Chapter 9

Thermochemistry: Energy Changes in Chemical Reactions

Chapter Outline

- 9.1 Energy as a Reactant or a Product
- 9.2 Transferring Heat and Doing Work
- 9.3 Enthalpy and Enthalpy Changes
- 9.4 Heating Curves and Heat Capacity
- 9.5 Heats of Reaction and Calorimetry
- 9.6 Hess’s Law and Standard Heats of Reaction
- 9.7 Heats of Reaction from Heats of Formation and Bond Energies
- 9.8 More Applications of Thermochemistry
What are bond energies? What heat changes occur in chemical reactions? Will a reaction occur? If we can show that the reaction gives off heat, then the answer is frequently yes.

\[
C_6H_{12}O_6(s) + 4KClO_3(l) \rightarrow 6CO_2(g) + 6H_2O(g) + 4KCl(s)
\]

**Why Study Thermochemistry?**

Chemical and physical changes frequently involve the **gain** or **loss** of HEAT -

physical changes (homogeneous mixtures):

\[
\begin{align*}
NaCl_{(aq)} &+ KBr_{(aq)} \rightarrow \text{COLD} \\
H_2SO_4_{(aq)} &+ H_2O_{(l)} \rightarrow \text{HOT}
\end{align*}
\]

\[\text{Physical mixing; no reaction}\]

chemical changes:

\[H_2SO_4_{(aq)} + C_6H_{12}O_6(s) \rightarrow \text{products + HEAT}\]

**HEAT** is a form of **ENERGY**
Energy Units

1 calorie (cal) = heat required to raise 1.0 gram of \( \text{H}_2\text{O} \) 1.0 °C

1 Joule = the KE of 2.0 kg mass moving 1.0 m/s

\[
= \frac{1}{2}mv^2
\]

\[
= \frac{1}{2} (2.0 \text{ kg}) (1.0 \text{ m/s})^2
\]

\[
= 1.0 \text{ kg m}^2/\text{s}^2
\]

\[
= 1.0 \text{ J}
\]

1.0 cal = 4.184 J

Definitions

Thermochemistry - the study of heat changes in chemical reactions

Heat - the transfer of thermal energy between two bodies at different temperatures

System - specific part of the Universe under study

Surroundings - the rest of the Universe outside the system
Energy and Work

ENERGY is the capacity to perform WORK

WORK is a force over a distance (F x d)

An object can possess energy in only two ways, (1) kinetic and (2) potential energy


Kinetic Energy

Kinetic energy (KE) = energy of motion

KE = \( \frac{1}{2} mv^2 \)  

m = mass 

v = velocity
Energy of position or stored energy

$$PE = mgh$$

- **m** = mass
- **g** = gravitational constant
- **h** = height

**Kinetic and Potential Energy at the Molecular Level**

**Kinetic Energy** - in any substance, whether it’s a solid, liquid, or gas, the individual particles are in constant, random, motion

- **Gas** = “bouncing” around
- **Liquids** = “sliding” around
- **Solids** = vibrations

The average Kinetic Energy is directly proportional to the absolute Kelvin temperature
Heat = Kinetic Energy

Heat “flows” from the hot object to the cold

Potential Energy in Atoms and Molecules

electron-proton attraction

Coulomb’s Law:
\[ F = k \frac{q_1 q_2}{d^2} \]
Coal is a complicated collection of organic molecules which when burned, releases a great amount of energy. The energy comes from the chemical bonds between atoms, which are broken during combustion.

Energy Changes in Chemical Reactions

In virtually every chemical reaction, heat is either lost or gained. How can we think of this in terms of kinetic and potential energy?

$$2 \text{C}_8\text{H}_{18} + 25 \text{O}_2 \rightarrow 16 \text{CO}_2 + 18 \text{H}_2\text{O} + \text{heat}$$

- high PE, low KE
- Low PE, high KE
Internal Energy, $\Delta E$

The sum of all the kinetic and potential energies (including chemical) of an object, or a collection of many objects.

Different types of molecular motion contribute to overall internal energy: (a) translational, (b) rotational, and (c) vibrational.

The First Law of Thermodynamics

(Conservation of Energy)

$$\Delta E = q + w$$

“internal energy”  Heat flow  Work ($F \times d$)
Energy Flow Diagrams

\[ \Delta E = q + w \]

It can be shown that the \( q \) that flows at constant pressure is known as Enthalpy:

\[ \Delta H = q_p \]

\( P = 1 \text{ atm} \)

Boiling water performs work on the surroundings

Heat flows into the system
**State functions** are properties that are determined by the state of the system, regardless of how that condition was achieved.

**State functions are PATH-INDEPENDENT**

energy, pressure, volume, temperature

\[
\Delta E = E_{\text{final}} - E_{\text{initial}} \\
\Delta P = P_{\text{final}} - P_{\text{initial}} \\
\Delta V = V_{\text{final}} - V_{\text{initial}} \\
\Delta T = T_{\text{final}} - T_{\text{initial}}
\]

Potential energy of the skier and hiker is the same even though they took different paths.

---

**State functions are PATH-INDEPENDENT**

“State Properties” of Denver:

Altitude 1 mile  
Latitude 39°43’ N  
Longitude 105°01’ W

“State Properties” of Chicago:

Altitude 656 ft.  
Latitude 41°51’ N  
Longitude 87°38’ W

Path values (distances between Chicago and Denver):

996 Miles via Int. 80  
1957 Miles via Memphis and Albuquerque on Int. 55, Int. 40, and Int. 25

State property differences:

\( \Delta (\text{altitude}) = 5,280 - 656 = 4,624 \text{ ft.} \)  
\( \Delta (\text{latitude}) = 39°43’ - 41°51’ = -2°08’ \)  
\( \Delta (\text{longitude}) = 105°01’ - 87°38’ = 17°23’ \)
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Isolated, Closed and Open Systems

(a) **Isolated system**: A thermos bottle containing hot soup with the lid screwed on tightly
(b) **Closed system**: A cup of hot soup with a lid
(c) **Open system**: An open cup of hot soup

- *isolated systems* can not exchange mass or energy
- *closed systems* can only exchange energy
- *open systems* can exchange mass and energy
**Exothermic and Endothermic Processes**

- Exothermic process: Heat flows *out* of the system to surroundings \((q < 0)\).
- Endothermic process: Heat flows *into* the system from surroundings \((q > 0)\).

**Pressure-Volume (P-V) Work**

\[
\Delta E = q + w
\]

- \(\Delta E > 0\) when heat flows in \((q > 0)\) or work is performed on the system \((w > 0)\)
- \(\Delta E < 0\) when heat flows out \((q < 0)\) or work is performed on the surroundings \((w < 0)\)
(a) Intake – air and fuel enters the cylinder

**(b) Compression** – heats up reaction mixture and ignites \( q > 0, w > 0, \Delta E > 0 \)

**(c) Power Stroke (expansion)** – combustion products perform work on the surroundings \( q < 0, w < 0, \Delta E < 0 \)

(d) Exhaust

---

**Example of P-V Work, p. 368-369**

Work = P \( \times \Delta V \) where \( \Delta V = V_f - V_i \) and \( P = \frac{F}{A} \)

Remember that energy (in Joules) is the capacity to do work, so \( P \times \Delta V \) has to have the same units as energy.

Units of a Joule = Newton x meters = \( \frac{kg\ m^2}{s^2} \)

Units of P = \( \frac{Newton}{m^2} = \frac{kg\cdot m/s^2}{m^2} = \frac{kg/s^2}{m} \)

Units: P \( \times \Delta V = \frac{kg/s^2}{m} \times m^3 = \frac{kg\ m^2}{s^2} = \) Joules

So \( \Delta E = q + w = q - P\Delta V \) There’s a minus sign because when \( \Delta V > 0 \), then system does work on the surroundings \( (w < 0) \)
Sample Exercise 9.2: Calculating P-V Work

A tank of compressed helium is used to inflate 100 balloons for sale at a carnival on a day when the atmospheric pressure is 1.01 atm. If each balloon is inflated with 4.8 L, how much P-V work is done by the compressed helium? Express your answer in Joules.

\[
\begin{align*}
\Delta V &= V_f - V_i \\
&= 4.8L - 0 = 4.8L \\
w &= -P \Delta V \\
&= -1.01 \text{ atm} \times \frac{4.8L}{\text{balloon}} \times 100 \text{ balloons} \times \frac{101.325 \text{ J}}{\text{L-atm}} \\
&= -4.9 \times 10^4 \text{ J} \\
&= -49 \text{ kJ} \checkmark
\end{align*}
\]

Sample Exercise 9.3: Relating \( \Delta E, q, \) and \( w \)

The racing cars in the figure are powered by V8 engines in which the motion of each piston in its cylinder displaces a volume of 0.733 L. If combustion of the mixture of gasoline vapor and air in one cylinder releases \(-1.68 \text{ kJ of energy}\), and if 33\% of the energy does P-V work, how much pressure, on average, does the combustion reaction mixture exert on each piston? How much heat flows from the reaction mixture to its surroundings?

Plan: \( \Delta E \rightarrow -P \Delta V \rightarrow P \rightarrow q \)

From \( \Delta E = q - P \Delta V \)

\[
\begin{align*}
\Delta V &= 0.733 \text{ L} \\
33\% &= \frac{\Delta V}{L}
\end{align*}
\]
Enthalpy and Enthalpy Changes

Many physical and chemical changes take place at constant pressure, e.g., biochemical reactions, laboratory reactions, etc.

The heat flow under constant pressure conditions is called Enthalpy (H)

\[ H = E + PV \]

Enthalpy is a measure of the system’s total energy:

H is hard to quantify exactly, but the change in enthalpy \( \Delta H \) can be easily measured.

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

and it can be shown that this equal to the heat flow at constant pressure \( q_p \)
Enthalpy Sign Conventions

<table>
<thead>
<tr>
<th>Description</th>
<th>Enthalpy Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exothermic</td>
<td>$\Delta H &lt; 0$</td>
</tr>
<tr>
<td>Endothermic</td>
<td>$\Delta H &gt; 0$</td>
</tr>
</tbody>
</table>

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**Heat Capacity ($C_p$)**

Note: the symbol is **upper case**

The heat required to raise the temperature of an object 1.0 °C (constant pressure)

Units are J/°C → **mass independent**

We will use Heat Capacity later in the chapter when we talk about calorimetry, as well as in the lab

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**Specific Heat ($c_p$)**

Note: the symbol is **lower case**

The heat required to raise the temperature of 1 gram of a substance 1 °C (constant pressure)

Units are J/g °C

We will be using Specific Heat in the lab
Calculating Heat Transfer Within the Same Phase

\[ q = m \cdot c_p \cdot \Delta T \]

\[ \Delta T = T_{\text{final}} - T_{\text{initial}} \]

units = g \cdot \frac{J}{g \cdot ^\circ C} = \text{Joules}

Sign Conventions

\[ \Delta T = T_{\text{final}} - T_{\text{initial}} \]

If \( T_{\text{final}} < T_{\text{initial}} \) then \( q < 0 \) and heat transferred OUT OF object (EXOTHERMIC)

If \( T_{\text{final}} > T_{\text{initial}} \) then \( q > 0 \) and heat transferred INTO object (ENDOTHERMIC)
Phase Changes and Heat Flow
\( \Delta H_{\text{fusion}} \) and \( \Delta H_{\text{vap}} \)

- **Endothermic**
  - Water vapor
  - \( \Delta H_{\text{vap}} = +40.67 \text{ kJ/mol} \)
  - Liquid water
  - \( \Delta H_{\text{fus}} = +6.01 \text{ kJ/mol} \)
  - Ice
  - \( \Delta H_{\text{solid}} = -6.01 \text{ kJ/mol} \)

- **Exothermic**

Calculating Heat Transfer Across a Phase Boundary

- **Molar heat of fusion:**
  - \( \Delta H_{\text{fus}} = \text{heat needed to convert 1 mole of a solid at its melting point to 1 mole of liquid.} \)
  - \( q = n \Delta H_{\text{fus}} \)

- **Molar heat of vaporization:**
  - \( \Delta H_{\text{vap}} = \text{heat needed to convert 1 mole of a liquid at its boiling point to 1 mole of vapor.} \)
  - \( q = n \Delta H_{\text{vap}} \)

- **The same sign conventions apply**
Heating Curves and Heat Capacity
Hot Soup on a Cold Day, p. 376
Sample Exercise 9.4: Calculating Heat Transfer Across Phase Boundaries

Between periods of a hockey game, and ice-resurfacing machine spreads $3.00 \times 10^2$ liters of hot (40.0 °C) water across a skating rink. How much heat must the water lose as it cools to its freezing point, freezes, and further cools to -10 °C? Assume that the water is the system, and that its density if 0.992 g/mL at 40.0 °C.

Heat Transfer from One Substance to Another Cold Drinks on a Hot Day, p. 379
Sample Exercise 9.5: Calculating a Final Temperature from Heat Gain and Loss

Suppose you wish to make a glass of freshly brewed iced tea. You start with exactly 1 cup (237 g) of hot (100.0 °C) brewed tea in an insulated mug and add 2.50 x 10² g of ice initially at -18.0 °C. All of the ice melts. What is the final temperature of the tea? Assume that the tea has the same thermal properties as water.

Determining Specific Heat, p. 381
Determining Specific Heat, p. 381

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Heats of Reaction and Calorimetry

The measurement of heat changes in a chemical reaction ($\Delta H$)

Heat changes in chemical reactions are determined by the temperature change of a water reservoir in contact with the reaction.

- temperature increases = exothermic reaction ($\Delta H < 0$)
- decreases = endothermic reaction ($\Delta H > 0$)

There are two types of calorimetry -

1. constant volume or "bomb" calorimetry, and
2. constant pressure or “coffee cup” calorimetry (like in lab)

Calorimetry requires the use of the Specific Heat ($c_p$) and the Heat Capacity ($C_p$) discussed previously.

Methods of Determining $\Delta H_{rxn}$

From calorimetry experiments:

- Constant Pressure (“coffee cup”) calorimetry: $q_{rxn} = - q_{calor}$
- Constant Volume (“bomb”) calorimetry: $\Delta H_{rxn} = -C_{p,calor} \Delta T$

From enthalpies of formation:

$$\Delta H_{rxn}^\circ = \Sigma n_p \Delta H_i^\circ (\text{products}) - \Sigma n_r \Delta H_i^\circ (\text{reactants})$$

$\Delta H_i^\circ$ values for substances in Appendix 4.

Using Hess’s Law (Section 9.6).

Heats of Reaction and Calorimetry

The measurement of heat changes in a chemical reaction ($\Delta H$)
Thermochemical Equations

The chemical equation of a reaction that includes heat as a “product” (exothermic) or as a “reactant” (endothermic)

Exothermic:

\[ 2 \text{C}_4\text{H}_{10}(g) + 13 \text{O}_2(g) \rightarrow 8 \text{CO}_2(g) + 10 \text{H}_2\text{O}(l) \quad \Delta H_{\text{rxn}} = -5754 \text{ kJ} \]

\[ 2 \text{C}_4\text{H}_{10}(g) + 13 \text{O}_2(g) \rightarrow 8 \text{CO}_2(g) + 10 \text{H}_2\text{O}(l) + 5754 \text{ kJ} \]

Endothermic:

\[ 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(l) \quad \Delta H_{\text{rxn}} = +286 \text{ kJ} \]

\[ 286 \text{ kJ} + 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(l) \]

Constant Pressure Calorimetry

“Coffee Cup Calorimetry”

NOTE: the book ignores the heat that leaks into the calorimeter itself, but we will take it into account.

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

\[ = - (q_{\text{water}} + q_{\text{cup}}) \]
Sample Exercise 9.6 (modified)
“Coffee Cup Calorimetry”

A “coffee-cup” calorimeter has a heat capacity, \( C_p \), equal to 52.1 J/°C. When 0.200 L of 0.200 M HCl is mixed with 0.200 L of 0.200 M NaOH, the temperature of the mixture increases from 22.15 °C to 23.48 °C. If the densities of the two solutions are 1.00 g/mL, what is the value of \( \Delta H_{rxn} \)?

Bomb Calorimetry (Constant V)

A bomb calorimeter is a constant-volume device used to measure the heat of a combustion reaction.
Sample Exercise 9.6: Calculating $\Delta H_{\text{rxn}}$ from Calorimetry Data

Before we can determine the energy change of a reaction run in a calorimeter, we must determine the heat capacity of the calorimeter, $C_{\text{calor}}$.

What is the value of $C_{\text{calor}}$ of a bomb calorimeter if burning 1.000 g of benzoic acid in it increases the temperature by 7.248 °C? The heat of combustion of benzoic acid is $\Delta H_{\text{comb}} = -26.38$ kJ/g.

Practice Exercise, p. 386

When a 0.500 g mixture of hydrocarbons is burned in the bomb calorimeter in the previous problem, its temperature rises by 6.76 °C. How much energy in kJ is released during the combustion? How much energy is released with the combustion of 1.000 g?
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Methods of Determining $\Delta H_{\text{rxn}}$

1. From calorimetry experiments:
   - Constant Volume: $\Delta H_{\text{rxn}} = -C_p \Delta T$
   - Constant Pressure: $q_{\text{rxn}} = -q_{\text{calor}}$

2. Using Hess’s Law

3. From enthalpies of formation:
   - $\Delta H_{\text{rxn}}^\circ = \Sigma n_p \Delta H_i^\circ(\text{products}) - \Sigma n_r \Delta H_i^\circ(\text{reactants})$
   - $\Delta H_i^\circ$ values for substances in Appendix 4.
Enthalpy: A State Function

- Depends only on the difference between initial and final state of the system.
  - Independent of path between states.

Hess’s Law

- Hess’s Law of constant heat of summation:
  - The $\Delta H$ of a reaction that is the sum of two or more reactions is equal to the sum of the $\Delta H$ values of the constituent reactions.

\[
\begin{align*}
1. \quad \text{CH}_4(g) + \text{H}_2\text{O}(g) & \rightarrow \text{CO}(g) + 3\text{H}_2(g) \quad \Delta H_1 \\
2. \quad \text{CO}(g) + \text{H}_2\text{O}(g) & \rightarrow \text{CO}_2(g) + \text{H}_2(g) \quad \Delta H_2 \\
3. \quad \text{CH}_4(g) + 2\text{H}_2\text{O}(g) & \rightarrow \text{CO}_2(g) + 4\text{H}_2(g) \quad \Delta H_3 \\
\end{align*}
\]

\[\Delta H_3 = \Delta H_1 + \Delta H_2\]
Hess’s Law (cont.)

Reactants taking an indirect path

\[
\begin{align*}
CO(g) + 3H_2(g) & \rightarrow +H_2O(g) \\
\Delta H^\circ_2 &= -41 \text{ kJ} \\
4H_2(g) + CO_2(g) & \rightarrow \\
\Delta H^\circ_1 &= +206 \text{ kJ}
\end{align*}
\]

Reactants taking a direct path

\[
\begin{align*}
CH_4(g) + H_2O(g) & \rightarrow \\
\Delta H^\circ_3 &= \Delta H^\circ_1 + \Delta H^\circ_2 = +165 \text{ kJ}
\end{align*}
\]

Calculations Using Hess’s Law

1. If a reaction is reversed, ΔH sign changes.

\[
\begin{align*}
N_2(g) + O_2(g) & \rightarrow 2NO(g) \quad \Delta H = 180 \text{ kJ} \\
2NO(g) & \rightarrow N_2(g) + O_2(g) \quad \Delta H = -180 \text{ kJ}
\end{align*}
\]

2. If the coefficients of a reaction are multiplied by an integer, ΔH is multiplied by that same integer.

\[
\begin{align*}
6NO(g) & \rightarrow 3N_2(g) + 3O_2(g) \quad \Delta H = 3(-180 \text{ kJ}) \\
\Delta H &= -540 \text{ kJ}
\end{align*}
\]
Problem: Using Hess’s Law

Using the following data, calculate the enthalpy change for the reaction:

\[ \text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) \quad \Delta H_{\text{rxn}} = ? \]

\[ \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad -285.8 \text{ kJ} \]
\[ \text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) + 2\text{CO}_2(g) \quad -1411 \text{ kJ} \]
\[ \text{C}_2\text{H}_6(g) + \frac{7}{2}\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(l) + 2\text{CO}_2(g) \quad -1560 \text{ kJ} \]

Methods of Determining \( \Delta H_{\text{rxn}} \)

1. From calorimetry experiments:
   - **Constant Volume**: \( \Delta H_{\text{rxn}} = -C_p \Delta T \)
   - **Constant Pressure**: \( q_{\text{rxn}} = -q_{\text{calor}} \)

2. Using Hess’s Law

3. From enthalpies of formation:
   - \( \Delta H_{\text{rxn}}^\circ = \Sigma n_p \Delta H_i^\circ(\text{products}) - \Sigma n_r \Delta H_i^\circ(\text{reactants}) \)
   - \( \Delta H_i^\circ \) values for substances in Appendix 4.
Standard Enthalpies of Formation

\[ \Delta H_f = \text{enthalpy change associated with the formation of 1 mole of a substance from the elements in their natural states} \]

\[ \Delta H^o_f = \text{STANDARD ENTHALPY OF FORMATION at 25 °C and 1 atmosphere of pressure (TABULATED)} \]

\[ \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H^o_f = -285.8 \text{ kJ/mol} \]

\[ \text{C}(s) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) \quad \Delta H^o_f = -74.8 \text{ kJ/mol} \]

Standard Enthalpies of Formation

Most standard enthalpies of formation are exothermic, but sometimes they are endothermic:

\[ 2\text{C}(s) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_2(\text{g}) \quad \Delta H^o_f = +226.7 \text{ kJ} \]

Compounds like acetylene (used in welding), which have endothermic enthalpies of formation, are good reservoirs of chemical potential energy.
Standard Enthalpies of Formation – cont’d

Note that $\Delta H^0_f$ for elements in their standard states (most stable form) are $= 0$

Forming an element in its standard state from the same element in its standard state amounts to no release of heat at all.

$$\Delta H^0_f (O_2) = 0 \quad \Delta H^0_f (C, \text{ graphite}) = 0$$
$$\Delta H^0_f (O_3) = 142 \text{ kJ/mol} \quad \Delta H^0_f (C, \text{ diamond}) = 1.90 \text{ kJ/mol}$$

Sample Exercise 9.9
Recognizing Formation Reactions

Which of the following reactions are formation reactions at 25°C? For those that are not, explain why not.

a. $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ_{\text{rxn}} = -241.4 \text{ kJ}$
b. $\text{C}_{\text{graphite}}(s) + 2 \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CH}_3\text{OH}(\ell) \quad \Delta H^\circ_{\text{rxn}} = -238.7 \text{ kJ}$
c. $\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \quad \Delta H^\circ_{\text{rxn}} = -802.3 \text{ kJ}$
d. $\text{P}_4(s, \text{ white}) + 6 \text{Cl}_2(g) \rightarrow 4 \text{PCl}_3(\ell) \quad \Delta H^\circ_{\text{rxn}} = -1278 \text{ kJ}$
Sample Exercise 9.10 – Calculating Standard Heats of Reaction from Standard Heats of Formation

Use the appropriate standard heat of formation values to calculate \( \Delta H_{\text{rxn}}^\circ \) for the combustion of propane:

\[
C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(g)
\]

\[
\Delta H_{\text{rxn}}^\circ = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})
\]

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\[ \Delta H^0 = \text{total energy input} - \text{total energy released} = \sum \text{BE(reactants)} - \sum \text{BE(products)} \]

**Break** = endothermic

**Make** = exothermic

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

**Bond energy** = the average energy required to break a particular type of bond.

<table>
<thead>
<tr>
<th>Bond Energy</th>
<th>( \Delta H^0 ) (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2(g) \rightarrow \text{H}(g) + \text{H}(g) )</td>
<td>436 kJ</td>
</tr>
<tr>
<td>( \text{Cl}_2(g) \rightarrow \text{Cl}(g) + \text{Cl}(g) )</td>
<td>243 kJ</td>
</tr>
<tr>
<td>( \text{HCl}(g) \rightarrow \text{H}(g) + \text{Cl}(g) )</td>
<td>431 kJ</td>
</tr>
<tr>
<td>( \text{O}_2(g) \rightarrow \text{O}(g) + \text{O}(g) )</td>
<td>495 kJ</td>
</tr>
<tr>
<td>( \text{N}_2(g) \rightarrow \text{N}(g) + \text{N}(g) )</td>
<td>941 kJ</td>
</tr>
</tbody>
</table>
Table of Average Covalent Bond Lengths and Bond Energies – can be used to estimate $\Delta H^\circ_{\text{rxn}}$

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length (pm)</th>
<th>Bond Energy (kJ/mol)</th>
<th>Bond</th>
<th>Bond Length (pm)</th>
<th>Bond Energy (kJ/mol)</th>
<th>Bond</th>
<th>Bond Length (pm)</th>
<th>Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>154</td>
<td>348</td>
<td>N—N</td>
<td>104</td>
<td>391</td>
<td>S—S</td>
<td>294</td>
<td>266</td>
</tr>
<tr>
<td>C≡C</td>
<td>134</td>
<td>614</td>
<td>N≡N</td>
<td>147</td>
<td>163</td>
<td>S—H</td>
<td>134</td>
<td>347</td>
</tr>
<tr>
<td>C≡N</td>
<td>120</td>
<td>839</td>
<td>N≡N</td>
<td>124</td>
<td>418</td>
<td>H—H</td>
<td>74</td>
<td>436</td>
</tr>
<tr>
<td>C≡N</td>
<td>147</td>
<td>293</td>
<td>N≡N</td>
<td>110</td>
<td>945</td>
<td>H—F</td>
<td>92</td>
<td>567</td>
</tr>
<tr>
<td>C≡N</td>
<td>127</td>
<td>615</td>
<td>N—O</td>
<td>136</td>
<td>201</td>
<td>H—Cl</td>
<td>127</td>
<td>431</td>
</tr>
<tr>
<td>C≡O</td>
<td>116</td>
<td>891</td>
<td>N≡O</td>
<td>122</td>
<td>607</td>
<td>H—Br</td>
<td>141</td>
<td>366</td>
</tr>
<tr>
<td>C≡O</td>
<td>143</td>
<td>135</td>
<td>N≡O</td>
<td>106</td>
<td>678</td>
<td>H—I</td>
<td>161</td>
<td>299</td>
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<tr>
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<td>743</td>
<td>O≡O</td>
<td>148</td>
<td>146</td>
<td>F—F</td>
<td>143</td>
<td>155</td>
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<tr>
<td>C≡O</td>
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<td>1072</td>
<td>O≡O</td>
<td>121</td>
<td>498</td>
<td>Cl—Cl</td>
<td>200</td>
<td>243</td>
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<tr>
<td>C≡H</td>
<td>110</td>
<td>413</td>
<td>O—H</td>
<td>96</td>
<td>463</td>
<td>Br—Br</td>
<td>228</td>
<td>193</td>
</tr>
<tr>
<td>C≡F</td>
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<td>485</td>
<td>S—O</td>
<td>151</td>
<td>265</td>
<td>I—I</td>
<td>266</td>
<td>151</td>
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<tr>
<td>C≡Cl</td>
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<td>328</td>
<td>S—O</td>
<td>143</td>
<td>523</td>
<td></td>
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</tbody>
</table>

*The bond energy of the C≡O bond in CO₂ is 799 kJ/mol.

Use bond energies to calculate the enthalpy change for:

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

$\Delta H^0 = \sum \text{BE(reactants)} - \sum \text{BE(products)}$

<table>
<thead>
<tr>
<th>Type of bonds broken</th>
<th>Number of bonds broken</th>
<th>Bond energy (kJ/mol)</th>
<th>Energy change (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of bonds formed</th>
<th>Number of bonds formed</th>
<th>Bond energy (kJ/mol)</th>
<th>Energy change (kJ)</th>
</tr>
</thead>
</table>