Topic 6.1-6.2

Endothermic and Exothermic Processes

Learning Objectives

- Understand the difference between endothermic and exothermic processes.
- Recognize that temperature changes in a system indicate changes in the internal energy of the system.
- Understand the meaning of positive and negative values of the change in the enthalpy of a system.
- Examine how dissolving a compound into solution produces changes in temperature and enthalpy.
- Use energy diagrams to represent changes in energy and enthalpy for each step of a reaction.

Topic Questions

- What is the difference between an endothermic and an exothermic reaction?
- What is a change in enthalpy and how is it related to heat transfer?
- Is the change in enthalpy positive or negative for an endothermic reaction? An exothermic reaction?
- How does dissolving an ionic compound in water affect the temperature and enthalpy of a solution?
- How can an energy diagram be constructed to show the changes in energy and and enthalpy for each step in a reaction?

6.1.01 Enthalpy as Internal Energy

[ENE-2.A.1 ENE-2.A.2 ENE-2.A.3]

An **exothermic reaction** is a process that **releases energy**, such as heat or light, from the system (ie, the reacting chemical species) to the surroundings, which includes the solution mixture, reaction vessel, and nearby environment. This is illustrated in Figure 6.1.

Exothermic reaction

Reactants → Products + Energy $\Delta H < 0$

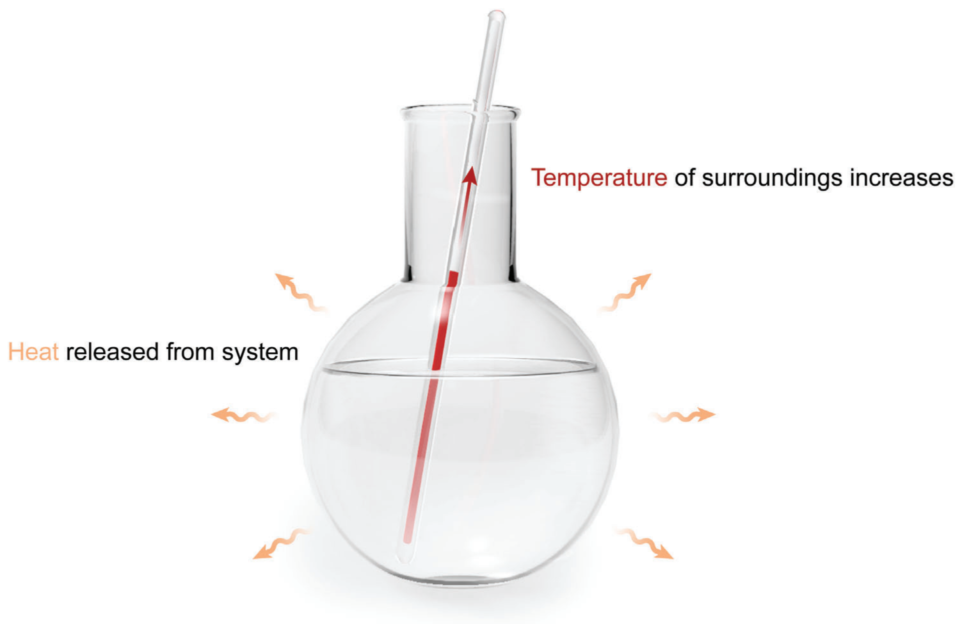

Figure 6.1 Exothermic reactions.

Because energy is released as a product of an exothermic reaction, the reaction mixture's temperature increases as heat is generated by the reaction. This heat is then transferred from the warmer reaction system to the cooler surrounding environment.

On the other hand, an **endothermic reaction** is a process that **absorbs energy** from the surroundings, as shown in Figure 6.2.

Endothermic reaction

Reactants + Energy → Products $\quad \Delta H > 0$

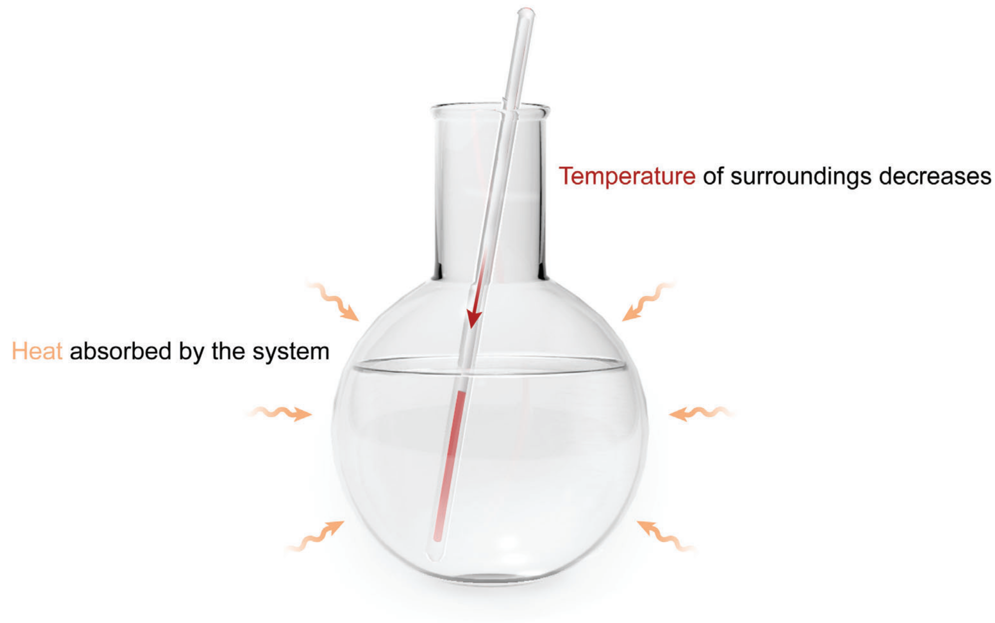

Figure 6.2 Endothermic reactions.

In an endothermic reaction, the reaction mixture's temperature decreases because heat is absorbed from the surrounding environment and used by the reaction system.

Exothermic reactions convert **internal energy** into **thermal energy** and release it as heat into the surroundings whereas endothermic reactions absorb thermal energy from the surroundings and convert the heat into stored internal energy. For reactions that occur under constant pressure, the **change in enthalpy** $\boldsymbol{\Delta H}$ evaluates the change in the total energy of the system (ie, the net heat transferred) during a reaction or process.

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

If the products have a lower enthalpy than the reactants, ΔH is negative (ie, thermal energy flows from the reactants to the surroundings). When the products have a higher enthalpy than the reactants, ΔH is positive (ie, thermal energy flows from the surroundings to the reactants).

6.1.02 Enthalpy of Dissolution

[ENE-2.A.4]

The **enthalpy of dissolution** is the amount of heat (ie, thermal energy) that is absorbed or released when a chemical compound (solute) is dissolved in a solvent under conditions of constant pressure. The amount of transferred thermal energy depends on the interactions between the particles of the substances.

For example, the process of dissolving an ionic compound (solute) in water (solvent) occurs by simultaneous steps that each involve either a negative or positive change in enthalpy ΔH:

- Δ*H* is positive for breaking the solute-solute interactions holding the cations and anions together (ie, the ionic bonds).
- Δ*H* is positive for breaking the solvent-solvent interactions between the water molecules (ie, hydrogen bonding).
- Δ*H* is negative for forming new solute-solvent interactions between the ions and the polar water molecules (ie, ion-dipole interactions).

Therefore, breaking the ionic bonds consumes heat from the solvent environment whereas forming new ion-dipole interactions releases heat. Figure 6.3 illustrates the dissolution process and shows the associated enthalpy contributions.

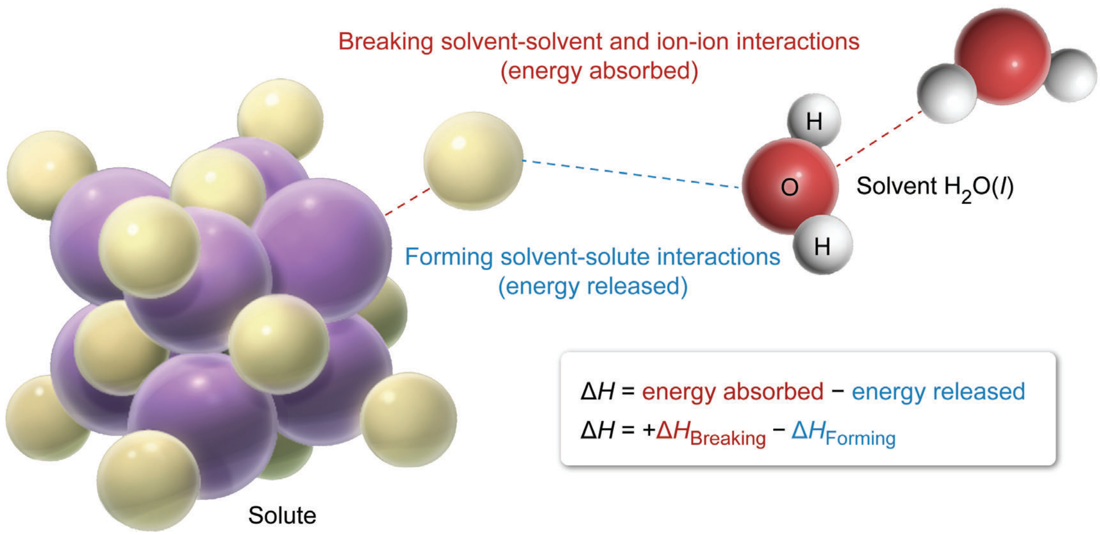

Figure 6.3 Enthalpy changes from interactions during dissolution.

Following the dissolution process, one of two outcomes is possible:

- If the total amount of heat absorbed by breaking the ionic bonds and solvent-solvent interactions is greater than the amount of heat released by forming new interactions, the process is endothermic, and the solution temperature decreases as heat is absorbed from the solvent. This outcome results in an overall **positive Δ*H***.
- If more heat is released by forming new interactions than is absorbed by breaking the ionic bonds and solvent-solvent interactions, the process is exothermic, and the solution temperature increases as heat is released to the solvent. This outcome results in an overall **negative Δ*H***.

6.2.01 Energy Diagrams

[ENE-2.B.1]

As described in Sub-Topic 5.6.01, energy diagrams (ie, graphs of energy versus reaction coordinate) show the energy of the reactants, transition states, any intermediates, and the products over the course of a reaction. For reactions in which the pressure does not change, the change in enthalpy Δ*H* is equal to the net amount of thermal energy that is absorbed or released as heat by a reaction. As such, if the enthalpy is plotted on the *y*-axis of an energy diagram, Δ*H* can be determined by evaluating the energy difference between the products and reactants because enthalpy is a state function.

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

As shown in Figure 6.4, if the products are lower in enthalpy than the reactants, ΔH is negative, and the overall reaction is exothermic (ie, it **releases heat** into the surroundings). On the other hand, if the products are higher in enthalpy than the reactants, ΔH is positive, and the overall reaction is endothermic (ie, it **absorbs heat** from the surroundings).

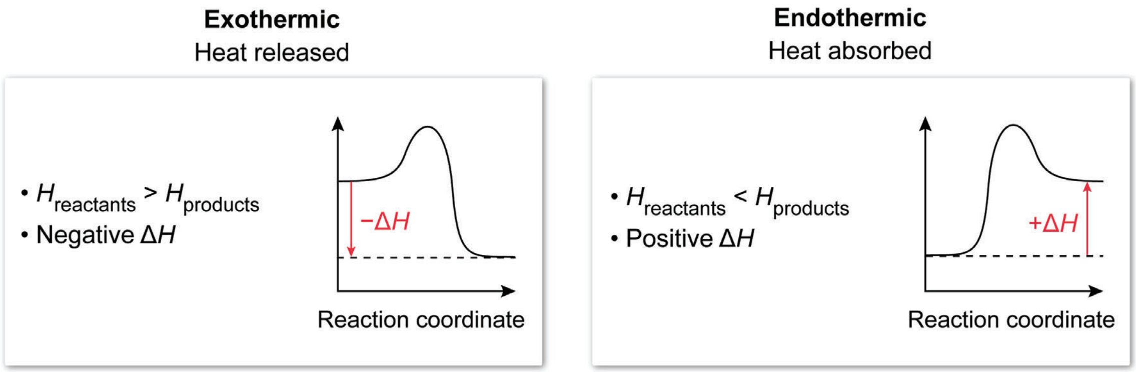

Figure 6.4 Exothermic and endothermic reaction energy diagrams.

Although an overall reaction will be either endothermic or exothermic, the nature of the individual elementary steps of the reaction may differ due to the relative energies of the participating chemical species in each step. For example, Figure 6.5 shows an energy diagram for a reaction that is exothermic overall but has both exothermic and endothermic steps.

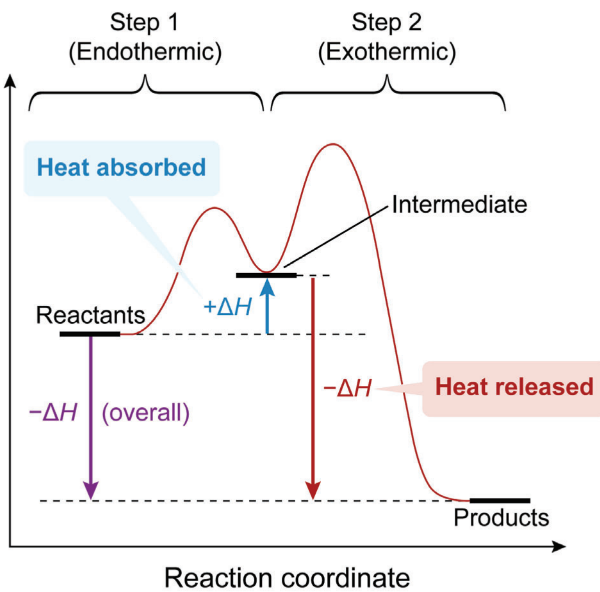

Figure 6.5 Endothermic and exothermic steps in a reaction.

As seen in Figure 6.5, Step 1 of the reaction is endothermic because the intermediate formed is higher in enthalpy than the initial reactants. In contrast, Step 2 of the reaction is very exothermic because the products formed are much lower in enthalpy than the reacting intermediate. Because Step 2 is more exothermic than Step 1 is endothermic, the overall enthalpy of the reaction is exothermic.

Topic 6.1-6.2 Endothermic and Exothermic Processes
Check for Understanding Quiz

$$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$

1. Solutions of $AgNO_3(aq)$ and $NaCl(aq)$ participate in an exothermic reaction represented by the equation above. Which of the following statements best describes the reaction?

   A. The reaction has $-\Delta H_{rxn}$, and heat is absorbed from the surrounding solution by the reaction.

   B. The reaction has $-\Delta H_{rxn}$, and heat is released from the reaction to the surrounding solution.

   C. The reaction has $+\Delta H_{rxn}$, and heat is absorbed from the surrounding solution by the reaction.

   D. The reaction has $+\Delta H_{rxn}$, and heat is released from the reaction to the surrounding solution.

2. The dissolution of $Mg(OH)_2(s)$ in water represented by the equation below is observed to be exothermic.

   $$Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2\ OH^-(aq)$$

   Which of the following is true about the thermal energy of the particle interactions during the dissolution process?

   A. The amount of heat released by forming new particle interactions in solution is greater than the amount of heat absorbed by breaking the ionic bonds.

   B. The amount of heat absorbed by breaking the ionic bonds is greater than the amount of heat released by forming new particle interactions in solution.

   C. The amount of heat absorbed by breaking the ionic bonds is equal to the amount of heat released by forming new particle interactions in solution.

   D. The amount of heat absorbed by breaking the ionic bonds cannot be compared to the amount of heat released by forming new particle interactions without more information.

3. Which of the following best describes the features of the energy diagram for an endothermic reaction that occurs by a two-step mechanism with one intermediate?

   A. The diagram has one peak, and the energy level of the reactants is lower than the energy level of the products.

   B. The diagram has two peaks, and the energy level of the reactants is higher than the energy level of the products.

   C. The diagram has two peaks, and the energy level of the reactants is lower than the energy level of the products.

   D. The diagram has three peaks, and the energy level of the reactants is higher than the energy level of the products.

Note: Answers to this quiz are in the back of the book (appendix).