Chapter 6: Thermochemistry

Chemical reactions obey 2 laws:
- conservation of mass (previous chapters)
- conservation of energy (this chapter)

6.1 Energy and Types of Energy

A. Definitions

- **Energy** - capacity to do work
- **Work** - (physicists) force x distance
  (chemists definition) directed energy change resulting from a process

B. Types of Energy

1. **Kinetic Energy** - energy produced by moving object
   \[ K.E = \frac{1}{2} m v^2 \] where \( m \) = mass and \( v \) = velocity

2. **Radiant energy** - (solar energy) energy from the sun; from chemical reactions of the sun; affect weather and plant growth

3. **Thermal energy** - associated with random motion of atoms and molecules.
   - may be calculated from the temperature and amount of molecules
   - Example: cup of coffee at 70 °C has less thermal energy than a bathtub of water at 40 °C

4. **Potential Energy** - energy available by virtue of an objects position, e.g., rock at the top of a cliff

5. **Chemical Energy** - energy stored in bonds; potential energy associated with chemical bonds:
bond breaking: energy is required
bond making: energy is liberated

All forms of energy may theoretically be converted to other forms of energy.

**Law of Conservation of Energy** - the total quantity of energy in the Universe is constant.

### 6.2 Energy Changes in Chemical Reactions

These are as important as the mass changes, e.g., combustion of hydrocarbons is done to make use of the energy liberated in the reaction.

1. **Heat** - (generally the form of energy in chemical reactions) transfer of thermal energy between two bodies at different temperatures:
   
   \[ \text{hotter} \rightarrow \text{colder} \]

2. **Thermochemistry** - study of heat changes in chemical reactions

3. **System** - part of the Universe of interest to us (beaker, automobile.....)

4. **Surroundings** - rest of the Universe

5. **Types of Systems:**
   - **open system** - exchanges mass and energy (usually heat) with surroundings; e.g., open beaker of H2O (water can evaporate)
   - **closed system** - allows heat transfer, not mass transfer; e.g. beaker with lid
   - **isolated system** - allows no heat or mass transfer; e.g., insulated beaker with a lid
Exothermic process -
• gives off heat
• transfers heat to surroundings
• heat is essentially a product of the reaction
• system warms up

6. Endothermic process -
• heat must be supplied by the surroundings
• heat is essentially a reactant
• system cools off

\[
\begin{align*}
&\text{Exothermic: heat given off by the system to the surroundings} \\
\text{2H}_2(g) + \text{O}_2(g) &\rightarrow \text{2H}_2\text{O}(l) \\
\text{Endothermic: heat absorbed by the system from the surroundings} \\
\text{2Hg}(l) + \text{O}_2(g) &\rightarrow \text{2HgO}(s)
\end{align*}
\]
6.3 Introduction to Thermodynamics

*Thermodynamics* – (broader than thermochemistry)  
*scientific study of the interconversion of heat and other kinds of energy*

1. *State Functions*

   state of a system – defined by macroscopic properties, i.e. composition, energy, temperature, pressure, volume

   our concern – change in the system from the point of initial and final states

   so if the volume changes we want to know \( \Delta V = V_f - V_i \)

   Energy is a state function

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*Figure 6.4*  Gain in potential energy is the same here (gravitational pull) regardless of pathway.
**First Law of Thermodynamics**

*Energy can be converted from one form to another, but cannot be created or destroyed.*

Potential energy to kinetic energy

Example is a chemical reaction, e.g., burning sulfur

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

cannot know exactly the total energy in the S, O₂, and SO₂, but can measure the change in energy (in this case heat evolved)

\[
\Delta E = E_{\text{prod}} - E_{\text{reac}}
\]

\[
\Delta E_{\text{system}} = \Delta E_{\text{surroundings}}
\]

\[
\Delta E_{\text{system}} = q + w \quad \text{where } q = \text{heat exchanged}; w = \text{work}
\]

\( q \) and \( w \) are **negative** if heat moves **out** of system or work is **done by** the system

and \( w \) are **positive** if heat is **added to** system or work is **done on** the system
Work involving gases

Figure 6.5
piston moves upward as gas expands
w = force x distance

\[ w = - P \Delta V \]

units of work = L-atm
conversion factor: 1 L-atm = 101.3 J

Example:
A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done in joules by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 4.00 atm.
6.4 Enthalpy, \( H \), of Chemical Reactions

- the total energy of a chemical system at constant pressure (conditions of most reactions)
- depends on amount of substance
- cannot measure enthalpy directly, but can measure changes in enthalpy
- \( \Delta H = H_{\text{products}} - H_{\text{reactants}} \)

**Endothermic reaction:** \( \Delta H > 0 \) (positive) -- heat is absorbed (deposit)

**Exothermic reaction:** \( \Delta H < 0 \) (negative) -- heat is released (withdrawal)

This semester we'll be concerned primarily with \( \Delta H \) and not \( \Delta E \)

**Enthalpy and the First Law of Thermodynamics**

Enthalpy (\( H \)) of system:

\[
H = E + PV
\]

Change in enthalpy (at constant pressure)

(change is what we can easily measure)

\[
\Delta H = \Delta E + \Delta PV
\]

or rearranged

\[
\Delta E = \Delta H - \Delta PV
\]

remember that \( \Delta E_{\text{system}} = q + w \)

so \( q = \Delta H \) at constant pressure

and \( PV = nRT \), so

\[
\Delta H = \Delta E + RT\Delta n
\]

\[
\Delta E = \Delta H - RT\Delta n
\]
Thermochemical Equations

Example: One mole of ice melts to liquid at 0 °C. (1 atmosphere, a standard condition)

- 18 grams (1 mole) of ice
- 6.01 kJ of energy absorbed
- \( \Delta H = 6.01 \text{ kJ} \)
- If the process is reversed, i.e., the liquid water is frozen, then \( \Delta H = -6.01 \text{ kJ} \)

Some energy conversion factors

\[
1 \text{ Joule} = 1 \text{ J} = 1 \text{ Kg m}^2/\text{s}^2 = 1 \text{ N} \cdot \text{m}
\]

where \( N = \text{Newton}, m = \text{meters}, s = \text{seconds} \)

- 1 kJ = 1000 J
- 4.184 J = 1 cal
- 1000 cal = 1 Kcal = 1 Calorie (Food Calorie)

For example: The reaction for the combustion of ethylene:

\[
\text{C}_2\text{H}_4 (g) + 3 \text{ O}_2 (g) \rightarrow 2 \text{ CO}_2 (g) + 2 \text{ H}_2\text{O} (l)
\]

\( \Delta H^\circ = -1,411 \text{ kJ} \) (very exothermic)

i.e., 1,411 kJ of heat energy are released in the reaction of 1 mole of \( \text{C}_2\text{H}_4 \) with 3 moles of \( \text{O}_2 \)

Rules for thermochemical equations:

- work in moles
- reversing an equation reverses the sign of \( \Delta H \)
- multiplying the equation by a factor applies to \( \Delta H \) as well as to moles
- must specify state of reaction and products

Example: If 10.0 g of \( \text{C}_2\text{H}_4 \) are burned, how much heat is produced?

\[
10.0 \text{ g} \times \frac{1 \text{ mole} \text{C}_2\text{H}_4}{28.0 \text{ g}} \times \frac{1411 \text{ kJ}}{\text{mole} \text{C}_2\text{H}_4} = 504 \text{ kJ}
\]
6.5 Calorimetry

measurement of heat change

A. **Specific Heat** \((s)\) - amount of heat needed to raise the temperature of 1 gram of a substance by 1 °C. (units are J/g.°C) (intensive property)

B. **Heat Capacity** \((C)\) - amount of heat required to raise the temperature of a given quantity substance by 1 °C. (extensive property)

Example: specific heat of water is 4.184 J/g . °C

heat capacity of 60.0g of water is

\[
\frac{60.0 \text{ g} \times 4.184 \text{ J}}{\text{g.°C}} = \frac{251 \text{ J}}{\text{°C}}
\]

C. Calculating amount of heat from \(s\) and change in temperature \((Δt)\)

\[
q = msΔt \quad \text{where } m = \text{mass}
\]

\[
q = CΔt \quad Δt = \left| \text{change in temperature} \right|
\]

\(q\) is positive for endothermic process
\(q\) is negative for exothermic process

Example:
An iron bar of mass 869 g cools from 94 °C to 5 °C. Calculate the heat released in kJ.

\[
q = msΔt
\]

\[
Δt = 94 \text{ °C} - 5 \text{ °C} = 89 \text{ °C}
\]

from Table 6.1, p. 210: \(s = 0.444 \text{ J/g . °C}\)

\[
q = 869 \text{g} \times \frac{0.444 \text{ J}}{\text{g.°C}} \times 89 \text{ °C} = 34339 \text{ J}
\]

\[
q = -34.3 \text{ kJ} \quad \text{(heat released)}
\]
D. Constant Volume Calorimetry

see Figure 6.8 (isolated system - no heat leaves or enters)
thermometer insulated jacket
ignition wire O₂ inlet
calorimeter bucket bomb
sample cup

Procedure:
• measure starting temperature
• measure mass of sample
• ignite sample
• measure temperature after reaction

\[ q_{\text{out of rexn}} = q_{\text{into the bomb and water}} \]
\[ q_{\text{system}} = q_{\text{water}} + q_{\text{bomb}} + q_{\text{rxn}} = 0 \]

**but we can also say**

\[ |q_{\text{rxn}}| = |(q_{\text{water}} + q_{\text{bomb}})| \]

\[ q_{\text{water}} = ms\Delta t = (m_{\text{water}})(4.184 \text{ J/g } ^\circ\text{C})\Delta t \]

\[ q_{\text{bomb}} = C_{\text{bomb}}\Delta t \]

\[ C_{\text{bomb}} = (m_{\text{bomb}})(s_{\text{bomb}}) \]

\[
q_{\text{out of rexn}} = q_{\text{into the bomb and water}}
\]

**Example**

A quantity of 1.922 g of methanol (CH\(_3\)OH) was burned in a bomb calorimeter. Consequently, the temperature of the H\(_2\)O rose by 4.20 \(^\circ\text{C}\). If the quantity of water surrounding the calorimeter was exactly 2000 g and the heat capacity of the calorimeter was 2.02 kJ/\(^\circ\text{C}\), calculate the molar heat of combustion of methanol.

\[
|q_{\text{rxn}}| = |(q_{\text{water}} + q_{\text{bomb}})|
\]

\[
q_{\text{out of rexn}} = q_{\text{into the bomb and water}}
\]

\[
|q_{\text{rxn}}| = \left[ \left( \frac{2.02 \times 10^3 \text{ J}}{\text{\degree C}} \right) \times 4.20 \text{ \degree C} \right] + \left( 2000 \text{ g} \times \frac{4.184 \text{ J}}{\text{g} \text{ \degree C}} \times 4.20 \text{ \degree C} \right)
\]

\[ q_{\text{rxn}} = 8484 \text{ J} + 35145.6 \text{ J} = 43,629.6 \text{ J} = 43.6 \text{ kJ} \]

BUT we know that the rexn was EXOTHERMIC so the \( q_{\text{rxn}} \) is \(- 43.6 \text{ kJ} \) !!!!!

Calculate the molar heat of combustion:

\[
1.922 \text{ g} \times \frac{1 \text{ mole CH}_3\text{OH}}{32.00 \text{ g}} = 0.0601 \text{ moles}
\]

\[
\frac{-43.6 \text{ kJ}}{0.0601 \text{ moles}} = -725 \text{ kJ/mole}
\]
6.6 Standard Enthalpy of Formation and Reaction

cannot measure absolute enthalpy, only the change in enthalpy
thus use a standard (like sea level)- accepted convention

$$\Delta H^\circ_f = \Delta H^\circ \text{ for the formation of one mole of substance from its elements in their standard states at a pressure of one atmosphere}$$

**Standard State** = 1 atmosphere, 25 °C

\(\Delta H^\circ_f\) for some substances found in Table 6.4 and in Appendix 3

**\(\Delta H^\circ_f\) for elements in most stable form is 0**

e.g., \(O_2, \Delta H^\circ_f = 0\)

\(O_3, \Delta H^\circ_f = 142 \text{ kJ/mole}\)

\(C_{\text{graphite}}, \Delta H^\circ_f = 0\)

\(C_{\text{diamond}}, \Delta H^\circ_f = 1.90 \text{ kJ/mole}\)

Example of a "formation" reaction (remember: \(\Delta H^\circ_f\) applies to 1 mole of a compound formed from its elements):

\[H_2 (g) + 1/2 O_2 (g) \rightarrow H_2O (l)\]

\(\Delta H^\circ_f\) (liq water) = -286 kJ/mole

practice writing formation reactions -- e.g., \(Na_2SO_4\)

\[2 Na (s) + 2 O_2 (g) + S (s) \rightarrow Na_2SO_4 (s)\]

\(\Delta H^\circ_f = -1385 \text{ kJ/mole}\)
B. Standard Enthalpy of Reaction

\[ aA + bB \rightarrow cC + dD \]

\[ \Delta H^\circ_{\text{rexn}} = \sum \Delta H^\circ_f (\text{products}) - \sum \Delta H^\circ_f (\text{reactants}) \]

\[ \Delta H^\circ_{\text{rexn}} = [c \cdot \Delta H^\circ_f (C) + d \cdot \Delta H^\circ_f (D)] - [a \cdot \Delta H^\circ_f (A) + b \cdot \Delta H^\circ_f (B)] \]

1. **Direct Method** - applies when reactants are elements in most stable state

   \[ S \text{ (rhombic)} + 3 F_2 \text{ (g)} \rightarrow SF_6 \text{ (g)} \]

   In these cases may directly measure by doing the reaction

2. **Indirect method** (Hess's Law) (Law of Heat Summation)

   - When reactants are converted to products, the change in \( H \) is the same whether the reaction takes place in one or several steps.
   - This applies when compounds cannot be made directly from the elements

**Example**

Calculate the \( \Delta H^\circ_f \) of acetylene, \( \text{C}_2\text{H}_2 \) gas from its elements.

\[ 2 \text{C (graphite)} + \text{H}_2 \text{ (g)} \rightarrow \text{C}_2\text{H}_2 \text{ (g)} \]

The equations for each step and the corresponding enthalpy changes are:

\[ \text{C (graphite)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2 \text{ (g)} \quad \Delta H^\circ_f = -393.5 \text{ kJ} \]

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

\[ 2 \text{C}_2\text{H}_2 \text{ (g)} + 5 \text{O}_2 \text{ (g)} \rightarrow 4 \text{CO}_2 \text{ (g)} + 2 \text{H}_2\text{O} \text{ (l)} \quad \Delta H^\circ_{\text{rexn}} = -2598.8 \text{ kJ} \]

**First:** reverse last reaction to put the product (\( \text{C}_2\text{H}_2 \)) on the correct side of the equation

\[ 4 \text{CO}_2 \text{ (g)} + 2 \text{H}_2\text{O} \text{ (l)} \rightarrow 2 \text{C}_2\text{H}_2 \text{ (g)} + 5 \text{O}_2 \text{ (g)} \quad \Delta H^\circ = +2598.8 \text{ kJ} \]
Second: There is no H$_2$O or CO$_2$ in the formation equation, so place these reagents on opposite sides. The goal is to get these to cancel when the 3 reactions are summed.

\[ \text{C (graphite) + O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\circ_f = -393.5 \text{ kJ} \]
\[ \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ_f = -285.8 \text{ kJ} \]

Third: Multiply by appropriate factors to make sure the same number of each reagent that must be canceled occurs on right and left sides.

\[ 4 \left[ \text{C (graphite) + O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \right] \quad 4 \Delta H^\circ_f = -1574.0 \text{ kJ} \]
\[ 2 \left[ \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \right] \quad 2 \Delta H^\circ_f = -571.6 \text{ kJ} \]
\[ 4 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{C}_2\text{H}_2(\text{g}) + 5 \text{O}_2(\text{g}) \quad \Delta H^\circ = +2598.8 \text{ kJ} \]
\[ 4 \left[ \text{C (graphite) + H}_2(\text{g}) \rightarrow \text{2C}_2\text{H}_2(\text{g}) \right] \quad 4 \Delta H^\circ = 453.2 \text{ kJ} \]
\[ 2 \left[ \text{C (graphite) + H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_2(\text{g}) \right] \quad 2 \Delta H^\circ = 226.6 \text{ kJ} \]

### 6.7 Heat of Solution and Dilution
examples: dissolving salts, hot and cold packs in first aid kits

$\Delta H_{\text{soln}}$ - heat generated or absorbed when a solute dissolves

Lattice Energy ($U$) - energy required to completely separate one mole of a solid ionic compound into gaseous ions:

\[ \text{NaCl (s) + energy} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \]

$\Delta H_{\text{hyd}}$ - heat of hydration: enthalpy change associate with hydration

\[ \Delta H_{\text{soln}} = \Delta H_{\text{hyd}} + U \]

see Figure 6.11

\[ \text{NaCl (s)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \quad U = 788 \text{ kJ} \]
\[ \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \xrightarrow{\text{H}_2\text{O}} \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \quad \Delta H_{\text{hyd}} = -784 \text{ kJ} \]
\[ \text{NaCl (s)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \quad \Delta H_{\text{soln}} = 4 \text{ kJ} \]

Thus the mixture cools slightly.
1 calorie (cal) = 4.184 J  
1000 cal = 1 Calorie (Cal) = 1 food Calorie

These numbers can be determined in a bomb calorimeter.
### Periodic Table of the Elements

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