Chapter 6

Thermochemistry: Energy Flow and Chemical Change
Thermochemistry: Energy Flow and Chemical Change

6.1 Forms of Energy and Their Interconversion

6.2 Enthalpy: Heats of Reaction and Chemical Change

6.3 Calorimetry: Laboratory Measurement of Heats of Reaction

6.4 Stoichiometry of Thermochemical Equations

6.5 Hess’ s Law of Heat Summation

6.6 Standard Heats of Reaction ($\Delta H^0_{\text{rxn}}$)
Thermodynamics: First Law

Thermodynamics: Study and measure of the nature of heat and energy and its transformations

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

✔ Energy flow is key in science; understanding it will help us to understand WHY things occur. When energy is transferred from one object to another, it appears as work and/or as heat

Thermodynamics was developed independent of theory *through observation of bulk matter*

To deal with large groups of molecules and atoms we need to define THREE parameters: System, Surroundings and Thermodynamic Universe
Thermodynamics: First Law

**System:**
The part of the universe of immediate interest; composed of particles with their own internal energies (E or U). The system has an internal energy. When a change occurs, the internal energy changes. Can be closed, open or isolated;

**Surroundings:**
The portion of the universe that can exchange energy and matter with the system;

**Thermodynamic Universe:**
System + Surroundings

*Open System:* Exchanges both E and matter with Surroundings;

*Closed System:* Exchanges only E with Surroundings;

*Isolated System:* Exchanges NEITHER with Surroundings
The system in this case is the *contents* of the reaction flask. The surroundings comprise everything else, including the flask itself.
Open
An Auto

Closed
A Battery

Isolated
A perfect Thermos
Energy diagrams for the transfer of internal energy \((E)\) between a system and its surroundings.

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

A. E of system decreases

B. E of system increases
A system transferring energy as heat only.

**A** E lost as heat

- $T_{sys} > T_{surr}$
- Heat (q) lost to surroundings ($q < 0$)

**B** E gained as heat

- $T_{sys} = T_{surr}$
- Heat (q) gained from surroundings ($q > 0$)

Energy, E
A system losing energy as work only.

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Work ($w$)

Motion against an opposing force; a directed motion thru a distance; $w = F \Delta x$

Capacity of a system to do work is called Internal Energy ($U$)
Most important: $\Delta U = U_{\text{final}} - U_{\text{initial}}$

If E transfer is only due to work then $\Delta U = w$

Work is either expansion or nonexpansion
($\Delta V \neq 0$ vs. $\Delta V = 0$)

$w = -P_{\text{ext}} \Delta V$ (since $w = -$ when system does work)
Work

\[ w = - P_{\text{ext}} \Delta V \quad (P_{\text{ext}} \text{ must be constant}) \]

*Work is in L-atm: 1 L-atm = 101.325 J*

If \( P_{\text{ext}} = 0 \), then free expansion occurs

If \( P_{\text{ext}} \) does change in infinitesimally small amts, then process is *REVERSIBLE*: a process in which an infinitesimally small change in the opposite direction will cause the process to reverse direction.
Figure 6.5  Pressure-volume work.

\[ w = -P \Delta V \]
An expanding gas pushing back the atmosphere does \( PV \) work \((w = -P\Delta V)\).
Heat ($q$)

energy transfer due to a temperature difference

- More familiar way to transfer E
- Sys and Surr are at different T’s
- If no work is done, then $\Delta U = q$
- Temperature is not heat; it is directly proportional to it ($q \propto \Delta T$)!
- Temperature: a measure of the relative ‘hotness’ or “coldness” of an object
- $q = -q_{surr}$
- Exothermic vs Endothermic

Chapter 6: First Law
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.
Measuring Heat Using a Calorimeter

Constant Pressure

Constant Volume
Figure 6.7
Coffee-cup calorimeter.
Figure 6.8 A bomb calorimeter.
### Table 6.1 The Sign Conventions* for $q$, $w$, and $\Delta E$

<table>
<thead>
<tr>
<th>$q$</th>
<th>+</th>
<th>$w$</th>
<th>=</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ (heat <em>gained</em>)</td>
<td>+ (work done <em>on</em>)</td>
<td></td>
<td></td>
<td>+ (energy <em>increased</em>)</td>
</tr>
<tr>
<td>+ (heat <em>gained</em>)</td>
<td></td>
<td>− (work done <em>by</em>)</td>
<td></td>
<td>Depends on <em>sizes</em> of $q$ and $w$</td>
</tr>
<tr>
<td>− (heat <em>lost</em>)</td>
<td></td>
<td>+ (work done <em>on</em>)</td>
<td></td>
<td>Depends on <em>sizes</em> of $q$ and $w$</td>
</tr>
<tr>
<td>− (heat <em>lost</em>)</td>
<td></td>
<td>− (work done <em>by</em>)</td>
<td></td>
<td>− (energy <em>decreased</em>)</td>
</tr>
</tbody>
</table>

*From the perspective of the system.*
Selected Heat Capacities ($C_s$ and $C_m$)

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific heat capacity ($J\cdot(^\circ C)^{-1}\cdot g^{-1}$)</th>
<th>Molar heat capacity ($J\cdot K^{-1}\cdot mol^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>1.01</td>
<td>—</td>
</tr>
<tr>
<td>benzene</td>
<td>1.05</td>
<td>136</td>
</tr>
<tr>
<td>brass</td>
<td>0.37</td>
<td>—</td>
</tr>
<tr>
<td>copper</td>
<td>0.38</td>
<td>33</td>
</tr>
<tr>
<td>ethanol</td>
<td>2.42</td>
<td>111</td>
</tr>
<tr>
<td>glass (Pyrex)</td>
<td>0.78</td>
<td>—</td>
</tr>
<tr>
<td>granite</td>
<td>0.80</td>
<td>—</td>
</tr>
<tr>
<td>marble</td>
<td>0.84</td>
<td>—</td>
</tr>
<tr>
<td>polyethylene</td>
<td>2.3</td>
<td>—</td>
</tr>
<tr>
<td>stainless steel</td>
<td>0.51</td>
<td>—</td>
</tr>
<tr>
<td>water: solid</td>
<td>2.03</td>
<td>37</td>
</tr>
<tr>
<td>liquid</td>
<td>4.184</td>
<td>75</td>
</tr>
<tr>
<td>vapor</td>
<td>2.01</td>
<td>34</td>
</tr>
</tbody>
</table>

- Amt of heat to raise 10.0 g of water 5°C: 209.2 J
- Temp increase if same amount of heat is added to 10.0 g of gold ($C_s = 0.106$ J/g-C): 197.4 °C!
### Table 6.2 Specific Heat Capacities of Some Elements, Compounds, and Mixtures

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat Capacity (J/g·K)*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elements</strong></td>
<td></td>
</tr>
<tr>
<td>Aluminum, Al</td>
<td>0.900</td>
</tr>
<tr>
<td>Graphite, C</td>
<td>0.711</td>
</tr>
<tr>
<td>Iron, Fe</td>
<td>0.450</td>
</tr>
<tr>
<td>Copper, Cu</td>
<td>0.387</td>
</tr>
<tr>
<td>Gold, Au</td>
<td>0.129</td>
</tr>
<tr>
<td><strong>Compounds</strong></td>
<td></td>
</tr>
<tr>
<td>Water, H₂O(l)</td>
<td>4.184</td>
</tr>
<tr>
<td>Ethyl alcohol, C₂H₅OH(l)</td>
<td>2.46</td>
</tr>
<tr>
<td>Ethylene glycol, (CH₂OH)₂(l)</td>
<td>2.42</td>
</tr>
<tr>
<td>Carbon tetrachloride, CCl₄(l)</td>
<td>0.862</td>
</tr>
<tr>
<td><strong>Solid mixtures</strong></td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>1.76</td>
</tr>
<tr>
<td>Cement</td>
<td>0.88</td>
</tr>
<tr>
<td>Glass</td>
<td>0.84</td>
</tr>
<tr>
<td>Granite</td>
<td>0.79</td>
</tr>
<tr>
<td>Steel</td>
<td>0.45</td>
</tr>
</tbody>
</table>

*At 298 K (25°C)
Since $q = nC_m\Delta T$ then 

$$C_m = \frac{q}{n\Delta T} = \frac{q}{\Delta T} \quad (n = 1)$$

However, $q = \Delta U$ at constant volume or $q = \Delta H$ at constant pressure, so:

$$C_{m,V} = \frac{\Delta U}{n\Delta T} \quad \text{OR} \quad C_{m,P} = \frac{\Delta H}{n\Delta T}$$

and

$$C_{m,P} = C_{m,V} + R$$

For Ar: $C_{m,V} = 12.8 \text{ J/mol-K}$ and $C_{m,P} = 21.1 \text{ J/mol-K}$
Sample Problem 6.3  Finding the Quantity of Heat from Specific Heat Capacity

**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:** Given the mass, specific heat capacity and change in temperature, we can use \( q = c \times \text{mass} \times \Delta T \) to find the answer. \( \Delta T \) in °C is the same as for K.

**SOLUTION:**

\[
q = 0.387 \text{ J/g•K} \times 125 \text{ g} \times (300^\circ\text{C} - 25^\circ\text{C}) = 1.33 \times 10^4 \text{ J}
\]
Figure 6.4  Two different paths for the energy change of a system.

\[ \text{C}_8\text{H}_{18} (\text{octane}) + \frac{25}{2} \text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O} \]
First Law of Thermodynamics

The internal energy of an isolated system is constant

\[ \Delta U = q + w \]

• Isolated system, \( \Delta U = 0 \)
• Container walls can be either \textit{adiabatic} \( (q = 0) \) or \textit{diathermic} \( (w = 0) \)
• Both \( q \) and \( w \) are path dependent

Internal Energy \((U)\) is a \textit{State Function}

To determine the change in a state function, choose any \textit{convenient path} (even if the real path is too complicated to calculate)
\[ \Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} \]

**Units of Energy**

- **Joule (J)** \(1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2\)
- **calorie (cal)** \(1 \text{ cal} = 4.184 \text{ J}\)
- **British thermal unit (Btu)** \(1 \text{ Btu} = 1055 \text{ J}\)
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 CO₂ and H₂O 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 (ΔE) in J, kJ, and kcal.

PLAN: 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.

SOLUTION: \( q = -325 \text{ J} \quad w = -451 \text{ J} \)

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

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

\[
-0.776 \text{ kJ} \times \frac{\text{kcal}}{4.184 \text{ kJ}} = -0.185 \text{ kcal}
\]
Enthalpy (H)

The heat released or absorbed by a system at constant pressure

- For Constant Volume systems $\Delta U = q$
- Most Processes WE study are Constant Pressure systems
- Enthalpy is a State Function that allows us to keep track of $q$ at constant $P$; By definition: $H = U + PV$
- $\Delta H = \Delta U + P \Delta V = q - P_{ext} \Delta V + P \Delta V = q - P_{ext} \Delta V + P_{ext} \Delta V$
- So $\Delta H = q$
- Implication 1: At constant volume you measure $\Delta U$; at constant pressure you measure $\Delta H$
- Implication 2: The molar heat capacity $C_m = q/(n \Delta T)$ Therefore it will be different for a constant volume process than for a constant pressure process
The Meaning of Enthalpy

\[ w = -P \Delta V \]

\[ H = E + PV \]

where \( H \) is enthalpy

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

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

\[ \Delta H \approx \Delta E \] in

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 does change but \( q \) is \( \gg\gg P \Delta V \).
Mathematical Aspects of State Functions

Given $X$ is a state function, then:

- The change in $X$ is equal to the sum of the $X$ values for the products minus the reactants:
  \[ \Delta X = \Sigma n_i X_{pdts} - \Sigma n_j X_{rxtnts} \]

- The value for the reverse process is equal in magnitude BUT opposite in sign:
  \[ \Delta X_{rev} = -\Delta X_{fwd} \]

- Multiplication of a process by number multiplies the $X$ value by that number:
  If $A \rightarrow 2B \quad \Delta X_1 = 7$ then $3A \rightarrow 6B \quad \Delta X_2 = 3\Delta X_1 = 21$

- The sum of all of the $X$ values making up a process is equal to the $X$ overall for that process:
  \[ \Delta X_{total} = \Delta X_{step\ 1} + \Delta X_{step\ 2} + \Delta X_{step\ 3} + \ldots \]
Figure 6.6

Enthalpy diagrams for exothermic and endothermic processes.

A Exothermic process

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

\( \Delta H < 0 \)

B Endothermic process

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

\( \Delta H > 0 \)
### ΔH of Physical Processes

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>Freezing point (K)</th>
<th>ΔH$_{fus}^\circ$ (kJ·mol$^{-1}$)</th>
<th>Boiling point (K)</th>
<th>ΔH$_{vap}^\circ$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>CH$_3$COCH$_3$</td>
<td>177.8</td>
<td>5.72</td>
<td>329.4</td>
<td>29.1</td>
</tr>
<tr>
<td>ammonia</td>
<td>NH$_3$</td>
<td>195.4</td>
<td>5.65</td>
<td>239.7</td>
<td>23.4</td>
</tr>
<tr>
<td>argon</td>
<td>Ar</td>
<td>83.8</td>
<td>1.2</td>
<td>87.3</td>
<td>6.5</td>
</tr>
<tr>
<td>benzene</td>
<td>C$_6$H$_6$</td>
<td>278.6</td>
<td>10.59</td>
<td>353.2</td>
<td>30.8</td>
</tr>
<tr>
<td>ethanol</td>
<td>C$_2$H$_5$OH</td>
<td>158.7</td>
<td>4.60</td>
<td>351.5</td>
<td>43.5</td>
</tr>
<tr>
<td>helium</td>
<td>He</td>
<td>3.5</td>
<td>0.021</td>
<td>4.22</td>
<td>0.084</td>
</tr>
<tr>
<td>mercury</td>
<td>Hg</td>
<td>234.3</td>
<td>2.292</td>
<td>629.7</td>
<td>59.3</td>
</tr>
<tr>
<td>methane</td>
<td>CH$_4$</td>
<td>90.7</td>
<td>0.94</td>
<td>111.7</td>
<td>8.2</td>
</tr>
<tr>
<td>methanol</td>
<td>CH$_3$OH</td>
<td>175.2</td>
<td>3.16</td>
<td>337.8</td>
<td>35.3</td>
</tr>
<tr>
<td>water</td>
<td>H$_2$O</td>
<td>273.2</td>
<td>6.01</td>
<td>373.2</td>
<td>40.7</td>
</tr>
</tbody>
</table>

(44.0 at 25°C)
Heating Curves

Temperature (°C)

Heat supplied

Solid  Liquid  Liquid vaporizing  Vapor

Solid melting

Melting point

Boiling point

5.01 kJ·mol⁻¹

7.5 kJ·mol⁻¹

40.7 kJ·mol⁻¹

$\Delta H_{\text{fus}}$

$\Delta H_{\text{vap}}$

$q$

$q$

$q$

$T_1 (-5 \, \text{C})$

$T_2 (+120 \, \text{C})$

Chapter 6: First Law

Slide 6-33
Heating Curve Calculations

To take 0.5 mole (9.0 g) of ice from –5ºC to vapor at 120ºC:

Total heat = (heat to take 0.5 mol of ice from –5ºC to 0ºC) + (heat to melt 0.5 mol of ice) + (heat to take 0.5 mol of water from 0ºC to 100ºC) + (heat to vaporize 0.5 mol of ice) + (heat to take 0.5 mol of vapor from 100ºC to 120ºC)

\[
q_{\text{tot}} = nC_{m,P,\text{ice}} \Delta T + n\Delta H_{fus} + nC_{m,P,\text{liq}} \Delta T + n\Delta H_{vap} + nC_{m,P,\text{vap}} \Delta T
\]

\[
q_{\text{tot}} = 0.5 \text{ mol}(37 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1})(5 \text{ K}) + 0.5 \text{ mol}(6.01 \text{ kJ} \cdot \text{mol}^{-1}) + \]

\[
0.5 \text{ mol}(75 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1})(100 \text{ K}) + 0.5 \text{ mol}(40.7 \text{ kJ} \cdot \text{mol}^{-1}) + \]

\[
0.5 \text{ mol}(34 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1})(20 \text{ K}) = 27.5 \text{ kJ}
\]
\( \Delta H \) of Chemical Change

- Enthalpy change during chemical reactions important to understanding chemistry.

- Reaction Enthalpies: \( \Delta H \) or \( \Delta H_{rxn} \)

- \( \Delta H \) associated with Thermochemical Equations:
  \[
  2\text{Al (s) + 6HCl (aq)} \rightarrow 2\text{AlCl}_3 \text{ (aq) + H}_2 \text{ (g)} \quad \Delta H = -1049 \text{ kJ}
  \]

- \( \Delta H_{rxn} \) associated with certain types of reactions; corrected to a per mole basis; used in tabular collections of data:
  \[
  \Delta H_{\text{rxn}} = -524.5 \text{ kJ/mol for the HCl oxidation of Al}
  \]
  \[
  \Delta H_{\text{combustion}} = -1560 \text{ kJ/mol for ethane (C}_2\text{H}_6)\]

- Relation between \( \Delta H \) and \( \Delta U \):
  For reactions in which NO gas is generated: \( \Delta H = \Delta U \)
  For reactions in which gas is generated: \( \Delta H = \Delta U + \Delta n_{\text{gas}}RT \)
Standard Reaction Enthalpies $\Delta H^\circ$

$\Delta H$ depends on conditions and phases; to allow standardization for reporting the idea of Standard State was developed.

The standard state of a property $X$ (designated as $X^\circ$) is defined as such:

✓ Substances and elements: most stable form of that material at the $T$ of interest and 1 bar of pressure;

✓ Solutions: 1.0 M concentration;

   Allows the tabulation and reporting of data from various sources to be accomplished!
Common $\Delta H_x^\circ$'s

Enthalpy of Formation ($\Delta H_f^\circ$)

✔ Defined as: *the standard reaction enthalpy for the formation of one mole of a substance in its most stable form from its elements in their most stable form at the temperature of interest:*

\[
2 \text{Na}(s) + \text{C}(s, \text{gr}) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{Na}_2\text{CO}_3 (s)
\]

✔ By Definition $\Delta H_f^\circ \equiv 0$ of an element in its most stable state;

✔ Allows $\Delta H_{rxn}^\circ$ to be calculated using $\Delta H_f^\circ$ of pdts - rxtnts:

\[
aA + bB \rightarrow dD
\]

\[
\Delta H_f^\circ = [d\Delta H_f^\circ, D] - [a\Delta H_f^\circ, A - b\Delta H_f^\circ, B]
\]

Enthalpy of Combustion ($\Delta H_c^\circ$ or $\Delta H^\circ_{comb}$)

✔ Defined as: *the standard reaction enthalpy for the combustion of one mole of a substance in its most stable form at $T$ of interest:*

\[
\text{C}_2\text{H}_2(g) + \frac{5}{2} \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + \text{H}_2\text{O} (l)
\]
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) \( \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) + 285.8 \text{ kJ} \)

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

**PLAN:** Determine whether heat 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:**

![Enthalpy Diagram](image)
Sample Problem 6.4  Determining the Heat of a Reaction

PROBLEM:  You place 50.0 mL of 0.500 M NaOH in a coffee-cup calorimeter at 25.00°C and carefully add 25.0 mL of 0.500 M HCl, also at 25.00°C. After stirring, the final temperature is 27.21°C. Calculate $q_{\text{soln}}$ (in J) and $\Delta H_{\text{rxn}}$ (in kJ/mol). (Assume the total volume is the sum of the individual volumes and that the final solution has the same density and specific heat capacity as water: $d = 1.00$ g/mL and $c = 4.184$ J/g•K)

PLAN: We need to determine the limiting reactant from the net ionic equation. The moles of NaOH and HCl as well as the total volume can be calculated. From the volume we use density to find the mass of the water formed. At this point $q_{\text{soln}}$ can be calculated using the mass, $c$, and $\Delta T$. The heat divided by the $M$ of water will give us the heat per mole of water formed.
Sample Problem 6.4  

**Determining the Heat of a Reaction**

**SOLUTION:**  
\[ \text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l) \]
\[ \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) \]

For NaOH  \[ 0.500 \text{ M} \times 0.0500 \text{ L} = 0.0250 \text{ mol OH}^- \]

For HCl  \[ 0.500 \text{ M} \times 0.0250 \text{ L} = 0.0125 \text{ mol H}^+ \]

HCl is the limiting reactant. 0.0125 mol of H\(_2\)O will form during the reaction.

total volume after mixing = 0.0750 L

\[ 0.0750 \text{ L} \times 10^3 \text{ mL/L} \times 1.00 \text{ g/mL} = 75.0 \text{ g of water} \]

\[ q = \text{mass} \times \text{specific heat} \times \Delta T \]
\[ = 75.0 \text{ g} \times 4.184 \text{ J/g} \cdot ^\circ\text{C} \times (27.21^\circ\text{C} - 25.00^\circ\text{C}) \]
\[ = 693 \text{ J} \]

\[ (693 \text{ J}/0.0125 \text{ mol H}_2\text{O})(\text{kJ}/10^3 \text{ J}) = -55.4 \text{ kJ/mol H}_2\text{O formed} \]
Sample Problem 6.5  Calculating the Heat of a Combustion Reaction

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 heat capacity of the calorimeter = 8.151 kJ/K). The temperature increases 4.937°C. Is the manufacturer’s claim correct?

PLAN: \(- q_{\text{sample}} = q_{\text{calorimeter}}\)  (First Law of Thermodynamics)

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

1 Calorie = 1 kcal = 4.184 kJ

10 Calorie = 41.84 kJ

The manufacturer’s claim is true.
Figure 6.9

Summary of the relationship between amount (mol) of substance and the heat (kJ) transferred during a reaction.
The major source of aluminum in the world is bauxite (mostly aluminum oxide). Its thermal decomposition can be represented by

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

If aluminum is produced this way, how many grams of aluminum can form when 1.000 \times 10^3 \text{ kJ} of heat is transferred?

**SOLUTION:**

\[
1.000 \times 10^3 \text{ kJ} \times \frac{2 \text{ mol Al}}{1676 \text{ kJ}} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 32.20 \text{ g Al}
\]
Sample Problem 6.8 Using Hess’s Law to Calculate an Unknown \( \Delta H \)

PROBLEM: Two gaseous pollutants that form in auto exhausts are CO and NO. An environmental chemist is studying ways to convert them 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: \( \text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H_A = -283.0 \text{ kJ} \)

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

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 6.8

SOLUTION:

Multiply Equation B by $\frac{1}{2}$ and reverse it:

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

Add the manipulated equations together:

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

$\frac{1}{2}$ Equation B (reversed):

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

\[
\begin{align*}
\text{CO}(g) + \text{NO}(g) & \rightarrow \text{CO}_2(g) + \frac{1}{2} \text{N}_2(g) \\
\Delta H_{\text{rxn}} & = -373.3 \text{ kJ}
\end{align*}
\]
### Table 6.3: Selected Standard Heats of Formation at 25°C (298 K)

<table>
<thead>
<tr>
<th>Formula</th>
<th>( \Delta H_f^\circ ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td></td>
</tr>
<tr>
<td>Ca(s)</td>
<td>0</td>
</tr>
<tr>
<td>CaO(s)</td>
<td>−635.1</td>
</tr>
<tr>
<td>CaCO(_2)(s)</td>
<td>−1206.9</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
</tr>
<tr>
<td>C(graphite)</td>
<td>0</td>
</tr>
<tr>
<td>C(diamond)</td>
<td>1.9</td>
</tr>
<tr>
<td>CO(g)</td>
<td>−110.5</td>
</tr>
<tr>
<td>CO(_2)(g)</td>
<td>−393.5</td>
</tr>
<tr>
<td>CH(_4)(g)</td>
<td>−74.9</td>
</tr>
<tr>
<td>CH(_3)OH(l)</td>
<td>−238.6</td>
</tr>
<tr>
<td>HCN(g)</td>
<td>135</td>
</tr>
<tr>
<td>CS(_2)(l)</td>
<td>87.9</td>
</tr>
<tr>
<td>Chlorine</td>
<td></td>
</tr>
<tr>
<td>Cl(g)</td>
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<tr>
<td>Cl(_2)(g)</td>
<td>0</td>
</tr>
<tr>
<td>HCl(g)</td>
<td>−92.3</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
</tr>
<tr>
<td>H(g)</td>
<td>218.0</td>
</tr>
<tr>
<td>H(_2)(g)</td>
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<tr>
<td>Nitrogen</td>
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</tr>
<tr>
<td>N(_2)(g)</td>
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<tr>
<td>NH(_3)(g)</td>
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<tr>
<td>NO(_2)(g)</td>
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<tr>
<td>Oxygen</td>
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</tr>
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<td>O(_2)(g)</td>
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</tr>
<tr>
<td>O(_3)(g)</td>
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</tr>
<tr>
<td>H(_2)O(_2)(g)</td>
<td>−241.8</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>−285.8</td>
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<tr>
<td>Silver</td>
<td></td>
</tr>
<tr>
<td>Ag(s)</td>
<td>0</td>
</tr>
<tr>
<td>AgCl(s)</td>
<td>−127.0</td>
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<tr>
<td>Sodium</td>
<td></td>
</tr>
<tr>
<td>Na(s)</td>
<td>0</td>
</tr>
<tr>
<td>Na(g)</td>
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</tr>
<tr>
<td>NaCl(s)</td>
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<tr>
<td>S(_8)(rhombic)</td>
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<tr>
<td>S(_8)(monoclinic)</td>
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<tr>
<td>SO(_2)(g)</td>
<td>−296.8</td>
</tr>
<tr>
<td>SO(_3)(g)</td>
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</tbody>
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---

*Chapter 6: First Law*
Table 6.3  Selected Standard Enthalpies of Formation at 25°C (298K)

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\Delta H^\circ_f$ (kJ/mol)</th>
<th>Formula</th>
<th>$\Delta H^\circ_f$ (kJ/mol)</th>
<th>Formula</th>
<th>$\Delta H^\circ_f$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td></td>
<td>Cl$_2$(g)</td>
<td>0</td>
<td>Ag(s)</td>
<td>0</td>
</tr>
<tr>
<td>Ca(s)</td>
<td>0</td>
<td>HCl(g)</td>
<td>-92.3</td>
<td>AgCl(s)</td>
<td>-127.0</td>
</tr>
<tr>
<td>CaO(s)</td>
<td>-635.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$(s)</td>
<td>-1206.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td>Hydrogen</td>
<td></td>
<td>Sodium</td>
<td></td>
</tr>
<tr>
<td>C(graphite)</td>
<td>0</td>
<td>H(g)</td>
<td>218</td>
<td>Na(s)</td>
<td>0</td>
</tr>
<tr>
<td>C(diamond)</td>
<td>1.9</td>
<td>H$_2$(g)</td>
<td>0</td>
<td>Na(g)</td>
<td>107.8</td>
</tr>
<tr>
<td>CO(g)</td>
<td>-110.5</td>
<td>Nitrogen</td>
<td></td>
<td>NaCl(s)</td>
<td>-411.1</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>-393.5</td>
<td>N$_2$(g)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$(g)</td>
<td>-74.9</td>
<td>NH$_3$(g)</td>
<td>-45.9</td>
<td>S$_8$(rhombic)</td>
<td>0</td>
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<tr>
<td>CH$_3$OH(l)</td>
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<td>NO(g)</td>
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<td>S$_8$(monoclinic)</td>
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<td>Oxygen</td>
<td></td>
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<td>-296.8</td>
</tr>
<tr>
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<td>87.9</td>
<td>O$_2$(g)</td>
<td>0</td>
<td>SO$_3$(g)</td>
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</tr>
<tr>
<td>Chlorine</td>
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<td>O$_3$(g)</td>
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<tr>
<td>Cl(g)</td>
<td>121.0</td>
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<tr>
<td></td>
<td></td>
<td>H$_2$O(l)</td>
<td>-285.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Sample Problem 6.9  Writing Formation Equations

PROBLEM: Write balanced equations for the formation of 1 mol of the following compounds from their elements in their standard states and include $\Delta H^\circ_f$.

(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.

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 $\Delta H^\circ_f$ in Table 6.3 or Appendix B.
Sample Problem 6.9

SOLUTION:

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

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

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

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

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

$$\frac{1}{2}\text{H}_2(g) + \text{C(graphite)} + \frac{1}{2}\text{N}_2(g) \rightarrow \text{HCN}(g) \quad \Delta H_f^o = 135 \text{ kJ}$$
<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>$\Delta H^\circ_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>$C_6H_6(l)$</td>
<td>$-3268$</td>
</tr>
<tr>
<td>carbon</td>
<td>C(s, graphite)</td>
<td>$-394$</td>
</tr>
<tr>
<td>ethanol</td>
<td>$C_2H_5OH(l)$</td>
<td>$-1368$</td>
</tr>
<tr>
<td>ethyne (acetylene)</td>
<td>$C_2H_2(g)$</td>
<td>$-1300$</td>
</tr>
<tr>
<td>glucose</td>
<td>$C_6H_{12}O_6(s)$</td>
<td>$-2808$</td>
</tr>
<tr>
<td>hydrogen</td>
<td>$H_2(g)$</td>
<td>$-286$</td>
</tr>
<tr>
<td>methane</td>
<td>$CH_4(g)$</td>
<td>$-890$</td>
</tr>
<tr>
<td>octane</td>
<td>$C_8H_{18}(l)$</td>
<td>$-5471$</td>
</tr>
<tr>
<td>propane</td>
<td>$C_3H_8(g)$</td>
<td>$-2220$</td>
</tr>
<tr>
<td>urea</td>
<td>$CO(NH_2)_2(s)$</td>
<td>$-632$</td>
</tr>
</tbody>
</table>

*In a combustion, carbon is converted into carbon dioxide, hydrogen into liquid water, and nitrogen into nitrogen gas. More values are given in Appendix 2A.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>$\Delta H_f^\circ$</th>
<th>Substance</th>
<th>Formula</th>
<th>$\Delta H_f^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>NH$_3$(g)</td>
<td>−46.11</td>
<td>benzene</td>
<td>C$_6$H$_6$(l)</td>
<td>+49.0</td>
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<tr>
<td>carbon dioxide</td>
<td>CO$_2$(g)</td>
<td>−393.51</td>
<td>ethanol</td>
<td>C$_2$H$_5$OH(l)</td>
<td>−277.69</td>
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<tr>
<td>carbon monoxide</td>
<td>CO(g)</td>
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<td>ethyne (acetylene)</td>
<td>C$_2$H$_2$(g)</td>
<td>+226.73</td>
</tr>
<tr>
<td>dinitrogen tetroxide</td>
<td>N$_2$O$_4$(g)</td>
<td>+9.16</td>
<td>glucose</td>
<td>C$_6$H$_12$O$_6$(s)</td>
<td>−1268</td>
</tr>
<tr>
<td>hydrogen chloride</td>
<td>HCl(g)</td>
<td>−92.31</td>
<td>methane</td>
<td>CH$_4$(g)</td>
<td>−74.81</td>
</tr>
<tr>
<td>hydrogen fluoride</td>
<td>HF(g)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nitrogen dioxide</td>
<td>NO$_2$(g)</td>
<td>+33.18</td>
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<td>H$_2$O(g)</td>
<td>−241.82</td>
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</tr>
</tbody>
</table>

* A much longer list is given in Appendix 2A.
Hess’ Law of Heat Summation

Let's say we want to determine the reaction enthalpy for the following reaction:

$$\text{H}_2 (g) + \text{Cl}_2 (g) \rightarrow 2\text{HCl} (g) \quad \Delta H^\circ_{\text{rxn}} = ??$$

given the following individual reactions:

$$\text{NH}_3 (g) + \text{HCl} (g) \rightarrow \text{NH}_4\text{Cl} (s) \quad \Delta H^\circ_1 = -176.0 \text{ kJ}$$

$$\text{N}_2 (g) + 3\text{H}_2 (g) \rightarrow 2\text{NH}_3 (g) \quad \Delta H^\circ_2 = -92.22 \text{ kJ}$$

$$\text{N}_2 (g) + 4\text{H}_2 (g) + \text{Cl}_2 (g) \rightarrow 2 \text{NH}_4\text{Cl} (s) \quad \Delta H^\circ_3 = -628.66 \text{ kJ}$$

Start by adding two reactions that give us the reactants we want on the correct side:

**Step 1**

$$\text{N}_2 (g) + 4\text{H}_2 (g) + \text{Cl}_2 (g) \rightarrow 2 \text{NH}_4\text{Cl} (s) \quad \Delta H^\circ_3$$

$$2\text{NH}_3 (g) \rightarrow \text{N}_2 (g) + 3\text{H}_2 (g) \quad - (\Delta H^\circ_2)$$

$$2\text{NH}_3 (g) + \text{H}_2 (g) + \text{Cl}_2 (g) \rightarrow 2 \text{NH}_4\text{Cl} (s) \quad \Delta H^\circ(\text{step 1}) = \Delta H^\circ_3 + - (\Delta H^\circ_2)$$

**Step 2**

$$2\text{NH}_3 (g) + \text{H}_2 (g) + \text{Cl}_2 (g) \rightarrow 2 \text{NH}_4\text{Cl} (s) \quad \Delta H^\circ(\text{step 1})$$

$$2[\text{NH}_4\text{Cl} (s) \rightarrow \text{NH}_3 (g) + \text{HCl} (g)] \quad 2(-\Delta H^\circ_1)$$

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

So  \( \Delta H^\circ_{\text{rxn}} = \Delta H^\circ(\text{step 1}) + 2(-\Delta H^\circ_1) = \Delta H^\circ_3 + - (\Delta H^\circ_2) + 2(-\Delta H^\circ_1) \)

\( \Delta H^\circ_{\text{rxn}} = -184.64 \text{ kJ} \)
Figure 6.10

The general process for determining $\Delta H_{\text{rxn}}^\circ$ from $\Delta H_f^\circ$ values.

\[ \Delta H_{\text{rxn}}^\circ = \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants}) \]
Calculating the Heat of Reaction from Heats of Formation

**PROBLEM:** Nitric acid, whose worldwide annual production is about 10 billion kilograms, 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 \(\Delta H^\circ_{\text{rxn}}\) from \(\Delta H^\circ_{\text{f}}\) values.

**PLAN:** Look up the \(\Delta H^\circ_{\text{f}}\) values and use Hess’ s law to find \(\Delta H^\circ_{\text{rxn}}\).

**SOLUTION:**

\[
\Delta H^\circ_{\text{rxn}} = \sum m\Delta H^\circ_{\text{f}}\text{ (products)} - \sum n\Delta H^\circ_{\text{f}}\text{ (reactants)}
\]

\[
\begin{align*}
\Delta H^\circ_{\text{rxn}} &= \{4[\Delta H^\circ_{\text{f}}\text{ NO}(g)] + 6[\Delta H^\circ_{\text{f}}\text{ H}_2\text{O}(g)]\} - \{4[\Delta H^\circ_{\text{f}}\text{ NH}_3(g)] + 5[\Delta H^\circ_{\text{f}}\text{ O}_2(g)]\} \\
&= (4 \text{ mol})(90.3 \text{ kJ/mol}) + (6 \text{ mol})(-241.8 \text{ kJ/mol}) - \\
&[(4 \text{ mol})(-45.9 \text{ kJ/mol}) + (5 \text{ mol})(0 \text{ kJ/mol})]
\end{align*}
\]

\[
\Delta H^\circ_{\text{rxn}} = -906 \text{ kJ}
\]
Figure 6.11

The trapping of heat by the atmosphere.
End of Chapter 6

Silberberg HW: 10, 14, 15, 19, 35, 37, 39, 41, 48, 52, 54, 57, 59, 64, 65, 67, 71, 77, 79, 81, 82, 92, 97, 98, 100