Entropy:** Ludwig Bolzmann formulated an equation for entropy based on microstates and macrostates. The more microstates in a given macrostate, the more likely that macrostate is to occur.

2. **Entropy of Energy Quanta:** Quanta of energy tend to distribute themselves throughout matter evenly.
3. **Entropy and States of Matter:** Different states of matter have different amounts of entropy associated with them; in general, solids have the least entropy and gases have the most.
4. **Spontaneity and Gibb's Free Energy:** The Gibbs free energy equation allows us to determine the spontaneity of a chemical reaction.
5. **Coupling Reactions:** A nonspontaneous reaction can still occur if it is coupled to a spontaneous reaction.
6. **Chemical Equilibrium:** When a reaction has proceeded to the point where the Gibbs free energy has reached a minimum, the reaction has reached equilibrium.
7. **The Equilibrium Constant:** The equilibrium constant expresses the ratio of products to reactants at equilibrium. Reactions with high equilibrium constants favor the product side at equilibrium, while reactions with low equilibrium constants favor the reactant side.
8. **Le Chatelier's Principle:** A chemical reaction at equilibrium will react to resist any changes made to the system and return to equilibrium.
9. **Temperature and Equilibrium:** A change in temperature affects the equilibrium constant. Whether the equilibrium constant increases or decreases is a function of whether the reaction is endothermic or exothermic.

# Video

### Video Content

Light a match and chemical change happens in a one-way process: Reactants are transformed into products. But there are many chemical reactions called "equilibrium reactions" that operate in both directions: with reactants and products always present. The Unit 9 video will show how chemical equilibrium works, the essential role it plays in the function of the human body, and how it is exploited in chemical processes such as ammonia synthesis, a process that provides food for up to half the world's population.

### Host Introduction

Dr. Wilton Virgo, assistant professor at Wellesley College, introduces spontaneous and nonspontaneous chemical reactions by discussing the rusting of iron and the smelting of iron ore.

### Host Science Explanation
### "Dynamic Equilibrium"

Dr. Wilton Virgo explains chemical equilibrium as a state in which a chemical reaction runs forward and backward simultaneously. At equilibrium, both reactions continue to occur, but because they occur at the same rate, the concentrations of reactants and products remain constant. While the reaction rates are equal at equilibrium, the concentrations of reactants and products need not be. The equilibrium constant K is the ratio of product concentration to reactant concentration. When the value of K is high, products are favored at equilibrium. When the value of K is low, reactants are favored.

### Laboratory Demonstration
### "Le Chatelier's Principle"

Dr. Wilton Virgo demonstrates Le Chatelier's Principle using the reaction that forms the iron(III) thiocyanate complex: $Fe^{3+} + SCN^{-} \leftrightarrows FeSCN^{2+}$. Adding the reactant $Fe^{3+}$ shifts the reaction to the right, and precipitating the $Fe^{3+}$ shifts the reaction to the left.

### Real World Application
### "Counteracting Poison"

Dr. Daniel Deschler at the Massachusetts Eye and Ear Infirmary shows how manipulating two important equilibrium reactions in the blood can treat carbon monoxide poisoning.

### Laboratory Demonstration
### "Pressure and Le Chatelier's Principle"

Daniel Rosenberg, Lecture Demonstrator at Harvard University, demonstrates how changing pressure can shift the gaseous equilibrium reaction $2NO_2 \leftrightarrows N_2O_4$ according to Le Chatelier's Principle.

### Lab Demonstration
### "Temperature and Equilibrium"

Daniel Rosenberg demonstrates the effect of temperature on the equilibrium constant by heating and cooling tubes containing the $2NO_2 \leftrightarrows N_2O_4$ reaction.

### History of Chemistry
### "The Haber-Bosch Process"

Authors Thomas Hager and Sam Kean, and Nobel prize-winning MIT professor Dr. Richard Schrock, describe the race to produce artificial fertilizer in the early 1900s. Natural sources of fixed nitrogen were drying up, and without the ability to harness atmospheric nitrogen to fertilize crops, the world faced potential mass starvation. Fritz Haber found a way to react nitrogen and hydrogen gas at high temperature and pressure to create ammonia.

# Unit Text

### Content Overview

The text begins with an illustration of Ludwig Boltzmann's work in statistical mechanics using a simple example of gas particles distributing themselves throughout a container. This leads to definitions of the terms "microstate" and "macrostate." "Entropy" represents a quantity that reflects the number of microstates in a given macrostate. The entropy of energy quanta and states of matter is discussed. The text then introduces Gibb's free energy and shows how the spontaneity depends on the enthalpy change and entropy change of the system. Spontaneous reactions can drive non-spontaneous reactions; entropy can decrease in one part of a system as long as the overall entropy of the system increases.

The text then explains equilibrium and the equilibrium constant. It discusses Le Chatelier's Principle, which states that a chemical reaction at equilibrium will shift to counteract any changes (concentration, pressure, temperature) made to the system. The text concludes by examining how temperature affects equilibrium.

### Sidebar Content

1. **Osmosis and Entropy:** This sidebar explores the role of entropy in osmosis. It further explains the role of osmosis in food preservation and in the diseases cholera and cystic fibrosis.

2. **Q, the Reaction Quotient:** This sidebar introduces the reaction quotient and shows how to calculate it to predict the direction of a reaction.

# Interactives

### Historical Timeline of Chemistry

This interactive illustrates how different discoveries build upon, disprove, or reinforce previous theories. This not only reinforces basic chemistry concepts, but also emphasizes the nature of science. Scientists mentioned in this unit are also listed on the timeline.

### Control a Haber-Bosch Ammonia Plant Interactive

In this interactive, students attempt to maximize the profit of an ammonia plant. Ammonia production stops when the reaction reaches equilibrium. Using the principles in this unit, students will be able to manipulate the equilibrium to keep the ammonia flowing. Students must find the best combination of pressure and temperature to maximize production, as well as apply Le Chatelier's Principle. Please note that a lesson plan and student worksheet are available online with this interactive.

# During the Session

### Before Facilitating this Unit

The video provides students with a qualitative introduction to chemical equilibrium, the equilibrium constant, and Le Chatelier's Principle. The text approaches equilibrium from the point of view of thermodynamics. Students will learn that equilibrium is a state in which entropy is maximized; the Gibb's free energy has reached a minimum. After watching the history of the Haber-Bosch process in the video, students can see it in action with the Control a Haber-Bosch Ammonia Plant interactive.

### Tips and Suggestions

1. **The concept of entropy is difficult for many students to grasp.** Many teachers equate entropy with disorder, which can lead some students astray. To avoid this, emphasize the statistical origins of the concept of entropy.

2. **Entropy works on the level of particles.** While analogies like shuffling cards can be useful to get the concept of entropy across, some students can come away with the mistaken impression that entropy applies to macroscopic objects. The statistics behind entropy require that particles and quanta of energy move around randomly, and large everyday objects do not.

3. **This text approaches equilibrium from a thermodynamic point of view.** Many explanations of equilibrium start with kinetics; the kinetics approach is more accessible for many students and may be appropriate for introductory classes.

### Starting the Session: Checking Prior Thinking

You might assign students a short writing assignment based on the following questions, and then spend some time discussing prior thinking. This will help elicit prior thinking and misconceptions.

1. What does the word "equilibrium" mean to you? What does it mean in everyday life? What do you think equilibrium means in chemistry?

2. What is a spontaneous reaction?

3. Why do some chemical reactions occur and others do not? Why is it impossible to "unburn" something?

4. Our bodies burn glucose for energy in a spontaneous reaction. Plants "unburn" glucose when they photosynthesize. How can both these reactions happen, seemingly spontaneously?

5. If ten people flipped ten coins simultaneously, what would be the percentages of heads and tails? Would you expect it to be exactly 50/50? Why or why not? What if 100 people flipped the coins? A million?

## Before Watching the Video

Students should be given the following questions to consider while watching:

1. Why doesn't pure iron metal exist in nature?
2. Does a reaction at equilibrium stop?
3. At equilibrium, are the amounts of products and reactants equal?
4. What is the equilibrium constant (K)?
5. What is the role of hemoglobin in the blood?
6. How does the reaction shift when hemoglobin is in the lungs? In the tissues?
7. How does a change in temperature affect an equilibrium reaction?
8. Why can't plants use atmospheric nitrogen?
9. What was Haber's major contribution to chemistry? Why is it so important to humanity?

## Watch the Video

## After Watching the Video

Use these additional questions as follow-up, either as a group discussion or as short writing assignments.

1. What is an equilibrium reaction?
2. What is Le Chatelier's Principle?
3. How does hyperbaric oxygen treat carbon monoxide poisoning?
4. How does a change in pressure affect a gas-phase equilibrium reaction?
5. Hyperbaric oxygen is effective in treating carbon monoxide poisoning because pressure can have a large effect on gas-phase equilibriums. Why does pressure NOT have the same effect on aqueous reactions?
6. While Fritz Haber's process benefitted humanity greatly by harnessing nitrogen for fertilizer, what else was the process used for? What is the other side of Haber's legacy?

# Group Learning Activities

## Graphing Equilibrium

### Objective

This activity simulates a chemical system coming to equilibrium. Students will observe that the ratio of products to reactants at equilibrium is the same regardless of starting amounts.

### List of Materials

- Two 25-mL graduated cylinders
- Two different sized pipettes (one about twice the size of the other) or two straws or two tubes (one about twice the diameter of the other)
- Water

### Procedure 1

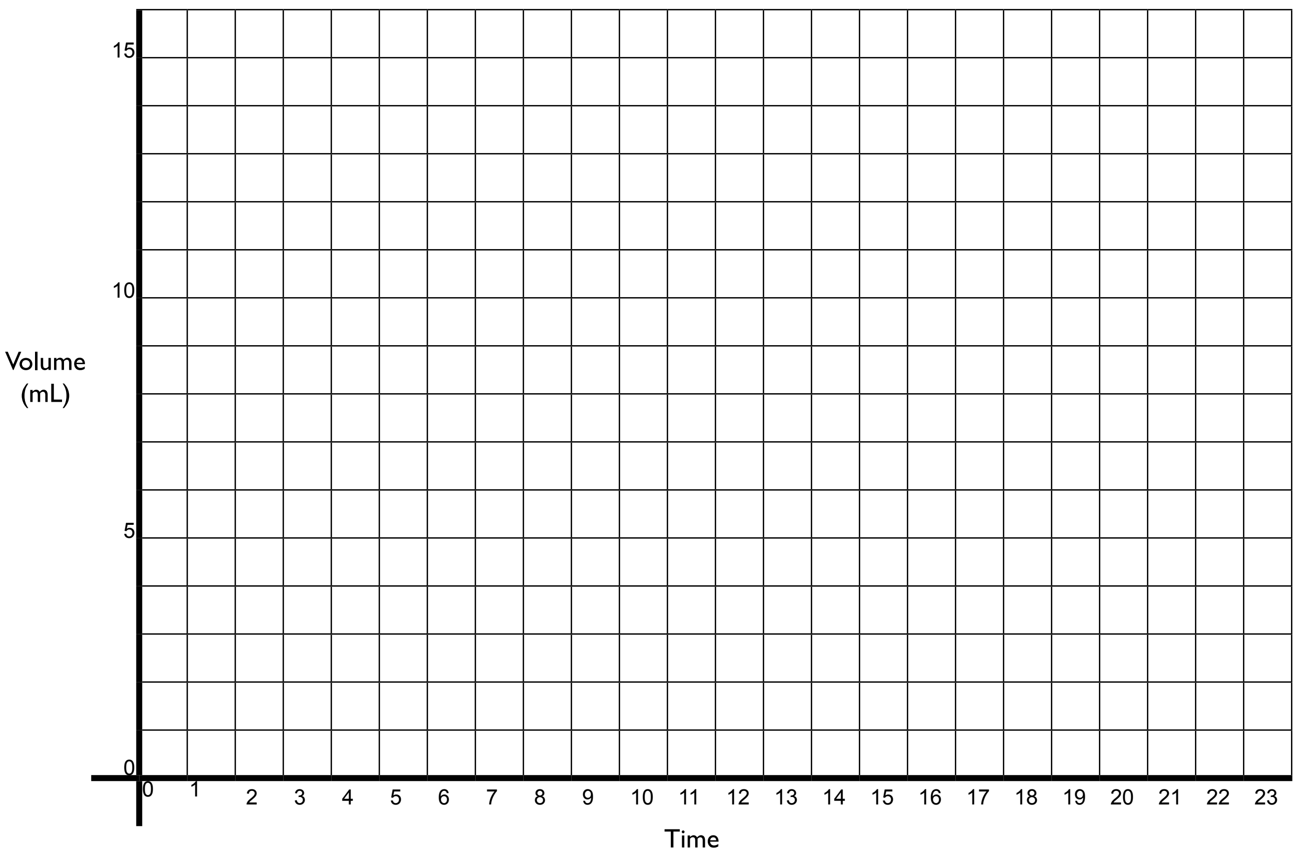
1. Place the two graduated cylinders on the bench; the one on the left will be designated "reactant" and the one on the right will be designated "product."

2. Add 15 mL of tap water to the reactant cylinder. Mark the volume that each cylinder contains on the graph below at time = 0.

3. SIMULTANEOUSLY insert the large pipette or tube into the reactant cylinder all the way the to bottom and the small pipette/ tube all the way into the product cylinder. Fill the pipettes/ tube with the water. To fill the tubes, squeeze the tubes with your thumb and middle finger and cover the tops of each tube with your index finger, then lift out the tubes. Transfer the water to the OPPOSITE cylinder.

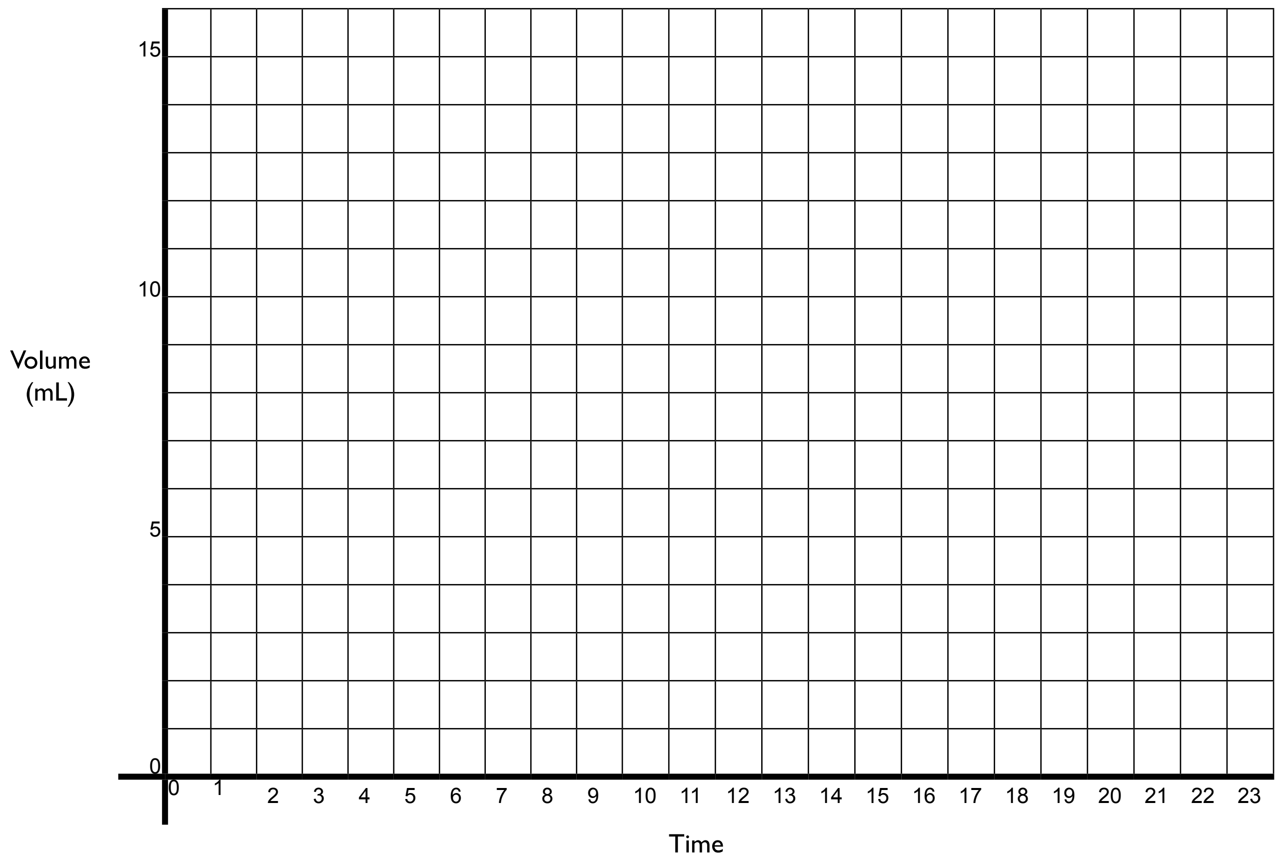
4. Record the volume of water in both tubes and record on the graph for time = 1. Use different colors on the graph to distinguish products and reactants.

5. Repeat steps 3 and 4 over and over until the amounts of products and reactants remain constant.



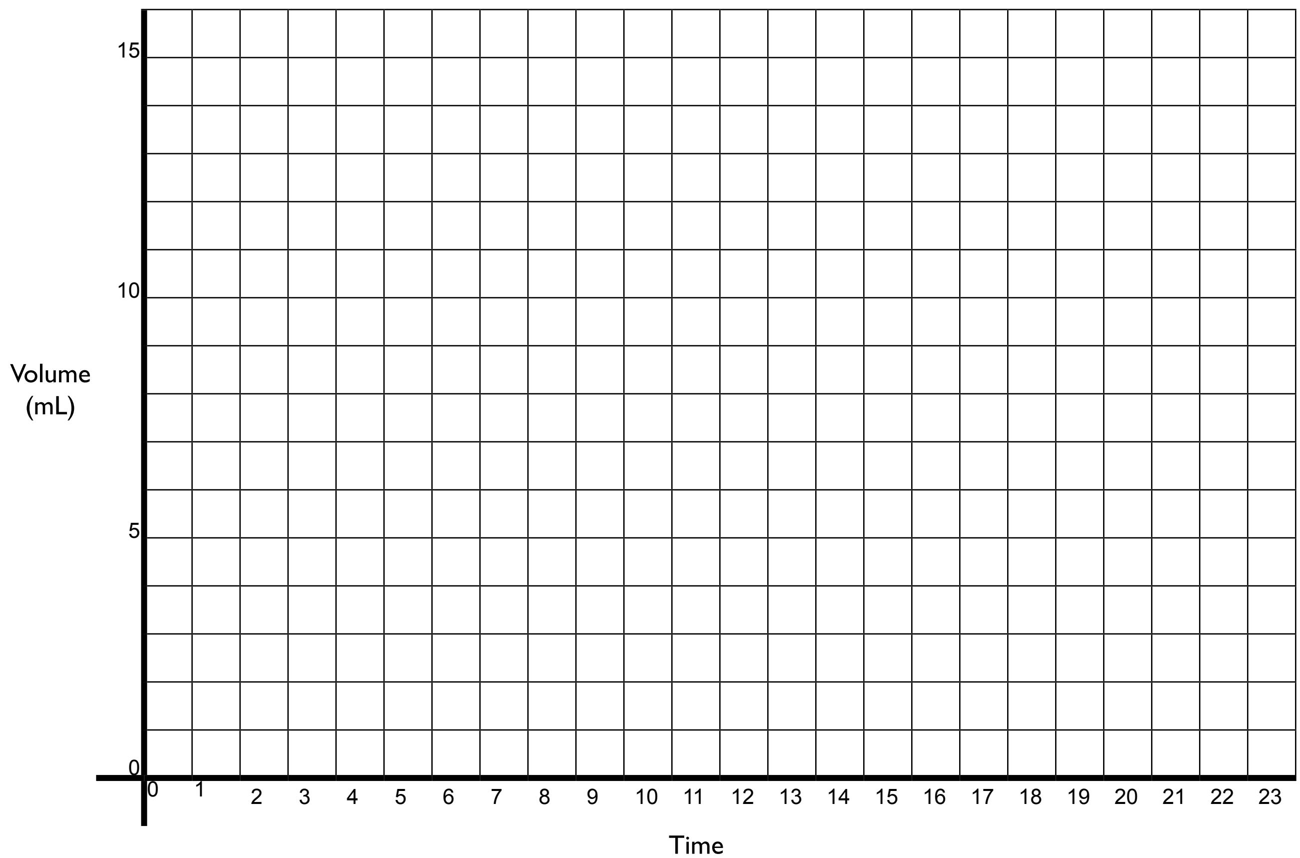
## Procedure 2

Repeat the same procedure, this time starting with the **reactant** cylinder **empty** and the **product** cylinder with 15 mL. Graph your data below.



## Procedure 3

Repeat the same procedure. This time, start out both cylinders with 7.5 mL of water. Graph your data below.




## Discussion

These questions can help guide students thinking during and after the activity:

1. How do you know when the reaction reaches equilibrium?
2. Once the reaction reaches equilibrium, do the reactions stop?
3. At equilibrium, are the rates of the forward and reverse reactions the same or different?
4. At equilibrium, do the amounts of reactants and products change?
5. Calculate the ratio of products to reactants for each reaction at equilibrium. Does this ratio depend on the starting amounts of products and reactants?

6. If the reaction has reached equilibrium, what would happen if more water were added to the reactant cylinder? The product cylinder?

7. What could you change about the experiment to make the final equilibrium ratio different from what you found?

### Hazards
Wear goggles to prevent water splashing into eyes.

### Disposal
There are no special disposal considerations.

## Gibb's Free Energy and Le Chatelier

### Objective
The contraction of a stretched rubber band is a spontaneous process. This demonstration allows students to figure out the signs of $\Delta H$ and $\Delta S$ for the following process:

stretched → contracted

The demo works best with thick, heavy rubber bands.

### List of Materials
- Thick heavy rubber bands
- Ring stand
- Hair dryer

### Procedure
1. Working in pairs, one student should stretch the rubber band and hold it in a stretched position for 20 seconds.

2. The other student should touch the middle of the rubber band, while the one holding the rubber band allows it to quickly contract. Be careful not to snap the rubber band on the other student's hand.

3. Repeat so the other student can feel the temperature of the rubber band as it expands and contracts.

### Discussion
The contracting band should feel cool, indicating that contraction is an endothermic process ($\Delta H$ is positive). If contraction is spontaneous but endothermic, the spontaneity must be due to an increase in entropy ($\Delta S$ is positive). The polymer strands have greater entropy when contracted, and less entropy when stretched; stretching the band puts the strands in a more parallel, ordered arrangement. The following questions can help guide students' thinking during this activity:

1. How does the temperature change when the rubber band contracts?

2. Does the temperature change indicate that the contraction is an exothermic or endothermic process? Why?

3. Is the rubber band contracting a spontaneous or nonspontaneous process?

4. If the contraction of the rubber band is spontaneous and it's an endothermic process, what must happen to the entropy? Why?

To introduce Le Chatelier's Principle you can also hang a rubber band from a ring stand and suspend a weight from the bottom so the band is partially stretched. Ask the students to predict whether the band will become longer or shorter when heated with a hair dryer. (The band will shorten according to Le Chatelier's Principle.)

### Hazards
Students should not snap rubber bands at other students. Wear safety glasses for added protection in the case of flyaway rubber bands.

### Disposal
There are no special disposal considerations.

# In-Class Chemical Demonstrations

## Le Chatelier's Principle with Copper(II) Chloride Complexes

### Objective
Students will see the following reaction shift according to Le Chatelier's Principle:

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \leftrightarrows [CuCl_4]^{2-} + 6H_2O$$

Adding chloride ions will shift the reaction to the right; diluting it will shift it left. This reaction also demonstrates how changes in temperature can change the equilibrium constant (K).

### List of Materials
- 0.5 M Solution of $CuCl_2$
- HCl
- Stirring rod
- Beaker

### Procedure
1. In a 0.5 M solution of $CuCl_2$ the copper ions form a complex with water which gives the solution a light blue color $[Cu(H_2O)_6]^{2+}$.

2. While stirring constantly, slowly pour in HCl.

3. The following equilibrium will shift to the right, and the solution will turn light green due to the presence of $[CuCl_4]^{2-}$ ions.

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \leftrightarrows [CuCl_4]^{2-} + 6H_2O$$

4. The reaction will shift the other way when diluted with distilled water.

5. The above reaction is endothermic; you can demonstrate this by heating the solution to make it greener and chilling it to make it bluer.

### Discussion

These questions can help guide students thinking during and after the activity:

1. When the chloride ions were added by adding HCl, which way did the equilibrium shift, and why?

2. When the solution was diluted, which way did the equilibrium shift, and why?

3. Silver ions combine with chloride ions to form the insoluble precipitate AgCl. If silver ions were added to the copper(II) chloride solution, which way would the equilibrium shift? What color change would you expect?

4. Compare the heated solution with the cooled solution. At which temperature were there more products?

5. Based on your answer to question 4, does the equilibrium constant for this reaction increase or decrease as temperature increases?

6. Based on your answer to question 4, is the reaction endothermic or exothermic?

### Hazards

It is good lab practice to review a chemical's Material Safety Data Sheet (MSDS) before working with any chemical. Follow instructions on the MSDS and encourage students to review them. Wear proper protective gear at all times: chemical splash goggles, chemical-resistant apron, lab coat, and gloves. Copper(II) chloride: Highly toxic by ingestion and inhalation. LD50 140 mg/kg. Hydrochloric acid: Toxic by ingestion or inhalation; severely corrosive to skin and eyes.

### Disposal

Check local regulations for proper disposal of chemicals.

## Going Deeper (In-Class Discussion or Reflection)

Instructors should allow up to 30 minutes for discussion at the end of the session, or students can use the time to reflect on one or more of these questions in journals.

1. Someone throws four coins in the air and they all end up showing heads. Does this

contradict the Second Law of Thermodynamics? Why or why not? Explain in terms of microstates and macrostates.

2. A ten-year-old boy tells his mother that there's no point to cleaning up his room because the Second Law of Thermodynamics says it will inevitably get messed up again. Is this argument valid?

3. What real-life example of equilibrium can you think of? If this equilibrium were disturbed, would it resist the change according to Le Chatelier's Principle?

4. Find examples of spontaneous and nonspontaneous chemical reactions or processes. Can you think of a process that can be spontaneous in the forward direction under certain conditions, and spontaneous in the reverse direction under different conditions?

## Before the Next Unit

Students should read the Unit 9 text if they haven't already done so. They may be assigned one or more reading assignments or activities from the list below, or if you choose to have them use the course materials outside of class, they can watch the Unit 10 video and/or read the Unit 10 text as an assignment before the next session.

## References and Additional Resources

Lightman, Alan P. "The Conservation of Energy." *Great ideas in physics: the conservation of energy, the second law of thermodynamics, the theory of relativity, and quantum mechanics*. 3rd ed. New York: McGraw-Hill, 2000.

Lower, Stephen. "Thermodynamics of chemical equilibrium." *Steve Lower Stuff.* Accessed August 7, 2012. http://www.chem1.com/acad/webtext/thermeq/index.html

Phet Interactive Simulations. "Energy Forms and Changes." University of Colorado at Boulder. Accessed August 12, 2013. http://phet.colorado.edu/en/simulation/energy-forms-and-changes

Phet Interactive Simulations. "Reversible Reactions." University of Colorado at Boulder. Accessed August 12, 2013. http://phet.colorado.edu/en/simulation/reversible-reactions

The Royal Society of Chemistry. "The quantum casino." *Presenting Science*. Accessed August 7, 2012. http://www.presentingscience.com/quantumcasino/index.html

# For Professional Development

In addition to watching the videos, reading the text, and going through the activities listed in the course guide, participants taking this course for professional development should read the following papers and answer the corresponding reflection questions, then complete the professional development assignments.

## Further Reading & Reflection Questions

Lambert, Frank L. "Disorder- A Cracked Crutch for Supporting Entropy Discussions." *Journal of Chemical Education*. 79: 2 (2002): 187-192. Accessed August 5, 2013. http://www.researchgate.net/publication/231265843_Disorder_-_A_Cracked_Crutch_for_Supporting_Entropy_Discussion

1. Do you agree with the author that teaching entropy as disorder is misleading and damaging? Why or why not? Use specific examples in this paper or from your teaching experience to support your position.

2. Does this paper influence how you will approach teaching entropy? If so, how? If not, why not?

Tyson, Louise and David F. Treagust. "The Complexity of Teaching and Learning Chemical Equilibrium." *Journal of Chemical Education*. 76: 4 (1999): 554-558. Accessed on August 5, 2013. http://www3.fsa.br/fabricio/images/Chemical_equilibrium_JCE_Tyson_et_al.pdf

1. Compare and contrast the benefits and challenges associated with using Le Chatelier's Principle, Equilibrium Law, and collision theory in teaching about equilibrium? Do you agree with the author's recommendations for how to use these explanations?

2. Have you encountered students who were confused by equilibrium terminology such as equilibrium, closed system, or equilibrium shift/position? What are some ways you might be able to address these discrepancies in language use?

3. Were you surprised that students are confused by the difference between physical and chemical equilibrium? Why or why not? How could you avoid introducing this kind of confusion to your students?

## Professional Development Assignments

1. After reading the papers above and reflecting on the questions presented, develop a lesson plan designed to teach the material presented in this unit.

2. Using a group activity or classroom demonstration presented in this course guide, show how you would implement it in your classroom. Where would it fit into your curriculum or standards? Would you change the demonstration or activity in any way? How would you assess student learning?