

Thermochemistry

SECTION 1

OBJECTIVES

- Define *temperature* and state the units in which it is measured.
- Define *heat* and state its units.
- Perform specific-heat calculations.
- Explain enthalpy change, enthalpy of reaction, enthalpy of formation, and enthalpy of combustion.
- Solve problems involving enthalpies of reaction, enthalpies of formation, and enthalpies of combustion.

Virtually every chemical reaction is accompanied by a change in energy. Chemical reactions usually absorb or release energy as heat. You learned in Chapter 10 that energy is also absorbed or released in physical changes, such as melting a solid or condensing a vapor. **Thermochemistry** is the study of the transfers of energy as heat that accompany chemical reactions and physical changes.

Heat and Temperature

The energy absorbed or released as heat in a chemical or physical change is measured in a **calorimeter**. In one kind of calorimeter, known quantities of reactants are sealed in a reaction chamber, which is immersed in a known quantity of water in an insulated vessel. Therefore, the energy given off (or absorbed) during the reaction is equal to the energy absorbed (or given off) by the known quantity of water. The amount of energy is determined from the temperature change of the known mass of surrounding water. The data collected from calorimetry experiments are temperature changes because energy cannot be measured directly; but temperature, which is affected by the transfer of energy as heat, is directly measurable. To see why this is so, let us look at the definitions of heat and temperature and at how temperature is measured.

Temperature is a measure of the average kinetic energy of the particles in a sample of matter. The greater the kinetic energy of the particles in a sample, the higher the temperature is and the hotter it feels. To assign a numerical value to temperature, it is necessary to define a temperature scale. For calculations in thermochemistry, we use the Celsius and Kelvin scales. Celsius and Kelvin temperatures are related by the following equation.

$$K = 273.15 + ^\circ C$$

For most calculations in this book, 273.15 is rounded to 273.

The ability to measure temperature is thus based on energy transfer. The amount of energy transferred as heat is usually measured in joules. A **joule** is the SI unit of heat as well as all other forms of energy. The joule, abbreviated J, is derived from the units for force and length.

$$N \times m = \frac{\text{kg} \times \text{m}^2}{\text{s}^2}$$

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Topic: Heat/Temperature

Code: HC60726

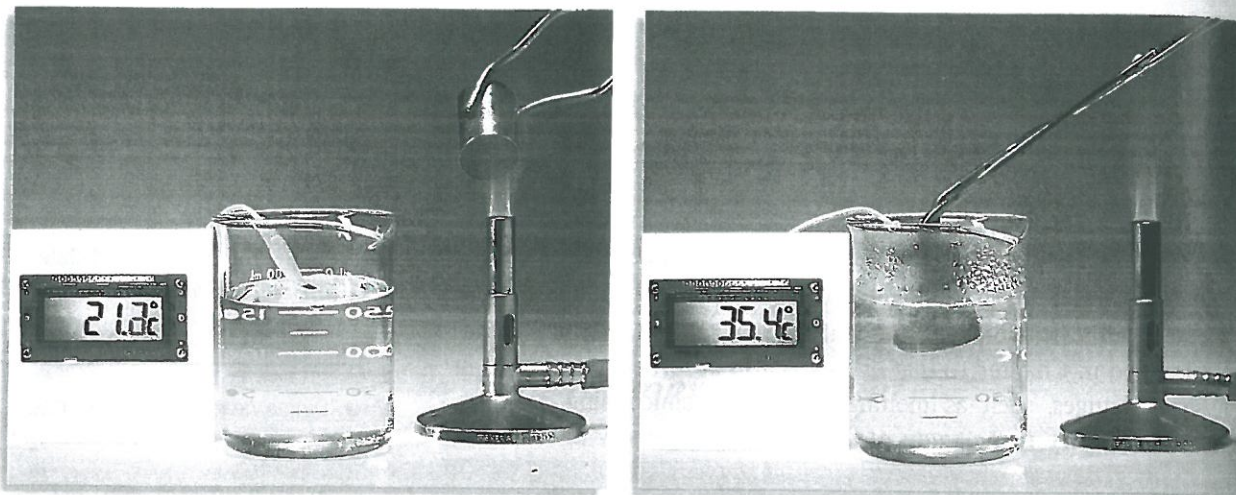


FIGURE 1 The direction of energy transfer is determined by the temperature differences between the objects within a system. The energy is transferred as heat from the hotter brass bar to the cooler water. This energy transfer will continue until the bar and the water reach the same temperature.

Heat can be thought of as the energy transferred between samples of matter because of a difference in their temperatures. Energy transferred as heat always moves spontaneously from matter at a higher temperature to matter at a lower temperature, as shown in **Figure 1**. The temperature of the cool water in the beaker increases as energy flows into it. Likewise, the temperature of the hot brass bar decreases as energy flows away from it. When the temperature of the water equals the temperature of the brass bar, energy is no longer transferred as heat within the system.

Specific Heat

The quantity of energy transferred as heat during a temperature change depends on the nature of the material changing temperature, the mass of the material changing temperature, and the size of the temperature change. One gram of iron heated to 100.0°C and cooled to 50.0°C in a calorimeter transfers 22.5 J of energy to the surrounding water. But one gram of silver transfers 11.8 J of energy under the same conditions. The difference depends on the metals' differing capacities for absorbing this energy. A quantity called specific heat can be used to compare heat absorption capacities for different materials. **Specific heat** is the amount of energy required to raise the temperature of one gram of a substance by one Celsius degree (1°C) or one kelvin (1 K) (because the sizes of the degree divisions on both scales are equal). Values of specific heat can be given in units of joules per gram per Celsius degree, J/(g·°C), joules per gram per kelvin, J/(g·K), or calories per gram per Celsius degree, cal/(g·°C). **Table 1** gives the specific heats of some common substances. Notice the extremely high specific heat of water, one of the highest of most common substances.

Specific heat is usually measured under constant pressure conditions, so its symbol, c_p , contains a subscripted p as a reminder to the reader.

TABLE 1 Specific Heats of Some Common Substances at 298.15 K

Substance	Specific heat J/(g·K)
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Benzene (l)	1.74
Ethanol (l)	2.44
Ethanol (g)	1.42
Aluminum (s)	0.897
Calcium (s)	0.647
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Mercury (l)	0.140
Lead (s)	0.129

In the following mathematical equation, c_p is the specific heat at a given pressure, q is the energy lost or gained, m is the mass of the sample, and ΔT represents the difference between the initial and final temperatures.

$$c_p = \frac{q}{m \times \Delta T}$$

This equation can be rearranged to give an equation that can be used to find the quantity of energy gained or lost with a change in temperature.

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

SAMPLE PROBLEM A

A 4.0 g sample of glass was heated from 274 K to 314 K, a temperature increase of 40. K, and was found to have absorbed 32 J of energy as heat.

- What is the specific heat of this type of glass?
- How much energy will the same glass sample gain when it is heated from 314 K to 344 K?

SOLUTION

- 1 **ANALYZE** Given: $m = 4.0 \text{ g}$
 $\Delta T = 40. \text{ K}$
 $q = 32 \text{ J}$
Unknown: c_p in J/(g·K)

2 PLAN

- a. The specific heat, c_p , of the glass is calculated using the equation given for specific heat.

$$c_p = \frac{q}{m \times \Delta T}$$

- b. The rearranged specific heat equation is used to find the energy gained when the glass was heated.

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

3 COMPUTE

a. $\frac{32 \text{ J}}{(4.0 \text{ g})(40. \text{ K})} = 0.20 \text{ J}/(\text{g}\cdot\text{K})$

b. $\frac{0.20 \text{ J}}{(\text{g}\cdot\text{K})} (4.0 \text{ g})(344 \text{ K} - 314 \text{ K})$

$$\frac{0.20 \text{ J}}{(\text{g}\cdot\text{K})} (4.0 \text{ g})(30 \text{ K}) = 24 \text{ J}$$

4 EVALUATE

The units combine or cancel correctly to give the specific heat in $\text{J}/(\text{g}\cdot\text{K})$ and the energy in J.

PRACTICE

Answers in Appendix E

- Determine the specific heat of a material if a 35 g sample absorbed 96 J as it was heated from 293 K to 313 K.
- If 980 kJ of energy are added to 6.2 L of water at 291 K, what will the final temperature of the water be?

extension

Go to go.hrw.com for more practice problems that ask you to calculate using specific heat.



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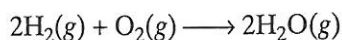
Enthalpy of Reaction

The energy absorbed as heat during a chemical reaction at constant pressure is represented by ΔH . The H is the symbol for a quantity called *enthalpy*. It is not practical to talk just about enthalpy as a quantity, because we have no way to directly measure the enthalpy of a system. Only *changes* in enthalpy can be measured. The Greek letter Δ (“delta”) stands for “change in.” Therefore, ΔH is read as “change in enthalpy.” An **enthalpy change** is the amount of energy absorbed by a system as heat during a process at constant pressure. The enthalpy change is always the difference between the enthalpies of the products and the reactants. The following equation expresses an enthalpy change for a reaction.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

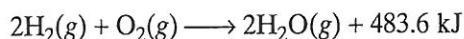
The **enthalpy of reaction** is the quantity of energy transferred as heat during a chemical reaction. You can think of enthalpy of reaction as the difference between the stored energy of the reactants and the products. Enthalpy of reaction is sometimes called “heat of reaction.”

If a mixture of hydrogen and oxygen is ignited, water will form and energy will be released explosively. The energy that is released comes from the reactants as they form products. Because energy is released, the reaction is *exothermic*, and the energy of the product, water, must be less than the energy of the reactants. The following chemical equation for this reaction indicates that when 2 mol of hydrogen gas at room temperature are burned, 1 mol of oxygen gas is consumed and 2 mol of water vapor are formed.

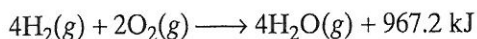


The equation does not tell you that energy is evolved as heat during the reaction. Experiments have shown that 483.6 kJ of energy are evolved when 2 mol of gaseous water are formed from its elements at 298.15 K.

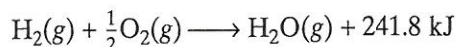
Modifying the chemical equation to show the amount of energy as heat released during the reaction gives the following expression.



This expression is an example of a **thermochemical equation**, an equation that includes the quantity of energy released or absorbed as heat during the reaction as written. In any thermochemical equation, we must always interpret the coefficients as *numbers of moles* and never as *numbers of molecules*. The quantity of energy released as heat in this or any other reaction depends on the amounts of reactants and products. The quantity of energy as heat released during the formation of water from H_2 and O_2 is proportional to the quantity of water formed. Producing twice as much water vapor would require twice as many moles of reactants and would release 2×483.6 kJ of energy as heat, as shown in the following thermochemical equation (which is simply the previous thermochemical equation, multiplied by two).



Producing one-half as much water would require one-half as many moles of reactants and would release only one-half as much energy, or $\frac{1}{2} \times 483.6$ kJ. The thermochemical equation for this reaction would be as follows.



The situation is reversed in an *endothermic* reaction because products have a larger enthalpy than reactants. The decomposition of water vapor is endothermic; it is the reverse of the reaction that forms water vapor. The amount of energy as heat absorbed by water molecules to form hydrogen and oxygen equals the amount of energy as heat released when the elements combine to form the water. This is to be expected because the difference between the energy of reactants and products is unchanged. Enthalpy now appears on the reactant side of the thermochemical equation that follows, indicating that it is an endothermic reaction.

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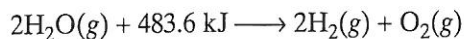
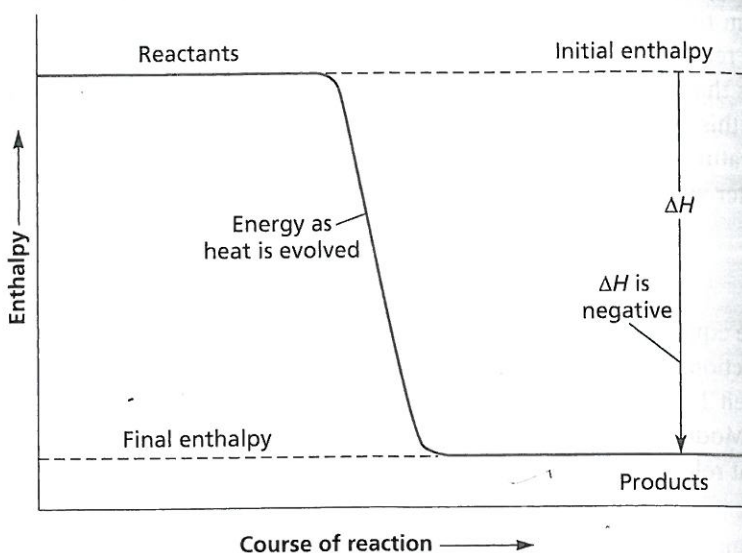
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FIGURE 2 In an exothermic chemical reaction, the enthalpy change is negative, meaning energy is released from the system as heat.

Exothermic Reaction Pathway



The physical states of reactants and products must always be included in thermochemical equations because they influence the overall amount of energy as heat gained or lost. For example, the energy needed for the decomposition of water would be greater than 483.6 kJ if we started with ice, because extra energy would be needed to melt the ice and to change the liquid into a vapor.

Thermochemical equations are usually written by designating the value of ΔH rather than writing the energy as a reactant or product. For an exothermic reaction, ΔH is always negative because the system loses energy. So, the thermochemical equation for the exothermic formation of 2 mol of gaseous water from its elements now has the following form.

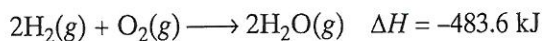
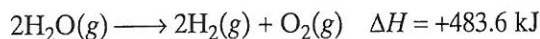


Figure 2 graphically shows the course of an exothermic reaction. The initial enthalpy of the reactants is greater than the final enthalpy of the products. This means energy as heat is evolved, or given off, during the reaction; this is described as a negative enthalpy change.

For an endothermic reaction, ΔH is always positive because the system gains energy. Thus, the endothermic decomposition of 2 mol of gaseous water has the following thermochemical equation.



The course of an endothermic reaction is illustrated in **Figure 3**. Energy as heat is absorbed in this reaction, meaning that the initial enthalpy of

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Endothermic Reaction Pathway

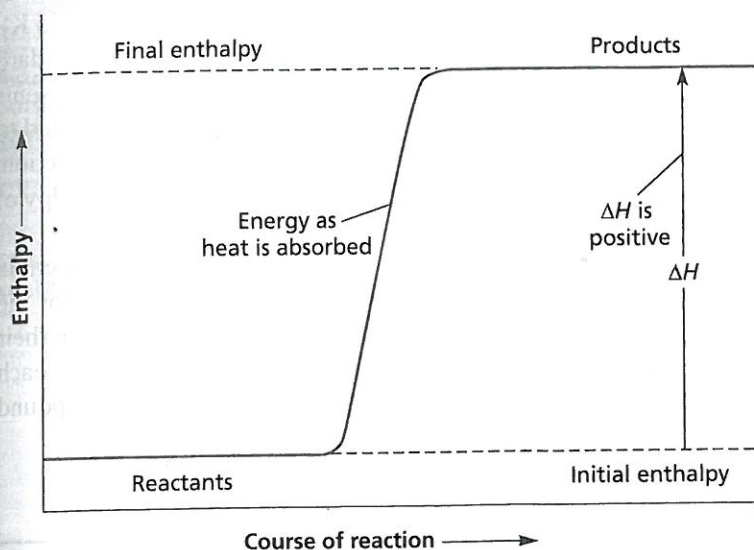


FIGURE 3 In an endothermic chemical reaction, the enthalpy change is positive because energy is absorbed into the system as heat.

the reactants is lower than the final enthalpy of the products. In this case, ΔH is designated as positive.

Keep in mind the following when using thermochemical equations.

1. The coefficients in a balanced thermochemical equation represent the numbers of *moles* of reactants and products and never the numbers of *molecules*. This allows us to write these coefficients as fractions rather than whole numbers when necessary.
2. The physical state of the product or reactant involved in a reaction is an important factor and therefore must be included in the thermochemical equation.
3. The change in enthalpy represented by a thermochemical equation is directly proportional to the number of moles of substances undergoing a change. For example, if 2 mol of water are decomposed, twice as much enthalpy, 483.6 kJ, is needed than for the decomposition of 1 mol of water.
4. The value of the enthalpy change, ΔH , is usually not significantly influenced by changing temperature.

Enthalpy of Formation

The formation of water from hydrogen and oxygen is a composition reaction—the formation of a compound from its elements in their standard form. Thermochemical data are often recorded as the enthalpies of such composition reactions. *The molar enthalpy of formation is the enthalpy change that occurs when one mole of a compound is formed from its elements in their standard state at 25°C and 1 atm.*

To make comparisons meaningful, enthalpies of formation are given for the standard states of reactants and products—these are the states found at atmospheric pressure and, usually, room temperature (298.15 K). Thus, the standard state of water is liquid, not gas or solid. The standard state of iron is solid, not a molten liquid. To signify that a value represents measurements on substances in their standard states, a ⁰ sign is added to the enthalpy symbol, giving ΔH^0 for the standard enthalpy of a reaction. Adding a subscript *f*, as in ΔH_f^0 , further indicates a standard enthalpy of formation.

Some standard enthalpies of formation are given in Appendix Table A-14. Each entry in the table is the enthalpy of formation for the synthesis of *one mole* of the compound listed from its elements in their standard states. The thermochemical equation to accompany each enthalpy of formation shows the formation of one mole of the compound from its elements in their standard states.

Stability and Enthalpy of Formation

If a large amount of energy as heat is released when a compound is formed, the compound has a large negative enthalpy of formation. Such compounds are very stable.

Elements in their standard states are *defined* as having $\Delta H_f^0 = 0$. The ΔH_f^0 of carbon dioxide is -393.5 kJ/mol of gas produced. Therefore, carbon dioxide is more stable than the elements from which it was formed. You can see in Appendix Table A-14 that the majority of the enthalpies of formation are negative.

Compounds with relatively positive values of enthalpies of formation, or only slightly negative values, are typically unstable. For example, hydrogen iodide, HI, is a colorless gas that decomposes somewhat when stored at room temperature. It has a relatively high positive enthalpy of formation of $+26.5$ kJ/mol. As it decomposes, violet iodine vapor, I₂, becomes visible throughout the container of the gas.

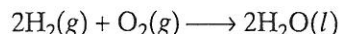
Compounds with a high positive enthalpy of formation are sometimes very unstable and may react or decompose violently. For example, ethyne (acetylene), C₂H₂ ($\Delta H_f^0 = +226.7$ kJ/mol), reacts violently with oxygen and must be stored in cylinders as a solution in acetone. Mercury fulminate, HgC₂N₂O₂, has a very large enthalpy of formation of $+270$ kJ/mol. Its instability makes it useful as a detonator for explosives.

Enthalpy of Combustion

Combustion reactions produce a considerable amount of energy in the form of light and heat when a substance is combined with oxygen. The enthalpy change that occurs during the complete combustion of one mole of a substance is called the **enthalpy of combustion** of the substance.

Activation Energy

Consider the reaction for the formation of water from the diatomic gases oxygen and hydrogen according to the following equation.



The enthalpy of formation is quite high: $\Delta H_f^0 = -285.8$ kJ/mol at 298.15 K. The free-energy change is also large: $\Delta G^0 = -237.1$ kJ/mol. Why, then, don't oxygen and hydrogen combine spontaneously and immediately to form water when they are mixed at room temperature?

Hydrogen and oxygen gases exist as diatomic molecules. When the molecules approach each other, the electron clouds repel each other, so the molecules might not meet. For a reaction to occur, the colliding molecules must have enough kinetic energy to intermingle the valence electrons. In other words, the bonds of these molecular species must be broken in order for new bonds to be formed between oxygen and hydrogen atoms. Bond breaking is an endothermic process, and bond forming is exothermic. Even though the net process for forming water is exothermic, an initial input of energy is needed to overcome the repulsion forces that occur between reactant molecules when they are brought very close together. This initial energy input activates the reaction.

Once an exothermic reaction is started, the energy released is enough to sustain the reaction by activating other molecules. Thus, the reaction rate keeps increasing. It is limited only by the time required for

reactant particles to acquire the energy and make contact. Energy from an outside source may start exothermic reactants along the pathway of reaction. A generalized reaction pathway for an exothermic reaction is shown as the forward reaction in **Figure 4**. The minimum amount of energy needed to activate this reaction is the activation energy represented by E_a . **Activation energy** is the minimum energy required to transform the reactants into an activated complex.

The reverse reaction, decomposition of water molecules, is endothermic because the water molecules lie at an energy level lower than that of the hydrogen and oxygen molecules. The water molecules require a larger activation energy before they can decompose to re-form oxygen and hydrogen. The energy needed to activate an endothermic reaction is greater than that required for the original exothermic change and is represented by E_a' in **Figure 4**. The difference between E_a' and E_a is equal to the energy change in the reaction, ΔE . This energy change has the same numerical value for the forward reaction as it has for the reverse reaction but with the opposite sign.

Reaction Pathways for Forward and Reverse Reactions

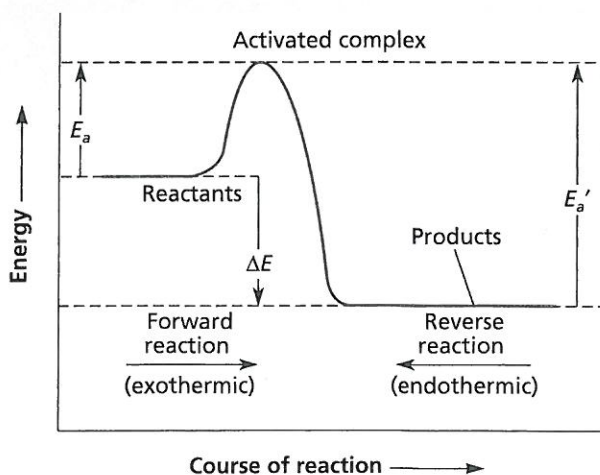


FIGURE 4 The difference between the activation energies for the reverse and forward reactions of a reversible reaction equals the energy change in the reaction, ΔE . The quantity for ΔE is the same for both directions, but is negative for the exothermic direction and positive for the endothermic direction.