Chapter 6
Thermochemistry

Every chemical and physical process involves an exchange of energy between the reaction and the rest of the universe. Thermochemistry involves the study of this exchange of energy.

Energy

- **energy** is broadly defined as the capacity to do work. (includes force × distance as well as electrical work)
- potential energy: energy due to position or composition
- kinetic energy: energy of motion

System, Surroundings, and Universe; Heat and Work

- **internal energy, E**: sum of potential and kinetic energy of all particles that make up system
  \[
  \Delta E = E_{\text{FINAL}} - E_{\text{INITIAL}} = E_{\text{PRODUCTS}} - E_{\text{REACTANTS}}
  \]
- **heat, q**: energy transfer as a result of a difference in temperature (ONLY)
- **work, w**: energy transfer when an object is moved by a force (also includes electrical work)
  \[
  \Delta E_{\text{SYS}} = q + w
  \]
  pressure-volume work: work in which volume changes against an external pressure.
  \[
  w = -P\Delta V
  \]

First Law of Thermodynamics aka Law of Conservation of Energy

Energy is “conserved”; you can convert energy from one form to another but you cannot create or destroy energy.

\[
\Delta E_{\text{SYS}} + \Delta E_{\text{Surr}} = \Delta E_{\text{Univ}} = 0
\]

Units of Energy

SI: joule (J) \(1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \) (= 1 N·m, units of force × distance)

In chemistry and many other sciences, the **calorie** (cal) still common
1 cal = 4.184 J

NOTE: the nutritional Calorie = 1000 chemical calories (= 1 kcal)
State Functions

- A state function depends only on the present state of the system, not on the path taken to get there.
  - E.g., \( T, P, V, \Delta E \)
  - State functions usually written with capital letter symbols.

Enthalpy, \( \Delta H \)

- Enthalpy is the heat of a reaction at constant pressure.
- Enthalpy always written as \( \Delta H \), not just \( H \). No convenient uniform reference point to set as zero point.
- In many cases, \( \Delta E \approx \Delta H \) at constant \( P \) if little or no work.
  
  This is not so if \( w \) is very large, i.e., if \( P \Delta V \) is a large quantity (a large \( \Delta V \) either way).

Names for Signs of Enthalpy Change

- **Exothermic**: “heat out” \( \Delta H \) negative
- **Endothermic**: “heat in” \( \Delta H \) positive

Types of Enthalpy Change

- **Heat of reaction** (\( \Delta H_{\text{RXN}} \)): enthalpy change for a chemical reaction
  
  \[
  2\text{Al(s)} + \text{Fe}_2\text{O}_3(\text{s}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 2\text{Fe(s)} \quad \Delta H = \Delta H_{\text{RXN}} = -851 \text{ kJ}
  \]

- **Heat of combustion** (\( \Delta H_{\text{COMB}} \)): enthalpy change for the chemical reaction when 1 mole of a substance reacts with \( \text{O}_2 \) (combustion)
  
  \[
  \text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O(l)} \quad \Delta H = \Delta H_{\text{COMB}} = -2202 \text{ kJ}
  \]

- **Heat of formation** (\( \Delta H_f \)): enthalpy change for the chemical reaction when 1 mole of a compound is produced from its component elements
  
  \[
  \text{Na(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)} \quad \Delta H = \Delta H_f = -411.1 \text{ kJ}
  \]

- **Heat of fusion** (\( \Delta H_{\text{FUS}} \)): enthalpy change for the melting of 1 mole of a substance
  
  \[
  \text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)} \quad \Delta H = \Delta H_{\text{FUS}} = +6.0 \text{ kJ}
  \]

- **Heat of vaporization** (\( \Delta H_{\text{VAP}} \)): enthalpy change for the vaporization of 1 mole of a substance
  
  \[
  \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)} \quad \Delta H = \Delta H_{\text{VAP}} = +44.0 \text{ kJ}
  \]

**Protip**

Heat of fusion and heat of vaporization are both always endothermic. For a substance, the heat of vaporization is always larger than the heat of fusion.
**Bond Energies and Enthalpy**

$\Delta H_{\text{RXN}}$ results primarily from differences in the strengths of bonds in the reactants and products.

Breaking bonds is **ENDO**thermic.
Forming bonds is **EXO**thermic.

- **Average Bond Enthalpy:** the amount of energy required to break 1 mole of bonds in the gas phase.
  Table of average bond enthalpies in **Table 9.2**.

Example: Estimate $\Delta H_{\text{RXN}}$:

\[
\begin{align*}
\text{CH}_4(g) + 2\text{O}_2(g) &\rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \\
\end{align*}
\]

$\Delta H = \Sigma nD(\text{bonds broken}) - \Sigma nD(\text{bonds formed})$  
[“$D$” for bond “D”issociation energy, old-fashioned name for bond enthalpy]
Heat Capacity

- **specific heat capacity, c**: quantity of heat required to raise temperature of 1 gram of material by 1 K (or 1 °C); an intensive property. (molar heat capacity $C_m$ is similar for 1 mole of substance)

Constant-Pressure Calorimeter

- **SYSTEM** = reaction
- **SURROUNDINGS** = water, thermometer, cups, stirrer, everything else!

Hess’s Law of Heat Summation

- **Hess’s law**: if a reaction is carried out in a number of steps, $\Delta H$ for the overall reaction is the sum of $\Delta H$ for each individual step.

Example: What is $\Delta H$ for this reaction

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

given the following information:

$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H = -802 \text{ kJ}$$

$$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H = +44 \text{ kJ}$$

- reverse equation: change sign of $\Delta H$
- multiply all coefficients by a constant: multiply $\Delta H$ by same constant
- add equations: add $\Delta H$ values
Standard States (e.g., \(\Delta H^\circ\))

1. Compounds
   - gas: \(\text{P} = 1\ \text{bar} (1\ \text{bar} = 100\ \text{kPa} \approx 1\ \text{atm})\)
   - liquids/solids: most stable form at \(T\) of interest and \(\text{P} = 1\ \text{bar}\)
   - aqueous solution: 1 M concentration

2. Elements: most stable form at \(T\) of interest and \(\text{P} = 1\ \text{bar}\)
   - \(\Delta H^\circ\) usually tabulated at 25 °C (298 K)

Standard Heat of Formation, \(\Delta H^\circ_F\)

- always tabulated per one mole of substance
- extensive list of \(\Delta H^\circ_F\) values in Appendix B of text

Note:
1. \(\Delta H^\circ_F\) for element in standard state = 0 (KNOW)
2. Most compounds have negative \(\Delta H^\circ_F\) (some don’t)

\[
\Delta H_{\text{RXN}} = \sum n\Delta H^\circ_F(\text{products}) - \sum n\Delta H^\circ_F(\text{reactants})
\]

Example: Calculate \(\Delta H^\circ_{\text{RXN}}\):

\[
\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})
\]

\[
\Delta H^\circ_F
\]

\[
\text{__________} \quad \text{__________} \quad \text{__________} \quad \text{__________} \quad \text{__________}
\]