Thermochemistry: Energy Flow and Chemical Change

6.1 Forms of Energy and Their Interconversion

6.2 Enthalpy: Heats of Reaction and Chemical Change

Thermodynamics is the study of heat and its transformations.

Thermochemistry is a branch of thermodynamics that deals with the heat involved with chemical and physical changes.

Fundamental premise

When energy is transferred from one object to another, it appears as work and/or as heat.

For our work we must define a system to study; everything else then becomes the surroundings.

The system is composed of particles with their own internal energies ($E$ or $U$). Therefore the system has an internal energy. When a change occurs, the internal energy changes.

\[ \Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{products}} - E_{\text{reactants}} \]
Figure 6.3 A system transferring energy as heat only.

Figure 6.4 A system losing energy as work only.

Energy, $E$

Zn(s) + 2H^+(aq) + 2Cl^−(aq) → H_2(g) + Zn^{2+}(aq) + 2Cl^−(aq)

$\Delta E < 0$

Work ($w$) done on surroundings ($w < 0$)

$H_2(g) + Zn^{2+}(aq) + 2Cl^−(aq)$

Figure 6.5 Some interesting quantities of energy.

Sample Problem 6.1 Determining the Change in Internal Energy of a System

PROBLEM: When gasoline burns in a car engine, the heat released causes the products CO_2 and H_2O to expand, which pushes the pistons outward. Excess heat is removed by the car’s cooling system. If the expanding gases do 451 J of work on the pistons and the system loses 325 J to the surroundings as heat, calculate the change in energy ($\Delta E$) in J, kJ, and kcal.

SOLUTION: Define system and surroundings, assign signs to $q$ and $w$ and calculate $\Delta E$. The answer should be converted from J to kJ and then to kcal.

$$q = -325 \text{ J}$$

$$w = -451 \text{ J}$$

$$\Delta E = q + w = -325 \text{ J} + (-451 \text{ J}) = -776 \text{ J}$$

$$\Delta E = 776 \text{ J} \times \frac{1 \text{ kcal}}{4.184 \times 10^3 \text{ J}} = 0.185 \text{ kcal}$$

$-776 \text{ J}$

$-0.776 \text{ kcal}$

$0.185 \text{ kcal}$

Table 6.1 The Sign Conventions* for $q$, $w$ and $\Delta E$

<table>
<thead>
<tr>
<th>$q$</th>
<th>$w$</th>
<th>$\Delta E$</th>
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<tbody>
<tr>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>+</td>
<td>-</td>
<td>depends on $q$ and $w$</td>
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<td>-</td>
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<td>depends on $q$ and $w$</td>
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* For $q$: + means system gains heat; - means system loses heat.
* For $w$: + means work done on system; - means work done by system.

$\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$

Units of Energy

Joule (J) \hspace{1cm} 1 J = 1 kg$\cdot$m$^2$/s$^2$

Calorie (cal) \hspace{1cm} 1 cal = 4.184 J

British Thermal Unit \hspace{1cm} 1 Btu = 1055 J
The Meaning of Enthalpy

\[ w = -P \Delta V \]
\[ H = E + PV \]

where \( H \) is enthalpy

\[ \Delta H = \Delta E + P \Delta V \]

1. Reactions that do not involve gases.
2. Reactions in which the number of moles of gas does not change.
3. Reactions in which the number of moles of gas changes but \( P \) is \( \gg \) \( \Delta V \).

\[ q_p = \Delta E + P \Delta V = \Delta H \]

Sample Problem 6.2  Drawing Enthalpy Diagrams and Determining the Sign of \( \Delta H \)

**PROBLEM:** In each of the following cases, determine the sign of \( \Delta H \), state whether the reaction is exothermic or endothermic, and draw an enthalpy diagram.

(a) \( H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) + 285.8 \text{ kJ} \)
(b) \( 40.7 \text{ kJ} + H_2O(l) \rightarrow H_2O(g) \)

**PLAN:** Determine whether \( \Delta H \) is a reactant or a product. As a reactant, the products are at a higher energy and the reaction is endothermic. The opposite is true for an exothermic reaction.

**SOLUTION:**

(a) The reaction is exothermic.

\[ \begin{align*}
\Delta H &= -285.8 \\
\text{EXOTHERMIC} &
\end{align*} \]

(b) The reaction is endothermic.

\[ \begin{align*}
\Delta H &= +40.7 \text{ kJ} \\
\text{ENDOTHERMIC} &
\end{align*} \]