Objectives

- ➔ Describe the process of heat transfer in systems.
- ➔ Explain how energy can be converted to less useful forms.
- ➔ Describe how energy transfer can be modeled mathematically.

Key Terms

Thermodynamics
Exothermic
Endothermic
Heat
Temperature
Enthalpy
Specific heat
Specific heat capacity
Thermal energy
First law of thermodynamics
Second law of thermodynamics
Entropy
Atmospheric thermodynamics

Thermodynamics

As you know, energy cannot be created or destroyed. So what happens to energy when an object is heated or cooled? Let's think about what happens when you place your hands around a mug of hot chocolate. Is heat energy released to the surroundings (your hands), or is it absorbed by the hot chocolate? Your hands start to warm up from holding the hot chocolate; therefore, the heat energy must be released by the hot chocolate and absorbed by your hands. This physical reaction is called exothermic.

Thermodynamics is the science that deals with the relationship between heat, pressure, density, and temperature in a substance. Thermodynamics specifically focuses largely on how the transfer of heat is related to various energy changes within a physical system. Those changes in heat usually result in work being done by the system. The changes are guided by the laws of thermodynamics.

An **exothermic** reaction can be a chemical or a physical object that releases heat energy to its surroundings. The opposite of this reaction is endothermic. An **endothermic** reaction absorbs heat from its surroundings. Figure 1 shows an example of exothermic and endothermic phenomena you are probably familiar with.

Heat and temperature are not the same thing. **Heat** is a form of energy; it is measured in calories or joules. **Temperature** is a measure of the average kinetic energy of the particles in a substance; it is measured in kelvins or degrees.

Exothermic releases energy

Endothermic absorbs energy

Figure 1

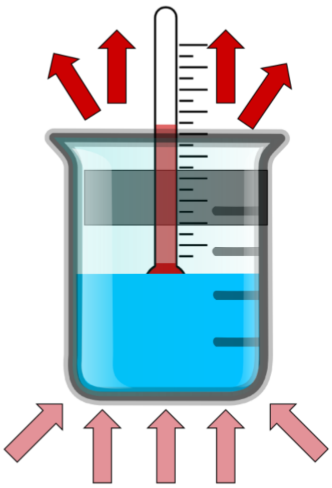

Figure 2

Enthalpy

Scientists use the term **enthalpy** when referring to the total heat of a system, taking into account the amount of volume and the pressure on the system (figure 2). The change in enthalpy, or ΔH, refers to energy differences between the reactants and products of a chemical reaction. When reactions occur under constant-pressure conditions, all this energy is in the form of heat. ΔH is often expressed in either joules (J) or calories (cal). One calorie is equivalent to 4.184 joules.

Temperature changes measured during a chemical reaction inside a calorimeter (a device that can measure changes in enthalpy or heat) cannot be used directly to measure the enthalpy change (ΔH) of the reaction. Instead, the temperature change must be inserted into a mathematical equation, along with other factors, to calculate the enthalpy change of the reaction.

Thermodynamic System

The transfer of heat (heat flow) within a system and its surroundings is designated by the letter (q), meaning quantity of heat. According to the law of conservation of energy and the **first law of thermodynamics**, if a known mass of hot lead is immersed in water in a closed system calorimeter, the heat lost by the lead equals the heat gained by the water. Heat lost (-q) = heat gained (q).

When a system is heated, energy moves from the surroundings to the system. The system gains energy, and q is positive. When a system is cooled, energy moves from the system to the surroundings. The system loses energy, and q is negative.

Heat	Energy Moves from	Energy Moves to	Value of “q”
Heat added	Surroundings	System	q is positive
Heat reduced	System	Surroundings	q is negative

Determining Changes in Enthalpy

Here are some various terms that need to be discussed before performing any calculations. First, if pressure remains constant during a reaction, ΔH (change in enthalpy) of a chemical system is equivalent to the heat of the system (q):

$$\Delta H_{system} = q$$

Second, ΔH of a chemical system is equal to the difference between the sum of the enthalpies of products and reactants:

$$\Delta H_{system} = \Sigma H_{products} - \Sigma H_{reactants} = q$$

Now that we have reviewed the meanings of these terms, we can turn to another equation that relates q to other factors that scientists can measure in a lab:

$$q = m \times c \times \Delta T$$

In this equation, m is the mass of the system (measured in grams), c is the specific heat of the system, and ΔT is the change in temperature of the system. This equation allows a scientist to measure the temperature change of a chemical reaction in a calorimeter and to then use that temperature change to calculate the change in enthalpy for that reaction.

The scientist must also measure the system's mass (m) and know the system's specific heat (c). For a chemical reaction, the system is composed of the substances undergoing reaction and the solvent.

Specific Heat

Specific heat is a property of a substance. Each substance has a unique specific heat. To think about this, consider what it feels like to stand on a sandy beach on a hot, summer day, as shown in figure 3. When it is very hot, the sand becomes scorching—so hot that it hurts to walk barefoot across the beach to the water. Yet, when you step into the water, it feels cool. You might wonder why the sand is so hot and the water is so cool when both are exposed to the same conditions of air temperature and sunlight. How can the concept of specific heat solve this puzzle?

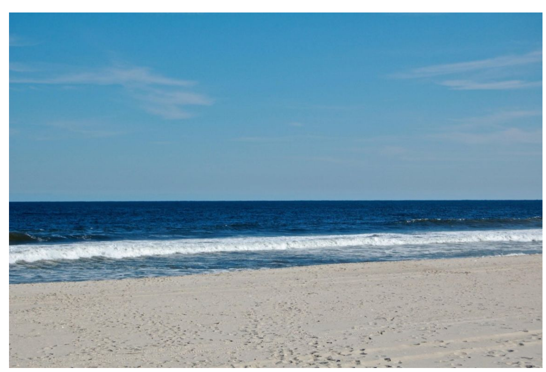

Figure 3

All substances respond differently to being heated. Each substance requires a different amount of heat energy to raise its temperature. The **specific heat capacity** of a substance is defined as the amount of heat needed to raise one gram of a substance one degree Celsius. Specific heat is expressed in joules per gram degree celsius (J/g°C). It is sometimes used for identifying an unknown substance. Different substances heat at different rates, and specific heat reference tables provide these known values at standard pressure (figure 4). Once you experimentally find the specific heat (c_p) of an unknown metal in the laboratory, you can use a specific heat reference chart to determine the identity of the metal.

For reactions taking place in water, the mass is the sum of the water and other reactants. Only the specific heat of water is used, because it is present in such high amounts compared to the other substances.

Specific Heat of Common Materials

Material	Specific Heat (Joules/gram°C)
Liquid water	4.18
Solid water (ice)	2.11
Water vapor	2.00
Dry air	1.01
Basalt	0.84
Granite	0.79
Iron	0.45
Copper	0.38
Lead	0.13

Figure 4

Measuring the Enthalpy Change for a Reaction

The procedure for determining ΔH, or change in enthalpy of a chemical system, begins with laboratory work and then proceeds to calculations, as outlined below.

1. **Measure the masses of reactants.**
   The masses of the reactants will be important later on during the calculation phase of the procedure.

2. **Measure the temperature of reactants.**
   Reactants should be allowed to achieve the same initial temperature. Measure and record this value as the initial temperature, $T_{initial}$.

3. **Monitor the temperature until the reaction is complete.**
   The temperature will rise if the reaction is exothermic; the temperature will fall if the reaction is endothermic. Record the temperature every 30 seconds until it levels off. This indicates the reaction has come to a stop. The temperature reading corresponding to this time point can be taken as the ending temperature of the reaction, T_{final}.

4. **Calculate ΔT.**

   Subtract $T_{initial}$ from T_{final} to determine ΔT:

$$\Delta T = T_{final} - T_{initial}$$

   The ΔT can be positive or negative. A positive ΔT indicates an endothermic reaction, whereas a negative ΔT indicates an exothermic reaction.

5. **Calculate q.**

   Use the following equation to calculate the enthalpy change for the reaction (q). Sum the measured masses of the reactants to obtain the mass of the reaction solution (m). Use ΔT (calculated above). The value for specific heat (c_p) can be obtained from reference sources. For aqueous solutions, use the specific heat of water (4.184 J/g · °C).

$$q = m \times c_p \times \Delta T$$

Example 1:
Suppose you place a 67 g piece of copper into a beaker of water. The initial temperature of the water was 25°C. The water heated to a final temperature of 55°C. Using the table on the previous page (with specific heats), calculate the amount of energy absorbed by the water.

Solution: To determine q, calculate ΔT, and then multiply by c_p (specific heat) and m (mass).

$q = m \times c_p \times \Delta T$
$m = 67$ g
$c_p = 0.385$ J/g·°C
$\Delta T = 55°C - 25°C = 30°C$

$q = (67\text{ g}) \cdot (.385\text{ J/g·°C}) \cdot (30°C)$
$q = 773.85$ J

Energy Transformation

A system that interacts with and exchanges energy with its surroundings is a thermodynamic system. **Thermal energy**, often referred to as heat, is the average kinetic energy of the atoms and molecules of a substance. Thermal energy is measured by temperature and can be transferred within a system. The first law of thermodynamics states that heat is a form of energy that is conserved. This means that heat energy cannot be created or destroyed. It can, however, be transferred from one location to another and converted to and from other forms of energy.

There is a flow of energy between two systems when there is a temperature difference between them, and there is a path between them that is thermally conducting. The flow of heat will continue as long as there is a difference in temperature, until both systems reach the same temperature. When both systems reach the same temperature, they are at thermal equilibrium with each other, and the flow of energy ceases. This is diagrammed in figure 5.

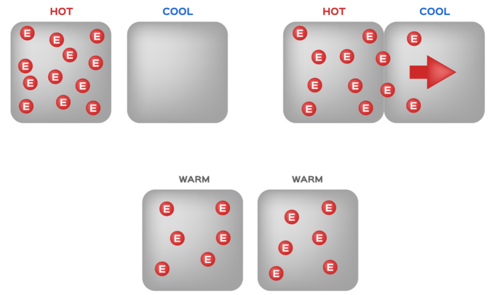

Figure 5

Second Law of Thermodynamics

Figure 6

The **second law of thermodynamics** is about the quality of energy found in a system. It states that as energy is transferred or transformed, energy can be transformed to less useful forms of energy. The second law also states that there is a natural tendency of any isolated system to regulate its energy such that it is more uniform. Figure 6 shows a cup of coffee in a traditional cup. What is happening to the thermal energy in the coffee?

What does all this mean? Essentially, when looking at forms of energy, we want it to be in a form that we can use, such as gasoline for our cars. We want to get as much kinetic energy as possible from the potential chemical energy found in the bonds of the gasoline compounds. However, we know that some cars are more efficient than others and get more mileage out of a gallon of gas than others. Why is that? More efficient cars transform more chemical potential energy in the gasoline to kinetic energy and minimize the amount of energy transformed into heat. Based on the second law, there will never be a machine that is 100% efficient, as some energy will always be transformed to a less useful form of energy.

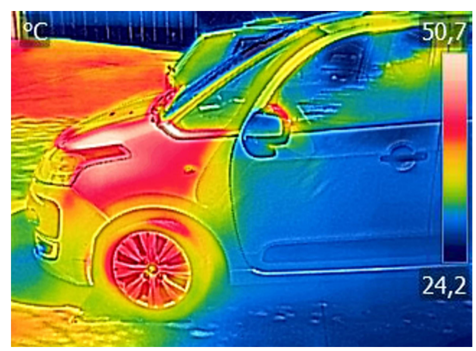

Figure 7

When looking at a car, you have an open system, as it interacts with the surroundings at all times, as you can see in figure 7. But what about an isolated or closed system that has no interaction with the surroundings? How is the second law applied to this kind of system? In the case of an isolated system, instead of the energy being transformed into a less useful form, the energy of the system will regulate in such a way that there is a uniform distribution of the energy. For example, an isolated system contains water that is 100°C and ice cubes that are 0°C. The water molecules contain more energy and will come in contact with the molecules in the ice with less energy. Eventually, the energy of the two substances will reach equilibrium. The overall system has more disorder or **entropy**.

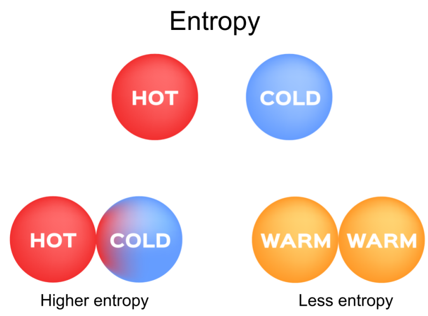

Figure 8

Uncontrolled systems, or open systems, will always evolve toward more stable states—that is, toward more uniform energy distribution within the system or between the system and its environment (figure 8). For example, water flows downhill, and objects that are hotter than their surrounding environment cool down. Any object or system that can degrade with no added energy is unstable. Eventually it will change or fall apart, although in some cases, such as long-lived radioactive isotopes, it may remain in the unstable state for a long time before decaying.

The Nature of Science in Action

Scientific Knowledge Assumes an Order and Consistency in Natural Systems

Science assumes the universe is a vast, single system in which basic laws are consistent.

The law of thermodynamics is consistent throughout all systems, from man-made machinery to involuntary bodily functions in humans.

Energy Capture Not Efficient

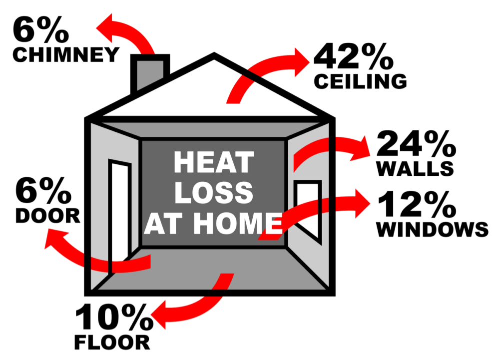

Figure 9

Living organisms use the flow of energy in metabolic processes, and engineers use the flow of energy in a turbine, a piston and crankshaft, a sail, or wind-turbine blades. In each of these applications, energy is transformed (some of it, but not all) into useful work. The transfer of energy is not completely efficient. It is true that energy cannot be destroyed, but when converted, some energy transforms into less useful forms. Engineers design for maximum efficiency when planning an energy storage or distributing system. This allows for the largest fraction of the original amount of energy to be transferred for its purpose and the least amount of energy to be given away to unwanted avenues such as friction. Reduction in costs, waste, and harmful environmental impacts can all occur when we increase efficiency in energy transfer processes. There will always be a loss of energy to the environment around the system; therefore, no system is 100% efficient. This energy is usually lost in the form of heat. Consider any electronic device you own, such as a computer, cell phone, or car. They all get warm or hot to the touch after extended use. The energy conversion efficiency is a machine's or system's ability to convert energy from one form to another. Some systems have a great energy conversion efficiency, such as a wind turbine, which has 90% efficiency. Others, such as combustion engines, only have 10–50% efficiency. As energy moves beyond the original source and spreads out, it becomes harder to use for more energy form transfers.

The Nature of Science in Action

Science Is a Human Endeavor

Technological advances have influenced the progress of science, and science has influenced advances in technology.

Scientists are striving to increase efficiency in all electronics, from our refrigerators to our cell phones. While no system is 100% efficient, scientists will continue to perfect materials that act as insulators and conductors to provide more efficient energy conversions.

Advanced Topics

It may seem somewhat obvious, but it is worth noting that heat can only “flow” from a hotter object to a colder one. The term *heat* really refers to the amount of energy an object gains or loses due to the interactions it has with another object on a molecular level. What happens when you mix some cold milk into your hot coffee? The two substances mix together, and the resulting temperature of the mixture is somewhere between that of the original hot coffee and the cold milk. On a microscopic scale, the cold, slow-moving particles of the milk collide with the much faster (and therefore hotter) particles of the coffee. Conservation of energy and momentum tells us that in this type of collision, the faster-moving coffee particles will slow down (or get colder) and the slower-moving milk particle will speed up (or get hotter). Another way of saying this would be to say that the coffee loses energy and the milk gains that energy. This process is described using the term *heat*, or describing heat flowing from the hot coffee to the cold milk, until they reach some sort of equilibrium. Because interactions of objects with different temperatures always come down to collisions of individual particles, either through mixing liquids or two surfaces coming in contact with each other, hotter (more energetic) objects will always give energy to colder (less energetic) objects.

So how do you make an object colder? You make it interact with something that has less energy. Refrigerators, through a rather complex process, create very cold, fast-moving coolant that runs through pipes in the walls of the interior compartment. This very cold coolant is much cooler than the items placed in the refrigerator, which means that items stored inside will be the hotter object and will transform some energy and become colder.

Beyond the Classroom

Atmospheric thermodynamics is the study of heat-to-work transformations (and their reverse) that take place in Earth's atmosphere and manifest as weather or climate. Atmospheric thermodynamics use the laws of classical thermodynamics to describe and explain such phenomena as the properties of moist air, the formation of clouds, atmospheric convection, boundary-layer meteorology, and vertical instabilities in the atmosphere. Atmospheric thermodynamic diagrams are used as tools in the forecasting of storm development. Atmospheric thermodynamics are used in many climate models. Given the level of devastation that some communities have experienced in the last 20 years, it is understandable how many have come to rely on these models for preparation as storms approach.

Some of the most memorable natural disasters of recent years were Hurricanes Katrina, Sandy, and Harvey. We recall these storms causing millions of dollars worth of damage. When looking at the scenes of devastation and wreckage left by these storms, they may seem very similar. But there are some major differences we can see when looking at Hurricane Sandy.

Katrina and Harvey were both textbook tropical cyclones. The circular, low-pressure center allowed for strong winds to circulate in a symmetrical wind field. The warm core gained energy from the warm Atlantic Ocean it travelled over. Most cyclones follow a similar path of gaining energy from the warm, tropical waters they travel over. Sandy had a similar start as it travelled through the tropics. But as the storm moved along the Atlantic US coast, it merged with another weather system approaching from the west. This resulted in the formation of an extratropical cyclone.

Research the difference between a tropical cyclone and an extratropical cyclone, and create a model that explains how energy at the microscopic level results in the macroscopic manifestations of these devastating storms.

Thermodynamics Review

Reviewing Key Terms

Use each of the following terms in a separate sentence.

1. Thermal energy
2. First law of thermodynamics
3. Temperature
4. Specific heat

Use the correct key term to complete each of the following sentences.

1. ________ is the amount of heat required to raise one gram of a substance by one degree Celsius.
2. The relationship between heat, pressure, density, and temperature in a substance is known as ________.
3. The ________ law of thermodynamics states that as energy is transformed, some energy will be transformed to a less useful form.

Reviewing Main Ideas

1. What quantity of heat is required to raise the temperature of 450 grams of water from 15°C to 85°C? The specific heat capacity of water is 4.18 J/g °C.
   a. 1.21×10^{-5}J
   b. 1.32×10^{5}J
   c. 1.52×10^{-5}J
   d. 1.52×10^{5}J

2. The first law of thermodynamics is observed when–
   a. there is no longer a change in temperature in a system.
   b. the flow of energy between two systems ceases.
   c. thermal equilibrium occurs.
   d. all of the above occur.

3. When a cold stick of butter is left out on the kitchen counter–
   a. heat is transferred to the surroundings.
   b. heat is transferred to the system from the surroundings.
   c. there is no flow of heat.

Making Connections

1. Describe the relationship between *q* and energy in the melting of an ice cube.

2. Use the second law of thermodynamics to explain why there may appear to be a loss of energy in a system.

Open-Ended Response

1. Explain how the first law of thermodynamics is observed when a cold spoon is placed in a pot of boiling water.

2. Why is it important to understand the interaction a system has with the surroundings?