

5.2: Enthalpy and Reactions

Learning Objectives

- To know the key features of a state function.
- To understand why enthalpy is an important state function.

To study the flow of energy during a chemical reaction, we need to distinguish between a system, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundings, the rest of the universe, including the container in which the reaction is carried out (Figure 5.2.1). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

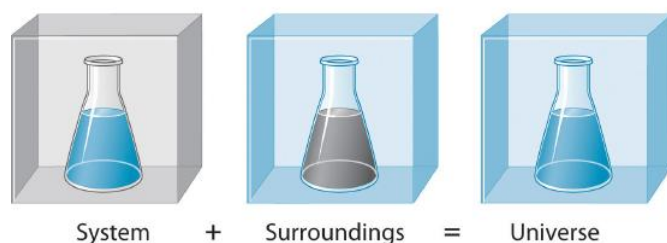


Figure 5.2.1 A System and Its Surroundings The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.

Three kinds of systems are important in chemistry. An open system, a system that can exchange both matter and energy with its surroundings, can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A closed system, a system that can exchange energy but not matter with its surroundings, can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An isolated system, a system that can exchange neither energy nor matter with its surroundings, exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system, a complete description of the system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter, is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function, a property of a system whose magnitude depends on only the present state of the system, not its previous history, is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure 5.2.2). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.

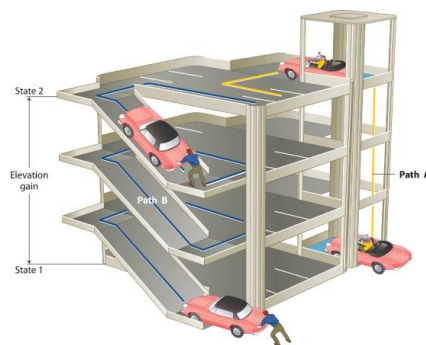
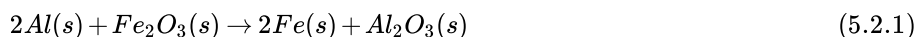


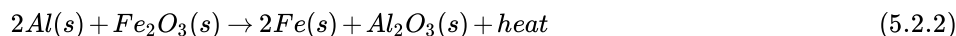
Figure 5.2.2 Elevation as an Example of a State Function The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are not state functions.

Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (see chapter opening image). The balanced chemical equation for the reaction is as follows:



We can also write this chemical equation as



to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system to its surroundings is described as exothermic. A process in which heat (q) is transferred *from* a system *to* its surroundings. By convention, $q < 0$ for an exothermic reaction.

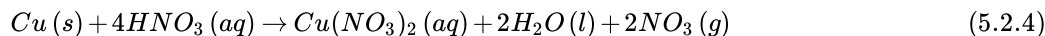
When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:



When heat is transferred to a system *from* its surroundings, the process is endothermic. A process in which heat $q > 0$ is transferred to a system *from* its surroundings. By convention, $q > 0$ for an endothermic reaction.

Enthalpy of Reaction

We have stated that the change in energy (ΔE) is equal to the sum of the heat produced and the work performed (Equation 9.1.3). Work done by an expanding gas is called *pressure-volume work*, also called *PV work*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:



If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 5.2.3). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of *PV work* done by multiplying the external pressure P by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure)

$$w = -P\Delta V \quad (5.2.5)$$

The negative sign associated with *PV work* done indicates that the system loses energy. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

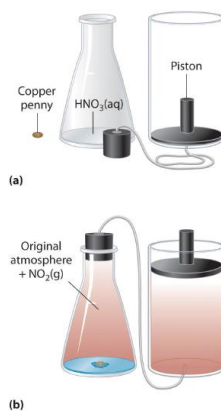


Figure 5.2.3 An Example of Work Performed by a Reaction Carried Out at Constant Pressure (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO₂ gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.

The symbol E in Equation 5.2.3 represents the internal energy. The sum of the kinetic and potential energies of all of a system's component. Internal energy is a state function, of a system, which is the sum of the kinetic energy and potential energy of all its components. Additionally, $\Delta E = q + w$, where q is the heat produced by the system and w is the work performed by the system. It is the change in internal energy that produces heat plus work. Substituting Equation 8.1.5 we find that

$$\Delta E = q - P\Delta V \quad (5.2.6)$$

Thus, if a reaction were carried out in a constant volume system (a pressure cooker for example)

$$\Delta E = q_v \quad (5.2.7)$$

Where the subscript v in q_v indicates that the process is carried out at constant volume. Thus, if the volume is held constant, the change in internal energy is equal to the heat flowing into or out of the system. However, we live in a constant pressure world, not a constant volume one. The atmospheric pressure at the surface of the earth where we live is roughly constant allowing for variation in barometric pressure due to weather or altitude.

To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called enthalpy (H). The sum of a system's internal energy E and the product of its pressure P and volume V (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy E plus the product of its pressure P and volume V :

$$H = E + PV \quad (5.2.8)$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (for a given P , $\Delta P = 0$), the change in enthalpy (ΔH). At constant pressure, the amount of heat transferred from the surroundings to the system or $\Delta H = q$ is

$$\Delta H = \Delta(E + PV) = \Delta E + \Delta PV = \Delta E + P\Delta V \quad (5.2.9)$$

Substituting $q + w$ for ΔE (Equation 5.2.9) and $-w$ for $P\Delta V$ (Equation 5.2.5), we obtain

$$\Delta H = \Delta E + P\Delta V = q_p + w - w = q_p \quad (5.2.10)$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 5.2.10 we see that at constant pressure the change in enthalpy, ΔH of the system, defined as $H_{\text{final}} - H_{\text{initial}}$, is equal to the heat gained or lost.

$$\Delta H = H_{\text{final}} - H_{\text{initial}} = q_p \quad (5.2.11)$$

Just as with ΔE , because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. The enthalpy change is the same even if the process does *not* occur at constant pressure. Most importantly, the change in enthalpy for a reaction can be determined by measuring the flow of heat into or out of the system. As we will see

below, there are also cases where we want to know the amount of heat generated by a reaction, as for example for combustion of fuel. In that case knowing the molar change in enthalpy provides the information needed.

Finally, looking at Equation 9.2.9 shows that for reactions where the volume does not change, or better put does not change much, $\Delta H_{\text{rxn}} \sim \Delta E_{\text{rxn}}$. As a practical matter, this includes all reactions where all the products and reactants are either in the solid, liquid or aqueous phases. This is not generally true when there are gases on either side of the equation, a question which we will discuss in the chapter on gases.

Note the Pattern

To find ΔH , measure q_p .

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}) The change in enthalpy that occurs during a chemical reaction., the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus $\Delta H_{\text{rxn}} < 0$ for an exothermic reaction, and $\Delta H_{\text{rxn}} > 0$ for an endothermic reaction. In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, an exothermic reaction is *energetically downhill* (part (a) in Figure 5.2.4). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, an endothermic reaction is *energetically uphill* (part (b) in Figure 5.2.4). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

Note the Pattern

Bond breaking requires an input of energy; bond making releases energy.

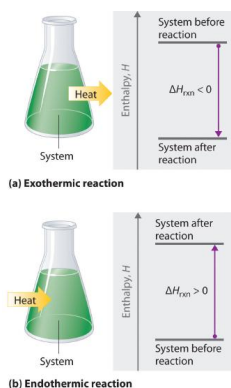
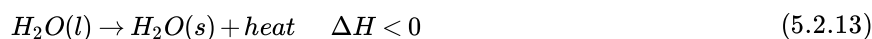


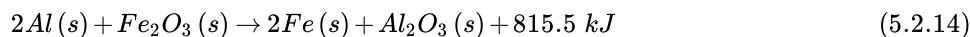
Figure 5.2.4 The Enthalpy of Reaction Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill.

- Reversing a reaction or a process changes the sign of ΔH . Ice absorbs heat when it melts (electrostatic interactions are broken), so liquid water must release heat when it freezes (electrostatic interactions are formed):



In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider [Equation 9.2.12](#), which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3 , and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:



Thus $\Delta H = -851.5 \text{ kJ/mol}$ of Fe_2O_3 . We can also describe ΔH for the reaction as -425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide -851.5 kJ by 2. When a value for ΔH , in kilojoules rather than kilojoules per mole, is written after the reaction, as in [Equation 9.2.13](#), it is the value of ΔH corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:



If 4 mol of Al and 2 mol of Fe_2O_3 react, the change in enthalpy is $2 \times (-851.5 \text{ kJ}) = -1703 \text{ kJ}$. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

$$-\frac{851.5 \text{ kJ}}{2 \text{ mol Al}} = -\frac{425.8 \text{ kJ}}{1 \text{ mol Al}} = -\frac{1703 \text{ kJ}}{4 \text{ mol Al}} \quad (5.2.16)$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in [Example 5.2.1](#).

✓ Example 5.2.1

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ at 0°C and constant pressure, how much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.

B Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given ΔH for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by ΔH ($+6.01 \text{ kJ/mol}$):

$$\begin{aligned} \text{moles } \text{H}_2\text{O} &= 1.00 \times 10^6 \text{ metric tons } \text{H}_2\text{O} \left(\frac{1000 \text{ kg}}{1 \text{ metric ton}} \right) \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol } \text{H}_2\text{O}}{18.015 \text{ g } \text{H}_2\text{O}} \right) \\ &= 5.55 \times 10^{10} \text{ mol } \text{H}_2\text{O} \end{aligned}$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01 \text{ kJ}}{\text{mol } \text{H}_2\text{O}} \right) (5.55 \times 10^{10} \text{ mol } \text{H}_2\text{O}) = 3.34 \times 10^{11} \text{ kJ}$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown in the table below.

Possible sources of the approximately $3.34 \times 10^{11} \text{ kJ}$ needed to melt a 1.00×10^6 metric ton iceberg

Possible sources of the approximately 3.34×10^{11} kJ needed to melt a 1.00×10^6 metric ton iceberg

Combustion of 3.8×10^3 ft³ of natural gas

Combustion of 68,000 barrels of oil

Combustion of 15,000 tons of coal

1.1×10^8 kilowatt-hours of electricity

? Exercise 5.2.1

If 17.3 g of powdered aluminum are allowed to react with excess Fe_2O_3 , how much heat is produced?

Answer

273 kJ

Key Equations

definition of enthalpy

Equation 5.2.6: $H = E + PV$

pressure-volume work

Equation 5.2.5: $w = -P\Delta V$

enthalpy change at constant pressure

Equation 5.2.8: $\Delta H = \Delta E + P\Delta V$

Equation 5.2.9: $\Delta H = q_p$

Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**.

Enthalpy is a state function used to measure the heat transferred from a system to its surroundings or vice versa at constant pressure. Only the **change in enthalpy** (ΔH) can be measured. A negative ΔH means that heat flows from a system to its surroundings; a positive ΔH means that heat flows into a system from its surroundings. For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn} . The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion** (ΔH_{fus}) and the **enthalpy of vaporization** (ΔH_{vap}), respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion** (ΔH_{comb}) is the enthalpy change that occurs when a substance is burned in excess oxygen. The **enthalpy of formation** (ΔH_f) is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH_f°) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** ($\Delta H_{\text{rxn}}^\circ$) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the “products minus reactants” rule. The **enthalpy of solution** (ΔH_{soln}) is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Key Takeaway

- Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure.

Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Conceptual Problems.

- Heat implies the flow of energy from one object to another. Describe the energy flow in an
 - exothermic reaction.
 - endothermic reaction.
- When a thermometer is suspended in an insulated thermos that contains a block of ice, the temperature recorded on the thermometer drops. Describe the direction of heat flow.
- In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. State whether each process is endothermic or exothermic.
 - Water is added to sodium hydroxide pellets, and the flask becomes hot.
 - The body metabolizes glucose, producing carbon dioxide and water.
 - Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.
- In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. Determine whether each process is endothermic or exothermic.
 - Concentrated acid is added to water in a flask, and the flask becomes warm.
 - Water evaporates from your skin, causing you to shiver.
 - A container of ammonium nitrate detonates.
- Is Earth's environment an isolated system, an open system, or a closed system? Explain your answer.
- Why is it impossible to measure the absolute magnitude of the enthalpy of an object or a compound?
- Determine whether energy is consumed or released in each scenario. Explain your reasoning.
 - A leaf falls from a tree.
 - A motorboat maneuvers against a current.
 - A child jumps rope.
 - Dynamite detonates.
 - A jogger sprints down a hill.
- The chapter states that enthalpy is an extensive property. Why? Describe a situation that illustrates this fact.
- The enthalpy of a system is affected by the physical states of the reactants and the products. Explain why.
- Is the distance a person travels on a trip a state function? Why or why not?
-

Contributors

- Anonymous

Modified by Joshua Halpern

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