Chapter 6

Thermochemistry: Energy Flow and Chemical Change

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.

Open System: Exchanges both E and matter with Surroundings;
Closed System: Exchanges only E with Surroundings;
Isolated System: Exchanges NEITHER with Surroundings.

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.

Sign is from the point of view of the System.

Figure 6.1 A chemical system and its surroundings.

The system in this case is the contents of the reaction flask. The surroundings comprise everything else, including the flask itself.

An Auto A Battery A perfect Thermos

Open Closed Isolated
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 system transferring energy as heat only.

\[ \text{A system losing energy as work only.} \]

Chapter 6: First Law

A system transferring energy as heat only.

Chapter 6: First Law

Work (w)

Motion against an opposing force; a directed motion thru a distance: \( w = F \cdot s \)  

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)

If \( P_{\text{ext}} \) does change in infinitesimally small units, then process is REVERSIBLE; a process in which an infinitesimally small change in the opposite direction will cause the process to reverse direction.

Work

If \( P_{\text{ext}} \) is constant, then work is done on the system.

Figure 6.5 Pressure-volume work.
An expanding gas pushing back the atmosphere does \( PV \) work (\( w = -P \Delta V \)).

Heat (\( q \))

- More familiar way to transfer \( E \)
- \( \text{Sys and Surr are at different } T \)'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
- \( q = -q_{\text{surr}} \)
- Exothermic vs Endothermic

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

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

A bomb calorimeter.

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Table 6.1
<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat Capacity (J/g•°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>4.184</td>
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<tr>
<td>Ethanol</td>
<td>2.46</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.902</td>
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<tr>
<td>Solid metals</td>
<td></td>
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<td>Wood</td>
<td>1.76</td>
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<tr>
<td>Copper</td>
<td>0.05</td>
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<td>Graphite</td>
<td>0.10</td>
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<td>Brass</td>
<td>0.37</td>
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<tr>
<td>Copper</td>
<td>0.38</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.900</td>
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</table>

Selected Heat Capacities ($C_s$ and $C_m$)

- 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 ($C_s = 0.106 \text{ J/g•C}$): 197.4 °C

\[ C_{m,V} = \frac{\Delta U}{\Delta T} \]
\[ C_{m,P} = \frac{\Delta H}{\Delta T} \]

\[ C_{m,V} = C_{m,P} + R \]

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/gK.

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:

\[ q = 0.387 \text{ J/gK} \times 125 \text{ g} \times (300°C - 25°C) = 1.33 \times 10^4 \text{ J} \]
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 adiabatic (\( q = 0 \)) or diathermic (\( w = 0 \))
- Both \( q \) and \( w \) are path dependent

Internal Energy (\( U \)) is a State Function

To determine the change in a state function, choose any convenient path (even if the real path is too complicated to calculate)

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 \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) to expand, which pushes the pistons outward. Excess heat is removed by the car’s cooling system. If the expanding gases do \( +451 \text{ J} \) of work on the pistons and the system loses \( -325 \text{ J} \) to the surroundings as heat, calculate the change in energy. Answer 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:

- \( \Delta E = q + w = 325 \text{ J} + (-451 \text{ J}) = -126 \text{ J} \)
- \( -126 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -0.126 \text{ kJ} \)
- \( -0.126 \text{ kJ} \times \frac{4.184 \text{ kcal}}{1 \text{ kJ}} = -0.526 \text{ kcal} \)

Enthalpy (H)

The heat released or absorbed by a system at constant pressure

- For Constant Volume systems \( \Delta H = q \)
- 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: \( H = U + PV \)
- \( \Delta H = \Delta U + P \Delta V = q - P_\text{ext} \Delta V + P \Delta V = q - P_\text{ext} \Delta V + P_\text{int} \Delta V \)
- 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

- \( w = \Delta P V \)
- \( H = E + PV \)
- \( \Delta H \equiv \Delta E \) 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 \( \gg \) \( P \Delta V \).

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:
  \( \Delta X = \Delta n_{X_{\text{prod}}} - \Delta n_{X_{\text{rnt}}} \)
- The value for the reverse process is equal in magnitude BUT opposite in sign:
  \( \Delta X_{\text{rev}} = -\Delta X_{\text{fwd}} \)
- Multiplication of a process by number multiplies the \( X \) value by that number:
  If \( A \rightarrow 2B \) \( \Delta X_A = 7 \) then \( 3A \rightarrow 6B \) \( \Delta X_A = 3 \Delta X_A = 21 \)
- The sum of all of the \( X \) values making up a process is equal to the \( X \) overall for that process:
  \( \Delta X_{\text{overall}} = \Delta X_{\text{step 1}} + \Delta X_{\text{step 2}} + \Delta X_{\text{step 3}} + \ldots \)
ΔH of Physical Processes

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>Freezing point (K)</th>
<th>ΔHfus (kJ/mol)</th>
<th>Boiling point (K)</th>
<th>ΔHvap (kJ/mol)</th>
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</thead>
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<tr>
<td>acetone</td>
<td>CH₃COCH₃</td>
<td>177.0</td>
<td>3.73</td>
<td>369.4</td>
<td>287.4</td>
</tr>
<tr>
<td>ammonia</td>
<td>NH₃</td>
<td>195.4</td>
<td>6.63</td>
<td>217.7</td>
<td>27.4</td>
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<td>acetaldehyde</td>
<td>C₂H₄O</td>
<td>82.0</td>
<td>1.2</td>
<td>187.6</td>
<td>49.5</td>
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<td>butane</td>
<td>C₄H₁₀</td>
<td>278.4</td>
<td>15.35</td>
<td>335.2</td>
<td>108.8</td>
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<td>ethanol</td>
<td>C₂H₅OH</td>
<td>138.7</td>
<td>4.69</td>
<td>311.5</td>
<td>46.1</td>
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<td>He</td>
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<td>0.021</td>
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<td>methane</td>
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<td>1.99</td>
<td>383.7</td>
<td>49.5</td>
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<td>ethane</td>
<td>C₂H₆</td>
<td>373.2</td>
<td>5.96</td>
<td>407.4</td>
<td>20.5</td>
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<tr>
<td>water</td>
<td>H₂O</td>
<td>273.2</td>
<td>4.93</td>
<td>373.2</td>
<td>46.1</td>
</tr>
</tbody>
</table>

ΔH of Chemical Change

- Enthalpy change during chemical reactions important to understanding chemistry.
- Reaction Enthalpies: ΔH or ΔHₓ
- ΔH associated with Thermochemical Equations:
  2Al(s) + 6HCl(aq) → 2AlCl₃(aq) + H₂(g) ΔH = −1049 kJ
- ΔHₓ associated with certain types of reactions; corrected to a per mole basis; used in tabular collections of data: ΔHₓ = −524.5 kJ/mol for the HCl oxidation of Al
- Relation between ΔH and ΔU:
  - For reactions in which NO gas is generated: ΔH = ΔU + nC_p,TΔT
  - For reactions in which gas is generated: ΔH = ΔU + nC_p,TΔT + nC_v,TΔT

Heating Curve Calculations

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

<table>
<thead>
<tr>
<th>ΔH</th>
<th>q_wol</th>
<th>q_vap</th>
<th>q_mat</th>
<th>q_pd</th>
<th>q_kin</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mol(37 J/mol·K)(−5 K)</td>
<td>0.5 mol(6.0 J/mol)</td>
<td>0.5 mol(40.7 J/mol)</td>
<td>0.5 mol(34 J/mol·K)(20 K)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Standard Reaction Enthalpies ΔH°

ΔH° depends on conditions and phases; to allow standardization for reporting the idea of Standard State was developed.

- 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 $\Delta H_c^{\circ}$'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 at the temperature of interest.
- By definition, $\Delta H_f^{\circ}$ of an element in its most stable state:
- Allows $\Delta H_f^{\circ}$ to be calculated using $\Delta H_f^{\circ}$ of products - reactants:
  $$\Delta H_f^{\circ} = [\Delta H_f^{\circ}_{pdts} - \Delta H_f^{\circ}_{rxtnts}]$$

**Enthalpy of Combustion ($\Delta H_c^{\circ}$ or $\Delta H_{comb}^{\circ}$)**
- Defined as: the standard reaction enthalpy for the combustion of one mole of a substance in its most stable form at $T$ of interest:
  $$C_2H_6(g) + 5/2 O_2(g) \rightarrow 2 CO_2(g) + H_2O(0)$$

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 $q_{\text{mix}}$ (in J) and $\Delta H_f^{\circ}$ (in kJ/mol).

**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 $q_{\text{mix}}$ can be calculated using the mass, $c$, and $T$. The heat divided by the $M$ of water will give us the heat per mole of water formed.

**SOLUTION:**

1. **Calculating mass of water formed:**
   - $M_{\text{H}_2O} = 18.015$ g/mol
   - From the volume of 0.0750 L, the mass is calculated as:
   $$m = \rho \cdot V = 1.00 \text{ g/mL} \cdot 0.0750 \text{ L} = 75.0 \text{ g of water}$$

2. **Calculating the total volume after mixing:**
   - Total volume = 0.0750 L

3. **Calculating the heat divided by the water's mass:**
   - $c = 4.184 \text{ J/g} \cdot \text{K}$
   - $T = 27.21 - 25.00 = 2.21 \text{ K}$
   - $q_{\text{mix}} = c \cdot M \cdot T = 75.0 \text{ g of water} \cdot 4.184 \text{ J/g} \cdot \text{K} \cdot 2.21 \text{ K} = 693 \text{ J}$
   - $q_{\text{mix}} / M_{\text{H}_2O} = 693 \text{ J} / 0.0750 \text{ L} \cdot 18.015 \text{ g/mol} = 40.24 \text{ kJ/mol}$

4. **Conclusion:** The manufacturer's claim is correct.

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 O$_2$ (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)
- $q_{\text{sample}} = \text{heat capacity} \times \Delta T$
- $\Delta T = 4.937 \text{ K}$
- $q_{\text{sample}} = 8.151 \text{ kJ/K} \times 4.937 \text{ K} = 40.24 \text{ kJ}$

**SOLUTION:**
- 1 Calorie = 1 kcal = 4.184 kJ
- 10 Calorie = 41.84 kJ

The manufacturer’s claim is correct.
Sample Problem 6.8

Using the Heat of Reaction (ΔH rxn) to Find Amounts

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

\[ \text{Al}_2\text{O}_3(s) \rightarrow 2\text{Al}(l) + 1.5\text{O}_2(g) \quad \Delta H_{rn} = 1676 \text{ kJ} \]

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

**PLAN:**

**SOLUTION:**

\[
\text{2 mol Al} \times \frac{1676 \text{ kJ}}{1 \text{ mol Al}} = 3352 \text{ kJ}
\]

\[
3352 \text{ kJ} \times \frac{1 \text{ mol Al}}{2 \text{ mol Al}} = 1676 \text{ kJ}
\]

\[
= 32.20 \text{ g Al}
\]

---

Sample Problem 6.8

**SOLUTION:**

Multiply Equation B by ½ and reverse it:

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

\[ \text{Add the manipulated equations together:} \]

Equation A: CO(g) + ½ O₂(g) → CO₂(g) \quad \Delta H = -283.0 \text{ kJ} \]

½ Equation B (reversed):

\[ \text{½ NO(g)} \rightarrow \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) \quad \Delta H = -45.9 \text{ kJ} \]

\[ \text{CO(g)} + \text{NO(g)} \rightarrow \text{CO}_2(g) + \frac{1}{2} \text{N}_2(g) \quad \Delta H_{rn} = -373.3 \text{ kJ} \]

---

Table 6.3 Selected Standard Enthalpies of Formation at 25°C (298K)

<table>
<thead>
<tr>
<th>Formula</th>
<th>∆H° f (kJ/mol)</th>
<th>Formula</th>
<th>∆H° f (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(l)</td>
<td>0</td>
<td>CCl(g)</td>
<td>-92.3</td>
</tr>
<tr>
<td>CaCO₃(s)</td>
<td>-935.1</td>
<td>HCl(g)</td>
<td>218</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td>N₂(g)</td>
<td>0</td>
</tr>
<tr>
<td>Cl₂</td>
<td>-1206.9</td>
<td>H₂(g)</td>
<td>0</td>
</tr>
<tr>
<td>C(graphite)</td>
<td>1.9</td>
<td>Cl₂(g)</td>
<td>0</td>
</tr>
<tr>
<td>CO(g)</td>
<td>-110.5</td>
<td>N₂(g)</td>
<td>0</td>
</tr>
<tr>
<td>CO₂(g)</td>
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<td>N₂(g)</td>
<td>0</td>
</tr>
<tr>
<td>CH₄(g)</td>
<td>-74.9</td>
<td>NH₄(g)</td>
<td>45.9</td>
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<tr>
<td>CH₃OH(l)</td>
<td>-238.6</td>
<td>NH₄(g)</td>
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<tr>
<td>CH₄(s)</td>
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<td>NiO(g)</td>
<td>90.3</td>
</tr>
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<td>Cl₂</td>
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<td>NiO₃(s)</td>
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<td>Cl₂</td>
<td>-214.2</td>
<td>O₂(g)</td>
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</tbody>
</table>

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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 ∆H° rxn:

(a) Silver chloride, AgCl, a solid at standard conditions.
(b) Calcium carbonate, CaCO₃, 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 ∆H° rxn in Table 6.3 or Appendix B.

---

Sample Problem 6.9

Using Hess's Law to Calculate an Unknown ∆H

**PROBLEM:** Two gaseous pollutants that form in auto exhausts are CO and NO. An environmental chemist is trying 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 ∆H:

\[ \text{CO}_2(g) \rightarrow \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \quad \Delta H_{rxn} = 1676 \text{ kJ} \]

\[ \text{CO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g) + \text{O}_2(g) \quad \Delta H_{rxn} = -283.0 \text{ kJ} \]

\[ \text{CO}(g) + \text{NO}(g) \rightarrow \text{CO}_2(g) + \frac{1}{2} \text{N}_2(g) \quad \Delta H_{rxn} = ? \]

**PLAN:** Manipulate Equations A and/or B and their ∆H values to get to the target equation and its ∆H. All substances except those in the target equation must cancel.
Sample Problem 6.9

**SOLUTION:**

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

\[
Ag(s) + \frac{1}{2}Cl_2(g) \rightarrow AgCl(s) \quad \Delta H_f^\circ = -127.0 \text{ kJ}
\]

(b) Calcium carbonate, CaCO₃, a solid at standard conditions.

\[
Ca(s) + C(graphite) \rightarrow CaCO_3(s) \quad \Delta H_f^\circ = -1206.9 \text{ kJ}
\]

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

\[
\frac{1}{2}N_2(g) + H_2(g) \rightarrow HCN(g) \quad \Delta H_f^\circ = 130 \text{ kJ}
\]

---

**Table 6.4 Standard Enthalpies of Combustion at 25°C (kJ mol⁻¹)**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>(\Delta H_f^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>C₆H₆(l)</td>
<td>-3269</td>
</tr>
<tr>
<td>Carbon</td>
<td>C(石墨)</td>
<td>-394</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH(l)</td>
<td>-1360</td>
</tr>
<tr>
<td>Ethyne (acetylene)</td>
<td>C₂H₂(g)</td>
<td>-1500</td>
</tr>
<tr>
<td>Glucose</td>
<td>C₆H₁₂O₆(s)</td>
<td>-2808</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H₂(g)</td>
<td>-286</td>
</tr>
<tr>
<td>Methane</td>
<td>C₂H₆(g)</td>
<td>-890</td>
</tr>
<tr>
<td>Octane</td>
<td>C₈H₁₈(g)</td>
<td>-5871</td>
</tr>
<tr>
<td>Propene</td>
<td>C₃H₆(g)</td>
<td>-2230</td>
</tr>
<tr>
<td>Ammonia</td>
<td>CO₂H₂(g)</td>
<td>-632</td>
</tr>
</tbody>
</table>

*As in a combustion, carbon is converted into carbon dioxide, hydrogen into liquid water, and nitrogen into nitrogen gas. More values are given in Appendix 2B.

---

**Hess’ Law of Heat Summation**

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

\[ H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \quad \Delta H_f^\circ = ? \]

Given the following individual reactions:

- \( NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) \quad \Delta H_f^\circ = -75.0 \text{ kJ} \)
- \( N_2(g) + 3H_2(g) \rightarrow 2NH_3(s) \quad \Delta H_f^\circ = -906 \text{ kJ} \)
- \( N_2(g) + 4HCl(g) \rightarrow 2NH_4Cl(s) \quad \Delta H_f^\circ = -268.6 \text{ kJ} \)

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

**Step 1**

\[ \begin{align*}
2NH_3(g) + 2H_2(g) + 3HCl(g) &\rightarrow 2NH_4Cl(s) + H_2(g) \\
\Delta H_f^\circ &\text{of step 1} = \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants}) \\
&= \Delta H_f^\circ (\text{Products}) - \Delta H_f^\circ (\text{Reactants})
\end{align*} \]

**Step 2**

\[ \begin{align*}
2NH_4Cl(s) + H_2(g) &\rightarrow 2NH_3(g) + HCl(g) \\
\Delta H_f^\circ &\text{of step 2} = \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants}) \\
&= \Delta H_f^\circ (\text{Products}) - \Delta H_f^\circ (\text{Reactants})
\end{align*} \]

So \[ \Delta H_f^\circ = \Delta H_f^\circ (\text{step 1}) + 2\cdot\Delta H_f^\circ (\text{step 2}) + \Delta H_f^\circ (\text{step 2}) \]

\[ \Delta H_f^\circ = -184.64 \text{ kJ} \]

---

**Sample Problem 6.9**

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:

\[ 4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g) \]

Calculate \(\Delta H_f^\circ\) from \(\Delta H_f^\circ\) values.

**PLAN:**

Look up the \(\Delta H_f^\circ\) values and use Hess’s law to find \(\Delta H_f^\circ\).

**SOLUTION:**

\[ \Delta H_f^\circ = \sum n\Delta H_f^\circ (\text{products}) - \sum n\Delta H_f^\circ (\text{reactants}) \]

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

\[ = (4 \text{ mol}) \times (90.3 \text{ kJ mol}^{-1}) + (6 \text{ mol}) \times (-241.8 \text{ kJ mol}^{-1}) - \left[ (4 \text{ mol}) \times (-45.9 \text{ kJ mol}^{-1}) + (5 \text{ mol}) \times 0 \text{ kJ mol}^{-1}) \right] \]

\[ \Delta H_f^\circ = -906 \text{ kJ} \]
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, 76, 81, 82, 92, 97, 98, 100