Thermochemistry: Energy Flow and Chemical Change

Forms of Energy and Their Interconversion

• An object has potential energy by virtue of its position and kinetic energy due to its motion.

• The potential energy of a weight raised above the ground is converted to kinetic energy as it falls.

• When the weight hits the ground, it transfers some kinetic energy to the soil, causing some particles to move, doing work. Also, some of the transferred kinetic energy appears as heat.

• Potential energy in chemical bonds of foods and fuels is converted to kinetic energy giving the ability to do work and generate heat.

• Whenever energy is transferred from one object to another, it appears as work, $w$, and/or as heat, $q$. 
Concept 6-1 distinction between a system and its surroundings

Energy Flow to and from a System

• To measure a change in energy, we must define a system; that part of the universe whose change is to be measured.

• The sum of the kinetic and potential energies of all the particles in the system is its internal energy, $E$.

• As a chemical system changes from reactants to products, the internal energy of the system changes.

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

• The energy change appears as heat and/or work. $\Delta E = q + w$
A reacting chemical system can change its internal energy in either of two ways:

1. By losing some energy to the surroundings:

\[ E_{\text{final}} < E_{\text{initial}} \]
\[ \Delta E < 0 \]

2. By gaining some energy from the surroundings:

\[ E_{\text{final}} > E_{\text{initial}} \]
\[ \Delta E > 0 \]
**Concept 6-2** How energy is transferred to or from a system as heat and/or work

- Consider a system that does no work but transfers energy only as heat \(q\); \(w = 0\), so \(\Delta E = q\).

- Internal energy decreases as heat flows out of the system, so \(\Delta E < 0\) so \(q < 0\)

- Ice water will gain energy as heat from the surroundings until its temperature and that of the surroundings are equal.

\[\Delta E > 0\] so \(q > 0\)
Concept 6-3 The relation between the internal energy change, heat, and work

• Consider a system that transfers energy only as work \( w \) being done.

\[
q = 0 \text{ and } \Delta E = w
\]

• Energy is lost by the system in the form of work, so \( \Delta E < 0 \), and \( w \) is negative.

• This type of work, in which a volume change occurs against an external pressure, is called pressure-volume work (PV work).

• Raising external pressure would decrease the volume of the system, increasing \( E \) by doing work on it: \( \Delta E \) is positive and \( w \) is positive.
\[ \Delta E = q + w \]

**The Sign Conventions of \( q \), \( w \), and \( \Delta E \)**

<table>
<thead>
<tr>
<th>( q )</th>
<th>( w )</th>
<th>( \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>Depends on size of ( q ) and ( w )</td>
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<tr>
<td>-</td>
<td>+</td>
<td>Depends on size of ( q ) and ( w )</td>
</tr>
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<td>-</td>
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</tbody>
</table>

**Units of Energy**

- The SI unit is the joule (J), a derived unit: \( 1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2 \). Both heat and work are expressed in joules.
- The calorie (cal) was defined originally as the amount of energy needed to raise the temperature of one gram of water by 1°C. \( 1 \text{ cal} \equiv 4.184 \text{ J} \)
- The energy changes in chemical reactions are often large; use the kilojoule (kJ): \( 1 \text{ kJ} = 1000 \text{ J} = 0.2390 \text{ kcal} = 239.0 \text{ cal} \)
• Force has the SI base units of mass times acceleration:

\[ F = m \times a \text{ in units of } \text{kg} \times \text{m/s}^2 \]

• Work done on a mass is force (F) times the distance (d) the mass travels.

\[ \bar{w} = F \times d \text{ in units of } (\text{kg} \cdot \text{m/s}^2) \times \text{m} = \text{kg} \cdot \text{m}^2/\text{s}^2 = \text{J} \]

• The calorie (cal) was defined originally as the amount of energy needed to raise the temperature of one gram of water by 1°C.

\[ 1 \text{ cal} = 4.184 \text{ J} \]

• The energy changes in chemical reactions are often large; use the kilojoule (kJ):

\[ 1 \text{ kJ} = 1000 \text{ J} = 0.2390 \text{ kcal} = 239.0 \text{ cal} \]
Concept 6-4  The meaning of energy conservation.

The Law of Energy Conservation

• Whenever a system gains energy, the surroundings supply that energy and thus lose an equivalent amount. The reverse is also true.

• Energy can be converted from one form into another as it is transferred, but it cannot be created or destroyed.

• The law of conservation of energy (first law of thermodynamics) states that the total energy of the universe is constant.

• The energy of the system plus the energy of the surroundings remains constant: energy is conserved.

\[ \Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0 \]
Determining the Energy Change of a System

Skill 6-1. Interconverting energy units

Problem: Gasoline burns in an engine. Heat released causes the gases to expand. Determine \( \Delta E \) in J, kJ, and kcal if expanding gases do 451 J of work on the pistons and the system loses 325 J to the surroundings as heat.

Plan: System = reactants + products of reaction. Heat is released by the system, so \( q \) is negative. Pistons are pushed outward, so work is done by the system and \( w \) is negative. \( \Delta E \) is the sum of \( q \) and \( w \).

Solution: Calculating \( \Delta E \) in J:

\[
q = -325 \text{ J} \quad w = -451 \text{ J}
\]

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

Converting from J to kJ:

\[
\Delta E = -776 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -0.776 \text{ kJ}
\]

Converting kJ to kcal:

\[
\Delta E = -0.776 \text{ kJ} \times \frac{0.2390 \text{ kcal}}{1 \text{ kJ}} = -0.185 \text{ kcal}
\]
Concept 6-5 The meaning of a state function and why $\Delta E$ is constant even though $q$ and $w$ vary.

- $\Delta E$ does not depend on how the change takes place, only on the initial and final states of the system.
- A system in its initial state consists of one mole of octane together with enough oxygen for its combustion.

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$$

initial state ($E_{\text{initial}}$)     final state ($E_{\text{final}}$)

- Some energy from the fuel mixture is released to heat and/or do work on the surroundings, so $\Delta E$ is negative.
- If octane is burned in the open, the energy change appears mostly as heat.
- In an automobile engine, a much larger portion (~30%) of the energy change appears as work.
• Amount of work and heat available from a change depend on how the change occurs; total $\Delta E$, the sum of heat and work, does not.

$\Delta E$ is constant, but $q$ and $w$ can vary.

• The internal energy ($E$) of a system is a state function, a property of the system that can be determined completely by its current state.

  Changes in $E$, $P$, and $V$ depend only on the initial and final states.

• Heat ($q$) and work ($w$) are not state functions since they do depend on the path the system takes in undergoing the change in energy.
Concept 6-5 The meaning of enthalpy and the relation between $\Delta E$ and $\Delta H$.

- Most physical and chemical changes occur under virtually constant atmospheric pressure: in an open flask, in a lake, in an organism, etc.

- A thermodynamic variable called enthalpy takes constant pressure into account.

A gas expands against a constant pressure:

$$PV \text{ work done} = P \times \Delta V \quad \text{or} \quad P(V_{\text{final}} - V_{\text{initial}})$$

The work done by an expanding gas on the surroundings is $$w = -P \Delta V$$
• Combining equations: \[ \Delta E = q + w = q + (-P\Delta V) = q - P\Delta V \]

• Solving for heat at constant pressure (q_{\text{p}}) : \[ q_{\text{p}} = \Delta E + P\Delta V \]

• Enthalpy is defined such that, \( \Delta H \), the change in enthalpy is equal to \( q_{\text{p}} \), the heat gained or lost by the system at constant pressure, so: \[ \Delta H = \Delta E + P\Delta V \]

• \( E, P, \) and \( V \) are state functions, so \( H \) is also a state function.

• So, \( \Delta H \) depends only on the difference between \( H_{\text{final}} \) and \( H_{\text{initial}} \).

• Most chemical changes occur at constant pressure, so \( \Delta H \) is more relevant and easier to obtain than \( \Delta E \): to find \( \Delta H \), we measure \( q_{\text{p}} \).
• If the reaction involves no volume change, $P\Delta V = 0$, so $\Delta H = \Delta E$.
• Many reactions involve little or no PV work, so most (or all) of the energy change occurs as heat.

**Case 1.** Reactions that do not involve gases.

$$2\text{KOH}(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{K}_2\text{SO}_4(aq) + 2\text{H}_2\text{O}(l)$$

**Case 2.** The total moles of gaseous reactants equals the total moles of gaseous products. Example: $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$

Here $V$ is constant, so $\Delta V = 0$, $P\Delta V = 0$, and $\Delta H = \Delta E$.

**Case 3.** Number of gas moles changes in the reaction, so $P\Delta V \neq 0$. But $q_P$ is usually larger than $P\Delta V$, most of $\Delta E$ is heat and $\Delta H \approx \Delta E$.

$$2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g)$$

$\Delta H = -483.6 \text{ kJ}$ and $P\Delta V = -2.5 \text{ kJ}$
**Concept 6-7.** The meaning of $\Delta H$ and the distinction between exothermic and endothermic reactions

- The enthalpy change during a reaction is called the heat of reaction or enthalpy of reaction, $\Delta H_{\text{rxn}}$.

\[
\Delta H = H_{\text{final}} - H_{\text{initial}} = H_{\text{products}} - H_{\text{reactants}}
\]

- The sign of $\Delta H$ shows whether heat is absorbed or released.

- Determine its sign by imagining the heat as a “reactant” or “product.”

- When methane burns in air, heat is released, so show it on the right:

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

- The products (CO$_2$ and 2H$_2$O) have less enthalpy than the reactants (CH$_4$ and 2O$_2$) by the amount of heat released.

  Since heat is released, $\Delta H$ ($H_{\text{final}} - H_{\text{initial}}$) is negative.
• A process like combustion that results in a decrease in the enthalpy of the system is **exothermic**.

\[ H_{\text{final}} < H_{\text{initial}} \quad \Delta H < 0 \]

• **Endothermic** changes occur with an increase in the system enthalpy.

\[ \Delta H (H_{\text{water}} - H_{\text{ice}}) \text{ is positive.} \]
Skill 6-2 Drawing enthalpy diagrams for chemical and physical changes

Problem: For (a) and (b), give the sign of $\Delta H$, whether the reaction is exo- or endothermic and draw an enthalpy diagram for each.

(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: See if heat is a “product” (exothermic; $\Delta H < 0$) or a “reactant” (endothermic; $\Delta H > 0$). For exothermic reactions, reactants are above products in the enthalpy diagram.

Solution: (a) Heat is on the right (product), so $\Delta H < 0$ and the reaction is exothermic.
(b) Heat is on the left (reactant), so \( \Delta H > 0 \) and the reaction is endothermic.

- Certain enthalpy changes represent such common processes that they are given specific names:
- One mole of a substance combines with oxygen in a combustion reaction; the heat of reaction is the heat of combustion (\( \Delta H_{\text{comb}} \)):
  \[ \text{C}_4\text{H}_{10}(l) + \frac{13}{2}\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 5\text{H}_2\text{O}(g) \quad \Delta H = \Delta H_{\text{comb}} \]
- When one mole of compound forms from its elements, the heat of reaction is the heat of formation (\( \Delta H_f \)):
  \[ \text{K}(s) + \frac{1}{2}\text{Br}_2(l) \rightarrow \text{KBr}(s) \quad \Delta H = \Delta H_f \]
• When one mole of substance melts, the enthalpy change is the heat of fusion ($\Delta H_{\text{fus}}$):

$$\text{NaCl}(s) \rightarrow \text{NaCl}(l) \quad \Delta H = \Delta H_{\text{fus}}$$

• When one mole of a substance vaporizes, the enthalpy change is the heat of vaporization ($\Delta H_{\text{vap}}$):

$$\text{C}_6\text{H}_6(l) \rightarrow \text{C}_6\text{H}_6(g) \quad \Delta H = \Delta H_{\text{vap}}$$

**Where Does the Heat Come from?**

• Any change in a system’s total energy occurs through changes in the kinetic and potential energy components:

$$\Delta E_{\text{total}} = \Delta E_k + \Delta E_p$$

• A molecule’s $E_k$ contributions come from its motion through space, the rotation and the vibration of the molecule.

• $E_p$ contributions are forces in atoms between nuclei and electrons, between the nucleons and between atoms in each chemical bond.
Concept 6-8. How changes in bond strength account for the heat of reaction

- The energy released or absorbed during a reaction is due mostly to difference in PE between the reactant bonds and the product bonds.

Breaking and Forming Bonds

- In a chemical reaction, reactant bonds are broken and product bonds are formed. $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O(}\text{g})$

- When 2 g H$_2$ (1 mol) and 16 g O$_2$ (0.5 mol) react at 25°C, 18 g water vapor (1 mol) forms and 242 kJ of heat is released.

- Total reactant bond energy (1 mol H$_2$ bonds and 0.5 mol O$_2$ bonds) is greater than the total product bond energy (1 mol H$_2$O bonds).

- The difference is released as heat (242 kJ)
Bond energies in fuels and foods

- Most common fuels are hydrocarbon compounds and coal; those for organisms are fats and carbohydrates.
- Both have molecules with C–C and C–H bonds that break in combustion; the atoms become bonded to O (CO$_2$ and H$_2$O).

Heats of Combustion ($\Delta H_{\text{comb}}$) of Some Carbon Compounds

<table>
<thead>
<tr>
<th>NAME (FORMULA)</th>
<th>STRUCTURAL FORMULA</th>
<th>SUM OF C–C AND C–H BONDS</th>
<th>SUM OF C–O AND O–H BONDS</th>
<th>$\Delta H_{\text{comb}}$ (kJ/mol)</th>
<th>$\Delta H_{\text{comb}}$ (kJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-carbon compounds</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane (C$_2$H$_6$)</td>
<td></td>
<td>7</td>
<td>0</td>
<td>$-1560$</td>
<td>$-51.88$</td>
</tr>
<tr>
<td>Ethanol (C$_2$H$_5$OH)</td>
<td></td>
<td>6</td>
<td>2</td>
<td>$-1367$</td>
<td>$-29.67$</td>
</tr>
</tbody>
</table>
### TABLE 6.3 Heats of Combustion of Some Fats and Carbohydrates

<table>
<thead>
<tr>
<th>SUBSTANCE</th>
<th>$\Delta H_{\text{comb}}$ (kJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fats</strong></td>
<td></td>
</tr>
<tr>
<td>Vegetable oil</td>
<td>37.0</td>
</tr>
<tr>
<td>Margarine</td>
<td>30.1</td>
</tr>
<tr>
<td>Butter</td>
<td>30.0</td>
</tr>
<tr>
<td><strong>Carbohydrates</strong></td>
<td></td>
</tr>
<tr>
<td>Table sugar (sucrose)</td>
<td>16.2</td>
</tr>
<tr>
<td>Brown rice</td>
<td>14.9</td>
</tr>
<tr>
<td>Maple syrup</td>
<td>10.4</td>
</tr>
</tbody>
</table>
Calorimetry: Laboratory Measurement of Heats of Reaction

**Concept 6-9.** relation between specific heat capacity and heat transferred.

- The amount of heat released or absorbed by a system is related to its temperature change and its heat capacity.

**Specific Heat Capacity of Substances**

- Experience shows that the more heat an object absorbs, the higher its temperature becomes.
  \[ \text{Heat} \propto \Delta T \quad \text{or} \quad \text{heat} = \text{constant} \times \Delta T \]

- Heat capacity is the proportionality constant in the equation:
  \[ \text{Heat capacity} = \frac{\text{heat}}{\Delta T} \quad [\text{in J/K}] \]
• **Specific heat capacity** (C), is the amount of heat needed to change the temperature of one gram of a substance by one kelvin:

\[
\text{Specific heat capacity (C)} = \frac{\text{heat}}{\text{grams} \times \Delta T} \quad \text{[in units of J/g \cdot K]}
\]

• **Molar heat capacity** is the amount of heat required to change the temperature of one mole of the substance by one kelvin:

\[
\text{Molar heat capacity} = \frac{\text{heat}}{\text{moles} \times \Delta T} \quad \text{[in units of J/mol \cdot K]}
\]

The specific heat capacity of liquid water is 4.184 J/g\cdot K, so:

\[
\text{Molar heat capacity of H}_2\text{O}(l) = 4.184 \ \frac{\text{J}}{\text{g} \cdot \text{K}} \times \frac{18.02\ \text{g}}{1\ \text{mol}} = 75.40 \ \frac{\text{J}}{\text{mol} \cdot \text{K}}
\]

• Table 6.4 has specific heat capacities of some elements, compounds, and materials.
Given specific heat capacity and mass of a substance being heated, measure its temperature change to calculate the heat change, \( q \):

\[
q = C \times \text{mass} \times \Delta T
\]

If an object becomes hotter, \( \Delta T \) (i.e., \( T_{\text{final}} - T_{\text{initial}} \)) is positive, the object gains heat, and \( q > 0 \).

**Skill 6-3.** Solving problems involving specific heat capacity, change in temperature, and heat of reaction

**Problem:** How much heat is needed to raise the temp. of 125g of Cu from 25°C to 300°C? Specific heat capacity of Cu = 0.387 J/g•K.

**Solution:** Calculating \( q \):

\[
\Delta T = T_{\text{final}} - T_{\text{initial}} = 300°C - 25°C = 275°C = 275 \text{ K}
\]

\[
q = C \times \text{mass} \times \Delta T = 0.387 \text{ J/g} \cdot \text{K} \times 125 \text{ g} \times 275 \text{ K} = 1.33 \times 10^4 \text{ J}
\]
Concept 6-10. How constant-pressure (coffee-cup) and constant-volume (bomb) calorimeters work

Calorimetry

- Calorimeters are used to measure the heat released (or absorbed) by a physical or chemical process.
- Heat lost by the system is gained by the surroundings.
- Measure their $\Delta T$ to determine the heat transferred by the system.

“coffee-cup” calorimeter
• To determine the specific heat capacity of an unknown solid:

- Weigh the solid (system), heat to a known temperature, and add it to water (surroundings) of known temp. and mass in the calorimeter.

- Measure the final water temperature, which is also the final temp. of the solid. (Heat lost = heat gained)

\[-q_{\text{solid}} = q_{\text{water}}\]

\[-(C_{\text{solid}} \times \text{mass}_{\text{solid}} \times \Delta T_{\text{solid}}) = C_{\text{H}_2\text{O}} \times \text{mass}_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}\]

• All the quantities are known or measured except \(C_{\text{solid}}\), which is calculated:

\[C_{\text{solid}} = -\frac{C_{\text{H}_2\text{O}} \times \text{mass}_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}}{\text{mass}_{\text{solid}} \times \Delta T_{\text{solid}}}\]
**Problem:** A 25.64 g sample of solid is heated to 100.00°C and added to a calorimeter holding 50.00 g water. The water temperature rises from 25.10°C to 28.49°C. Find the specific heat capacity of the solid.

**Solution:** It is helpful to summarize the information given:

<table>
<thead>
<tr>
<th></th>
<th>MASS (g)</th>
<th>C (J/g · K)</th>
<th>$T_{\text{initial}}$ (°C)</th>
<th>$T_{\text{final}}$ (°C)</th>
<th>$\Delta T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>25.64</td>
<td>?</td>
<td>100.00</td>
<td>28.49</td>
<td>-71.51</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>50.00</td>
<td>4.184</td>
<td>25.10</td>
<td>28.49</td>
<td>3.39</td>
</tr>
</tbody>
</table>

Calculating $C_{\text{solid}}$:

$$C_{\text{solid}} = - \frac{C_{\text{H}_2\text{O}} \times \text{mass}_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}}{\text{mass}_{\text{solid}} \times \Delta T_{\text{solid}}}$$

$$= - \frac{4.184 \text{ J/g} \cdot \text{K} \times 50.00 \text{ g} \times 3.39 \text{ K}}{25.64 \text{ g} \times (-71.51 \text{ K})} = 0.387 \text{ J/g} \cdot \text{K}$$
We assumed that all the heat lost by the solid was gained by water.

- In fact, some heat is gained by the other parts of the calorimeter.
- For accurate work, the heat capacity of the entire calorimeter must be known.

- Bomb calorimeters measure precisely the heat released in combustion reactions.
Problem: A dietetic dessert is claimed to have less than 10 Calories per serving. A bomb calorimeter with a heat capacity of 8.151 kJ/K is used to test the claim. One serving of the dessert is burned in O$_2$; the temperature increases 4.937°C. Is the claim correct?

Solution: Calculating the heat gained by the calorimeter:

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

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

One serving of the dessert has slightly less than 10 Calories (41.84 kJ), so the manufacturer’s claim is correct.
• The energy released in a bomb calorimeter cannot do PV work because the volume is constant and so $P\Delta V = 0$.

• The energy change measured by a bomb calorimeter is the heat at constant volume ($q_V$), which equals $\Delta E$, not $\Delta H$:

$$\Delta E = q + w = q_V + 0 = q_V$$

**Stoichiometry of Thermochemical Equations**

**Concept 6-11.** relation between $\Delta H^\circ_{\text{rxn}}$ and amount of substance.

• Thermochemical equations are balanced equations that also state the heat of reaction for the amounts of substances specified.

• $\Delta H_{\text{rxn}}$ has 2 parts— a sign showing the direction of the change and a magnitude that depends on the amount of reacting substances:
1. **Sign of ΔH.** The ΔH of a forward reaction is identical in magnitude but opposite in sign to the ΔH of the reverse reaction.

- Decomposition of 2 mol water into its elements (endothermic):

  \[ 2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \quad \Delta H_{\text{rxn}} = 572 \text{ kJ} \]

- Formation of 2 mol water from its elements (exothermic):

  \[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) \quad \Delta H_{\text{rxn}} = -572 \text{ kJ} \]

2. **Magnitude of ΔH.** The size of ΔH is proportional to the amount of substance in the reaction.

- Formation of 1 mol water from its elements (1/2 the above):

  \[ \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H_{\text{rxn}} = -286 \text{ kJ} \]
• To show the magnitude of $\Delta H_{rxn}$ for a certain amount of substance, thermochemical equations may have fractional coefficients.

In the reaction $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H_{rxn} = -286 \text{ kJ}$

286 kJ is thermochemically equivalent to 1 mol H$_2$(g),
286 kJ is thermochemically equivalent to 1/2 mol O$_2$(g),
286 kJ is thermochemically equivalent to 1 mol H$_2$O(l).

• Use these thermochemically equivalent quantities to find the heat change when a given amount of substance reacts or is produced.

• Use the heat of reaction, in kJ/mol, to convert moles of a substance to the equivalent heat change.
Skill 6-4  Relating the heat of reaction and the amount of substances changing.

Problem: Thermal decomposition of bauxite ore can be represented:

$$\text{Al}_2\text{O}_3(s) \xrightarrow{\Delta} 2\text{Al}(s) + \frac{3}{2}\text{O}_2(g) \quad \Delta H_{\text{rxn}} = 1676 \text{ kJ}$$

Produced this way, how many grams of aluminum could be made when $1.000 \times 10^3 \text{ kJ}$ of heat was utilized?

Plan:

1. $1670 \text{ kJ} = 2 \text{ mol Al}$
2. $\mathcal{M} \text{ (g/mol)}$
3. Heat (kJ) $\rightarrow$ Moles of Al $\rightarrow$ Mass (g) of Al

Solution: Converting from heat available to mass of Al:

$$\text{Mass (g) of Al} = (1.000 \times 10^3 \text{ kJ}) \times \frac{2 \text{ mol Al}}{1676 \text{ kJ}} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

$$= 32.20 \text{ g Al}$$
**Concept 6-12.** The importance of Hess’s law and the manipulation of $\Delta H$ values

- Since enthalpy is a state function, $\Delta H$ for complex reactions can be defined irrespective of how the reaction actually occurs.

- **Hess’s law:** the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps.

  - **Equation 1:** $S(s) + O_2(g) \rightarrow SO_2(g)$ \hspace{1cm} $\Delta H_1 = -296.8$ kJ
  - **Equation 2:** $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ \hspace{1cm} $\Delta H_2 = -198.4$ kJ
  - **Equation 3:** $S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g)$ \hspace{1cm} $\Delta H_3 =$ ?

- Alter eq’ns 1 and 2 so that the substances sum to equation 3, then $\Delta H_3$ is the sum of the altered enthalpy changes of eq’ns 1 and 2.

- Equations 1 and 3 contain the same amount of sulfur, so leave equation 1 unchanged.
• Equation 2 contains twice as much SO\textsubscript{3} as needed, so multiply it by \( \frac{1}{2} \), being sure to halve \( \Delta H_2 \) as well.

• Add equation 1 to the halved equation 2 and eliminate terms that appear on both sides of the equation:

\[
\begin{align*}
\text{Equation 1:} & \quad S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta H_1 = -296.8 \text{ kJ} \\
\frac{1}{2} \text{ equation 2:} & \quad SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g) \quad \frac{1}{2}\Delta H_2 = -99.2 \text{ kJ} \\
\hline
S(s) + O_2(g) + SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_2(g) + SO_3(g) \\
\text{Or} & \quad S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g) \\
\Delta H_3 &= \Delta H_1 + \frac{1}{2}\Delta H_2 = -296.8 \text{ kJ} + (-99.2 \text{ kJ}) = -396.0 \text{ kJ}
\end{align*}
\]
Skill 6-5. Using Hess’s law to find an unknown $\Delta H$

**Problem:** A chemist is studying ways to convert CO and NO to less harmful gases through the following equation:

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

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

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

Equation B: $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \quad \Delta H_B = 180.6$ kJ

Adding the altered equations to obtain the target equation:

| Equation A: $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H = -283.0$ kJ |
| $\frac{1}{2}$ equation B reversed: $\text{NO}(g) \rightarrow \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \quad \Delta H = -90.3$ kJ |

Target: $\text{CO}(g) + \text{NO}(g) \rightarrow \text{CO}_2(g) + \frac{1}{2}\text{N}_2(g) \quad \Delta H = -373.3$ kJ
Concept 6-13. The meaning of a formation equation and the standard heat of formation

• ΔH varies with conditions, so use ΔH values representing standardized conditions, to compare thermodynamic data.

The standard states are:

• For a gas, the standard state is 1 atm.

• For a substance in aqueous solution, the standard state is 1 M concentration (1 M = 1 mol/L).

• For an element or compound, the standard state is the most stable form at 1 atm and the temperature of interest; usually 25°C (298 K).

• ΔH\text{rxn} measured with all substances in their standard states, is the standard heat of reaction, ΔH°\text{rxn}.
Formation Reactions and Their Standard Enthalpy Changes

- In a formation reaction, one mole of a compound forms from its elements.

- The standard heat of formation ($\Delta H_f^\circ$) is the enthalpy change of the formation reaction with all substances in their standard states.

For the formation of methane (CH$_4$):

$$\text{C(graphite)} + 2\text{H}_2(g) \rightarrow \text{CH}_4(g) \quad \Delta H_f^\circ = -74.9 \text{ kJ}$$

- Table 6.5 shows $\Delta H_f^\circ$ values for several elements and compounds.

- Note that:
  1. An element in its standard state is assigned a $\Delta H_f^\circ$ of 0.
  2. Most compounds have a negative $\Delta H_f^\circ$; compounds are usually more stable than their component elements.
Skill 6-6. Writing formation equations and using $\Delta H_f^\circ$ values to find $\Delta H_{\text{rxn}}^\circ$

**Problem:** Write balanced equations for the formation of one mole of the following compounds from their elements and include $\Delta H_f^\circ$.

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

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

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

**Solution:**

(a) $\text{Ag(s) + \frac{1}{2}Cl}_2(g) \rightarrow \text{AgCl(s)}$ \hspace{1cm} $\Delta H_f^\circ = -127.0 \text{ kJ}$

(b) $\text{Ca(s) + C(graphite) + \frac{3}{2}O}_2(g) \rightarrow \text{CaCO}_3(s)$ \hspace{1cm} $\Delta H_f^\circ = -1206.9 \text{ kJ}$

(c) $\frac{1}{2}\text{H}_2(g) + \text{C(graphite) + \frac{1}{2}N}_2(g) \rightarrow \text{HCN(g)}$ \hspace{1cm} $\Delta H_f^\circ = 135 \text{ kJ}$
**Concept 6-14.** How a reaction combines the decomposition of reactants and the formation of products

- Using $\Delta H_f^\circ$ values and applying Hess’s law, $\Delta H_{\text{rxn}}^\circ$ for any chemical change can be calculated. Steps:

  **Step 1:** Break each reactant down into its elements. (reverse of formation reaction), std. enthalpy change for each reactant is $-\Delta H_f^\circ$.

  **Step 2:** The appropriate elements form each product; (formation reaction). The std. enthalpy change for each product is $+\Delta H_f^\circ$. 
Calculating the reaction enthalpy change from formation enthalpies:

Find $\Delta H_{\text{rxn}}$ for: $\text{TiCl}_4(l) + 2\text{H}_2\text{O}(g) \rightarrow \text{TiO}_2(s) + 4\text{HCl}(g)$

Write the equation as the sum of 4 equations, one for each compound:

$\text{TiCl}_4(l) \rightarrow \text{Ti}(s) + 2\text{Cl}_2(g)$  \hspace{2cm} $-\Delta H_f^0 [\text{TiCl}_4(l)]$

$2\text{H}_2\text{O}(g) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$  \hspace{2cm} $-2\Delta H_f^0 [\text{H}_2\text{O}(g)]$

$\text{Ti}(s) + \text{O}_2(g) \rightarrow \text{TiO}_2(s)$  \hspace{2cm} $\Delta H_f^0 [\text{TiO}_2(s)]$

$2\text{H}_2(g) + 2\text{Cl}_2(g) \rightarrow 4\text{HCl}(g)$  \hspace{2cm} $4\Delta H_f^0 [\text{HCl}(g)]$

$\text{TiCl}_4(l) + 2\text{H}_2\text{O}(g) + \text{Ti}(s) + \text{O}_2(g) + 2\text{H}_2(g) + 2\text{Cl}_2(g) \rightarrow$

$\text{Ti}(s) + 2\text{Cl}_2(g) + 2\text{H}_2(g) + \text{O}_2(g) + \text{TiO}_2(s) + 4\text{HCl}(g)$

Or

$\text{TiCl}_4(l) + 2\text{H}_2\text{O}(g) \rightarrow \text{TiO}_2(s) + 4\text{HCl}(g)$
• In general, the $\Delta H^\circ_{\text{rxn}}$ is the sum of the $\Delta H^\circ_f$ of the products minus the sum of the $\Delta H^\circ_f$ of the reactants:

$$\Delta H^\circ_{\text{rxn}} = \Sigma m \Delta H^\circ_f (\text{products}) - \Sigma n \Delta H^\circ_f (\text{reactants})$$

where $\Sigma$ means “sum of,” and $m$ and $n$ are the coefficients of the reactants and products from the balanced equation.

**Problem**: The first step in the industrial production of nitric acid is the oxidation of ammonia according to the following equation:

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

Calculate $\Delta H^\circ_{\text{rxn}}$ from $\Delta H^\circ_f$ values (Table 6.5).

**Solution**: Calculating $\Delta H^\circ$ rxn:

$$\Delta H^\circ_{\text{rxn}} = \Sigma m \Delta H^\circ_f (\text{products}) - \Sigma n \Delta H^\circ_f (\text{reactants})$$
\[4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightarrow 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)\]

\[\Delta H^0_{\text{rxn}} = \sum m \Delta H^0_f(\text{products}) - \sum n \Delta H^0_f(\text{reactants})\]

\[= 4 \Delta H^0_f[\text{NO}(g)] + 6 \Delta H^0_f[\text{H}_2\text{O}(g)] - \{4 \Delta H^0_f[\text{NH}_3(g)] + 5 \Delta H^0_f[\text{O}_2(g)]\}\]

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

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

\[= 361 \text{ kJ} - 1451 \text{ kJ} + 184 \text{ kJ} - 0 \text{ kJ}\]

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