



## What Theories Explain Energy?

Thermodynamics is the study of energy change accompanying physical and chemical changes. In chemical systems, these changes are described through the ideas of heat and work, enthalpy, entropy, and Gibbs free energy. These explanations are best understood at the microscopic scale, where the energy can be characterized through the motions of particles and the relative position of particles. While these concepts are abstract, the investigations, videos, and readings in this section give students practical experience with the concepts and rules that govern how matter and energy interact.

- Lab Investigation—Entropy & Enthalpy Changes
- Lab Investigation—Energy & Entropy of a Stretched Rubber Band
- *ChemMatters* Reading—Why Cold Doesn't Exist

# Entropy & Enthalpy Changes | A Lab Investigation

## Summary

In this investigation, students will explore basic thermodynamic concepts, including spontaneity, entropy, and enthalpy through a series of guided questions and procedures.

## Objective

Given prior knowledge of the thermodynamic terms entropy, enthalpy, and spontaneous processes, students will gain a deeper understanding of how  $\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$  expresses the second law of thermodynamics by exploring energy transfer between system and surroundings as salts dissolve.

## Safety

- Be sure you and the students wear properly fitting goggles.
- Ammonium chloride can be an irritant to body tissues. In the event of contact, wash affected areas with water.
- Ammonium nitrate is a strong oxidizer. May emit toxic vapors of  $\text{NO}_x$  and  $\text{NH}_3$  when heated to decomposition. Can be an irritant to body tissues. In the event of contact, wash affected areas with water.
- Calcium chloride can be an irritant to body tissues. In the event of contact, wash affected areas with water.
- Acetone is flammable. Avoid flames or sparks. Irritating to body tissues. Avoid body tissue contact. Slightly toxic by ingestion. Skin contact causes dermatitis. Vapor may cause weakness, fatigue, nausea, and headache. Work in a well-ventilated area.
- Dispose of solutions according to local regulations.

## Materials for Each Group

- 10 g ammonium chloride or ammonium nitrate
- 5 g calcium chloride
- Thermometer
- 100-mL graduated cylinder
- 3 150-mL beakers, stirring rod

## Optional Materials for the Post-Lab Demo

- Digital thermometer
- 10-mL graduated cylinder
- 10 mL acetone

### *Time Required*

One class period, approximately 45–50 minutes.

### *Lab Tips*

This lab is designed for students to work together, discussing and answering the questions posed while proceeding through the step-by-step treatment of the second law.

### *Pre-Lab Discussion*

What does spontaneous mean? What kinds of processes in your experience happen spontaneously? Are there any differences between them?

### *Incorporating into the Curriculum*

This investigation could be incorporated into a unit on chemical changes or thermodynamics.

## PREPARING TO INVESTIGATE

Thermodynamics is a way of describing energy transformations when a system changes from one state to another. The entire architecture of thermodynamics is built on carefully defined terms, many of which have an everyday meaning that is not exactly what chemists mean when they use the term. For example, one way that chemists state the second law of thermodynamics is that in any *spontaneous* change, the *entropy* of the *universe* increases. The underlined words have a very particular meaning that we need to know before we can understand the second law.

The second law of thermodynamics may be expressed in many ways, and it has been used by chemists to understand everything from the work of a steam engine to the direction of time. It grew in the nineteenth century out of observations made about big things like steam engines, and today it is often used to illuminate the conceptual, chemical world of tiny things like atoms, ions, and molecules. In this activity we will use careful observations of the process of dissolving salts in water to more deeply understand the second law.

### *What is a Spontaneous Change?*

A spontaneous change is any change that happens freely in time. For example, you can drop a ball from above your head and it falls to the floor (spontaneous) but you need to provide energy to the ball to place it over your head again. Being able to predict what processes will be spontaneous is how we apply the second law.

Which of the following processes are spontaneous?

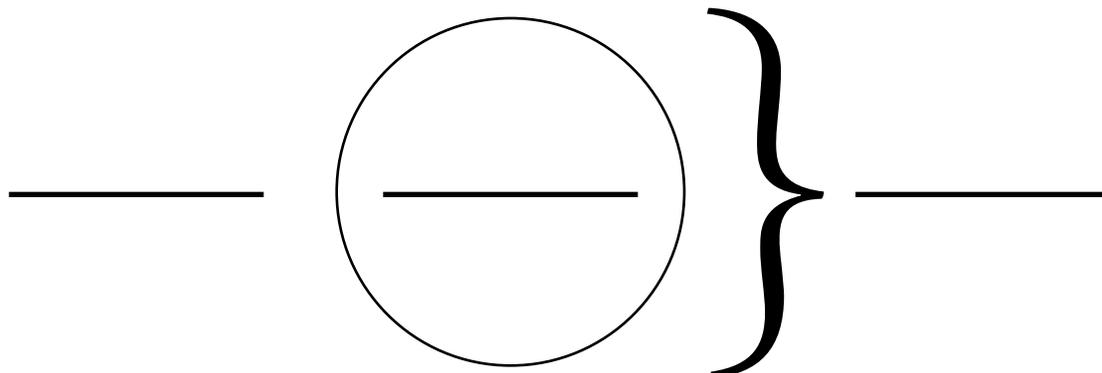
- Ice melts when dropped in a cup of warm water.
- Water evaporates when it is spilled on a hot surface.
- Water in a glass on your desk decomposes to hydrogen and oxygen.
- Iron rusts in air.
- The smell of perfume spray spreads throughout a room.
- Equal volumes of olive oil and vinegar dissolve together to make a salad dressing.

*Good to know: spontaneous  $\neq$  instantaneous!* Even if a change is spontaneous, this doesn't necessarily mean that it happens quickly. The second law tells us that all diamonds are spontaneously turning into coal, but this process is so slow we will never observe it taking place.

### *System, Surroundings, Universe*

The system is the specific part of the universe we are considering, where a change is taking place. It can be any size—a test tube, a beaker, a human body, or an ocean. The surroundings are everything outside the system. The universe consists of the system and the surroundings together.

Fill in the blanks below. Label the regions with the terms *system*, *surroundings*, and *universe*.



## GATHERING EVIDENCE

1. Place 5.0 g of ammonium nitrate in a 150-mL beaker, then put the beaker on the portion of the diagram above that you have labeled as the system. Write the formula for ammonium nitrate and identify its solid type.



Formula:

Identify by underlining: Ionic Solid      Covalent Solid      Metallic Solid

2. Record your observations of the macroscopic properties of the salt:
  
  
  
  
  
  
  
  
  
  
3. Complete the sentence: Ammonium nitrate is an \_\_\_\_\_ solid, and the individual particles in its lattice structure are \_\_\_\_\_.

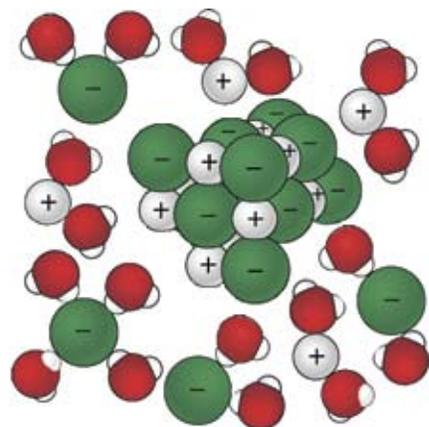
### *Defining Entropy and Looking at Entropy Changes in a System*

Entropy is a mathematically defined property in thermodynamics. It can often help to understand it as a measure of the possible arrangements of the atoms, ions, or molecules in a substance.

The symbol for entropy is  $S$ , and a change in entropy is shown as “delta”  $S$  or  $\Delta S$ . If the entropy of a system increases,  $\Delta S$  is positive. If the entropy of a system decreases,  $\Delta S$  is negative.

1. Pour 100 mL of water over the salt in the beaker and stir. Can you still see the ammonium nitrate?
2. Make and record your observations:

3. Using the terms *cation*, *anion*, *solute*, *solvent*, and *solution*, label the diagram on the right.



4. Given the physical state of ammonium nitrate before it dissolves, how do the possible arrangements of the ions in the salt compare to their possible arrangements when free to move within the solution?
5. Does your answer to the preceding item suggest that the entropy of the ammonium nitrate increased or decreased upon dissolving?
6. Would  $\Delta S$  for this change be positive or negative?

But more is going on than just ions leaving the solid and moving about more freely. Note in the figure above that the polar water molecules are attracted to and oriented around the dissolved ions. The ions are solvated. This orientation of a lot of the water molecules reduces their freedom to move about in the liquid, so the number of possible arrangements of the water molecules is reduced when the ions are present.

7. Would  $\Delta S$  for this change in the arrangement of water molecules be positive or negative?

The change in entropy for the reaction system  $\Delta S_{\text{sys}}$  has to include both the positive change for the ions and the negative change for the water molecules. Which one predominates? For most salts with single charges on their cations and anions, like NaCl, KBr, or LiNO<sub>3</sub>, the positive change in entropy for the ionic solid separating into its ions in solution will predominate.

8. Did dissolution of ammonium nitrate happen spontaneously?
9. If the overall  $\Delta S_{\text{sys}}$  for the dissolution of ammonium nitrate is positive, which  $\Delta S$  in the system predominates:  $\Delta S$  for the ions, or  $\Delta S$  for the water molecules?

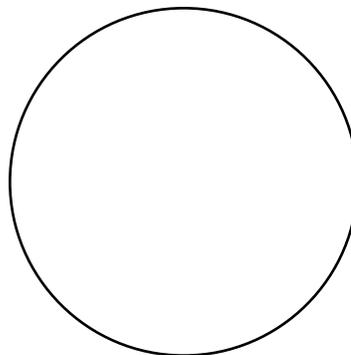
### *Looking at Entropy Changes in the Surroundings by Defining Enthalpy*

We will now consider entropy changes in the surroundings by looking at another thermodynamic term, *enthalpy*. The enthalpy of a system has a definition in thermodynamics that relates to its internal energy, the pressure on the system, and the volume of the system. It is useful in understanding the second law, however, because at constant pressure and volume, a change in enthalpy is the same as the thermal energy transferred from the system to the surroundings, or from the surroundings to the system.

The symbol for the enthalpy of a system is  $H$ , and a change in enthalpy is shown as “delta”  $H$  or  $\Delta H$ . If thermal energy transfers from the system to the surroundings during a physical or chemical change, the  $\Delta H$  is negative and the change is *exothermic*. If thermal energy transfers from the surroundings to the system during a change, the  $\Delta H$  is positive and the change is *endothermic*.

### **Case one for enthalpy**

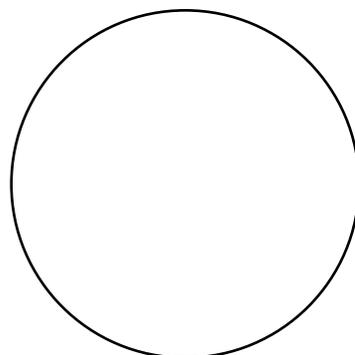
1. Measure out 100 mL of water in a clean 150-mL beaker. Once again, label the “system” and the “surroundings” in the diagram below.
2. Place the beaker on your paper in the region labeled “system” below, then measure the temperature of its contents with a thermometer and record.
3. Add 5.0 g of ammonium chloride or ammonium nitrate.
4. While holding the beaker at its base, stir, and make and record your observations, including the final temperature of the mixture.
5. Your hand at the base of the beaker can be considered part of the surroundings. Was thermal energy transferred to your hand from the beaker, or away from your hand to the beaker?
6. Label the diagram below with an arrow, showing the direction of the transfer of thermal energy. Is thermal energy transferred from the surroundings to the system, or from the system to the surroundings?



7. Is the change endothermic or exothermic?
8. Is  $\Delta H$  of the system positive or negative?

### Case two for enthalpy

1. Measure 100 mL of water in a clean 150-mL beaker.
2. Place the beaker in the “system” below, and measure and record the temperature of its contents. Add 5.0 g of calcium chloride.
3. While holding the beaker at its base, stir, and make and record your observations, including the final temperature of the mixture.
4. Was thermal energy transferred to your hand from the beaker, or away from your hand to the beaker?
5. Label the diagram below with an arrow, showing the direction of the transfer of thermal energy. Is thermal energy transferred from the surroundings to the system, or from the system to the surroundings?



6. Is the change endothermic or exothermic?
7. Is  $\Delta H$  of the system positive or negative?

### Relating the change in enthalpy ( $\Delta H$ of the system) to a change in entropy of the surroundings ( $\Delta S$ of the surroundings)

We are going to look at how entropy changes in the surroundings, depending on the sign of  $\Delta H$  of the system. Before we do, however, let's review.

1. When thermal energy is transferred from region A to region B, the molecules in region B, on average, \_\_\_\_\_ (speed up or slow down?).
2. When the average speed of the molecules in a region is high, there are \_\_\_\_\_ (more or fewer?) high-speed molecules. When the average speed of the molecules in a region is low, there are \_\_\_\_\_ (more or fewer?) high-speed molecules.

3. When the average speed of the molecules in a region is high, there are \_\_\_\_\_ (more or fewer?) possible arrangements for the molecules among the molecular speeds. When the average speed of the molecules in a region is low, there are \_\_\_\_\_ (more or fewer?) possible arrangements for molecules among the molecular speeds.

Now consider what happens in the *surroundings* during the process of thermal energy transfer.

4. When thermal energy is transferred in an endothermic change, will the molecules of the surroundings speed up or slow down?
5. How will this affect the entropy of the surroundings, will it increase or decrease?
6. In this case, is  $\Delta S$  of the surroundings positive or negative?
7. When thermal energy is transferred in an exothermic change, will the molecules of the surroundings speed up or slow down?
8. How will this affect the entropy of the surroundings, will it increase or decrease?
9. In this case, is  $\Delta S$  of the surroundings positive or negative?

### Looking at entropy changes in the universe and the second law

In any spontaneous change, the entropy of the universe increases, or  $\Delta S_{\text{universe}} > 0$ .

We have seen that we can consider the entropy of the system and the entropy of the surroundings separately. Since the universe is composed of the system and the surroundings, then we will consider both when determining the change in entropy of the universe:

$$\Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$$

- When both the change in entropy of the system and the change in entropy of the surroundings are positive, the change in entropy of the universe must be positive, so the reaction will always be spontaneous, under the given conditions.
- If both terms are negative, the reaction is never spontaneous under the given conditions.
- If one term is positive and the other is negative, then whichever has the largest absolute value determines whether  $\Delta S_{\text{universe}}$  is positive (spontaneous reaction) or negative (reaction is not spontaneous) under the given conditions.

Complete the following:

1. In an exothermic reaction,  $\Delta S_{\text{surroundings}}$  is \_\_\_\_\_ (positive or negative?).
2. In an endothermic reaction,  $\Delta S_{\text{surroundings}}$  is \_\_\_\_\_ (positive or negative?).
3. In a spontaneous, endothermic reaction, thermal energy is spontaneously \_\_\_\_\_ (absorbed or released?) by the system from the surroundings.
4. In a spontaneous, exothermic reaction, thermal energy is spontaneously \_\_\_\_\_ (absorbed or released?) to the surroundings from the system.

## ANALYZING EVIDENCE

### Application of Free Energy

Thermodynamics also defines a term known as free energy,  $G$ ; the change,  $\Delta G$ , when a system undergoes a change, is often considered the energy of the system available to do work. Free energy also relates to the second law, since *in any spontaneous process the change in free energy ( $\Delta G$ ) for the system is negative*. The definition for the change in free energy summarizes our discussion of entropy changes in the system and in the surroundings:

$$\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

We have seen that whenever  $\Delta H_{\text{sys}}$  is negative (exothermic) the  $\Delta S_{\text{sur}}$  increases, or is positive.

1. So if  $\Delta H_{\text{sys}}$  is negative and  $\Delta S_{\text{sys}}$  is positive, what will the sign of  $\Delta S$  universe always be?
2. Under these conditions, is the reaction spontaneous?
3. And under these conditions, what will the sign of  $\Delta G$  always be?

This famous relationship of free energy change to changes in enthalpy and entropy shows us the balance between entropy changes in the system and the surroundings, and how that balance depends on temperature. Note that  $T$  stands for the absolute temperature in Kelvin, so its value is always positive.

Use the relationship  $\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$  to complete the chart below:

If $\Delta H_{\text{system}}$ is	Then $\Delta S_{\text{surroundings}}$ will be (+ or -)	And if $\Delta S_{\text{system}}$ is	And $\Delta S_{\text{universe}}$ will be (+ or -)	The $\Delta G$ will be (+ or -)	And the reaction is (spontaneous or not spontaneous)
negative or exothermic		positive (any temperature conditions)			
positive, or endothermic		negative (any temperature conditions)			
negative or exothermic		negative (high temperature conditions)			

negative or exothermic		negative (low temperature conditions)			
positive, or endothermic		positive (high temperature conditions)			
positive, or endothermic		positive (low temperature conditions)			

## INTERPRETING EVIDENCE

### *Decomposition of Baking Soda*

The mysteries of bread making began to be simplified in the 1800s with the use of baking soda. Although it was also combined with sour milk to lighten the texture of heavy bread, it could produce a lightening effect in bread dough on its own when it decomposed:



1. Gases are produced in the decomposition, therefore the sign of  $\Delta S_{\text{sys}}$  for the process is likely to be \_\_\_\_\_.
2. Heat is absorbed in the process so the sign of  $\Delta H_{\text{sys}}$  is \_\_\_\_\_.
3. Apply this information to  $\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$ . When is it likely that  $\Delta G$  will be negative, in other words, when will the process be spontaneous, at high T or at low T?  
\_\_\_\_\_
4. If the values of  $\Delta H_{\text{sys}}$  and  $\Delta S_{\text{sys}}$  are found, we can predict the temperature needed for the baking soda to decompose, and adjust our baking temperature accordingly!

### *Melting Point of Water*

Consider the process:



1. Determine the sign for  $\Delta H_{\text{sys}}$ . Explain your choice.
2. Determine the sign for  $\Delta S_{\text{sys}}$ . Explain your choice.
3. Will  $\Delta G$  be negative at high or at low temperatures?
4. We can use  $\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$  to predict the temperature at which a substance will melt, if we have values for  $\Delta H_{\text{sys}}$  and  $\Delta S_{\text{sys}}$ . At some temperature (T),  $\Delta G$  will change from positive to negative. What will be the value of  $\Delta G$  at the temperature of this change?

5. Substitute this value for  $\Delta G$  and rearrange  $\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$  to solve for T. This value of T will be what?

### *Production of Ozone*

Ozone ( $\text{O}_3$ ) is an unstable form of oxygen that is formed in the stratosphere. The ozone layer in the upper atmosphere protects life on the earth's surface from high-energy ultraviolet light from the sun. Ozone is produced from oxygen gas:



1. In this process, \_\_\_\_\_ moles of oxygen gas produce \_\_\_\_\_ moles of gaseous ozone. Are there more possible arrangements (higher entropy) for the reactants or the products? \_\_\_\_\_ Therefore, is  $\Delta S_{\text{sys}}$  positive or negative?
2. The process is endothermic, so  $\Delta H_{\text{sys}}$  is \_\_\_\_\_.
3. Use  $\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$  to consider: At what T will the reaction be spontaneous?
4. If a system will never spontaneously absorb thermal energy from the surroundings to undergo a change, does that mean the change is impossible? Could energy somehow be forced into the system, for example, by doing "work" on the system?
5. In the case of the production of ozone in stratosphere, which goes on every day, what kind of energy could be "working" on the oxygen gas?

### *Decomposition of Hydrogen Peroxide*

If you have ever used hydrogen peroxide to disinfect an open cut, you may have seen bubbles form when the hydrogen peroxide decomposes:



1. What must be forming in the bubbles?
2. When a gas is formed from a liquid, is the sign of  $\Delta S_{\text{sys}}$  positive or negative?
3. This decomposition is exothermic, so what is the sign of  $\Delta H$ ?
4. So the decomposition of hydrogen peroxide is spontaneous at \_\_\_\_\_ temperatures.
5. Consider that the bottle you bought from the store has been sitting on the shelf for some time, and still contains  $\text{H}_2\text{O}_2$ . Does the conclusion that a reaction is spontaneous at all temperatures mean that the reaction happens quickly? What could have caused the reaction to speed up when the hydrogen peroxide was applied to your open cut?

## REFLECTING ON THE INVESTIGATION

### Demo

1. Place the measuring end of a digital thermometer into a 10-mL graduated cylinder full of acetone.
2. Have students note the temperature, then remove the thermometer, waving it a bit in the air to rapidly evaporate the acetone. The temperature quickly falls.
3. Have students analyze the process from the point of view of thermodynamic properties (the endothermic  $\Delta H_{\text{vap}}$ , the positive  $\Delta S_{\text{system}}$ , and the spontaneity of the process).

### Cross Link

Students can explore the basic mechanics of evaporative cooling in the investigation *The Energy of Evaporation* on page 65.

### Practice Problem

Now that we've observed the qualitative relationships between  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ , let's calculate the quantitative value of  $\Delta G^{\circ}_{\text{rxn}}$  for the dissolution of solid ammonium nitrate in water at 25 °C:



	$\Delta H$ (kJ/mol)	$S_o$ (J/mol K)
$\text{NH}_4\text{NO}_3 (\text{s})$	-365.6	151
$\text{NH}_4^+ (\text{aq})$	-132.80	112.8
$\text{NO}_3^- (\text{aq})$	-206.57	146.4

Remember that  $\Delta H^{\circ}_{\text{rxn}} = \sum n \Delta H^{\circ}_f (\text{products}) - \sum n \Delta H^{\circ}_f (\text{reactants})$  and  $\Delta S^{\circ}_{\text{sys}} = \sum n S_o (\text{products}) - \sum n S_o (\text{reactants})$ . Then use  $\Delta G = \Delta H_{\text{rxn}} - T \Delta S_{\text{sys}}$  to find the change in free energy. Pay attention to units as  $\Delta H^{\circ}_{\text{rxn}}$  will be calculated in kJ and  $\Delta S^{\circ}_{\text{sys}}$  will be calculated in J. Be sure to reconcile units before finding  $\Delta G$ .

- $\Delta H^{\circ}_{\text{rxn}} =$
- $\Delta S^{\circ}_{\text{sys}} =$
- $\Delta G^{\circ}_{\text{rxn}} =$

Do your lab observations support your results? Explain.

## TEACHER'S KEY

Which of the following processes are spontaneous?

- Ice melts when dropped in a cup of warm water.

*Spontaneous*

- Water evaporates when it is spilled on a hot surface.

*Spontaneous*

- Water in a glass on your desk decomposes to hydrogen and oxygen.

*Not spontaneous*

- Iron rusts in air.

*Spontaneous*

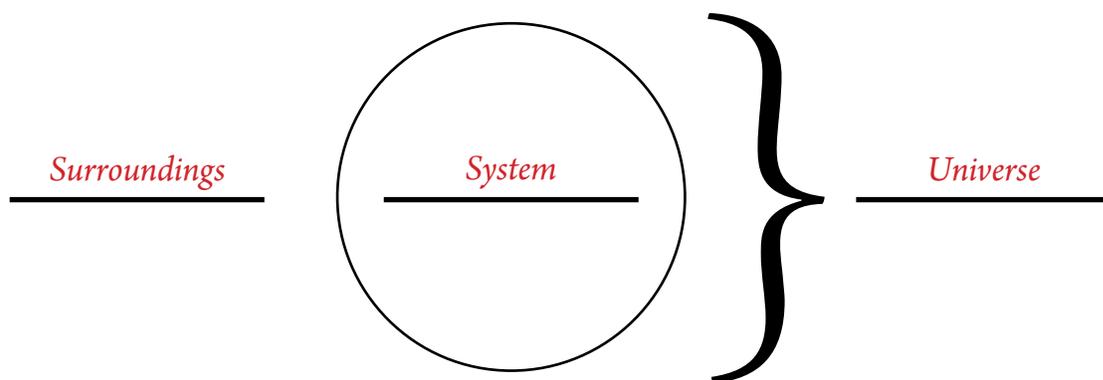
- The smell of perfume spray spreads throughout a room.

*Spontaneous*

- Equal volumes of olive oil and vinegar dissolve together to make a salad dressing.

*Not spontaneous*

Fill in the blanks below. Label the regions with the terms *system*, *surroundings*, and *universe*.



### Gathering Evidence

1. Place 5.0 g of ammonium nitrate in a 150-mL beaker, then put the beaker on your lab sheet where you have designated the system. Write the formula for ammonium nitrate and identify what type of solid it is.

Formula:  $NH_4NO_3$

Identify by underlining:    *Ionic Solid*    *Covalent Solid*    *Metallic Solid*

2. Observe the macroscopic properties of the salt:

*White crystalline solid, small pellets 2–3 mm in diameter*

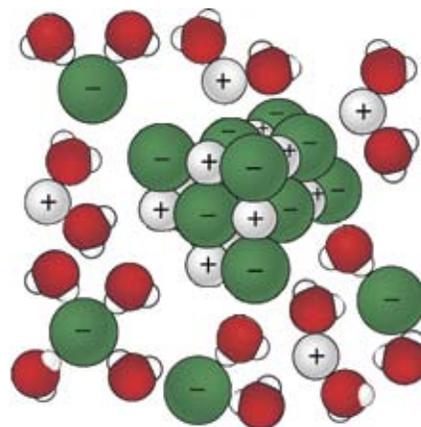
3. Complete the sentence: Ammonium nitrate is an *ionic* solid, and the individual particles in its lattice structure are *ions*.

### *Defining Entropy and Looking at Entropy Changes in a System*

1. Pour 100 mL of water over the salt in the beaker and stir. Can you still see the ammonium nitrate?

*After stirring, the ammonium nitrate disappears; the solution appears transparent.*

2. Make and record your observations.
3. Using the terms *cation*, *anion*, *solute*, *solvent*, and *solution*, label the diagram at right:



4. Given the physical state of ammonium nitrate before it dissolves, how do the possible arrangements of the ions in the salt compare to their possible arrangements when free to move within the solution?

*There are many more possible arrangements or possible positions for the ions after they have dissolved in water.*

5. Does your answer to the preceding item suggest that the entropy of the ammonium nitrate increased or decreased upon dissolving?

*Entropy for the ions in ammonium nitrate has increased.*

6. Would  $\Delta S$  for this change be positive or negative?

*Positive*

7. Would  $\Delta S$  for this change in the arrangement of water molecules be positive or negative?

*There are fewer arrangements possible for the water molecules so the  $\Delta S$  for the water molecules is negative.*

8. Did dissolution of ammonium nitrate happen spontaneously?

*Yes*

9. If the overall  $\Delta S_{\text{sys}}$  for the dissolution of ammonium nitrate is positive, which  $\Delta S$  in the system predominates:  $\Delta S$  for the ions, or  $\Delta S$  for the water molecules?

*Since  $\Delta S$  for the ions is positive and  $\Delta S$  for the water molecules is negative, the  $\Delta S$  for the ions must predominate if the  $\Delta S_{\text{sys}}$  is positive.*

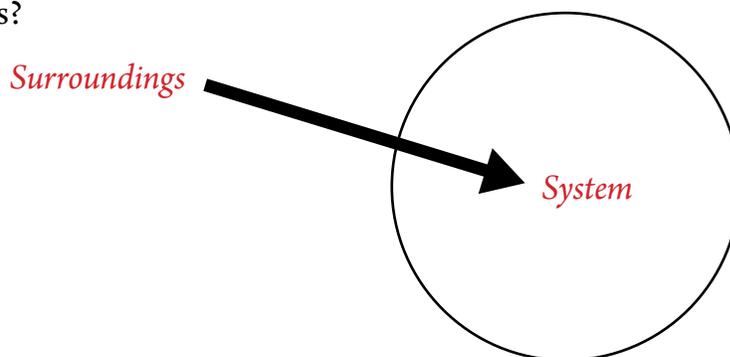
### Defining Enthalpy and Looking at Entropy Changes in the Surroundings

#### Case one for enthalpy

1. Measure out 100 mL of water in a clean 150-mL beaker. Once again, label the “system” and the “surroundings” in the diagram below.
2. Place the beaker on your paper in the region labeled “system” below, then measure the temperature of its contents with a thermometer and record.
3. Add 5.0 g of ammonium chloride or ammonium nitrate.
4. While holding the beaker at its base, stir, and make and record your observations, including the final temperature of the mixture.
5. Your hand at the base of the beaker can be considered part of the surroundings. Was thermal energy transferred to your hand from the beaker, or away from your hand to the beaker?

*Since my hand feels cooler, thermal energy is being transferred from my hand to the beaker.*

6. Label the diagram below with an arrow, showing the direction of the transfer of thermal energy. Is thermal energy transferred from the surroundings to the system or from the system to the surroundings?



7. Is the change endothermic or exothermic?

*Endothermic*

8. Is  $\Delta H$  of the system positive or negative?

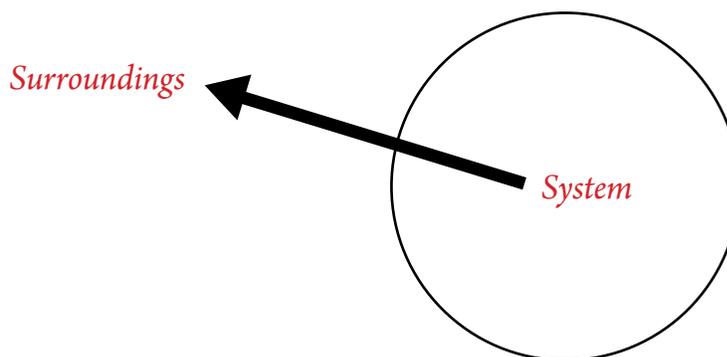
*Positive*

## Case two for enthalpy

1. Measure 100 mL of water in a clean 150-mL beaker.
2. Place the beaker in the “system” below, and measure and record the temperature of its contents. Add 5.0 g of calcium chloride.
3. While holding the beaker at its base, stir, and make and record your observations, including the final temperature of the mixture.
4. Was thermal energy transferred to your hand from the beaker, or away from your hand to the beaker?

*Since my hand feels warmer, thermal energy is being transferred from the beaker to my hand.*

5. Label the diagram below with an arrow, showing the direction of the transfer of thermal energy. Is thermal energy transferred from the surroundings to the system or from the system to the surroundings?



6. Is the change endothermic or exothermic?

*Exothermic*

7. Is  $\Delta H$  of the system positive or negative?

*Negative*

## Relating the change in enthalpy ( $\Delta H$ of the system) to a change in entropy of the surroundings ( $\Delta S$ of the surroundings)

We are going to look at how entropy changes in the surroundings, depending on the sign of  $\Delta H$  of the system. Before we do, however, let's review.

1. When thermal energy is transferred from region A to region B, the molecules in region B, on average, *speed up*.
2. When the average speed of the molecules in a region is high, there are *more* high-speed molecules. When the average speed of the molecules in a region is low, there are *fewer* high-speed molecules.
3. When the average speed of the molecules in a region is high, there are *more* possible arrangements for the molecules among the molecular speeds. When the average speed of the molecules in a region is low, there are *fewer* possible arrangements for molecules among the molecular speeds.

Now consider what happens in the *surroundings* during the process of thermal energy transfer.

4. When thermal energy is transferred in an endothermic change, will the molecules of the surroundings speed up or slow down?

*Slow down*

5. How will this affect the entropy of the surroundings, will it increase or decrease?

*Decrease*

6. In this case is  $\Delta S$  of the surroundings positive or negative?

*Negative*

7. When thermal energy is transferred in an exothermic change, will the molecules of the surroundings speed up or slow down?

*Speed up*

8. How will this affect the entropy of the surroundings, will it increase or decrease?

*Increase*

9. In this case, is  $\Delta S$  of the surroundings positive or negative?

*Positive*

## Looking at entropy changes in the universe and the second law

Complete the following:

1. In an exothermic reaction,  $\Delta S_{\text{surroundings}}$  is *positive*.
2. In an endothermic reaction,  $\Delta S_{\text{surroundings}}$  is *negative*.
3. In a spontaneous, endothermic reaction, thermal energy is spontaneously *absorbed* by the system from the surroundings.
4. In a spontaneous, exothermic reaction, thermal energy is spontaneously *released* to the surroundings from the system.

### Analyzing Evidence

1. So if  $\Delta H_{\text{sys}}$  is negative and  $\Delta S_{\text{sys}}$  is positive, what will the sign of  $\Delta S$  universe always be?

*Positive*

2. Under these conditions, is the reaction spontaneous?

*Yes*

3. And under these conditions, what will the sign of  $\Delta G$  always be?

*Negative*

If $\Delta H_{\text{system}}$ is	Then $\Delta S_{\text{surroundings}}$ will be (+ or -)	And if $\Delta S_{\text{system}}$ is	And $\Delta S_{\text{universe}}$ will be (+ or -)	The $\Delta G$ will be (+ or -)	And the reaction is (spontaneous or not spontaneous)
negative or exothermic	+	positive (any temperature conditions)	+	-	spontaneous
positive, or endothermic	-	negative (any temperature conditions)	-	+	not spontaneous
negative or exothermic	+	negative (high temperature conditions)	-	+	not spontaneous

negative or exothermic	+	negative (low temperature conditions)	+	-	spontaneous
positive, or endothermic	-	positive (high temperature conditions)	+	-	spontaneous
positive, or endothermic	-	positive (low temperature conditions)	-	+	not spontaneous

### Interpreting Evidence

#### Decomposition of baking soda

1. Gases are produced in the decomposition, therefore the sign of  $\Delta S_{\text{sys}}$  for the process is likely to be *positive*.
2. Heat is absorbed in the process so the sign of  $\Delta H_{\text{sys}}$  is *negative*.
3. Apply this information to  $\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$ . When is it likely that  $\Delta G$  will be negative, in other words, when will the process be spontaneous, at high T or at low T?

*High T*

#### Melting point of water

1. Determine the sign for  $\Delta H_{\text{sys}}$ . Explain your choice.

*Positive. Energy must be provided to a system in order to melt a substance.*

2. Determine the sign for  $\Delta S_{\text{sys}}$ . Explain your choice.

*Positive. The liquid state has higher entropy than the solid state.*

3. Will  $\Delta G$  be negative at high or at low temperatures?

*Negative*

4. We can use  $\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$  to predict the temperature at which a substance will melt, if we have values for  $\Delta H_{\text{sys}}$  and  $\Delta S_{\text{sys}}$ . At some temperature (T),  $\Delta G$  will change from positive to negative. What will be the value of  $\Delta G$  at the temperature of this change?

*Zero*

5. Substitute this value for  $\Delta G$  and rearrange  $\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$  to solve for T. This value of T will be what?

*$T = \Delta H_{\text{sys}} / \Delta S_{\text{sys}}$ . This value of T will be the melting point.*

## Production of ozone

1. In this process, *three* moles of oxygen gas produce *two* moles of gaseous ozone. Are there more possible arrangements (higher entropy) for the reactants or the products? Therefore, is  $\Delta S_{\text{sys}}$  positive or negative?

*Reactants, negative.*

2. The process is endothermic, so  $\Delta H_{\text{sys}}$  is *positive*.
3. Use  $\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$  to consider: At what T will the reaction be spontaneous?

*At no T.*

4. If a system will never spontaneously absorb thermal energy from the surroundings to undergo a change, does that mean the change is impossible? Could energy somehow be forced into the system, for example, by doing “work” on the system?

*No, change is not impossible. Energy is absorbed from another source.*

5. In the case of the production of ozone in the stratosphere, which goes on every day, what kind of energy could be “working” on the oxygen gas?

*High-energy radiant energy from the sun.*

## Decomposition of hydrogen peroxide

1. What must be forming in the bubbles?

*Oxygen*

2. When a gas is formed from a liquid, is the sign of  $\Delta S_{\text{sys}}$  positive or negative?

*Positive*

3. This decomposition is exothermic, so what is the sign of  $\Delta H$ ?

*Negative*

4. So the decomposition of hydrogen peroxide is spontaneous at *all* temperatures.
5. Consider that the bottle you bought from the store has been sitting on the shelf for some time, and still contains  $\text{H}_2\text{O}_2$ . Does the conclusion that a reaction is spontaneous at all temperatures mean that the reaction happens quickly? What could have caused the reaction to speed up when the hydrogen peroxide was applied to your open cut?

*Something in the blood or on your skin—a catalyst.*

### Practice Problem

- $\Delta H_{\text{rxn}}^{\circ} = 26.2 \text{ kJ}$   
 $\Delta H_{\text{rxn}}^{\circ} = -132.80 \text{ kJ} + (-206.57 \text{ kJ}) - (-365.6 \text{ kJ}) = 26.2 \text{ kJ}$
- $\Delta S_{\text{sys}}^{\circ} = 108 \text{ J/mol K}$   
 $\Delta S_{\text{sys}}^{\circ} = 112.8 \text{ J/mol K} + 146.4 \text{ J/mol K} - 151 \text{ J/mol K} = 108 \text{ J/mol K}$
- $\Delta G_{\text{rxn}}^{\circ} = -5.98 \text{ kJ}$   
 $\Delta G_{\text{rxn}}^{\circ} = 26.2 \text{ kJ} - (298 \text{ K})(108 \times 10^{-3} \text{ kJ/K}) = -5.98 \text{ kJ}$

Do your lab observations support your results? Explain.

*The change in enthalpy has a positive value, and our observation was that the reaction was endothermic. The entropy of the system increased, which is consistent with a salt dissolving when the positive entropy change for the ions predominates over the negative entropy change for the water molecules. And the reaction happened spontaneously, which is consistent with a negative delta G.*

# Energy & Entropy of a Stretched Rubber Band

## A Lab Investigation

### *Summary*

In this investigation, students work with a real-world item, a rubber band, to explore the concepts of Gibbs free energy, enthalpy, and entropy and their relation to the spontaneity of a physical process. They make observations of any thermal energy absorbed or given off by the rubber band as it is stretched and as it is allowed to contract by touching the band to their forehead. Then, they heat a stretched rubber band and observe whether its length stretches further, contracts, or stays the same.

### *Objective*

Students learn about Gibbs free energy, enthalpy, and entropy, and the idea of assigning positive or negative values to each. They are then related to the spontaneity of stretching or contracting a rubber band.

### *Safety*

- It is recommended that students wear goggles for this investigation, as rubber bands can break and could do so in a student's face.
- When heating the rubber bands, students should be careful not to hold the hair dryer or heat gun on one part of the rubber band for an extended period of time, as the rubber could melt and/or burn.
- If you elect to use the optional high-intensity light bulbs, be aware they get very hot. Also, without some sort of shade, they can be bright for the eyes.

### *Materials*

- Wide rubber band for each student
- Several hair dryers or heat guns for class to share
- Materials for students to design set-up in step 6 (see Lab Tips below)

### *Time Required*

One class period, approximately 45–50 minutes.

### *Lab Tips*

Various lab equipment items could be placed in the laboratory area to inspire students as they design their method in step 6 to test the stretch/contraction of the rubber band as it is heated. These could include: ring stands, clamps, digital balances, weights, rulers, paper clips, safety pins, binder clips, and scissors. Different lab set-ups to measure a change in the rubber band could be:

1. Attach one end of a cut rubber band to a clamp that is attached to a ring stand. Attach a weight to the other end of the band. Adjust so the weight is partially resting on a digital balance, so only part of its weight registers. Any change in the length of the band will result in an increase or decrease in the balance reading.
2. Attach one end of a cut rubber band to a clamp that is attached to a ring stand. Attach a weight to the other end of the band. Use a ruler or other measurement scale next to the weight to observe any change in length. A wooden splint could be attached to the weight, with the end sticking out from the side of the weight, to more easily view any changes.
3. An uncut band could be looped around a doorknob or drawer pull, with a weight or heavy object looped through the bottom of the band. Use a ruler or other measurement scale next to the weight to observe any change in length. A wooden splint could be attached to the weight or object, with the end sticking out from the side of the weight, to more easily view any changes.

The best results are obtained if the band is stretched close to its maximum length. Instead of a hair dryer or heat gun, high-intensity light bulbs could be used.

### *Pre-Lab Discussion*

This investigation introduces the concepts of Gibbs free energy (G), enthalpy (H), entropy (S), and spontaneity. These terms, their symbols, and their connection to each other in the equation  $\Delta G = \Delta H - T\Delta S$  could be discussed before the lab; however, the investigation can be done without this discussion.

It can be pointed out that whether a process is spontaneous or not is not related to how quickly the process occurs. Other examples of spontaneous physical changes could be discussed. One common example is the melting of ice, which at ordinary pressures is spontaneous at temperatures above 0 °C.

### *Integrating into the Curriculum*

This investigation would fit into units on thermodynamics and polymers.

## PREPARING TO INVESTIGATE

In this investigation, you will make observations of an everyday item, a rubber band. Based on what you already know about rubber bands and how they behave, consider the following:

1. Picture holding a rubber band by looping your thumbs through the band so the band sits on your thumbs, but is unstretched. If you wait, will the band ever spontaneously stretch and fall off your thumbs?
2. Picture holding a rubber band between your thumbs as before, but this time stretched to nearly its limit. If you quickly pull a thumb out of the band, will the band spontaneously remain stretched out?

The two situations above may sound ridiculous. They describe the opposite of your past experiences with rubber bands. Anyone who has ever let fly a rubber band from her fingers or had a rubber band suddenly break knows that she can reasonably expect a stretched rubber band to contract when released. This change is spontaneous, and at everyday temperatures and pressures happens quite quickly. The reverse change, for a rubber band to go from a contracted position to a stretched position without an outside force acting on it, such as the pull of your thumbs, is not spontaneous.

Is there a way to determine if a change will be spontaneous or not? There is a quantity called Gibbs free energy ( $G$ ) that can help. For a change in a system, if the amount of free energy decreases, that is, if  $\Delta G < 0$ , the change is spontaneous.

Different variables contribute to  $\Delta G$ . Expressed as an equation,  $\Delta G = \Delta H - T\Delta S$ , where  $\Delta H$  is change in enthalpy,  $T$  is temperature in Kelvin, and  $\Delta S$  is change in entropy. All quantities are from the viewpoint of the system. Enthalpy is a measure of the internal energy of the system. We cannot measure the enthalpy of a system directly, but can measure changes in enthalpy as the thermal energy released or absorbed when changes in the system occur at constant pressure. From the viewpoint of the system, if thermal energy is released by the system, it has been transferred out of the system, and  $\Delta H$  would have a negative sign. Entropy is a way of expressing how many different ways the particles and energy of a system can be arranged. For changes, nature favors increases in entropy ( $\Delta S > 0$ ) that will maximize the number of different possible arrangements of particles and energy in the system.

In this investigation, you will observe whether thermal energy is absorbed or released from a rubber band as it is stretched and allowed to contract. Then, you will design a way to measure any stretching or contraction of a rubber band when it is heated. Using your observations, you will consider the changes in enthalpy and entropy that occur in the system of the rubber band, and how they contribute to the system's free energy changes.

## GATHERING EVIDENCE

1. Obtain a wide rubber band. Hook both your thumbs into the rubber band, so you can use your thumbs to stretch out the band.



2. Hold the rubber band hooked on your thumbs so that the band is just snug enough to remain on your thumbs, but is not stretched out. Hold the wide, flat part of the band to your forehead. Does it feel warmer, cooler, or the same as your forehead? Repeat this step a few times to be sure of your initial observation.
3. Hold the rubber band hooked on your thumbs. Hold it near your forehead but not touching it. Quickly stretch the band out to the sides and immediately touch the wide, flat part of the band to your forehead. In the “Observations” column of the data table below, record your observations of whether it feels warmer, cooler, or the same as your forehead. Repeat this step a few times to be sure of your initial observation. In between the different tries, allow the band to contract to its original size and hold it unstretched for about 20 seconds to be sure it is at its original temperature.
4. Hold the rubber band hooked on your thumbs. Stretch the band out to the sides. Keep the band stretched out for about 20 seconds to be sure it is at its original temperature. While still looping your thumbs into the band, quickly allow the band to contract to its original position and immediately touch the wide, flat part of the band to your forehead. In the “Observations” column of the data table below, record your observations of whether it feels warmer, cooler, or the same as your forehead. Repeat this step a few times to be sure of your initial observation.
5. Based on your observations in steps 3 and 4, predict what will happen if you heat a stretched rubber band.
6. Design and set up a method, using materials your instructor has made available, to qualitatively measure any change, stretching, contracting, or staying the same, in the length in a stretched rubber band as it is heated with a hair dryer or heat gun. You may cut the rubber band into a single long strip if you wish. Keep the hair dryer or heat gun moving slowly to avoid overheating and melting the rubber band.
7. Use your method to observe any change in the length of the stretched rubber band as it is heated with a hair dryer or heat gun. In the “Observations” column of the data table below, record your observations.

Process	Observations	System absorbs or gives off thermal energy?	$\Delta H$ +/-	Process spontaneous? yes/no	$\Delta G$ +/-
stretching band (step 3)					
contracting band (step 4)					
heating band (step 7)					

## ANALYZING EVIDENCE

1. Based on the temperature changes you observed when you held the stretched rubber band and the contracted rubber band to your forehead in steps 3 and 4, determine whether the system (the rubber band) absorbs or gives off thermal energy in these cases. Use this information to fill in the column “System absorbs or gives off thermal energy?” for “stretching band (step 3)” and “contracting band (step 4).”
2. Did the system (the rubber band) absorb or give off thermal energy when you used the hair dryer/heat gun in step 7? Use this information to fill in the column “System absorbs or gives off thermal energy?” for “heating band (step 7).”
3. Is the change in enthalpy ( $\Delta H$ ) for a system positive or negative if the system absorbs thermal energy? If the system gives off thermal energy? Remember, the sign is from the perspective of the system. Has the thermal energy in the system increased or decreased? Use this information to fill in the column “ $\Delta H$  +/-” with the appropriate signs.
4. Fill in the column “Process spontaneous? yes/no,” depending on whether the change that occurred was spontaneous.
5. Is the change in free energy ( $\Delta G$ ) for a system positive or negative when the system undergoes a spontaneous reaction? Use this information to fill in the column “ $\Delta G$  +/-” with the appropriate signs.

## INTERPRETING EVIDENCE

1. If the process of a stretched rubber band returning to its original size by contracting was written as the equation: stretched band  $\longrightarrow$  contracted band, would “thermal energy” be shown in the equation as a reactant or product? Explain.
2. Is allowing a stretched band to contract an exothermic or endothermic reaction? Describe the direction of the flow of thermal energy between the system of the rubber band and its surroundings, which include your forehead.
3. As discussed in Preparing to Investigate, a rubber band contracting is a spontaneous process, meaning  $\Delta G$  for that process is negative. Using the equation below and based on your observations during the investigation, label the variables  $\Delta G$ ,  $\Delta H$ , and  $T$  with the appropriate sign, + or –, for the contraction process.

$$\Delta G = \Delta H - T\Delta S$$

4. What should the sign for  $\Delta S$  be in the equation above for the contraction process to be spontaneous?
5. How did your observations in steps 3 and 4 when you touched the rubber band to your forehead relate to the result you saw in step 7 when you heated the rubber band?

## REFLECTING ON THE INVESTIGATION

1. Based on the sign for  $\Delta S$ , positive or negative, that you answered for question 4 in Interpreting Evidence, explain how the arrangement of the cross-linked polymer chains in the rubber band can result in an increase or decrease in entropy when it is contracted compared to when it is stretched. Explain or draw what happens on the molecular level.
2. How does the action of the heated rubber band in step 7 compare with what happens when other everyday materials, such as metal, are heated?
3. Picture using the method and set-up you designed in step 6 of Gathering Evidence, but instead of heating the stretched band, you cool it. Predict what would happen. Explain.

## TEACHER'S KEY

In this investigation, students work with a real-world item, a rubber band, to explore the concepts of Gibbs free energy, enthalpy, and entropy, and their relation to the spontaneity of a physical process.

### Analyzing Evidence

Process	Observations	System absorbs or gives off thermal energy?	$\Delta H$ +/-	Process spontaneous? yes/no	$\Delta G$ +/-
stretching band (step 3)	<i>feels warm</i>	<i>gives off thermal energy</i>	-	<i>no</i>	+
contracting band (step 4)	<i>feels cool</i>	<i>absorbs thermal energy</i>	+	<i>yes</i>	-
heating band (step 7)	<i>band contracts</i>	<i>absorbs thermal energy</i>	+	<i>yes</i>	-

### Interpreting Evidence

1. If the process of a stretched rubber band returning to its original size by contracting was written as the equation: stretched band  $\longrightarrow$  contracted band, would “thermal energy” be shown in the equation as a reactant or product? Explain.

*Thermal energy would be shown as a reactant. Thermal energy is added to the system, the rubber band, as it contracts. This is why the band feels cool on the forehead, since energy flows from the forehead to the band.*

2. Is allowing a stretched band to contract an exothermic or endothermic reaction? Describe the direction of the flow of thermal energy between the system of the rubber band and its surroundings, which include your forehead.

*It is an endothermic reaction. Thermal energy flows from the surroundings (forehead) to the system (rubber band). This makes the band feel cool on the forehead.*

3. As discussed in Preparing to Investigate, a rubber band contracting is a spontaneous process, meaning  $\Delta G$  for that process is negative. Using the equation below and based on your observations during the investigation, label the variables  $\Delta G$ ,  $\Delta H$ , and  $T$  with the appropriate sign, + or -, for the contraction process.

$$\Delta G = \Delta H - T\Delta S$$

*(-) = (+) - (+)(\Delta S)*

4. What should the sign for  $\Delta S$  be in the equation above for the contraction process to be spontaneous?

*The sign for  $\Delta S$  must be positive in order for the right-hand side of the equation to be negative to agree with the sign of the left-hand side.*

5. How did your observations in steps 3 and 4 when you touched the rubber band to your forehead relate to the result you saw in step 7 when you heated the rubber band?

*When the band stretched, it gave off thermal energy, which made the forehead feel warm. When the band contracted, it absorbed thermal energy, which made the forehead feel cool. When the band was heated with a hair dryer, the system was absorbing thermal energy. The system absorbing thermal energy is connected with the process of contracting.*

### Reflecting on the Investigation

1. Based on the sign for  $\Delta S$ , positive or negative, that you answered for question 4 in Interpreting Evidence, explain how the arrangement of the cross-linked polymer chains in the rubber band can result in an increase or decrease in entropy when it is contracted compared to when it is stretched. Explain or draw what happens on the molecular level.

*When the band is stretched, the cross-linked polymer chains straighten out and are more aligned with each other, like a bundle of uncooked spaghetti noodles. There are fewer potential arrangements of particles in this situation. When the band is allowed to contract, the chains are not as straight and become more tangled, like a mass of cooked spaghetti noodles. There are more potential arrangements of particles in this situation.*

2. How does the action of the heated rubber band in step 7 compare with what happens when other everyday materials, such as metal, are heated?

*Typically, materials such as metal expand when they are heated, rather than contracting as the rubber band did.*

3. Picture using the method and set-up you designed in step 6 of Gathering Evidence, but instead of heating the stretched band, you cool it. Predict what would happen. Explain.

*Since thermal energy is being given off by the system, or removed from it, the rubber band should stretch.*

### Post-Lab Discussion

A review of the equation  $\Delta G = \Delta H - T\Delta S$ , its variables, and what a positive or negative sign for each variable means could be useful. Depending on their answers to Reflecting on the Investigation question 1, students might need a further discussion of what happens on the molecular level as a rubber band stretches/contracts.

### Extensions

Students could also investigate the effect of heating the rubber band to different temperatures, such as using low/high settings on a hair dryer or various settings on a heat gun. Does the temperature change the amount of contraction?

An additional polymer to explore is a toy called Shrinky Dinks. Pieces of this plastic can be decorated with colored pencils or markers, then baked. When heated, the plastic contracts dramatically, resulting in a piece approximately one-third its original length and width, but much thicker. The change of this material is not easily reversible and could be contrasted with that of rubber bands, which can be stretched and contracted over and over. Instead of buying commercially available kits, transparent deli containers with the recycle code #6 can also be used.

As an advanced, challenging extension, students could construct a rubber band heat engine using directions available online. The spokes on a bicycle wheel rim are replaced with rubber bands. Each spoke is cut, and the ends remaining on the wheel are bent into hooks so the rubber band can be looped around them. The wheel is then mounted so it can rotate freely. A heat lamp is placed near one area of the rubber bands. As the lamp heats the rubber bands, they contract, which moves the wheel. The heated rubber bands rotate away and cool down, with different rubber bands coming close to the lamp to heat up and continue the process. Directions are available online:

<http://bit.ly/highschoolnrg17>

Videos of constructed rubber band heat engines can also be found online. The engine was described by physicist Richard Feynman (Feynman, R. P.; Leighton, R. B.; Sands, M. *The Feynman Lectures on Physics*, Vol. I: The New Millennium Edition: Mainly Mechanics, Radiation, and Heat. New York: Basic Books, 2010, p 44-2):

<http://bit.ly/highschoolnrg18>

### Additional Resources

- Summerlin, L. R.; Ealy, J. L., Jr. *Chemical Demonstrations: A Sourcebook for Teachers*, Volume 1, second ed. Washington, DC: American Chemical Society, 1988, p 73.
- Hirsch, W. "Rubber Bands, Free Energy, and Le Châtelier's Principle." *J. Chem. Educ.*, 2002, 79 (2), pp 200A–B.

# Why COLD Doesn't Exist

By Michael Tinnesand



## Pop Quiz!

**Q: What happens when an ice cube is added to warm soda?**

- Heat is transferred from the soda to the ice.
- The ice cube's "cold content" is transferred to the soda.
- Both heat and cold are transferred between the ice and soda.

In our daily lives, we see many examples of warm objects that become colder, but it may not be obvious how it happens. Let's see how things become cold (and get the answer to our pop quiz).

## Collisions in your soft drink

In the case of the ice cubes in the soft drink, the soft drink becomes colder and the ice cubes warmer because energy is transferred from the soft drink to the ice, not the other way around, so the best answer is "a." The reason is that energy is always transferred from a body at higher temperature to a body at lower temperature and, as a result, there is no such thing as "cold" flowing from the ice to the beverage.

To understand how this works, let's consider the definitions of "temperature" and "kinetic energy." In any sample of matter, particles—atoms, ions, or molecules—can move in three different ways: They can vibrate (wiggle about a fixed position), translate (move from one location to another), or rotate (spin around).

At any time, these particles are constantly moving—slowly in solids, and more noticeably in liquids and gases, and as they do,

Water molecules in the ice move relatively slowly

Soft-drink molecules move faster

When the faster moving soft drink molecules collide with the slower-moving water molecules in the ice cubes, the water molecules are ejected from the ice cubes. The result? The ice melts and the soft drink cools.

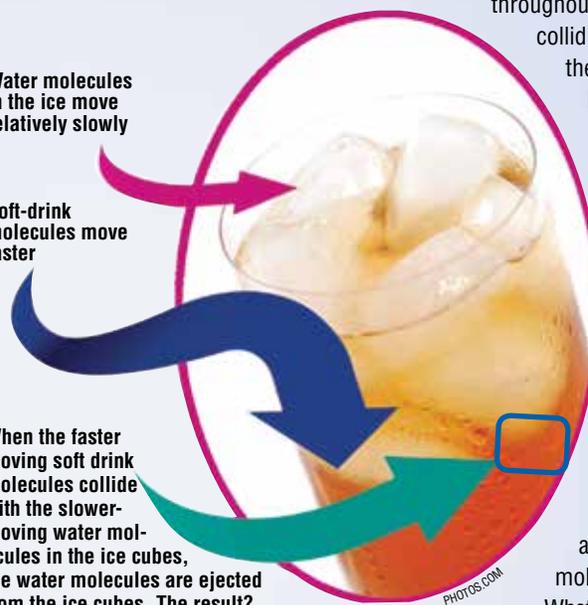
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they collide with one another. Each time these collisions occur, the speeds and directions of the colliding particles change. So the particles have a wide range of speeds and, similarly, a wide range of kinetic energies (because kinetic energy is proportional to the square of the speed). The values of the kinetic energies of all the particles follow a distribution that looks like the one shown in Fig. 1.

A common way to discuss the kinetic energy of all the particles in a sample is to

use their average kinetic energy, which lies around the peak of the distribution. This average kinetic energy varies with temperature (Fig. 1). The more the particles vibrate, translate, or rotate, the greater the temperature of the sample.

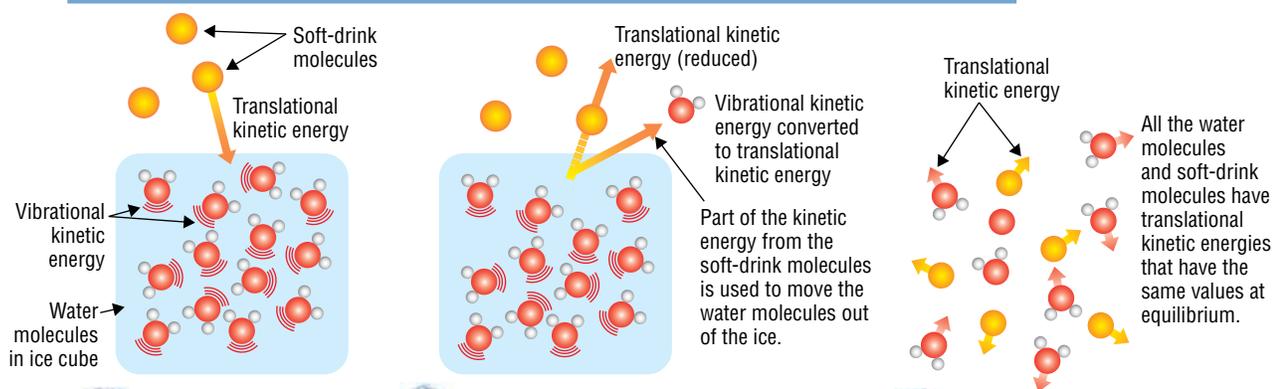
Let's return to the example of ice in a warm soft drink. The particles in the soft drink move throughout the space of the container, colliding with each other and with the walls of the container. This is known as translational kinetic energy, and it is the main form of kinetic energy for gases and liquids. The water molecules in the ice vibrate about a fixed position and, as a result, their kinetic energy is mainly vibrational. The molecules in the soft drink move faster than the water molecules in the ice cubes because they are at a higher temperature and, therefore, have a higher average kinetic energy than the water molecules.

What does the energy transfer look like? When the faster-moving soft-drink molecules collide with the slower-moving water molecules, part of the kinetic energy of the soft-drink molecules is used to move the water molecules out of their crystal lattice. The net effect is that the kinetic energy of the soft-drink molecules is reduced and the water molecules have the same kinetic energy that they initially had in the ice crystal, except that this kinetic energy is translational rather than vibrational. The total amount of energy transferred from the soft-drink molecules to the water molecules in the ice cubes is called heat.



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# How Ice Cubes Melt and Cool Your Soft Drink

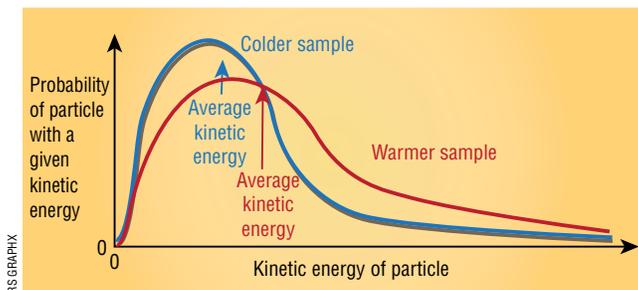


**A** The molecules of water in the ice cubes vibrate (they have vibrational kinetic energies), and the molecules in the soft drink move along straight lines in between collisions with other water molecules (they have translational kinetic energies).

**B** When a molecule in the soft drink collides with a water molecule, part of the translational kinetic energy is used to move the water molecule out of the ice, and the water molecule's vibrational kinetic energy is converted to translational kinetic energy.

**C** As more collisions between soft-drink molecules and water molecules occur, the soft-drink molecules keep transferring energy to the water molecules, until the temperatures of the soft-drink and water molecules are identical. This is known as equilibrium, in which case most of the ice cubes have melted, and both the soft-drink and water molecules are in liquid form.

ANTHONY FERNANDEZ



**Figure 1.** Distribution of the kinetic energies of particles in a sample at two different temperatures. The fraction of particles in the sample that have a given kinetic energy is shown by the height of the curve for that value of kinetic energy.

The collisions will continue to transfer energy until the temperatures of the ice molecules and soft-drink molecules are identical. This is known as thermal equilibrium. When thermal equilibrium has been reached, the average kinetic energy of both types of par-

ticles is equal, and the final temperature—assuming there is still ice left—will be about 0 °C.

## Cold finger

Thinking about heat and cold in this way can be useful in explaining how

heat transfer works in everyday life. It can help us explain common occurrences such as evaporation.

If you put your finger in water at the same temperature as your finger and then wave it in the air, it feels cooler. Why? Some of the water molecules with higher energy have enough energy to escape as water



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This happens over and over again, as higher energy water molecules vaporize, leaving water molecules with lower average kinetic energy, so heat transfer continues from your finger to the cooler water molecules. This net transfer of energy goes from your finger to the water, and your finger feels cooler.

So, does cold exist? Can we say that it is really cold outside? Yes, we can. Cold is a perfectly fine adjective to describe when something is not hot, or when its temperature is low. We sometimes use words to describe conditions that reflect the absence of something rather than the presence of something else. For example, there is no such thing as darkness. There is only light or lack of light. But that's a story for another time! **CM**

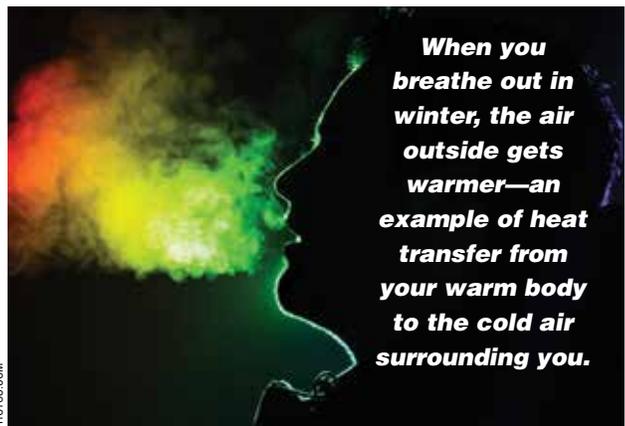
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**When you breathe out in winter, the air outside gets warmer—an example of heat transfer from your warm body to the cold air surrounding you.**

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