

Unit 7: The Energy in Chemical Reactions—Thermodynamics and Enthalpy



Unit Overview

The transfer of chemical energy to heat, light, and kinetic energy is striking in the vibrant display of fireworks, but the transfer of energy is also basic to all chemical reactions. Thermodynamics—the study of how and why energy moves—governs what can happen in a chemical reaction. By applying the laws of thermodynamics, chemists can measure, predict, and control the heat and energy of chemical reactions to help solve problems like making

cleaner burning rocket fuels and more efficient engines.

by Thomas van Geel

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Unit 7: *The Energy in Chemical Reactions—Thermodynamics and Enthalpy*

Section 1: Introduction

In science, energy represents the ability to do work or transfer heat. All living things require energy and have evolved ways to harness it from their environment. Plants absorb the energy of the sun directly, and animals acquire energy from food. Early humans acquired energy from food like other animals, but then developed new ways to capture it, starting with fire, a chemical reaction. (Figure 7-1)



Figure 7-1. Prometheus

In Greek mythology, Prometheus is credited with bringing fire to humankind from the gods. As the earliest example of humans harnessing chemical energy, fire's importance to the development of human culture cannot be overstated. The light from fire allowed humans to remain active after dark, and it provided protection from predators and insects. Cooking also makes food more digestible, allowing the body to extract more energy from it.

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Today, we use energy not just to power our bodies, but also to power vehicles, lights, computers—all of the machines and technology associated with modern life. Most of that energy comes from burning fossil fuels—which, as we will see, is also a chemical reaction.

Because energy is vital to so many aspects of our existence, a special branch of chemistry developed to study the energy of chemical reactions: **thermochemistry**. Energy takes many different forms: Objects in motion possess a certain kind of energy, and objects lifted against the force of gravity possess another. The most important types of energy for chemists are:

- Chemical energy—the energy stored in chemical bonds, and
- Thermal energy—the energy associated with temperature.

Thermochemistry focuses on energy changes that occur within a particular system, the place where the reaction is taking place, such as a laboratory container. A system can exchange energy with its surroundings through heat and work.

Energy is central to chemical reactions: Some release it, while others require energy to be added before they can take place. Understanding the role of energy in chemistry provides insight into all kinds of questions about daily life. For example, how does sweating cool us off on hot days? And why do vegans often eat larger meals than omnivores?

At a larger scale, thermochemistry is a critical part of many industrial and technological processes. It explains why societies typically shift from bio-based fuels such as wood to fossil fuels, which contain more energy per unit of fuel as they industrialize. (See Unit 12 to learn about nuclear chemistry as a way of obtaining even more energy from matter.)

Glossary

Thermochemistry

The study of energy in chemical reactions.

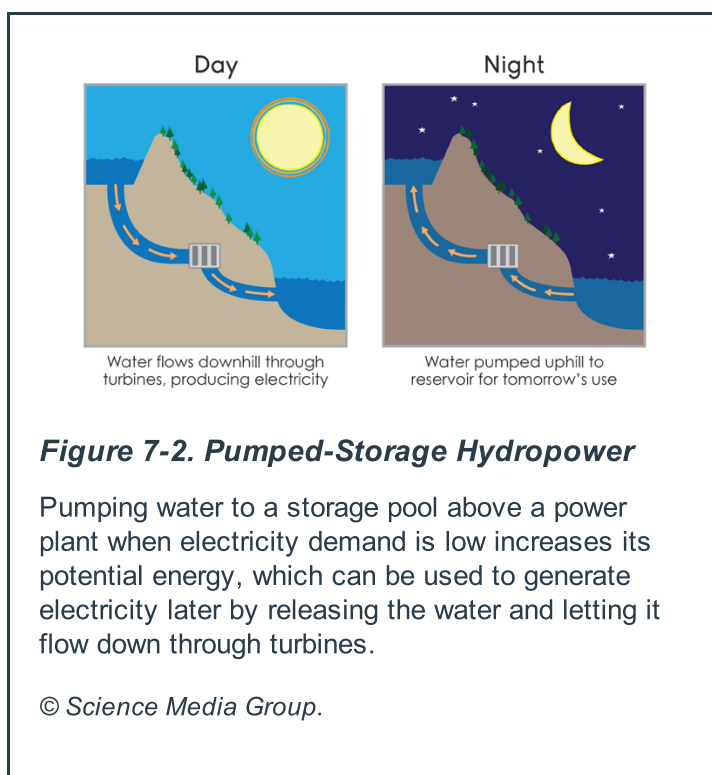
Unit 7: The Energy in Chemical Reactions—Thermodynamics and Enthalpy

Section 2: Kinetic and Potential Energy

The precursor to the modern concept of energy was the idea of **vis viva** (Latin for "living force"), which was proposed in the 17th century by Gottfried Wilhelm Leibniz (1646–1716), the German mathematician and philosopher who developed the differential and integral calculus. Scholars differed on the question of how to measure the *vis viva* possessed by an object, but agreed that it depended on an object's mass and **velocity**. The definition of *vis viva* is very similar to the modern definition of **kinetic energy**, which is one of two ways in which an object—for example, a molecule, a rock, or a rider on a bicycle—can possess energy. Kinetic energy is the energy of moving objects. The heavier the object is and the faster it moves, the more kinetic energy it has. An object's kinetic energy is represented by the formula:

$$\text{Kinetic Energy} = \frac{1}{2}mv^2$$

where *m* represents the object's mass and *v* represents its velocity (or speed).

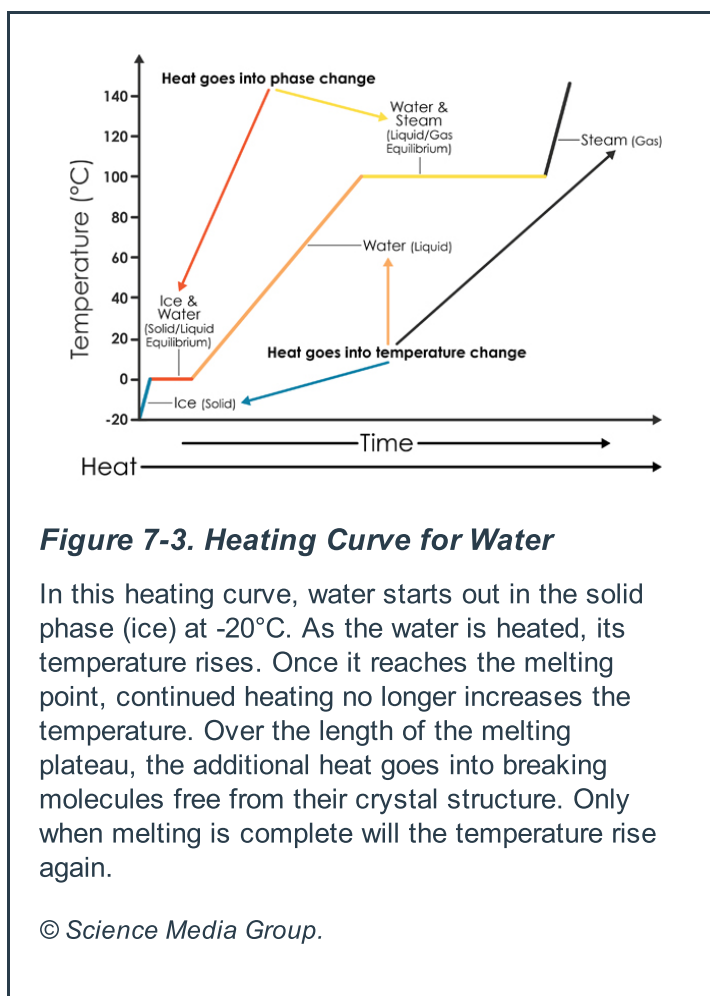


Objects can also possess **potential energy**. An object has potential energy because of its position in relation to other objects. When an object rises against the force of gravity, it gains potential energy; when it falls, it loses potential energy. The object stores this energy as it rises and releases it as it returns to Earth.

One familiar technology that taps potential energy is hydropower, which uses the energy of water flowing from a high point to a low point to generate electricity. Hydropower stations contain turbines that are positioned in the path of falling water—typically embedded in a dam. As water flows over the dam and through the turbines, it spins the machines' blades, powering generators that produce electricity. Potential energy (water at a high elevation) is converted into kinetic energy (falling water), which in turn generates electric power.

Some hydropower stations use a system called "pumped storage" to match their generating time to peak electricity demand phases. When demand is low (typically at night), the stations pump water uphill to storage ponds, increasing its potential energy. Then, when demand rises, the water is released and flows back through the turbine, generating power. (Figure 7-2)

As we learned in Unit 2, when a substance goes through a phase change, its particles gain or lose kinetic energy. For ice to change to water or for water to change to steam, the water molecules must gain enough energy to overcome the intermolecular forces that hold them together. For boiling, this energy is called the "**heat of vaporization**"; for melting, it is referred to as the "**heat of fusion**."



Although it may seem counterintuitive, water's temperature does not change while it is undergoing a phase change such as melting or boiling. This is because during the phase change, all of the energy added to the system (i.e., to the pot of water) is used to break the bonds between water molecules. In other words, it is providing potential energy. If we continue to add heat after all of the bonds have been broken and the water has turned to steam, it will flow into the system as kinetic energy that raises the temperature of the steam. We can see the relationship between the water's temperature and the amount of heat added to it in a diagram of water's heating curve. (Figure 7-3)

Glossary

Heat of fusion

The amount of heat needed to melt one mole of a substance.

Heat of vaporization

The amount of heat needed to boil one mole of a substance.

Kinetic energy

The energy of an object due to its motion.

Potential energy

The energy of an object due to its position.

Velocity

The rate of change of the position of an object.

Vis viva

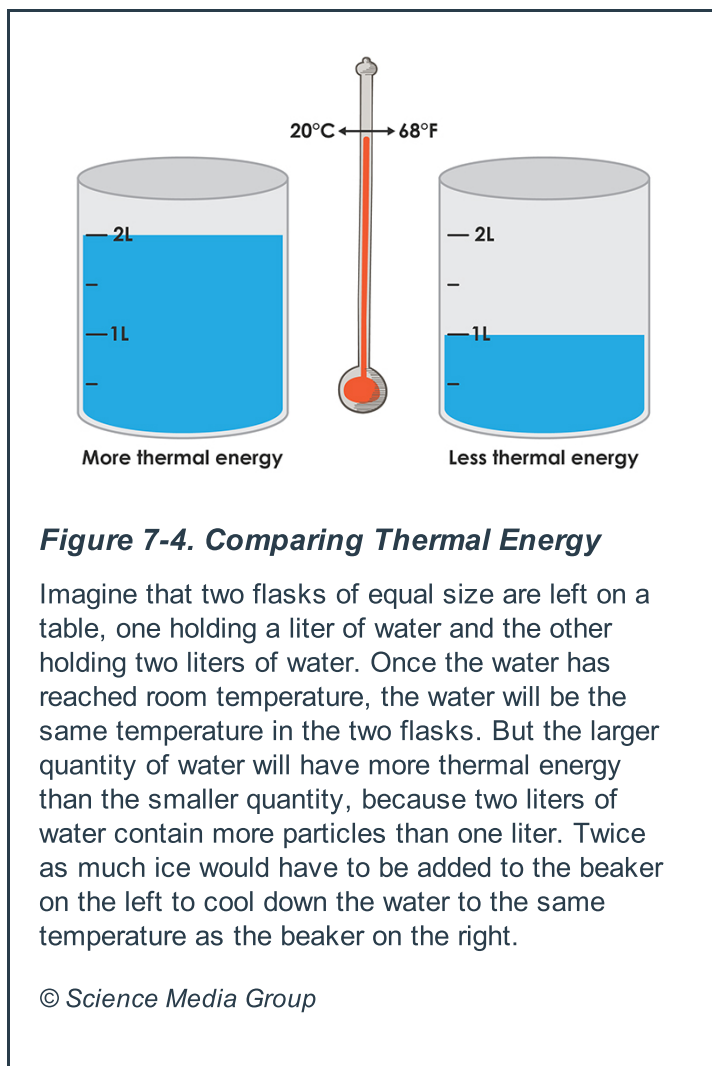
Latin for "living force." *Vis viva* was the precursor to the modern concept of kinetic energy.

Unit 7: The Energy in Chemical Reactions—Thermodynamics and Enthalpy

Section 3: Energy Changes in Chemistry

Chemicals in a laboratory can possess potential or kinetic energy, just as a baseball or a person sitting on a bicycle can. **Chemical energy** is potential energy that is stored in chemical bonds. Different types of bonds store different amounts of energy, which can be released by exchanging high-energy bonds for low-energy bonds. For example, the bonds that hold together a molecule of gasoline are rearranged when the molecule of fuel combusts; the new chemical bonds are formed in the products— CO_2 and H_2O . Because of the different energies associated with the bonds in the products and the reactants, this reaction will release energy to its surroundings. The engine uses the chemical energy released by the reaction to move the car. (Section 9 will go into more detail on the energies associated with individual bonds.)

As we have seen in our discussions of phase changes, molecules of chemical substances also have kinetic energy. They are in constant, random motion; as a substance heats up, its molecules move faster and faster. The total energy of all the molecules in a substance is called its "**thermal energy**."

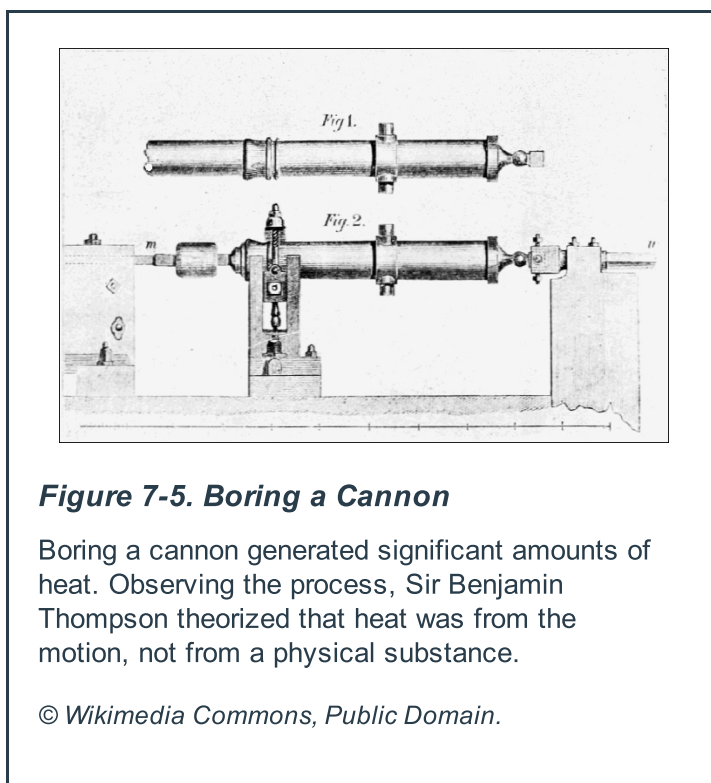


A substance's thermal energy is related to its temperature, which is the average kinetic energy of the particles in the substance. As the substance becomes hotter, its temperature increases and so does its thermal energy. But since thermal energy is the total amount of kinetic energy of all the particles, it

depends on the number of the particles in the object, while temperature does not. This can be visualized by imagining two different volumes of water that are the same temperature. (Figure 7-4)

Thermal energy is often incorrectly referred to as **heat**. Heat is actually the energy that flows from a high temperature object to a lower temperature object when objects are placed in thermal contact. We can say that a certain amount of heat flows from one metal to another, but it is not correct to say that a piece of metal *contains* a certain amount of heat.

Through the 18th century, scientists thought that heat was a kind of fluid that could flow between substances. Early chemists, including pioneers such as the French nobleman Antoine Lavoisier (1743–1794), called this purported heat fluid "**caloric**" from the Greek word for "heat."



Massachusetts native Sir Benjamin Thompson (1753–1814), later known as Count von Rumford, helped disprove the caloric theory. In a famous experiment, he boiled water with the thermal energy generated by boring a cannon—drilling a hole through a cylinder of solid brass to create the gun barrel of the cannon (the tube through which cannon balls were fired was called a "bore"). (Figure 7-5)

The friction of metal grinding against metal generated so much heat that it warmed a bath of water in which the cannon barrel was submerged. After 2.5 hours, the water boiled, to observers' amazement. Thompson reasoned that if caloric was a physical substance inside the cannon barrel, it should eventually run out. But boring out the cannon seemed to produce an inexhaustible supply. "[A]nything which any insulated body, or system of bodies, can continue to furnish without limitation cannot possibly be a material substance," Thompson concluded. The experiment showed that thermal energy had a "mechanical equivalent." Heat was not a fluid contained in matter. Rather, it was a result of the motion.

Scientists began measuring heat in **calories** in the 1820s, when French physicist and chemist Nicolas Clément (1779–1842) introduced the unit. He defined it as the amount of heat needed to increase the temperature of one kilogram of water by one degree Celsius. Today, food labels continue to use calories to indicate the energy content of food.¹ There is also a specific term for what this physical quantity is often called: the "heat capacity" or the "specific heat" for a substance. It is defined as the amount of heat it takes to raise one gram of a substance by one degree. For water, the heat capacity is 1 calorie/g °C. It turns out that water actually has a very high heat capacity, which is why tanks of water are often used as storage for heat energy collected from solar panels.

Modern chemists use a different unit: the **joule**, after James Prescott Joule (1818–1889), a British physicist. One joule is equal to 4.18 calories. A joule is a small unit: Driving a small, efficient car one mile burns enough gasoline to release 3 million joules. A nuclear reactor can produce 300 trillion joules *in one day*. Consequently, large increments of energy are usually measured in megajoules (one million joules), gigajoules (one billion joules), or even larger units.

¹Clément's calorie is properly referred to as a "kilocalorie" or "large calorie," and is written with a capital C to distinguish it from a "small calorie"—the amount of heat required to raise the temperature of one gram of water by 1°C.

Glossary

Caloric

A precursor to the modern understanding of heat. Caloric was believed to be an invisible fluid capable of carrying heat.

Calorie

A unit of energy equal to the amount of energy needed to raise 1 gram of water by 1 degree Celsius.

Chemical energy

The energy of a system due to the arrangement and bonding of atoms.

Heat

The transfer of thermal energy between a system and its surroundings.

Joule

The International System of Units (SI) unit of energy, equal to one newton-meter.

Thermal energy

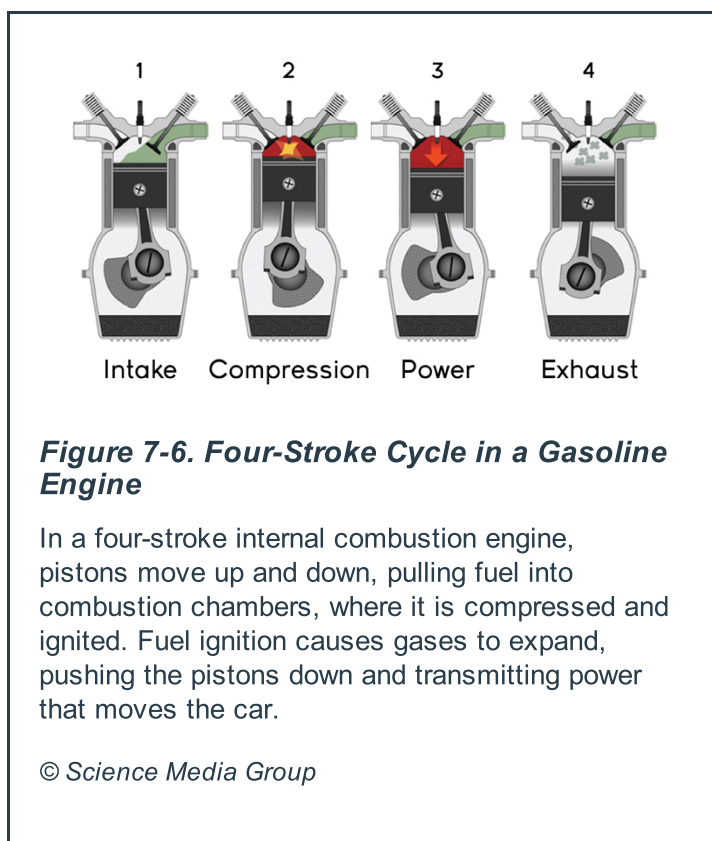
The energy in a system that relates to the temperature of the system.

Unit 7: The Energy in Chemical Reactions—Thermodynamics and Enthalpy

Section 4: Heat, Work, and Internal Energy

To keep track of how energy moves and changes in chemical reactions, it is important to strictly define the boundaries of the chemical system under study. In many lab experiments, the system is often a beaker or a flask in which chemical reactions occur. More generally, a **system** is the particular part of the universe under study. This can mean practically anything so long as the boundaries are well defined: a piston in a car engine, a human body, a nuclear reactor, or a star. The rest of the environment outside the system is called the **surroundings**.

Energy can enter and leave a chemical system as heat (represented by the variable q). Heat enters a system when the container contacts a hotter object such as a laboratory hot plate: Thermal energy conducts from the hotter object into the cooler one. Conversely, heat will leave the system when it contacts something at a lower temperature like an ice bath. When heat enters the system, the sign of q is positive; when heat leaves, q is negative.



Energy can also enter and leave a chemical system as **work** (represented by the variable w). One type of work is **pressure-volume work**; this occurs when the volume of the system expands or contracts. The amount of work done is equal to the change in volume of the system times the exterior pressure. Compression adds energy to the system, and the sign of w is positive. Expansion removes energy, and w is negative. The cylinders in a gasoline engine release energy as pressure-volume work. In the cylinder, a spark plug ignites a mixture of gasoline and air. The burning gasoline inside the cylinder drives the piston out; the piston delivers this energy to the crankshaft to move the car. (Figure 7-6)

A battery is an example of a chemical system that releases energy as **electrical work**. Electrical work leaves the system when the battery powers a light or a motor, and energy enters the system when the battery recharges. (We will discuss electrochemistry in Unit 11.)

State Functions

The change in internal energy of a system is a state function; that is, the value does not depend on the particular way in which the internal energy was changed. For example, consider a battery that starts out fully charged and ends up completely dead. The battery could have lost its energy by many different paths, but the particular path has no influence on the amount. It might have powered a cell phone, flashlight, electric motor, or any combination of these. The amount of internal energy lost simply depends on the initial state of the battery and the final state of the battery.

In contrast, heat and work are path-dependent functions. The value of a path-dependent function changes depending on the history of the system. Let's look at the battery again. It starts out fully charged, and then powers an electric heater until it is completely dead. In this case, the battery expended all its energy as heat. Starting again with a full charge, the battery powers an electric motor until it is completely dead; this time it expended all its energy as work. The battery could also power the heater until half its energy is spent, and then power the fan until it dies. It could expend its energy in many different combinations of heat and work. In other words, the amount of heat and/or work released depends on what the battery did; heat and work are path-dependent functions.

A quick analogy for this is a trip from Boston to Los Angeles. Some of the values of properties that describe this trip are path-dependent functions while others are state functions. For example, the distance we travel on the trip is dependent on the path we take there, and can vary significantly, especially if we decide to visit our aunt in Seattle on our way to Los Angeles. However, the total net distance traveled, the displacement of how far we were from the starting city, is a state function. It only depends on where we started and ended, and has nothing to do with how we took the trip in between.

The energy inside a system is called the **internal energy** (which is given the variable U), and includes the thermal energy of the substances, the energy due to their phases (latent heat), and their chemical energy. Determining the sum total of all these energies is complex; it is more important to know how the internal energy of a system *changes*. For example, the amount of energy a lump of coal happens to contain is not a useful number, but it is important to know how much energy will be released when the coal burns. When writing an equation, the change in a value is represented by the uppercase Greek letter delta (Δ). The change in energy of a system (ΔU) is the amount of heat (q) and work (w) gained or lost by the system:

$$\Delta U = q + w$$

Note: There are different conventions for the signs of q and w . In this text, all energy entering the system will have a positive sign, and all energy leaving the system will have a negative sign. (Table 7-1)

Table 7-1. Changes in Internal Energy Produced by Heat and Work

System absorbs heat	q is positive
System releases heat	q is negative
System is compressed	w is positive
System expands	w is negative

Glossary

Electrical work

The work done on a charged particle by an electric field.

Internal energy

The sum total of all different types of energy in a system (thermal, chemical, etc.).

Pressure-volume work

Work done on or by a system due to compression or expansion of gases.

Surroundings

The area outside the boundaries of the system being studied.

System

The part of the universe being studied.

Work

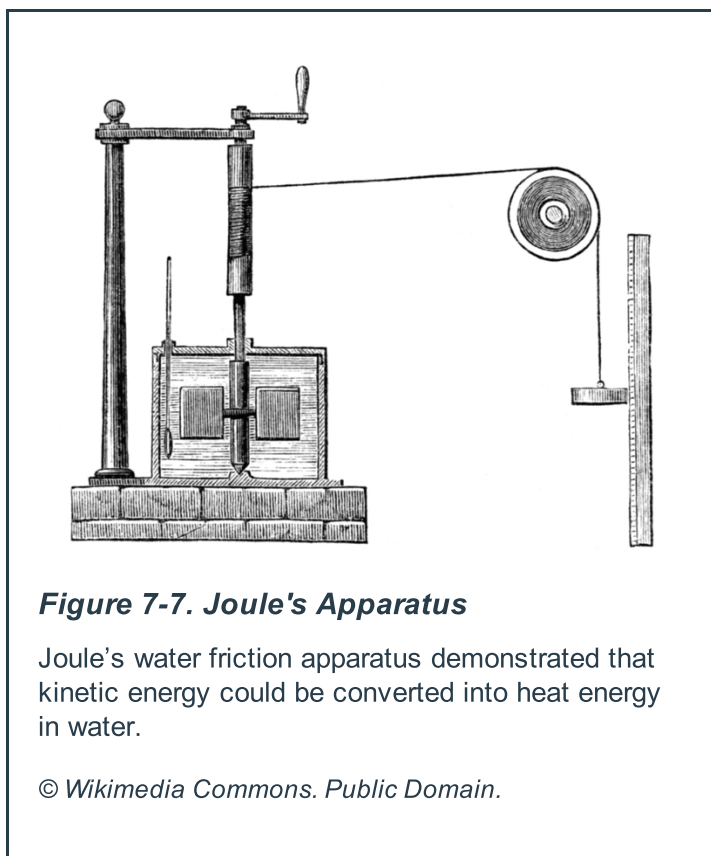
The way a system exchanges energy with the surroundings, excluding heat transfers (pressure-volume work, electrical work, etc.).

Unit 7: The Energy in Chemical Reactions—Thermodynamics and Enthalpy

Section 5: Energy Conversions and Conservation

When a star burns out or a car runs out of gas, it may seem that energy has been used up. In fact, this energy did not disappear, but was converted to another form. In the same way, energy cannot be created. "Generators" that produce electricity actually convert chemical or thermal energy into electrical energy. Because energy cannot be created or destroyed, energy is conserved, just as matter is conserved. This principle is expressed in the **First Law of Thermodynamics**, which states that energy cannot be created or destroyed. In an isolated system, energy never increases or decreases. Though many people throughout history have tried, no one has ever invented a machine that produces more energy than it consumes.

The world is full of energy transformations. Rubbing two sticks together warms them up. Chemical energy in oil is converted to thermal energy to heat our homes. Plants convert radiant energy from the sun into chemical energy via photosynthesis. Electricity is converted to thermal energy in toasters, radiant energy in light bulbs, and kinetic energy in the electric motors that power washing machines, power tools, fans, and disk drives.



Though we take these energy transformations for granted, it wasn't always so. Building on the work of Sir Benjamin Thompson and his cannons, English physicist James Prescott Joule solidified and quantified the relationship between mechanical movement and thermal energy. To show this conversion, Joule reportedly spent time during his honeymoon in France measuring the difference in water temperature at the top and bottom of a waterfall. He theorized that water at the bottom of the falls should be warmer than at the top, because upon impact the kinetic energy of the water was transformed into thermal energy.

To show this conversion in the lab, Joule built the water friction apparatus shown in Figure 7-7. It consisted of a weight hung from a length of twine wrapped around a vertical rod. Paddles projected from the bottom of the rod, which was submerged in an insulated tub of water. When the weight fell, the rod and paddles would

spin, churning the water and raising its temperature.

By measuring the temperature change and the energy lost by the descending weight, Joule demonstrated that the energy gained by the water was proportional to the energy lost by the falling weight. His apparatus converted the potential energy of the weight into the thermal energy of the water.



Figure 7-8. Manufacturing Snow

Snow cannon at the Canmore Nordic Centre, Alberta, Canada.

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Joule showed that when work was put into a system, the temperature increased. A fire-starting device called a "**fire piston**" puts this directly to practical use. The user places a small piece of paper in a narrow cylinder made out of wood or metal. Rapidly driving the piston down heats up the air inside enough to start the tinder smoldering. A **diesel engine** uses the same technology; the mixture of gas and air heats up and ignites due to compression (without a spark plug).

Rapid expansion has the opposite effect. When a gas quickly expands, its temperature drops because energy leaves the system as work. Snow machines at ski slopes use this principle when nature hasn't been cooperative. A snow machine shoots out a mixture of cold water and compressed air. As the air expands, its temperature drops enough to freeze the water into snow. (Figure 7-8)

Glossary

Diesel engine

An internal-combustion engine in which the compression of fuel, not a spark plug, causes the fuel to ignite.

Fire piston

A fire-starting device that burns tinder by rapidly compressing a gas.

First Law of Thermodynamics

Energy can never be created or destroyed. The total energy in the universe is constant.

Unit 7: The Energy in Chemical Reactions—Thermodynamics and Enthalpy

Section 6: Enthalpy



Figure 7-9. Thermite Welding

Thermite welding in progress. Liquid iron produced by the thermite reaction will flow into the mold around the rail gap.

© Wikimedia Commons. Author: Skatebiker.

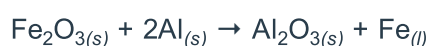
Many chemical reactions are useful because of the energy transformations that accompany them. All chemical reactions exchange energy with the surroundings by releasing or absorbing heat. Reactions that produce or consume gases also exchange energy as pressure-volume work.

The amount of heat exchanged with the surroundings is an important property of a chemical reaction. The amount of heat absorbed or released during a reaction under constant pressure is called "**enthalpy**" and is represented by the variable H . When the pressure of the system doesn't change, the change in enthalpy of a system equals the heat exchanged with the surroundings:

$$\Delta H = q$$

If a chemical reaction releases heat, it is **exothermic**. If a chemical reaction absorbs heat, it is **endothermic**. Many useful reactions are exothermic; we value them because we can harness the heat they release. Burning fuels such as coal and gasoline is an exothermic reaction; we use the heat produced by these reactions to power machinery and generate electricity. Digestion—the process by which our bodies break down nutrients from food—is an exothermic reaction that powers our movements and metabolism.

One of the most dramatic exothermic reactions is the thermite reaction, in which aluminum powder is mixed with a metal oxide, usually iron. Aluminum forms stronger bonds with oxygen than the metal does, so the aluminum reduces the oxide to metal:



The reaction releases so much heat that the iron produced is a liquid. This makes the thermite reaction useful in welding applications, such as fusing steel railroad tracks together. (Figure 7-9)

Sometimes, it is not desirable or useful for chemical reactions to release heat. The exothermic curing of concrete sometimes poses engineering challenges. For example, when workers poured the enormous blocks of concrete in the Hoover Dam, they embedded cooling pipes in the slabs. Without cold water flowing through these pipes, engineers estimated it would have taken 125 years for the dam to cool. A thorough knowledge of the enthalpy in the curing process was crucial to the project's success.

Because endothermic processes pull heat away from the surroundings, they cool things. Melting ice is endothermic, which is why ice packs reduce swelling from sports injuries. Chemical cold packs, which need no refrigeration, achieve the same thing with an endothermic chemical reaction. One of the common reactions inside cold packs is the dissolving of ammonium chloride:



The end result is the same: The endothermic chemical reaction cools the surroundings.

Glossary

Endothermic

Absorbing heat from the surroundings.

Enthalpy

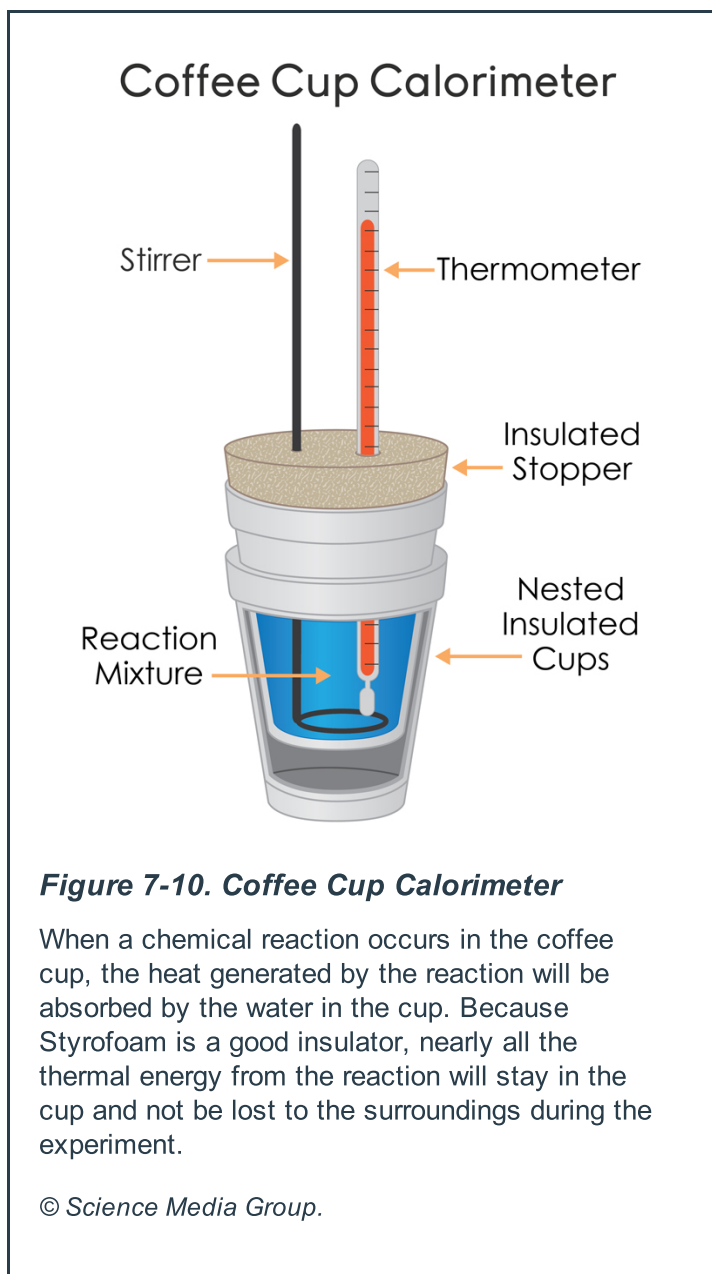
The amount of heat absorbed or released during a reaction or process under constant pressure.

Exothermic

Releasing heat to the surroundings.

Unit 7: The Energy in Chemical Reactions—Thermodynamics and Enthalpy

Section 7: Calorimetry

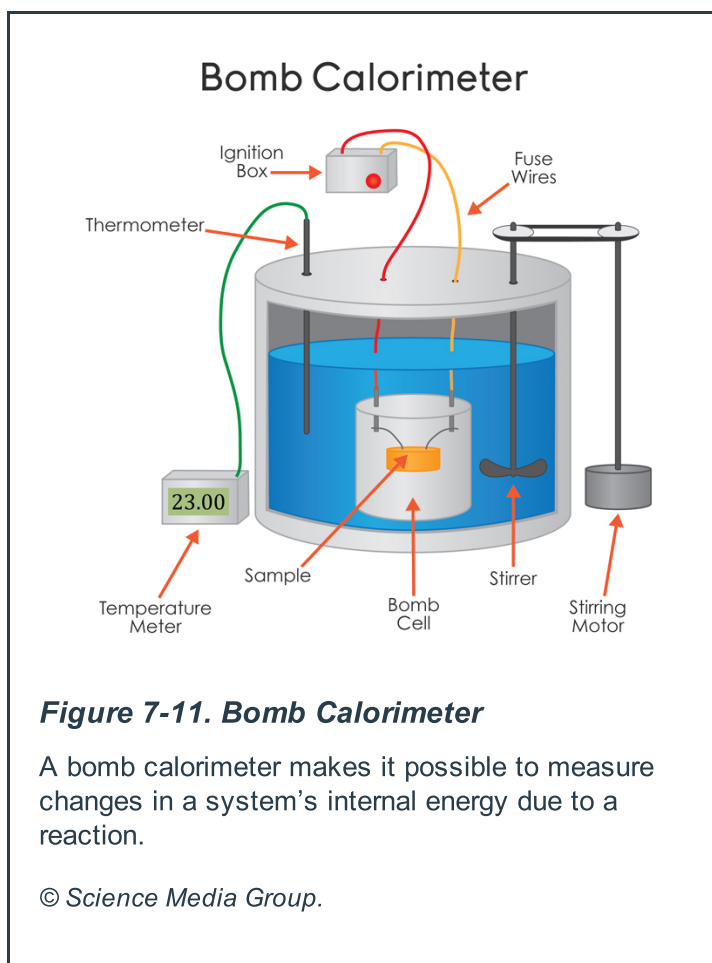


The amount of heat released or absorbed by any chemical process can be measured using an insulated container called a "**calorimeter**." If the reaction in question occurs in an aqueous solution, an effective calorimeter can be as simple as a Styrofoam coffee cup and a thermometer (Figure 7-10). In this case, because the Styrofoam cup is an open container, the pressure is constant, and measuring the heat is the same as measuring the change in enthalpy of a chemical reaction (ΔH).

When the reaction occurs, the change in temperature will be proportional to the enthalpy released by the reaction. For example, let's say that one mole of a substance can react inside 100 g of water inside the calorimeter so that the water absorbs all the heat, and the temperature of the water increases by 5 degrees. Using the mass of the water (m), the specific heat of the water (c), and the change in temperature (ΔT), we can calculate the heat released by the reaction:

$$q = mc\Delta T = 100\text{g} \cdot 4.18 \text{ J/g } ^\circ\text{C} \cdot 5^\circ\text{C} = 2090 \text{ J} = 2.09 \text{ kJ}$$

Because one mole of the substance dissolved, the value of ΔH is -2.09 kJ/mol . Note that this value is negative because the reaction gave off the enthalpy that the water absorbed.



However, many chemical reactions, such as combustion reactions, do not take place in a solution. To more efficiently measure the heat released by combustion reactions, chemists use a **bomb calorimeter**, which is a sealed vessel that contains a smaller container called a "bomb." The bomb (not related to a military weapon) is a container designed to withstand high pressure, and is equipped with valves for adding gases and electrical contacts for initiating combustion reactions. (Figure 7-11)

The basic principle is the same: A chemical reaction heats a quantity of water in an insulated container. In this case, however, the reaction takes place inside a sealed container, or bomb. The bomb contains the chemical to be analyzed and enough oxygen to make sure the sample burns completely. The bomb sits submerged in a container of water, and ignition wires start the combustion. Because the reaction takes place in a rigid, sealed container, no pressure-volume work is done by the reaction; all the energy will be released as heat, and none as work. In other words, a bomb calorimeter always measures the heat that is released by a reaction, but in this case the heat represents not the change in enthalpy (ΔH), but the change in internal energy (ΔU). Conveniently, there are simple calculations that can be done to convert the internal energy change into the enthalpy change chemists need.

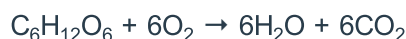
Food Energy

Throughout human evolutionary history, food has often been scarce. Because our ancestors were at the mercy of the seasons, we have evolved to store energy in our bodies to sustain us during times of famine. When we consume more energy in the form of food than we expend, we store the excess as fat. But why fat? We could have evolved to store the energy as protein or carbohydrates (the two other energy-containing nutrients), but natural selection has determined fat to be the best energy storage medium.

Gram for gram, fat can store far more energy than protein or carbohydrates. Below are the standard amounts of energy that each type of nutrient stores per gram.

- Carbohydrate: 4 Calories (16.7 kJ) per gram
- Protein: 4 Calories (16.7 kJ) per gram
- Fat: 9 Calories (37.7 kJ) per gram

Food scientists measure the amount of energy contained in fat, carbohydrates, and protein using a bomb calorimeter. When burned in the calorimeter, each gives off different amounts of energy. This method is most accurate for fat and carbohydrates because the combustion reaction in the calorimeter is the same as the reaction that occurs inside the body. Fats and carbohydrates are oxidized to carbon dioxide and water in reactions, like this one for glucose:



Note that this reaction is the reverse of the equation for photosynthesis. When plants photosynthesize, they form carbon dioxide and water into carbohydrates (plant tissue), using energy from sunlight to power the reaction. Digestion breaks down carbohydrates again, releasing energy in the process.

In a bomb calorimeter, the reaction takes place quickly. In the human body, the reaction takes place over a series of many intermediate reactions, gradually releasing energy along the way. Overall, however, the reactions are the same, and the amount of energy released is comparable.

Burning protein in a bomb calorimeter yields accurate values for its combustion, but that's not the same net reaction that's taking place in the body; so the number must be adjusted to compare to the chemistry of the body. Unlike fat and carbohydrates, protein contains a lot of nitrogen. When burned in a calorimeter, the nitrogen ends up as oxides of nitrogen. In the human body, the nitrogen ends up as urea ($\text{CH}_4\text{N}_2\text{O}$); this reaction releases less energy than in the calorimeter, and this difference must be taken into account.

Chemists have measured the change in enthalpy for thousands of different reactions and have collected them into tables that can be found in almost any chemistry book. So, there is no need for a chemist to perform calorimetry on a particular reaction, as that value can be found in a table of enthalpies of reactions. (Section 8 will explain how an enthalpy change for a reaction that is not in the table can be determined without doing a new calorimetry experiment.)

Glossary

Bomb calorimeter

A device used to measure the change in internal energy (ΔU) of a system at constant volume.

Calorimeter

A device used to measure either the change in the internal energy or the change in enthalpy of a system.

Unit 7: The Energy in Chemical Reactions—Thermodynamics and Enthalpy

Section 8: Hess's Law



Figure 7-12. Magnesium Ribbon Burning

A strip of magnesium burning. Because the reaction produces intense light, magnesium was the main component of photographic flash powder in the late 1800s. Today, many fireworks contain magnesium because it produces such brilliant white light.

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Because enthalpy is a state function (see *State Functions* sidebar in Section 4), the change in enthalpy of a chemical reaction depends only on the identity and phases of the reactants and products, and not on the specific way the reactants transform into the products. This useful fact is known as "**Hess's Law**," after Germain Henri Hess (1802–1850), a Russian chemist from the early 1800s. For example, let's imagine a reaction in which reactant A turns directly into product C. The ΔH for this reaction is x kJ per mole.

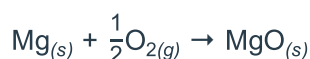


Reactant A might also be able to produce C by an alternate route. In this case, A might first turn into B, and B then turns into C. Each of these reactions also has a ΔH value, y and z , respectively:

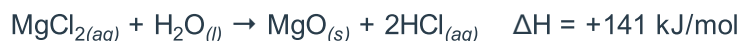
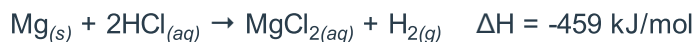


According to Hess's Law, the ΔH of the first reaction (converting A directly into C) must be equal to the sum of the ΔH values of the second and third reactions (converting A into C via B). Expressed mathematically, we have $x = y + z$.

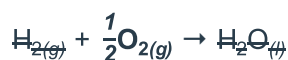
This allows chemists to figure out the ΔH of a reaction by combining other reactions and adding the ΔH of those reactions together. It is a useful way to calculate ΔH when calorimetry is impractical. For example, let's consider a highly exothermic reaction: the burning of magnesium metal (Figure 7-12):



To find the ΔH value for the burning of magnesium, we could look up the following information:



Note that combining the three reactions and canceling out the chemicals that appear as both reactants and products will produce the reaction for burning magnesium:



Because the three reactions "add up" to the reaction for burning magnesium, the sum of the three ΔH values will be the ΔH for burning magnesium:

$$\Delta H = -459 + 141 + (-286) = -604 \text{ kJ/mol}$$

The final result is a very large negative number, which makes sense because the reaction is quite exothermic and releases a significant amount of energy in the form of light and heat as the reaction occurs.

Glossary

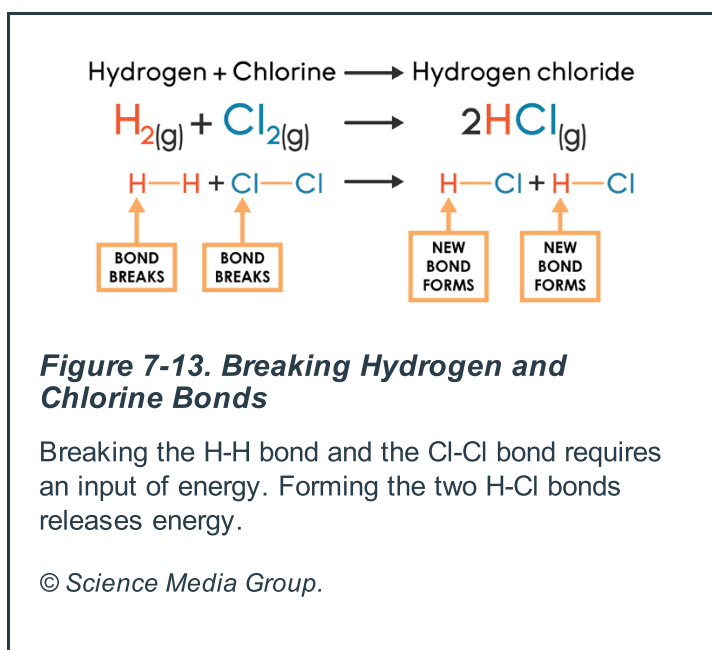
Hess's Law

The change in enthalpy of a reaction (ΔH) is the same if the reaction happens in a single step or in a series of steps. Thus, the series of steps must have individual enthalpy changes that add up to the total change in enthalpy for the process

Unit 7: The Energy in Chemical Reactions—Thermodynamics and Enthalpy

Section 9: Bond Enthalpies

During a chemical reaction, old bonds between atoms break and new bonds form. Breaking chemical bonds requires enthalpy; it is an endothermic process. Forming new bonds releases enthalpy; it is exothermic. When a chemical reaction occurs, the balance between these two processes determines if the reaction is endothermic or exothermic *overall*. A reaction will be endothermic if breaking the old bonds takes more enthalpy than the enthalpy released when the new bonds form. It will be exothermic if the new bonds release more enthalpy than the enthalpy needed to break the old bonds.

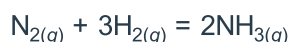


The amount of energy associated with a bond is called the "**bond enthalpy**," and it is measured in kilojoules per mole (kJ/mol). The bond that holds oxygen atoms together as an O_2 molecule has a bond enthalpy of 495 kJ/mol. In other words, breaking a mole of O_2 molecules into individual oxygen atoms requires an input of 495 kJ. Conversely, forming a mole of O_2 molecules from oxygen atoms would release 495 kJ.

Nitrogen's Triple Bond

Nitrogen molecules make up 78 percent of our atmosphere, yet the availability of nitrogen is often the limiting factor for plant growth. Nitrogen atoms are vital parts of the proteins and DNA found in all life. While nitrogen is abundant, diatomic nitrogen molecules (N_2) are impossible for most organisms to use. The strength of the triple bond holding the atoms together (941 kJ/mol) makes this form of nitrogen ($:\text{N} \equiv \text{N}:$) almost inert. It is so unreactive that food won't spoil quickly in a pure nitrogen atmosphere, so packages filled with nitrogen instead of air increase shelf life. The empty space inside some aircraft fuel tanks is filled with nitrogen to prevent explosions that could occur in the presence of oxygen.

Obtaining useful nitrogen from the atmosphere is called "nitrogen fixation." Plants can assimilate nitrogen in the form of nitrate ions (NO_3^-), not N_2 gas. Certain bacteria have the rare ability to turn atmospheric nitrogen into a useful form. Legumes, such as beans and peas, have evolved a unique symbiotic relationship with these bacteria. In exchange for carbohydrates and nutrients from the plant's roots, the bacteria provide nitrogen-rich compounds. These types of nitrogen compounds are a main component in inorganic fertilizers; however, there aren't enough legumes to keep up with the world demand. Without industrial nitrogen fixation to produce these fertilizers, the current world population would not be sustainable. The Haber-Bosch process, invented in the beginning of the 20th century, revolutionized the production of nitrogen fertilizer via the following reaction:



The ammonia (NH_3) is converted to ammonium (NH_4^+), nitrate (NO_3^-), and other compounds before use in agriculture.



High explosives, like the one used in the demolition shown above, release tremendous amounts of enthalpy very quickly due to the formation of high-enthalpy bonds. This, in turn, heats the air and the reactants, which then rapidly expand causing destruction. © Wikimedia Commons, Creative Commons License 3.0. Author: Heptagon, 2 December 2006.

While the fertilizer produced with the Haber-Bosch process has tremendously benefited humankind, the process also made the production of explosives much more economical. Nitrogen compounds have been a vital component of explosives since the invention of gunpowder, which contains saltpeter (KNO_3). Nitrogen is part of nitroglycerine, TNT, and C-4. All these explosives release enthalpy partly due to the highly exothermic formation of nitrogen triple bonds. For example, the combustion of nitroglycerine produces one and a half nitrogen molecules for every molecule exploded.

Nitroglycerine:



Chemists have measured and tabulated many bond enthalpy values because they provide yet another way, along with calorimetry and Hess's Law, to find the enthalpy change of a reaction. For example, in the reaction in Figure 7-13, two bonds break. The H-H bond requires 436 kJ/mol to break, and the Cl-Cl bond requires 242 kJ/mol; the total enthalpy input is 678 kJ/mol. When the two H-Cl bonds form, they release 862 kJ/mol (431 from each bond). Overall, the reaction will release 184 kJ/mol; the ΔH for this reaction is -184 kJ/mol.

It takes more enthalpy to break stronger bonds; conversely, forming stronger bonds releases more enthalpy. The strength of one particular bond has posed significant challenges for living things: the triple bond between nitrogen atoms. (See *Nitrogen's Triple Bond* sidebar)

Glossary

Bond enthalpy

The amount of enthalpy (or energy) needed to break one mole of a certain chemical bond.

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Section 10: Standard Enthalpies of Formation

When a chemical reaction describes *the formation of one mole of a compound from its constituent elements in their standard states*, the enthalpy change of the reaction is called the "standard enthalpy of formation" (ΔH_f°) for that compound. Standard state is the most stable state of that substance at a pressure of 1 atm and a temperature of 25°C. For liquid water, the equation would be:

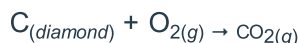


The equation fits all the criteria: One mole of water is formed. The hydrogen and oxygen are in standard states (they are in the gas phase, and they are diatomic).

The following equations **do not** have all the species in standard states...



...because nitrogen should be diatomic, and oxygen should be a gas, not a liquid, at 1 atm and 25°C.



...because at 1 atm and 25°C, the most stable form of carbon is graphite, not diamond.

Important fact: By definition, the ΔH_f° of an element in its standard state is zero.

Thousands of ΔH_f° values have been determined and recorded. Why do we care about them? These ΔH_f° values are very useful because they provide yet another way to determine the change in enthalpy of a reaction without doing it experimentally. It still uses Hess's Law, but it uses it on tables containing very specific enthalpy values for only formation reactions. Here's how it works.

Take the equation for the combustion of methane:



If we write the equations for the formation of everything in this equation and look up the ΔH_f° values on a table, we get:

$\text{CH}_{4(g)}$	$\text{C}_{(s)} + 2\text{H}_{2(g)} \rightarrow \text{CH}_{4(g)}$	-103.85 kJ/mol
$\text{O}_{2(g)}$	$\text{O}_{2(g)} \rightarrow \text{O}_{2(g)}$	0 kJ/mol
$\text{H}_2\text{O}_{(l)}$	$\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)}$	-285.8 kJ/mol
$\text{CO}_{2(g)}$	$\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$	-393.5 kJ/mol

Once we have these equations and values, we will always be able to use Hess's Law to find the ΔH of the overall reaction.



or



leaving us with



Notice that:

- The first equation is the ΔH_f° of $\text{CH}_{4(g)}$, only reversed.
- The third equation is double the ΔH_f° of $\text{H}_2\text{O}_{(l)}$.
- The fourth equation is the ΔH_f° of $\text{CO}_{2(g)}$.

And so, the ΔH of the reaction is:

$$\begin{aligned}\Delta H &= [(\Delta H_f^\circ \text{ of } \text{CO}_{2(g)}) + 2(\Delta H_f^\circ \text{ of } \text{H}_2\text{O}_{(l)})] - [(\Delta H_f^\circ \text{ of } \text{CH}_{4(g)}) + 2(\Delta H_f^\circ \text{ of } \text{O}_{2(g)})] \\ &= [-393.5 + 2(-285)] - [(-103.85) + 2(0)] = -859.65 \text{ kJ/mol}\end{aligned}$$

Because all the ΔH_f° values can be looked up in a table, we can determine the enthalpy change of the combustion reaction without burning any CH_4 . This technique always works, and is generalized by the formula below where n represents the stoichiometric coefficients of the substances in the balanced reaction:

$$\Delta H_{\text{rxn}} = \sum n\Delta H_f^\circ (\text{products}) - \sum n\Delta H_f^\circ (\text{reactants})$$

Put simply: To figure out the change in enthalpy for any equation, add up the ΔH_f° values of the products and multiply them by their coefficients; then subtract all the ΔH_f° values of the reactants multiplied by their coefficients.

Unit 7: *The Energy in Chemical Reactions—Thermodynamics and Enthalpy*

Section 11: Conclusion

As we have seen, if a chemist has a thermometer and can carefully perform a controlled chemical reaction, the result is a direct measure of the heat that this reaction involved. If this reaction was carried out under constant pressure, of which our planet is a good example, then this heat is really a change in enthalpy. In the end, chemists are looking for the change in enthalpy for a reaction.

This is the core of all thermochemistry. Chemists can either run new experiments or work with Hess's Law and tables of enthalpies or bond enthalpies compiled over the centuries to find that needed value. From the enthalpy change for a reaction, we can figure out which foods and fuels are best to eat or use in our cars, or how cool a cold pack from the local drug store can get.

However, thermochemistry is only one part of a larger field of thermodynamics. The early work in thermodynamics—understanding the way a system transfers energy to and from its surroundings—allowed scientists to maximize the efficiency of steam engines and paved the way for the Industrial Revolution. Understanding the way chemical reactions release and absorb energy continues to be critical to our understanding of modern engines. The field of thermodynamics is of vital importance to many aspects of science, from the chemical reactions that power our bodies to the nuclear reactions that power the stars. As we will see in Unit 9, further developments in thermodynamics explained the driving forces behind every physical process since the Big Bang. This will lead us to understand why some chemical reactions take place while others do not.



Unit 7: *The Energy in Chemical Reactions—Thermodynamics and Enthalpy*

Section 12: Further Reading

Biello, David. "Food versus Fuel: Native Plants Make Better Ethanol." *Scientific American* (blog), January 16, 2013, <http://www.scientificamerican.com/article.cfm?id=native-plants-on-marginal-lands-to-reduce-food-versus-fuel-from-biofuels>.

Kearney, Will. "That Beautiful Theory." *Chemical Heritage Magazine* 29 (2011).
<http://www.chemheritage.org/discover/media/magazine/articles/29-2-that-beautiful-theory.aspx>.

Lightman, Alan. "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.

Podolefsky, Noah, John Blanco, Ariel Paul, Emily Moore, Kathy Perkins, Trish Loeblein, "Energy Forms and Changes," *PHeT Interactive Simulations*. <http://phet.colorado.edu/en/simulation/energy-forms-and-changes>.