Chapter 5

Thermochemistry

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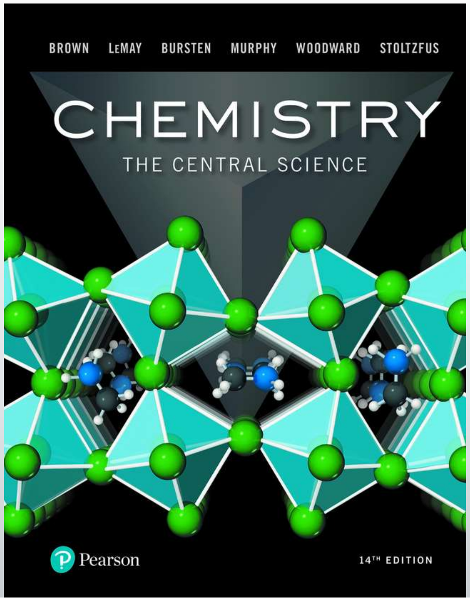


5.1 The Nature of Chemical Energy

- The study of energy and its transformations is known as **thermodynamics**.
- A portion of thermodynamics, which examines the relationships between chemical reactions and energy changes that involve heat, is called thermochemistry.
- Energy is released when chemical bonds are formed, whereas energy is consumed when chemical bonds are broken.

5.2 The First Law of Thermodynamics

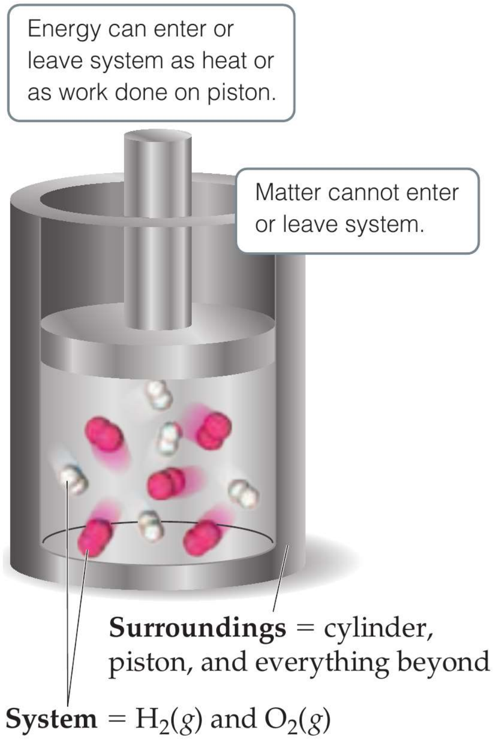
- The first law of thermodynamics: energy can be converted from one form to another, but it is neither created nor destroyed.

System and Surroundings

- The portion we single out for study is called the system; everything else is called the surroundings.
- **Example**: When we study the energy change that accompanies a chemical reaction in a laboratory, the reactants and products constitute the system. The container and everything beyond it are considered the surroundings.

5.2 The First Law of Thermodynamics

- Systems may be open, closed, or isolated.
- An **open system** is one in which matter and energy can be exchanged with the surroundings.
- **Example**: An uncovered pot of boiling water on a stove is an open system: Heat comes into the system from the stove, and water is released to the surroundings as steam.
- The systems we can most readily study in thermochemistry are called **closed systems**; systems that can exchange energy but not matter with their surroundings.



▲ Figure 5.4 A closed system.

5.2 The First Law of Thermodynamics

- An **isolated system** is one in which neither energy nor matter can be exchanged with the surroundings.
- An insulated thermos containing hot coffee approximates an isolated system.

Internal Energy

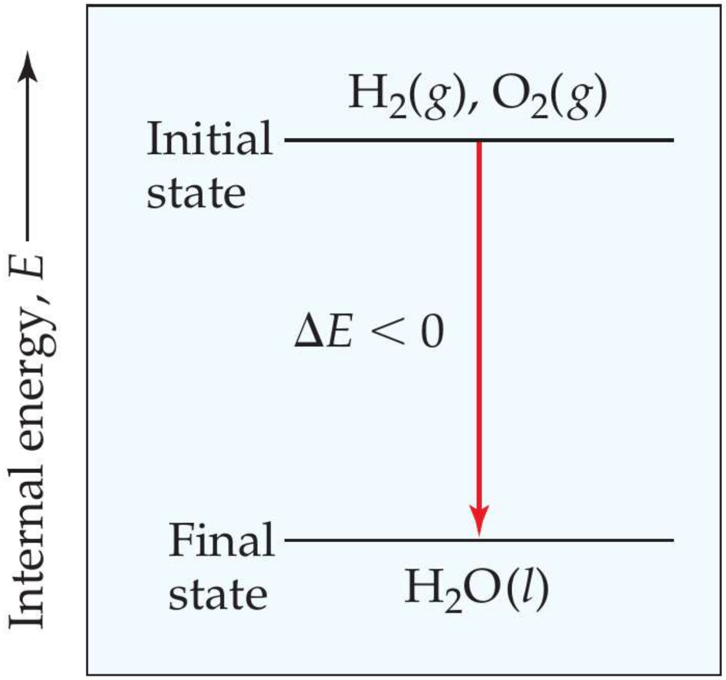
- The internal energy, E, of a system is the sum of all the kinetic and potential energies of the components of the system.
- We define the change in internal energy, denoted ΔE as:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

5.2 The First Law of Thermodynamics

- When $\Delta E > 0$, it indicates that the system has gained energy from its surroundings, whereas when $\Delta E < 0$, it indicates that the system has lost energy to its surroundings.
- In a chemical reaction, the initial state of the system refers to the reactants and the final state refers to the products.
- **Example**:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$$



$E_{initial}$ greater than E_{final}; therefore, energy is released from system to surroundings during reaction and $\Delta E < 0$.

5.2 The First Law of Thermodynamics

Relating Δ*E* to Heat and Work

- A system may exchange energy with its surroundings in two general ways: as heat (q) or as work (w).
- When a system undergoes any chemical or physical change, the accompanying change in internal energy, ΔE, is given by

$$\Delta E = q + w$$

- When heat is transferred to the system from the surroundings, q has a positive value.
- When work is done on the system by the surroundings, w has a positive value.

5.2 The First Law of Thermodynamics

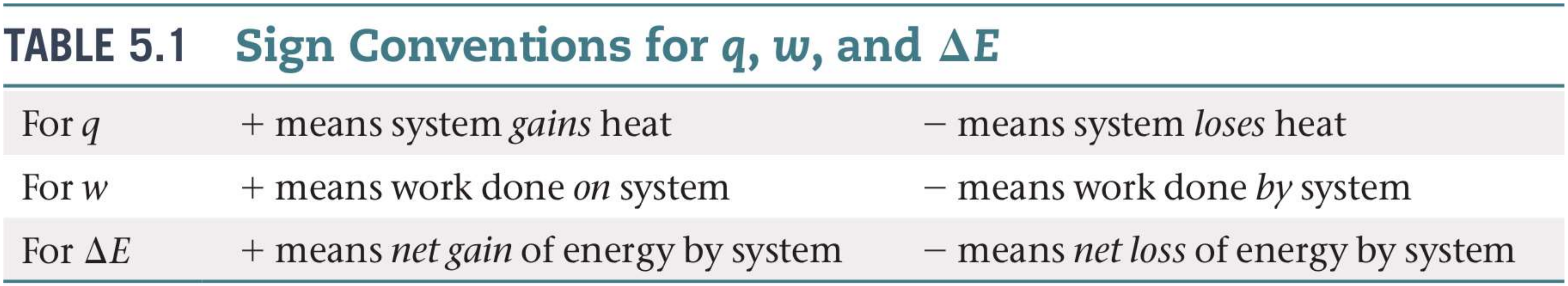


TABLE 5.1 Sign Conventions for q, w, and ΔE

For q	+ means system *gains* heat	− means system *loses* heat
For w	+ means work done *on* system	− means work done *by* system
For ΔE	+ means *net gain* of energy by system	− means *net loss* of energy by system

Sample Exercise 5.1

Gases A(g) and B(g) are confined in a cylinder-and-piston arrangement and react to form a solid product C(*s*): A(*g*) + B(*g*) → C(*s*). As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in the internal energy of the system?

$$\Delta E = q + w$$

$$= (-1150) + (480) = -670\ \mathrm{J}$$

5.2 The First Law of Thermodynamics

Endothermic and Exothermic Processes

- When a process occurs in which the system absorbs heat, the process is called endothermic.
- A process in which the system loses heat is called exothermic.

State Functions

- Internal energy is an example of a state function, a property of a system that is determined by specifying the system's condition, or state (in terms of temperature, pressure, and so forth).
- The value of a state function depends only on the present state of the system, not on the path the system took to reach that state.

5.2 The First Law of Thermodynamics

- This means that, although $\Delta E = q + w$ does not depend on how the change occurs, the specific amounts of heat and work depend on the way in which the change occurs.

5.3 Enthalpy

- Under the conditions of constant pressure there is a thermodynamic quantity called enthalpy (H), a state function, that is defined as the internal energy plus the product of the pressure, P, and volume, V, of the system: $H = E + PV$.

Pressure–Volume Work

- The work involved in the expansion or compression of gases is called pressure–volume work (P–V work).
- When pressure is constant in a process, the sign and magnitude of the pressure–volume work are given by

$$w = -P\Delta V$$

5.3 Enthalpy

- To express the work in the more familiar unit of joules, we use the conversion factor 1 atm·L = 101.325 J.
- When a gas expands, ΔV is positive (the volume increases) and w is negative, meaning the system does work on the surroundings.
- On the other hand, if the gas is compressed, ΔV is negative (the volume decreases) w is positive, meaning work is done on the system by the surroundings.

Sample Exercise 5.2

A fuel is burned in a cylinder equipped with a piston. The initial volume of the cylinder is 0.250 L, and the final volume is 0.980 L. If the piston expands against a constant pressure of 1.35 atm, how much work (in J) is done? (1 L·atm = 101.325 J)

$$w = -P\Delta V$$

$$= -(1.35)(0.980 - 0.250)\left(\frac{101.325\ \mathrm{J}}{1\ \mathrm{L} \cdot \mathrm{atm}}\right) = -99.9\ \mathrm{J}$$

5.3 Enthalpy

Enthalpy Change

- When a change occurs at constant pressure, the change in enthalpy, ΔH, is given by the relationship

$$\Delta H = \Delta E + P\Delta V$$

- At constant pressure,

$$\Delta H = q_{\mathrm{P}}$$

Sample Exercise 5.3

Indicate the sign of the enthalpy change, ΔH, in the following processes carried out under atmospheric pressure and indicate whether each process is endothermic or exothermic:

a. An ice cube melts

- ➢ The ice cube absorbs heat from the surroundings as it melts, so ΔH is positive and the process is endothermic.

b. 1 g of butane (C_4H_{10}) is combusted in sufficient oxygen to give complete combustion to CO_2 and H_2O.

- ➢ The combustion of butane in oxygen gives off heat, so ΔH is negative and the process is exothermic.

5.4 Enthalpies of Reaction

- The enthalpy change that accompanies a reaction is called either the enthalpy of reaction or the heat of reaction and is sometimes written ΔH_{rxn}.

$$\Delta H_{\mathrm{rxn}} = H_{\mathrm{products}} - H_{\mathrm{reactants}}$$

- Balanced chemical equations that show the associated enthalpy change in this way are called thermochemical equations.

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \qquad \Delta H = -483.6\ \mathrm{kJ}$$

5.4 Enthalpies of Reaction

❖ The following guidelines are helpful when using thermochemical equations and enthalpy diagrams:

1. Enthalpy is an extensive property: The magnitude of ΔH is proportional to the amount of reactant consumed in the process.
2. The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction.
3. The enthalpy change for a reaction depends on the states of the reactants and products.

Sample Exercise 5.4

How much heat is released when 4.50 g of methane gas is burned in a constant-pressure system?

$$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \qquad \Delta H = -890\ \mathrm{kJ}$$

$$n = \frac{m}{MM}$$

$$= \frac{4.50}{16.05} = 0.2804\ \mathrm{mol}$$

$$q_\mathrm{P} = 0.2804\ \mathrm{mol\ CH_4}\left(\frac{-890\ \mathrm{kJ}}{1\ \mathrm{mol\ CH_4}}\right) = -250\ \mathrm{kJ}$$

5.5 Calorimetry

- The measurement of heat flow is calorimetry; a device used to measure heat flow is a calorimeter.

Heat Capacity and specific Heat

- The heat capacity (C) of an object is the amount of heat required to raise its temperature by 1 K (or 1 °C).
- The greater the heat capacity, the greater the heat required to produce a given increase in temperature.
- The heat capacity of one mole of a substance is called its molar heat capacity, C_m.

5.5 Calorimetry

- The heat capacity of one gram of a substance is called its specific heat capacity, or merely its specific heat, C_s.

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

Sample Exercise 5.5

a. How much heat is needed to warm 250 g of water (about 1 cup) from 22 °C (about room temperature) to 98 °C (near its boiling point)?

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

$$= (4.184)(250)(98 - 22) = 7.9 \times 10^4 \text{ J}$$

b. What is the molar heat capacity of water?

$$C_m = 4.184 \frac{\text{J}}{\text{g} \cdot \text{K}} \left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 75.40 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$