Chapter 3

Thermochemistry: Energy Flow and Chemical Change

5.1 Forms of Energy and Their Interconversion

5.2 Enthalpy: Chemical Change at Constant Pressure

5.3 Calorimetry: Measuring the Heat of a Chemical or Physical Change

5.4 Stoichiometry of Thermochemical Equations

5.5 Hess’s Law: Finding $\Delta H$ of Any Reaction

5.6 Standard Enthalpies of Reaction ($\Delta_f H^\circ$)
Thermodynamics is the study of energy and its transformations.

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

When energy is transferred from one object to another, it appears as work and heat.
The system in this case is the contents of the reaction flask. The surroundings comprise everything else, including the flask itself.
System: Part of the Universe we are focusing on.

Surroundings: Everything else outside of the system

System + Surroundings = Universe

The internal energy, \( U \), of a system is the sum of the potential and kinetic energies of all the particles present.

The total energy of the universe remains constant. A change in the energy of the system must be accompanied by an equal and opposite change in the energy of the surroundings.

The total change in a system’s internal energy is the sum of the energy transferred as heat(\( q \)) and work(\( w \))

\[ \Delta U = q + w \]
Figure 5.2  Energy diagrams for the transfer of internal energy ($E$) between a system and its surroundings.

$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{products}} - E_{\text{reactants}}$
**Figure 5.3** The two cases where energy is transferred as heat only.

(A) Energy is released as heat.  
Heat ($q$) released to surroundings ($q < 0$)

(B) Energy is absorbed as heat.  
Heat ($q$) absorbed from surroundings ($q > 0$)
Figure 5.4A The two cases where energy is transferred as work only.

The system does work on the surroundings.
Figure 5.4B  The two cases where energy is transferred as work only.

The system has work done on it by the surroundings.

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Table 5.1 The Sign Conventions* for \( q \), \( w \), and \( \Delta U \)

\[
q + w = \Delta U
\]

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* For \( q \): + means system gains heat; - means system releases heat.

* For \( w \): + means work done on system; - means work done by system.
The Law of Energy Conservation

The first law of Thermodynamics states that the total energy of the universe is constant.

Energy is conserved, and is neither created nor destroyed. Energy is transferred in the form of heat and/or work.

\[ \Delta_{\text{universe}} U = \Delta_{\text{system}} U + \Delta_{\text{surroundings}} U = 0 \]
The SI unit of energy is the **joule** (J).

1 J = 1 kg·m$^2$/s$^2$

The **calorie** (cal) was once defined as the quantity of energy needed to raise the temperature of 1 g of water by 1°C.

1 cal = 4.184 J
Sample Problem 5.1  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$_2$O to expand, which pushes the pistons outward. Excess heat is removed by the car’s radiator. If the expanding gases do 451 J of work on the pistons and the system releases 325 J to the surroundings as heat, calculate the change in energy (Δ$U$) in J/mol, kJ/mol, and kcal/mol.

PLAN: Define the system and surroundings and assign signs to $q$ and $w$ correctly. Then $ΔU = q + w$. The answer can then be converted from J to kJ and to kcal.
Sample Problem 5.1

**SOLUTION:**

Heat is given out by a chemical reaction, so it makes sense to define the system as the reactants and products involved. The pistons, the radiator and the rest of the car then comprise the surroundings.

Heat is given out by the system, so \( q = -325 \text{ J} \)

The gases expand to push the pistons, so the system does work on the surroundings and \( w = -451 \text{ J} \)

\[ \Delta U = q + w = -325 \text{ J/mol} + (-451 \text{ J/mol}) = -776 \text{ J/mol} \]

\[ -776 \text{ J/mol} \times \frac{1 \text{ kJ}}{10^3 \text{ J/mol}} = -0.776 \text{ kJ} \]

\[ -0.776 \text{ kJ/mol} \times \frac{1 \text{ kcal}}{4.184 \text{ kJ/mol}} = -0.185 \text{ kcal} \]
5.2 Enthalpy: Chemical Change at Constant Pressure

- $\Delta U = q + w$
  - To determine $\Delta U$, both heat and work must be measured.

- The most common chemical work is *PV work*
  - the work done when the volume of a system changes in the presence of an external pressure.

- **Enthalpy (H)** is defined as $U + PV$ so
  \[ \Delta H = \Delta U + \Delta PV \]

- If a system remains at constant pressure and its volume does not change much, then
  \[ \Delta H \approx \Delta U \]
Even though $q$ and $w$ for the two paths are different, the total $\Delta U$ is the same for both.
An expanding gas pushing back the atmosphere does $pV$ work ($w = -P\Delta V$).
ΔU as a measure of ΔH

- ΔH is the change in heat for a system at constant pressure.
  \[ q_p = \Delta U + P\Delta V = \Delta H \]

- \( \Delta H \approx \Delta U \)
  - for reactions that do not involve gases
  - for reactions in which the total amount (mol) of gas does not change
  - for reactions in which \( q_p \) is much larger than \( P\Delta V \), even if the total mol of gas does change.
Figure 5.8

Enthalpy diagrams for exothermic and endothermic processes.

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(g)
\]

\[
\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)
\]

**A** Exothermic process
Heat is given out.

**B** Endothermic process
Heat is taken in.
PROBLEM: For 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: From each equation, note whether heat is a “reactant” or a “product”. If heat is taken in as a “reactant”, the process is endothermic. If heat is released as a “product”, the process is exothermic.

For the enthalpy diagram, the arrow always points from reactants to products. For endothermic reactions, the products are at a higher energy than the reactants, since the reactants take in heat to form the products.
Sample Problem 5.2

SOLUTION: (a) \( \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) + 285.8 \text{ kJ} \)

Heat is a “product” for this reaction and is therefore given out, so the reaction is exothermic. The reactants are at a higher energy than the products.
Sample Problem 5.2

SOLUTION: (b) $40.7 \text{ kJ} + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$

Heat is a “reactant” in this reaction and is therefore absorbed, so the reaction is endothermic. The reactants are at a lower energy than the products.
5.3 Calorimetry

The **specific heat capacity** \((c)\) of a substance is the quantity of heat required to change the temperature of 1 gram of the substance by 1 K.

\[
q = c \times m \times \Delta T
\]

- \(q\) = heat lost or gained
- \(c\) = specific heat capacity
- \(m\) = mass in g
- \(\Delta T = T_{\text{final}} - T_{\text{initial}}\)

The **heat capacity** is the heat required to change the temperature of the substance by 1K.

\[
q = \text{heat capacity} \times \Delta T
\]
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* at 298 K(25 °C)
Sample Problem 5.3

Finding the Quantity of Heat from a Temperature Change

PROBLEM: A layer of copper welded to the bottom of a skillet weighs 125 g. How much heat is needed to raise the temperature of the copper layer from 25°C to 300°C? The specific heat capacity (c) of Cu is 0.387 J/g·K.

PLAN: We know the mass (125 g) and c (0.387 J/g·K) of Cu and can find ΔT in °C, which equals ΔT in K. We can use the equation $q = cm\Delta T$ to calculate the heat.

SOLUTION: $\Delta T = T_{\text{final}} - T_{\text{initial}} = 300. - 25 = 275°C = 275 K$

$$q = cm\Delta T = \frac{0.387 \text{ J}}{\text{g} \cdot \text{K}} \times 125 \text{ g} \times 275 \text{ K} = 1.33 \times 10^4 \text{ J}$$
This device measures the heat transferred at constant pressure ($q_P$).
Sample Problem 5.4  Determining the Specific Heat Capacity of a Solid

**PROBLEM:** You heat 22.05 g solid in a test-tube to 100.00°C and then add the solid to 50.00 g of water in a coffee-cup calorimeter. The water temperature changes from 25.10°C to 28.49°C. Find the specific heat capacity of the solid.

**PLAN:** Since the water and the solid are in contact, heat is transferred from the solid to the water until they reach the same $T_{\text{final}}$. In addition, the heat given out by the solid ($-q_{\text{solid}}$) is equal to the heat absorbed by the water ($q_{\text{water}}$).

**SOLUTION:**

$$\Delta T_{\text{water}} = T_{\text{final}} - T_{\text{initial}} = (28.49°C - 25.10°C) = 3.39°C = 3.39 \text{ K}$$

$$\Delta T_{\text{solid}} = T_{\text{final}} - T_{\text{initial}} = (28.49°C - 100.00°C) = -71.51°C = -71.51 \text{ K}$$

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Sample Problem 5.4

\[ c_{\text{solid}} = \frac{c_{\text{H}_2\text{O}} \times \text{mass}_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}}{\text{mass}_{\text{solid}} \times \Delta T_{\text{solid}}} \]

\[ = \frac{4.184 \text{ J/g} \cdot \text{K} \times 50.00 \text{ g} \times 3.39 \text{ K}}{22.05 \text{ g} \times (-71.51 \text{ K})} = 0.450 \text{ J/g} \cdot \text{K} \]
Sample Problem 5.5  Determining the Enthalpy Change of an Aqueous Reaction

PROBLEM:  You place 50.0 mL of 0.500 M NaOH in a coffee-cup calorimeter at 25.00°C and add 25.0 mL of 0.500 M HCl, also at 25.00°C. After stirring, the final temperature is 27.21°C. (Assume that the total volume is the sum of the individual volumes, also assume that the final solution has the same density (1.00 g/mL) and specific heat capacity (table 5.2) as water.

(a) Calculate $q_{\text{soln}}$ (J)  (b) Calculate the change in enthalpy, $\Delta H$, of the reaction (kJ/mol of $\text{H}_2\text{O}$ formed).

PLAN:  Heat flows from the reaction (the system) to its surroundings (the solution). Since $-q_{\text{rxn}} = q_{\text{soln}}$, we can find the heat of the reaction by calculating the heat absorbed by the solution.
Sample Problem 5.5

SOLUTION:

(a) To find $q_{\text{soln}}$:

Total mass (g) of the solution = \((25.0 \text{ mL} + 50.0 \text{ mL}) \times 1.00 \text{ g/mL} = 75.0 \text{ g}\)

\[\Delta T_{\text{soln}} = 27.21^\circ \text{C} - 25.00^\circ \text{C} = 2.21^\circ \text{C} = 2.21 \text{ K}\]

\[q_{\text{soln}} = c_{\text{soln}} \times \text{mass}_{\text{soln}} \times \Delta T_{\text{soln}} = (4.184 \text{ J/g·K})(75.0 \text{ g})(2.21 \text{ K}) = 693 \text{ J}\]

(b) To find $\Delta H_{\text{rxn}}$ we first need a balanced equation:

\[\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)\]
Sample Problem 5.5

For HCl:

\[
25.0 \text{ mL HCl} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.500 \text{ mol}}{1 \text{ L}} \times \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol HCl}} = 0.0125 \text{ mol H}_2\text{O}
\]

For NaOH:

\[
50.0 \text{ mL NaOH} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.500 \text{ mol}}{1 \text{ L}} \times \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol NaOH}} = 0.0250 \text{ mol H}_2\text{O}
\]

HCl is limiting, and the amount of H\(_2\)O formed is 0.0125 mol.

\[
\Delta H_{\text{rxn}} = \frac{q_{\text{rxn}}}{\text{mol H}_2\text{O}} = \frac{-693 \text{ J}}{0.0125 \text{ mol}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = -55.4 \text{ kJ/mol H}_2\text{O}
\]
This device measures the heat released at constant volume \((q_V)\).
PROBLEM: A manufacturer claims that its new dietetic dessert has “fewer than 10 Calories per serving.” To test the claim, a chemist at the Department of Consumer Affairs places one serving in a bomb calorimeter and burns it in O₂. The initial temperature is 21.862°C and the temperature rises to 26.799°C. If the heat capacity of the calorimeter is 8.151 kJ/K, is the manufacturer’s claim correct?

PLAN: When the dessert (system) burns, the heat released is absorbed by the calorimeter:

\[-q_{\text{system}} = q_{\text{calorimeter}}\]

To verify the energy provided by the dessert, we calculate \(q_{\text{calorimeter}}\).
Sample Problem 5.6

SOLUTION:

\[ \Delta T_{\text{calorimeter}} = T_{\text{final}} - T_{\text{initial}} \]
\[ = 26.799^\circ C - 21.862^\circ C = 4.937^\circ C = 4.937 \text{ K} \]

\[ q_{\text{calorimeter}} = \text{heat capacity} \times \Delta T = 8.151 \text{ kJ/K} \times 4.937 \text{ K} = 40.24 \text{ kJ} \]

\[ 40.24 \text{ kJ} \times \frac{\text{kcal}}{4.184 \text{ kJ}} = 9.63 \text{ kcal or Cal} \]

The manufacturer’s claim is true, since the heat produced is less than 10 Calories.
5.4 Stoichiometry of Thermochemical Equations

• A *thermochemical equation* is a balanced equation that includes $\Delta_r H$.
  
  example: $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$ $\Delta H = 572$ kJ

• The sign of $\Delta H$ indicates whether the reaction is exothermic or endothermic.

• The magnitude of $\Delta H$ is *proportional to the amount of substance*.

• The value of $\Delta H$ can be used in a calculation in the same way as a mole ratio.
**Figure 5.11**

The relationship between amount (mol) of substance and the energy (kJ) transferred as heat during a reaction.
Sample Problem 5.7  Using the Enthalpy Change of a Reaction ($\Delta H$) to Find Amounts of Substance

PROBLEM: The major source of aluminum in the world is bauxite (mostly aluminum oxide). Its thermal decomposition can be represented by the equation:

$$\text{Al}_2\text{O}_3(s) \rightarrow 2\text{Al}(s) + \frac{3}{2} \text{O}_2(g) \Delta H = 1676 \text{ kJ}$$

If aluminum is produced this way, how many grams of aluminum can form when 1.000x$10^3$ kJ of heat is transferred?

PLAN: From the balanced equation and $\Delta H$, we see that 2 mol of Al is formed when 1676 kJ of heat is absorbed.

1.676 kJ = 2 mol Al

mass (g) of Al

multiply by $M$ (g/mol)
Sample Problem 5.7

SOLUTION:

\[
1.000 \times 10^3 \text{ kJ} \times \frac{2 \text{ mol Al}}{1676 \text{ kJ}} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 32.20 \text{ g Al}
\]
Hess’ law states that the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps.

\[ \Delta_{\text{overall}} H = \Delta_1 H + \Delta_2 H + \ldots + \Delta_n H \]

\( \Delta H \) for an overall reaction can be calculated if the \( \Delta H \) values for the individual steps are known.
Calculating $\Delta H$ for an overall process

- Identify the target equation, the step whose $\Delta H$ is unknown.
  - Note the amount of each reactant and product.

- Manipulate each equation with known $\Delta H$ values so that the target amount of each substance is on the correct side of the equation.
  - Change the sign of $\Delta H$ when you reverse an equation.
  - Multiply amount (mol) and $\Delta H$ by the same factor.

- Add the manipulated equations and their resulting $\Delta H$ values to get the target equation and its $\Delta H$.
  - All substances except those in the target equation must cancel.
Sample Problem 5.8  Using Hess’ s Law to Calculate an Unknown $\Delta H$

**PROBLEM:** Two pollutants that form in auto exhausts are CO and NO. An environmental chemist must convert these pollutants to less harmful gases through the following reaction:

$$\text{CO}(g) + \text{NO}(g) \rightarrow \text{CO}_2(g) + \frac{1}{2}\text{N}_2(g) \quad \Delta H = ?$$

Given the following information, calculate the unknown $\Delta H$:

Equation A: $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta_A H = -283.0 \text{ kJ/mol}$

Equation B: $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \quad \Delta_B H = 180.6 \text{ kJ/mol}$

**PLAN:** Manipulate Equations A and/or B and their $\Delta H$ values to get to the target equation and its $\Delta H$. All substances except those in the target equation must cancel.
Sample Problem 5.8

SOLUTION:

Multiply Equation B by $\frac{1}{2}$ and reverse it, $\Delta H$ sign changed

$\text{NO}(g) \rightarrow \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g); \Delta H = -90.3 \text{ kJ}$

Add the manipulated equations together:

Equation A: $\text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g)$ \hspace{1cm} $\Delta_A H = -283.0 \text{ kJ/mol}$

$-\frac{1}{2}$ Equation B: $\text{NO}(g) \rightarrow \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g)$ \hspace{1cm} $\Delta_{-\frac{1}{2}B} H = -90.3 \text{kJ/mol}$

$\begin{align*}
\text{CO}(g) + \text{NO}(g) & \rightarrow \text{CO}_2(g) + \frac{1}{2} \text{N}_2(g) \\
\Delta_C H & = -373.3 \text{ kJ/mol}
\end{align*}$
5.6 Standard Enthalpies of Reaction (\(\Delta_r H^\circ\))

**Standard Enthalpy of Reaction (\(\Delta_r H^\circ\))** is the enthalpy change of the reaction measured in **Standard State**.

- For a gas, standard state is 1 bar and ideal behavior
- For aqueous solutions, standard state is 1M concentration
- For a pure substance, standard state is the most stable form at 1 bar and the temperature of interest (usually 25°C)

**Standard Enthalpy of Formation (\(\Delta_f H^\circ\))** is the enthalpy change associated with the formation of 1 mol of a compound from its elements, in standard state

\[
\Delta_r H^\circ = \sum m \Delta_f H^\circ_{\text{(products)}} - \sum n \Delta_f H^\circ_{\text{(reactants)}}
\]

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<tr>
<td></td>
<td></td>
<td>AgCl(s)</td>
<td>-127.0</td>
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<tr>
<td>Sulfur</td>
<td></td>
<td>S$_8$(rhombic)</td>
<td>0</td>
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<tr>
<td></td>
<td></td>
<td>S$_8$(monoclinic)</td>
<td>0.3</td>
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<td></td>
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<td>SO$_2$(g)</td>
<td>-296.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO$_3$(g)</td>
<td>-396.0</td>
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<td></td>
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</table>

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Sample Problem 5.9  Writing Formation Equations

PROBLEM: Write a balanced formation equation for each of the following compounds including the value of $\Delta_f H^\circ$.

(a) AgCl\(_{(s)}\)  
(b) CaCO\(_3\)\(_{(s)}\)  
(c) HCN\(_{(g)}\).

PLAN: Write the elements as reactants and 1 mol of the compound as the product formed. Make sure all substances are in their standard states. Balance the equations and find the value of $\Delta_f H^\circ$ in Table 5.3 or Appendix B.
Sample Problem 5.9

SOLUTION:

(a) Silver chloride, AgCl, a solid at standard conditions.

\[ \text{Ag(s) + } \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{AgCl(s)} \quad \Delta_f H^\circ = -127.0 \text{ kJ/mol} \]

(b) Calcium carbonate, CaCO$_3$, a solid at standard conditions.

\[ \text{Ca(s) + C(graphite) + } \frac{3}{2} \text{O}_2(g) \rightarrow \text{CaCO}_3(s) \quad \Delta_f H^\circ = -1206.9 \text{ kJ/mol} \]

(c) Hydrogen cyanide, HCN, a gas at standard conditions.

\[ \frac{1}{2} \text{H}_2(g) + \text{C(graphite)} + \frac{1}{2} \text{N}_2(g) \rightarrow \text{HCN(g)} \quad \Delta_f H^\circ = 135 \text{ kJ/mol} \]
Figure 5.12

The two-step process for determining $\Delta_r H^\circ$ from $\Delta_f H^\circ$ values.

\[
\Delta_r H^\circ = \sum m \Delta_f H^\circ_{\text{products}} - \sum n \Delta_f H^\circ_{\text{reactants}}
\]
Sample Problem 5.10  Calculating $\Delta H^\circ_{\text{rxn}}$ from $\Delta H^\circ_{\text{f}}$ Values

PROBLEM: Nitric acid is used to make many products, including fertilizer, dyes, and explosives. The first step in the industrial production process is the oxidation of ammonia:

$$4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$$

Calculate $\Delta_r H^\circ$ from $\Delta_f H^\circ$ values.

PLAN: Use the $\Delta_f H^\circ$ values from Table 5.3 or Appendix B and apply the equation

$$\Delta H_{\text{rxn}} = \Sigma m \Delta_f H^\circ \text{ (products)} - \Sigma n \Delta_f H^\circ \text{ (reactants)}$$
Sample Problem 5.10

SOLUTION:

\[
\Delta r H = \Sigma m \Delta f H^\circ \text{ (products)} - \Sigma n \Delta f H^\circ \text{ (reactants)}
\]

\[
\Delta r H = [4(\Delta f H^\circ \text{of NO(g)}) + 6(\Delta f H^\circ \text{of H}_2\text{O(g)})]
- [4(\Delta H \text{ of NH}_3(g)) + 5(\Delta H \text{ of O}_2(g))]
\]

\[
= (4 \text{ mol})(90.3 \text{ kJ/mol}) + (6 \text{ mol})(-241.8 \text{ kJ/mol}) -
[(4 \text{ mol})(-45.9 \text{ kJ/mol}) + (5 \text{ mol})(0 \text{ kJ/mol})]
\]

\[
= -906 \text{ kJ/mol}
\]

\[
\Delta r H = -906 \text{ kJ/mol}
\]
Figure 8.8  The Born-Haber cycle for lithium fluoride.
A simple Born-Haber cycle can be represented as follows;

Unbound gaseous ions

Breaking bonds
Forming gases
Forming cations, anions

Metal and nonmetal

Lattice energy

Ionic compound
**Table 8.2** Average Bond Energies (kJ/mol) and Bond Lengths (pm)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy</th>
<th>Length</th>
<th>Bond</th>
<th>Energy</th>
<th>Length</th>
<th>Bond</th>
<th>Energy</th>
<th>Length</th>
<th>Bond</th>
<th>Energy</th>
<th>Length</th>
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<tr>
<td>H—H</td>
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<td>74</td>
<td>N—H</td>
<td>391</td>
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<td>Si—H</td>
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<td>148</td>
<td>S—H</td>
<td>347</td>
<td>134</td>
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<tr>
<td>H—F</td>
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<td>N—N</td>
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<td>146</td>
<td>Si—Si</td>
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<td>234</td>
<td>S—S</td>
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<td>204</td>
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<tr>
<td>H—Cl</td>
<td>427</td>
<td>127</td>
<td>N—P</td>
<td>209</td>
<td>177</td>
<td>Si—O</td>
<td>368</td>
<td>161</td>
<td>S—F</td>
<td>327</td>
<td>158</td>
</tr>
<tr>
<td>H—Br</td>
<td>363</td>
<td>141</td>
<td>N—O</td>
<td>201</td>
<td>144</td>
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<td>226</td>
<td>210</td>
<td>S—Cl</td>
<td>271</td>
<td>201</td>
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<tr>
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<td>161</td>
<td>N—F</td>
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<td>Si—F</td>
<td>565</td>
<td>156</td>
<td>S—Br</td>
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<td>109</td>
<td>N—Br</td>
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<td>Si—Br</td>
<td>310</td>
<td>216</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C—C</td>
<td>347</td>
<td>154</td>
<td>N—I</td>
<td>159</td>
<td>222</td>
<td>Si—I</td>
<td>234</td>
<td>240</td>
<td>F—F</td>
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<td>143</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F—Cl</td>
<td>193</td>
<td>166</td>
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<td>O—H</td>
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<td>O—O</td>
<td>204</td>
<td>148</td>
<td>P—P</td>
<td>200</td>
<td>221</td>
<td>Cl—Cl</td>
<td>243</td>
<td>199</td>
</tr>
<tr>
<td>C—S</td>
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<td>181</td>
<td>O—S</td>
<td>265</td>
<td>151</td>
<td>P—F</td>
<td>490</td>
<td>156</td>
<td>Cl—Br</td>
<td>215</td>
<td>214</td>
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<tr>
<td>C—F</td>
<td>453</td>
<td>133</td>
<td>O—F</td>
<td>190</td>
<td>142</td>
<td>P—Cl</td>
<td>331</td>
<td>204</td>
<td>Cl—I</td>
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<td>243</td>
</tr>
<tr>
<td>C—Cl</td>
<td>339</td>
<td>177</td>
<td>O—Cl</td>
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<td>164</td>
<td>P—Br</td>
<td>272</td>
<td>222</td>
<td>Br—Br</td>
<td>193</td>
<td>228</td>
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<tr>
<td>C—Br</td>
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<td>194</td>
<td>O—Br</td>
<td>234</td>
<td>172</td>
<td>P—I</td>
<td>184</td>
<td>246</td>
<td>Br—I</td>
<td>175</td>
<td>248</td>
</tr>
<tr>
<td>C—I</td>
<td>216</td>
<td>213</td>
<td>O—I</td>
<td>234</td>
<td>194</td>
<td></td>
<td></td>
<td></td>
<td>I—I</td>
<td>151</td>
<td>266</td>
</tr>
</tbody>
</table>

Multiple Bonds

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy</th>
<th>Length</th>
<th>Bond</th>
<th>Energy</th>
<th>Length</th>
<th>Bond</th>
<th>Energy</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡C</td>
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<td>134</td>
<td>N≡N</td>
<td>418</td>
<td>122</td>
<td>C≡C</td>
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<tr>
<td>C≡N</td>
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<td>127</td>
<td>N≡O</td>
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<td>891</td>
<td>115</td>
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<td>C≡O</td>
<td>745</td>
<td>123</td>
<td>O₂</td>
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<td>121</td>
<td>C≡O</td>
<td>1070</td>
<td>113</td>
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</table>

(799 in CO₂)
**Table 8.3 The Relation of Bond Order, Bond Length, and Bond Energy**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Order</th>
<th>Average Bond Length (pm)</th>
<th>Average Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—O</td>
<td>1</td>
<td>143</td>
<td>358</td>
</tr>
<tr>
<td>C≡O</td>
<td>2</td>
<td>123</td>
<td>745</td>
</tr>
<tr>
<td>C≡≡O</td>
<td>3</td>
<td>113</td>
<td>1070</td>
</tr>
<tr>
<td>C—C</td>
<td>1</td>
<td>154</td>
<td>347</td>
</tr>
<tr>
<td>C≡C</td>
<td>2</td>
<td>134</td>
<td>614</td>
</tr>
<tr>
<td>C≡≡C</td>
<td>3</td>
<td>121</td>
<td>839</td>
</tr>
<tr>
<td>N—N</td>
<td>1</td>
<td>146</td>
<td>160</td>
</tr>
<tr>
<td>N≡N</td>
<td>2</td>
<td>122</td>
<td>418</td>
</tr>
<tr>
<td>N≡≡N</td>
<td>3</td>
<td>110</td>
<td>945</td>
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</table>
The heat released or absorbed during a chemical change is due to differences between the bond energies of reactants and products.

\[ \Delta_r H^\circ = \Sigma \Delta_{\text{reactant bonds broken}} H^\circ + \Sigma \Delta_{\text{product bonds formed}} H^\circ \]
Figure 8.19  Using bond energies to calculate $\Delta H^\circ_{\text{rxn}}$ for HF formation.
Using bond energies to calculate $\Delta H^\circ_{\text{rxn}}$ for the combustion of methane.
Sample Problem 8.4  Using Bond Energies to Calculate $\Delta H^\circ_{\text{rxn}}$

**PROBLEM:** Calculate $\Delta H^\circ_{\text{rxn}}$ for the chlorination of methane to form trichloromethane (chloroform).

PROBLEM:

\[
\begin{align*}
\text{H--C--H + 3 Cl--Cl} & \rightarrow \text{Cl--C--Cl + 3 H--Cl} \\
\text{bonds broken} & \quad \Sigma \Delta H^\circ \text{ positive} \\
\text{bonds formed} & \quad \Sigma \Delta H^\circ \text{ negative}
\end{align*}
\]

**PLAN:** All the reactant bonds break, and all the product bonds form. Find the bond energies in Table 9.2 and substitute the two sums, with correct signs, into Equation 9.2.
Sample Problem 8.4

SOLUTION:

For bonds broken:

\[ 4 \times C-H = (4 \text{ mol})(413 \text{ kJ/mol}) = 1652 \text{ kJ} \]
\[ 3 \times Cl-Cl = (3 \text{ mol})(243 \text{ kJ/mol}) = 729 \text{ kJ} \]

\[ \sum \Delta \text{bonds broken} H^\circ = 2381 \text{ kJ} \]

For bonds formed:

\[ 3 \times C-Cl = (3 \text{ mol})(-339 \text{ kJ/mol}) = -1017 \text{ kJ} \]
\[ 1 \times C-H = (1 \text{ mol})(-413 \text{ kJ/mol}) = -413 \text{ kJ} \]
\[ 3 \times H-Cl = (3 \text{ mol})(-427 \text{ kJ/mol}) = -1281 \text{ kJ} \]

\[ \sum \Delta \text{bonds formed} H^\circ = -2711 \text{ kJ} \]

\[ \Delta_{\text{reaction}} H^\circ = \sum \Delta \text{bonds broken} H^\circ + \sum \Delta \text{bonds formed} H^\circ \]

\[ = 2381 \text{ kJ} + (-2711 \text{ kJ}) = -330 \text{ kJ} \]
Figure 8.21 Relative bond strength and energy from fuels.