Chapter 5
Thermochemistry
5.1 Energy and Energy Changes

- Energy is involved in all types of physical and chemical changes
- Energy: the capacity to do work or transfer heat
- All forms of energy are either
  - Kinetic
  - Potential
• **Kinetic energy** - energy of motion
  – Defining equation
  \[ E_k = \frac{1}{2}mu^2 \]
  – Where \( m \) is mass and \( u \) is velocity
  – Thermal - one form of kinetic energy associated with random motion
    • Monitor changes via changes in temperature
• **Potential energy** - energy of position
  – **Chemical energy** is stored within structural units of chemical substances.
  – **Electrostatic energy** is energy resulting from the interaction of charged particles.
    • Dependent on charges and distance between charges \((Q = \text{charge and } d = \text{distance})\)
    • Defining equation
    
      \[ E_{\text{el}} \propto \frac{Q_1 Q_2}{d} \]
    
      \( + E_{\text{el}} \): repulsive
    
    \( - E_{\text{el}} \): attractive
• Law of conservation of energy
  – Energy may be converted from one form to another.
  – The total amount of energy in the universe is constant.
  – Example
    • A chemical reaction (potential) gives off heat (thermal)
• Energy changes in chemical reactions
  – **System** is the part of the universe of interest.
    • Example
      – The reactants NaOH and HCl
  – **Surroundings** are the rest of the universe.
    • Example
      – When heat is given off from the reaction of NaOH and HCl, the energy is transferred from the system to the surroundings.
• **Thermochemistry**
  – The study of the transfer of heat (thermal energy) in chemical reactions.
  – **Exothermic** - transfer of heat from the system to the surroundings
  
  \[2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) + \text{energy}\]
  
  – **Endothermic** - the transfer of heat from the surroundings to the system
  
  \[\text{energy} + 2\text{HgO}(s) \rightarrow 2\text{Hg}(l) + \text{O}_2(g)\]
Comparison of Endothermic and Exothermic Processes

Exothermic:

\[ 2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \]

Endothermic:

\[ 2Hg(l) + O_2(g) \rightarrow 2HgO(s) \]

Heat given off by system

Heat absorbed by system
• Units of Energy
  – **Joule (J)** is the SI unit for energy.
  • The amount of energy possessed by a 2 kg mass moving at a speed of 1 m/s

\[ E_k = \frac{1}{2}mu^2 = \frac{1}{2}(2 \text{ kg})(1 \text{ m/s})^2 = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2 = 1 \text{ J} \]

1 J = 1 N \cdot m \quad \quad 1 \text{ N} = 1 \text{ kg} \cdot \text{m/s}^2

1 kJ = 1000 \text{ J}
- **Calorie (cal)** - commonly used on food labels
- 1 cal $\equiv$ 4.184 J
- 1000 cal = 1 Cal = 1 kcal
- Food calories (Cal) are really 1000 calories (cal).
Calculate the kinetic energy of a neon atom moving at a speed of 98 m/s.

\[ E_k = \frac{1}{2}mu^2 \]

\[
20.18 \text{ amu} \times \frac{1.661 \times 10^{-24} \text{ g}}{\text{amu}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 3.352 \times 10^{-26} \text{ kg}
\]

\[
E_k = \frac{1}{2} (3.352 \times 10^{-26} \text{ kg})(98 \text{ m/s})^2
\]

\[
E_k = 1.6 \times 10^{-22} \text{ J}
\]
5.2 Introduction to Thermodynamics

- Types of systems:
  - open (exchange of mass and energy)
  - closed (exchange of energy)
  - isolated (no exchange)
• **State functions** depend only on initial and final states of the system and not on how the change was carried out.
  
  – Energy \( (E) \)
  – Pressure \( (P) \)
  – Volume \( (V) \)
  – Temperature \( (T) \)
First Law of Thermodynamics

• Energy can be converted from one form to another but cannot be created or destroyed.
  – Based on the law of conservation of energy

• *Internal energy* \((U)\)
  – Kinetic energy - molecular motion
  – Potential energy - attractive/repulsive interactions
• The change in internal energy of a system between final (f) and initial (i) states is defined as:
  \[ \Delta U = \Delta U_f - \Delta U_i \]

• For a chemical system
  – Cannot calculate the total internal energy with any certainty
  – *Can* calculate the *change* in energy of the system experimentally
    \[ \Delta U = \Delta U_{(products)} - \Delta U_{(reactants)} \]
– Consider:

\[ S(s) + O_2(g) \rightarrow SO_2(g) \]

\[ \Delta U = U(\text{product}) - U(\text{reactants}) \]

= energy content of 1 mol SO\(_2\)(g) – energy content of 1 mol S(s) and 1 mol O\(_2\)(g)

– This reaction releases heat, therefore \( \Delta U \) is negative.
• When a system releases heat, some of the chemical energy is released as thermal energy to the surroundings but this does not change the total energy of the universe.

\[ \Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0 \]
• When a system undergoes a change in energy, the surroundings must undergo a change in energy equal in magnitude and opposite in sign.

\[ \Delta U_{\text{system}} = - \Delta U_{\text{surroundings}} \]
• Work and heat

\[ \Delta U_{\text{sys}} = q + w \]

where \( q \) is heat

\( w \) is work

TABLE 5.1 \ Sign Conventions for Heat (\( q \)) and Work (\( w \))

<table>
<thead>
<tr>
<th>Process</th>
<th>Sign</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat absorbed by the system (endothermic process)</td>
<td>( q ) is positive</td>
</tr>
<tr>
<td>Heat released by the system (exothermic process)</td>
<td>( q ) is negative</td>
</tr>
<tr>
<td>Work done on the system by the surroundings</td>
<td>( w ) is positive</td>
</tr>
<tr>
<td>(for example, a volume decrease)</td>
<td></td>
</tr>
<tr>
<td>Work done by the system on the surroundings</td>
<td>( w ) is negative</td>
</tr>
<tr>
<td>(for example, a volume increase)</td>
<td></td>
</tr>
</tbody>
</table>
Sign Conventions of $q$ and $w$
Calculate the overall change in internal energy for a system that absorbs 125 J of heat and does 141 J of work on the surroundings.

$q$ is + (heat absorbed)

$w$ is $-$ (work done)

$$\Delta U_{sys} = q + w = (+125 \text{ J}) + (-141 \text{ J})$$

$$= -16 \text{ J}$$
Reactions carried out at constant volume

- Pressure-volume work, \( w \), done by a system is
  \[
  w = -P \Delta V
  \]

- Constant volume, \( \Delta V = 0 \)
  \[
  \Delta U = q - P \Delta V
  \]

\[
q_v = \Delta U
\]
Decomposition of $\text{NaN}_3$ at Constant Volume

$$2\text{NaN}_3(s) \rightarrow 2\text{Na}(s) + 3\text{N}_2(g)$$
Reactions carried out at constant pressure

\[ \Delta U = q + w \]

\[ \Delta U = q_p - P\Delta V \]

\[ q_p = \Delta U + P\Delta V \]
Decomposition of NaN₃ at Constant Pressure

\[ 2\text{NaN}_3(s) \rightarrow 2\text{Na}(s) + 3\text{N}_2(g) \]
Enthalpy and enthalpy changes

- Enthalpy \((H)\) is a state function defined as

\[
H = U + PV
\]

- At constant pressure

\[
q_p = \Delta H
\]

- Enthalpy of reaction

\[
\Delta H = H(\text{products}) - H(\text{reactants})
\]

\(\Delta H\) is + for endothermic changes.

\(\Delta H\) is − for exothermic changes.
• Thermochemical Equations
  – Equations that represent both mass and enthalpy changes

\[ \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H = +6.01 \text{ kJ/mol} \]

• This is an endothermic process. It requires 6.01 kJ to melt one mole of ice, H\textsubscript{2}O(s).
• The enthalpy value will change if the number of moles varies from the 1:1 reaction stoichiometry.

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \quad \Delta H = -890.4 \text{ kJ/mol} \]

• This is an exothermic process. It releases 890.4 kJ when one mole of methane, CH\textsubscript{4}, reacts.
• The enthalpy value will change if the number of moles varies from the 1:2:1:2 reaction stoichiometry.
Comparison of Endothermic and Exothermic Changes

- **Endothermic Change**
  - $\text{H}_2\text{O}(l)$
  - Heat absorbed by the system from the surroundings
  - $\Delta H = +6.01 \text{ kJ/mol}$

- **Exothermic Change**
  - $\text{CH}_4(g) + 2\text{O}_2(g)$
  - Heat given off by the system to the surroundings
  - $\Delta H = -890.4 \text{ kJ/mol}$
  - $\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
• Thermochemical equation guidelines
  – Always specify state of reactants and products.
  – When multiplying an equation by a factor \((n)\), multiply the \(\Delta H\) value by the same factor.
  – Reversing an equation changes the sign but not the magnitude of the \(\Delta H\).
Given the following equation,

\[ \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \]

\[ \Delta H = -2803 \text{ kJ/mol} \]

calculate the energy released when 45.00 g of glucose is burned in oxygen.

\[
45.00 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} \times \frac{2803 \text{ kJ}}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} = 700.0 \text{ kJ}
\]
5.4 Calorimetry

- **Calorimetry** is the measurement of heat changes

- **Specific heat (s)** - the amount of heat required to raise the temp of 1 g of a substance by 1°C.
  - Units: J/g °C
  - Relation to amount of heat ($q$)

\[
q = ms\Delta T
\]

where $q$ is heat, $m$ is mass, $s$ is specific heat and $\Delta T$ = change in temp ($\Delta T = T_{\text{final}} - T_{\text{initial}}$)
<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat (J/g · °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(s)</td>
<td>0.900</td>
</tr>
<tr>
<td>Au(s)</td>
<td>0.129</td>
</tr>
<tr>
<td>C (graphite)</td>
<td>0.720</td>
</tr>
<tr>
<td>C (diamond)</td>
<td>0.502</td>
</tr>
<tr>
<td>Cu(s)</td>
<td>0.385</td>
</tr>
<tr>
<td>Fe(s)</td>
<td>0.444</td>
</tr>
<tr>
<td>Hg(l)</td>
<td>0.139</td>
</tr>
<tr>
<td>H$_2$O(l)</td>
<td>4.184</td>
</tr>
<tr>
<td>C$_2$H$_5$OH(l) (ethanol)</td>
<td>2.46</td>
</tr>
</tbody>
</table>
• **Heat capacity (C)** - the amount of heat required to raise the temp of an object by 1°C.

  – Units: J/°C
  – Relation to amount of heat (q)

\[
q = C \Delta T
\]

where \( q \) is heat, \( m \) is mass, \( C \) is heat capacity and \( \Delta T = \text{change in temp} \) \( (\Delta T = T_{\text{final}} - T_{\text{initial}}) \)
Calculate the amount of energy required to heat 95.0 grams of water from 22.5°C to 95.5°C.

\[ q = ms\Delta T \]

\[ \Delta T = T_{\text{final}} - T_{\text{initial}} = 95.5 \degree C - 22.5 \degree C \]

\[ \Delta T = 73.0 \degree C \]

\[ q = (95.0 \text{ g}) (4.184 \text{ J/g} \degree \text{C}) (73.0 \degree \text{C}) \]

\[ q = 2.90 \times 10^4 \text{ J} \text{ or } 29.0 \text{ kJ} \]
• Constant-pressure calorimetry

\[ q_{\text{sys}} = -ms\Delta T \]

– System: reactants and products

\[ q_{\text{sys}} = -q_{\text{surr}} \]
\[ q_{\text{surr}} = ms\Delta T \]

– Surroundings: water
– Used to measure
  • Specific heats
  • \( \Delta H \) values
# TABLE 5.3
Heats of Some Typical Reactions and Physical Processes Measured at Constant Pressure

<table>
<thead>
<tr>
<th>Type of Reaction</th>
<th>Example</th>
<th>$\Delta H$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of neutralization</td>
<td>HCl($aq$) + NaOH($aq$) $\rightarrow$ H$_2$O($l$) + NaCl($aq$)</td>
<td>$-56.2$</td>
</tr>
<tr>
<td>Heat of ionization</td>
<td>H$_2$O($l$) $\rightarrow$ H$^+$($aq$) + OH$^-$($aq$)</td>
<td>$+56.2$</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>H$_2$O($s$) $\rightarrow$ H$_2$O($l$)</td>
<td>$+6.01$</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>H$_2$O($l$) $\rightarrow$ H$_2$O($g$)</td>
<td>$+44.0^*$</td>
</tr>
</tbody>
</table>

*Measured at 25°C. At 100°C, the value is +40.79 kJ.*
A metal pellet with a mass of 85.00 grams at an original temperature of 92.5°C is dropped into a calorimeter with 150.00 grams of water at an original temperature of 23.1°C. The final temperature of the water and the pellet is 26.8°C. Calculate the heat capacity and the specific heat for the metal.
\[ q_{\text{water}} = ms \Delta T \]
\[ = (150.00 \text{ g}) (4.184 \text{ J/g}^\circ\text{C}) (3.7^\circ\text{C}) \]
\[ = 2300 \text{ J (water gained energy)} \]
\[ = -2300 \text{ J (pellet released energy)} \]

Heat capacity of pellet: \[ q = C \Delta T \]
\[ C = \frac{q}{\Delta T} \]
\[ = \frac{-2300 \text{ J}}{-65.7^\circ\text{C}} = 35 \text{ J/}^\circ\text{C} \]

Specific heat of pellet: \[ \frac{\text{J}}{\text{g}^\circ\text{C}} \]
\[ s = \frac{35 \text{ J/}^\circ\text{C}}{85.00 \text{ g}} = 0.41 \text{ J/g}^\circ\text{C} \]
• Constant-volume calorimetry
  
  – Isolated system

  \[ q_{\text{cal}} = -q_{\text{rxn}} \]

  \[ q_{\text{sys}} = -q_{\text{surr}} \]

  \[ q_{\text{cal}} = C_{\text{cal}} \Delta T \]

  \[ q_{\text{rxn}} = -C_{\text{cal}} \Delta T \]

  – Measures \( \Delta U \)
Typical procedure used in a bomb calorimeter

- Known amount of sample placed in steel container and then filled with oxygen gas
- Steel chamber submerged in known amount of water
- Sample ignited electrically
- Temperature increase of water is determined
A snack chip with a mass of 2.36 g was burned in a bomb calorimeter. The heat capacity of the calorimeter 38.57 kJ/°C. During the combustion the water temp rose by 2.70°C. Calculate the energy in kJ/g for the chip.
\[ q_{\text{rxn}} = - C_{\text{cal}} \Delta T \]
\[ = -(38.57 \text{ kJ/}^\circ\text{C}) (2.70^\circ\text{C}) \]
\[ = -104 \text{ kJ} \]

Energy content is a positive quantity.
\[ = 104 \text{ kJ/2.36 g} \]
\[ = 44.1 \text{ kJ/g} \]

Food Calories: 10.5 Cal/g
5.5 Hess’s Law

• *Hess’s Law*: The change in enthalpy that occurs when reactants are converted to products is the same whether the reaction occurs in one step or a series of steps.

• Used for calculating enthalpy for a reaction that cannot be determined directly.
• In using stepwise reactions to determine an overall reaction
  – Remember the rules for manipulating equations.
  – Add the $\Delta H$ values for each step together after proper manipulation to obtain the overall enthalpy for the desired reaction.
Given the following equations:

\[
\begin{align*}
H_3\text{BO}_3(aq) & \rightarrow HBO_2(aq) + H_2O(l) \quad \Delta H_{\text{rxn}} = -0.02 \text{ kJ} \\
H_2\text{B}_4\text{O}_7(aq) + H_2O(l) & \rightarrow 4 \text{ HBO}_2(aq) \quad \Delta H_{\text{rxn}} = -11.3 \text{ kJ} \\
H_2\text{B}_4\text{O}_7(aq) & \rightarrow 2 \text{ B}_2\text{O}_3(s) + H_2O(l) \quad \Delta H_{\text{rxn}} = 17.5 \text{ kJ}
\end{align*}
\]

Find the $\Delta H$ for this overall reaction.

\[
2H_3\text{BO}_3(aq) \rightarrow \text{ B}_2\text{O}_3(s) + 3H_2O(l)
\]
\[
2\text{H}_3\text{BO}_3(aq) \rightarrow 2\text{HBO}_2(aq) + 2\text{H}_2\text{O}(l) \quad \text{x 2} \\
\Delta H_{\text{rxn}} = 2(-0.02 \text{ kJ}) = -0.04 \text{ kJ}
\]

\[
2\text{HBO}_2(aq) \rightarrow \frac{1}{2}\text{H}_2\text{B}_4\text{O}_7(aq) + \frac{1}{2}\text{H}_2\text{O}(l) \quad \text{reverse, } \div 2 \\
\Delta H_{\text{rxn}} = +11.3 \text{ kJ}/2 = 5.65 \text{ kJ}
\]

\[
\frac{1}{2}\text{H}_2\text{B}_4\text{O}_7(aq) \rightarrow \text{B}_2\text{O}_3(s) + \frac{1}{2}\text{H}_2\text{O}(l) \quad \div 2 \\
\Delta H_{\text{rxn}} = 17.5 \text{ kJ}/2 = 8.75 \text{ kJ}
\]

\[
2\text{H}_3\text{BO}_3(aq) \rightarrow \text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(l) \\
\Delta H_{\text{rxn}} = 14.36 \text{ kJ}
\]
5.6 Standard Enthalpies of Formation

- **Standard enthalpy of formation**
  - Symbol: $\Delta H_f^\circ$
  - The enthalpy change that results when 1 mole of a compound is formed from its elements in their standard states.
  - $\Delta H_f^\circ$ for an element in its standard state is defined as zero.
  - Standard state: 1 atm, 25°C
  - Values found in reference tables
  - Used to calculate the $\Delta H^\circ_{\text{rxn}}$
• Defining equation for enthalpy of reaction:

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

where \( \Sigma \) denotes summation

\( n \) and \( m \) are the coefficients in the balanced equation
Calculate the $\Delta H^\circ_{\text{rxn}}$ for the following reaction from the table of standard values.

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

$$\Delta H^\circ_{\text{rxn}} = \sum n\Delta H_f^\circ \text{ (products)} - \sum m\Delta H_f^\circ \text{ (reactants)}$$

$$= [1(-393.5) + 2(-285.8)] - [1(-74.8) + 2(0)]$$

$$= -890.3 \text{ kJ/mol (exothermic)}$$
Key Points

• Energy and energy types
• Law of conservation of energy
• Energy associated with reactions
• System and surroundings
• Exothermic and endothermic
• Thermochemistry
• Systems - open, closed, isolated
Key Points

- First law of thermodynamics
- Enthalpy (heat of formation; heat of reaction)
- State function
- Calorimetry
- Specific heat
- Hess’s law
- Calculations involving enthalpy, specific heat, energy