Thermochemistry: Energy Changes in Reactions

Chapter 5
• Thermodynamics – The study of energy and its transformations

• Thermochemistry – The study of the relation between chemical reactions and changes in heat energy
Heat

- energy transferred between two objects as a result of the temperature difference between them.

Temperature

- A measure of kinetic energy
Heat Transfer

The process of heat energy flowing from one object into another.

Will reach thermal equilibrium.
Types of Energy

• Potential Energy –
  – Energy of position

• To a chemist –
  – The energy to be derived from a chemical reaction
  – Due to new atomic interactions
Kinetic Energy

- energy of motion
- thermal energy is kinetic
- $1/2 \, mv^2$
Energy can be converted from one form to another

\[ PE = mgh_1 \]

\[ u = 0 \therefore KE = 0 \]

\[ PE = mgh_2 \]
\[ KE = \frac{1}{2} mu^2 \]

\[ h_3 = 0 \therefore PE = 0 \]
\[ KE = \frac{1}{2} mu^2 \]
Conversion of potential energy to kinetic energy

\[ 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g) + \text{energy} \]
Systems, Surroundings, and the Flow of Energy

(a) Isolated System

(b) Closed System

(c) Open System

A thermos bottle with the lid screwed on tight

A cup of soup with a lid

Grated cheese

Crackers

Steam

Pepper mill

Water vapor

Chemistry: The Science in Context 2/e  Figure 5.8 © 2009 W. W. Norton & Company, Inc.
• In an Exothermic process, heat flows from a system into its surroundings.

• In an Endothermic process, heat flows from the surroundings into the system.
Surroundings

Energy out of system to surroundings: – sign

Energy into system from surroundings: + sign

System
Which of the pictures at the right represents the energy gauge for the system above when the $\Delta E_{\text{system}}$ is negative?
The diagram represents a chemical reaction involving the reactants $C(s)$ and $O_2(g)$ producing the product $CO_2(g)$. The change in internal energy is shown as $\Delta E < 0$ (negative) indicating an energy release for the system. The energy flow is from the system to the surroundings, with the change in energy for the surroundings being $\Delta E_{surr} > 0$ (positive).
Internal energy

C(s), O₂(g) \rightarrow \text{(products)}

\Delta E > 0 \text{ (positive)}

CO₂(g) \rightarrow \text{(reactant)}

\Delta E_{sys} > 0 \text{ (positive)}

\Delta E_{surr} < 0 \text{ (negative)}

System

Surroundings

Energy flow
1st Law of Thermodynamics

- The energy of the universe is constant.
- i.e. the energy of the universe is conserved
\[ \Delta E = E_{\text{final}} - E_{\text{initial}} \]

- $-\Delta E$ if energy leaves system
- $+\Delta E$ if energy enters system

- Note the $E$ of a system doesn’t depend on how system got there -- i.e. it is a state function
State Function

- A function or property whose value depends only on the present state (condition) of the system, not on the path used to arrive at that condition.
Energy Units

- Traditional unit – calorie
  - 1 calorie = energy to increase temperature of water by 1°C
  - 1 Calorie = food Calorie = 1kcal

- SI unit – joule
  - 4.184 joule = 1 cal
Energy can be either work or heat

\[ \Delta E = q + w \]

- Heat gain or loss
- Work done = \(-P\Delta V\)

Matches our earlier convention that \(E_{\text{in}}\) is + and \(E_{\text{out}}\) is –

Sample exercise 5.3
Sample exercise 5.4

Cross-sectional area = \( A \)

\[ \Delta V = A \times \Delta h \]

Initial state

Final state

Volume change
\[ E = q + w = q - PV \]

At constant pressure this becomes

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

Define

\[ H = E + PV \]

Or at constant pressure

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

Substituting \( \Delta E = q_p - P\Delta V \)

\[ \Delta H = \Delta E + P\Delta V = (q_p - P\Delta V) + P\Delta V = q_p \]
Enthalpy

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

\[ \Delta H = H_{\text{final}} - H_{\text{initial}} \]

\[ = H_{\text{products}} - H_{\text{reactants}} \]

Sample exercises 5.5, 5.6
HW 5.31 – 5.40
Specific Heat Capacity or Specific Heat (C) = \( \frac{q}{m \times \Delta T} \)

Tells how much heat is required to change the temp of a substance.

Some specific heats are

- Al 0.902 J/g °K
- Cu 0.385 J/g °K
- H₂O 4.184 J/g °K
A 55.0 g piece of metal was heated in boiling water to a temperature of 99.8°C and dropped into an insulated beaker with 225 mL of water (d = 1.00 g/ml) at 21.0 °C.

The final temperature of the metal and water is 23.1°C. Calculate the specific heat of the metal assuming that no heat was lost to the surroundings.
• Octane, $C_8H_{18}$, a primary constituent of gasoline, burns in air.

• $C_8H_{18}(l) + \frac{25}{2} O_2(g) \rightarrow 8 CO_2(g) + 9 H_2O(l)$

• Suppose that a 1.00 g sample of octane is burned in a calorimeter that contains 1.20 kg of water. The temperature of the water and the bomb rises from 25.00°C to 33.20°C. If the specific heat of the bomb, $C_{\text{bomb}}$, is known to be 837 J/°C, calculate the molar heat of reaction of $C_8H_{18}$.
A quantity of ice at 0°C is added to 90.0 g of water at 80°C. After the ice melted, the temperature of the water was 25°C. How much ice was added?

- specific heat of ice 2.06 J/g°C 37.1 J/mol°C
- specific heat of water 4.184 J/g°C 75.4 J/mol°C
- specific heat of steam 2.0 J/g°C 36 J/mol°C
- heat of fusion 333 J/g 6.01 kJ/mol
- heat of vaporization 2260 J/g 40.7 kJ/mol
• 50.0 g of ice at -20.0 °C are added to 342.0 g of water at 86.0 °C. What will be the final temperature of the sample?

• specific heat of ice 2.06 J/g°C 37.1 J/mol°C
• specific heat of water 4.184 J/g°C 75.4 J/mol°C
• specific heat of steam 2.0 J/g°C 36 J/mol°C
• heat of fusion 333 J/g 6.01 kJ/mol
• heat of vaporization 2260 J/g 40.7 kJ/mol

Sample exercise 5.7, 5.8, 5.9
HW #5.41 – 5.56
• A 33.14 g sample of copper and aluminum was heated to 119.25°C and dropped into a calorimeter containing 250.0 g of water at 21.00°C. The temperature rose to 23.05°C. Assuming no heat was lost to the surroundings, what is the percent copper in the sample?
Enthalpy

- Enthalpy transferred out of reactants $\rightarrow$ exothermic $\rightarrow \Delta H = -$ 

- Enthalpy transferred into products $\rightarrow$ endothermic $\rightarrow \Delta H = +$
Enthalpy

- $\Delta H_{\text{forward}} = -\Delta H_{\text{reverse}}$ (For reversible reactions)

- $\text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g)$
  $\Delta H = +241.8 \text{ kJ}$

- $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$
  $\Delta H = -241.8 \text{ kJ}$
Enthalpy

- The $\Delta H$ is proportional to the amount of substance undergoing change.

- $\text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g)$
  $\Delta H = +241.8 \text{ kJ}$

- $2 \text{H}_2\text{O}(g) \rightarrow 2 \text{H}_2(g) + 1 \text{O}_2(g)$
  $\Delta H = +483.6 \text{ kJ}$
Enthalpy

• The physical state of reactants and products is important.

• $\text{H}_2\text{O}(g) \longrightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g)$
  $\Delta H = +241.8 \text{ kJ}$

• $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g)$
  $\Delta H = +285.8 \text{ kJ}$
Enthalpy

• Enthalpy is a state function -- it doesn’t matter how you go from one place to another -- enthalpy and enthalpy changes are the same!!

• The $\Delta H$ value is the same no matter how you get from A$\rightarrow$B
Hess’s Law

The change in enthalpy for a stepwise process is the sum of the enthalpy changes of the steps.

\[ \Delta H_3 = \Delta H_1 + \Delta H_2 \]
Determine the $\Delta H$ for the sublimation of ice to water vapor at $0^\circ$C.

- $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ \hspace{1cm} $\Delta H = 6.02 \text{ kJ/reaction}$
- $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ \hspace{1cm} $\Delta H = 40.7 \text{ kJ/reaction}$
- $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(g)$ \hspace{1cm} $\Delta H = 46.7 \text{ kJ/reaction}$
Calculate the enthalpy change for the formation of methane, CH$_4$, from solid carbon (as graphite) and hydrogen gas.

C(s) + 2 H$_2$(g) $\rightarrow$ CH$_4$(g)

The enthalpies for the combustion of graphite, hydrogen gas and methane are given.

C(s) + O$_2$(g) $\rightarrow$ CO$_2$(g) $\quad$ $-393.5$ kJ

H$_2$(g) + $\frac{1}{2}$ O$_2$(g) $\rightarrow$ H$_2$O(l) $\quad$ $-285.8$ kJ

CH$_4$(g) + 2 O$_2$(g) $\rightarrow$ CO$_2$(g) + 2 H$_2$O(l) $\quad$ $-890.3$ kJ

Sample exercise 5.12, 5.13
Calculate the enthalpy change for the reaction

\[ \text{S(s)} + \text{O}_2(g) \rightarrow \text{SO}_2(g) \]

given

\[ 2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g) \quad \Delta H = -196 \text{ kJ} \]

\[ 2 \text{S(s)} + 3 \text{O}_2(g) \rightarrow 2 \text{SO}_3(g) \quad \Delta H = -790 \text{ kJ} \]
Standard Heat of Formation

- The enthalpy change, $\Delta H_f^o$, for the formation of 1 mol of a substance in the standard state from the most stable forms of its constituent elements in their standard states.

$\Delta H_f^o$

superscript $^o$ means standard state
25°C and 1 atm pressure

subscript $f$ means formation from most stable elements

Sample exercise 5.14
<table>
<thead>
<tr>
<th>Formula</th>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
<th>Formula</th>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
<th>Formula</th>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
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<td>Cl(g)</td>
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<td>Br$_2$(l)</td>
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<td>S$_8$(s, rhombic)</td>
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<td>CH$_4$(g)</td>
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<td>CH$_3$OH(l)</td>
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<td>C$_3$H$_6$O(l, acetone)</td>
<td>-248.4</td>
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\[ \Delta H^o_{rxn} = \sum n_p \Delta H^o_f \text{ (products)} - \sum n_r \Delta H^o_f \text{ (reactants)} \]
• Benzene, C₆H₆, is an important hydrocarbon. Calculate its enthalpy of combustion; that is, find the value of $\Delta H^\circ$ for the following reaction.

$\text{C}_6\text{H}_6(\text{l}) + \frac{15}{2} \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l})$

• Given

$\Delta H_f^\circ [\text{C}_6\text{H}_6(\text{l})] = +49.0 \text{ kJ/mol}$

$\Delta H_f^\circ [\text{CO}_2(\text{g})] = -393.5 \text{ kJ/mol}$

$\Delta H_f^\circ [\text{H}_2\text{O}(\text{l})] = -285.8 \text{ kJ/mol}$

Sample exercise 5.15, 5.16
Nitroglycerin is a powerful explosive, giving four different gases when detonated.

\[ 2 \text{C}_3\text{H}_5(\text{NO}_3)_3(\text{l}) \rightarrow 3 \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) + 6 \text{CO}_2(\text{g}) + 5 \text{H}_2\text{O}(\text{g}) \]

Given the enthalpy of formation of nitroglycerin, \( \Delta H_f^o \), is \(-364 \text{ kJ/mol}\), calculate the energy liberated when 10.0 g of nitroglycerin is detonated.
Enthalpies from Bond Energies

- Calculate the enthalpy of formation of water vapor from bond energies.

- $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$
  - (The experimental value is $-241.8 \text{kJ/mol}$)
### Table 7.1 Average Bond Dissociation Energies, $D$ (kJ/mol)*

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<th>Bond</th>
<th>Value (kJ/mol)</th>
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<td>H--H</td>
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<tr>
<td>C--H</td>
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<tr>
<td>N--H</td>
<td>390</td>
</tr>
<tr>
<td>O--H</td>
<td>460</td>
</tr>
<tr>
<td>F--F</td>
<td>159*</td>
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<tr>
<td>H--C</td>
<td>410</td>
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<tr>
<td>C--C</td>
<td>350</td>
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<td>O--C</td>
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<tr>
<td>Cl--Cl</td>
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<td>O--S</td>
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**Multiple covalent bonds †**

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<th>Bond</th>
<th>Value (kJ/mol)</th>
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<td>C≡C</td>
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<td>O≡O</td>
<td>498*</td>
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<tr>
<td>N≡N</td>
<td>945*</td>
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* Bond dissociation energies for diatomic molecules are exact.

† We’ll discuss multiple covalent bonds in Section 7.5.
• Oxygen difluoride, OF₂, is a colorless, very poisonous gas that reacts rapidly and exothermically with water vapor to produce O₂ and HF. Calculate the $\Delta H^o_f$ for OF₂.

• $\text{OF}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{HF}(\text{g}) + \text{O}_2(\text{g})$
  $\Delta H^o_{\text{rxn}} = -318 \text{ kJ}$

• The heats of formation for $\text{H}_2\text{O}(\text{g})$ and HF(g) are -241.8 kJ/mol and -271.1 kJ/mol respectively.
Energy Units

- 1 calorie = 4.184 J
- 1 food calorie = 1 Cal = 1 kcal = 1000 cal

Given the reaction below for the combustion of glucose to form carbon dioxide and water, calculate the Calories/g for carbohydrates.

\[
C_6H_{12}O_6(s) + 6 \text{O}_2(g) \rightarrow 6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l)
\]

\[
\Delta H_{\text{rxn}} = -2801.6 \text{ kJ}
\]
M & M candies consist of 70% carbohydrates, 21% fat, and 4.6% protein as well as other ingredients that do not have caloric value. What quantity of energy is generated if 47.9 g of M&Ms (1 small package) were burned in a bomb calorimeter? How long will I need to walk to use up the value of the M&Ms if 1 hour of walking uses up 400 Cal?

- 4 Cal/g carbs
- 4 Cal/g protein
- 9 Cal/g fat

Sample exercise 5.18
Stoichiometry using Enthalpy

• Consider the following reaction:
  2 Na(s) + Cl₂(g) → 2 NaCl(s)  ΔH = −821.8 kJ
• Is the reaction exothermic or endothermic?
• Calculate the amount of heat transferred when 8.0 g of Na(s) reacts according to this reaction.
• We generally expect that reactions evolving heat should proceed spontaneously and those that absorb heat should require energy to occur.
  – Mix barium hydroxide and ammonium chloride

\[
\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}(s) + 2 \text{NH}_4\text{Cl}(s) \\
\rightarrow \text{BaCl}_2(\text{aq}) + 2 \text{NH}_3(\text{g}) + 10 \text{H}_2\text{O}(\text{l})
\]
Entropy

- The amount of randomness, or molecular disorder, in a system.

- $S = \text{more positive to indicate greater disorder.}$
Gibbs Free Energy, $\Delta G$

- Determines whether a reaction is spontaneous and at what temperature it becomes spontaneous.

- Spontaneous -- A process that proceeds on its own without any continuous external influence.
\[ \Delta G = \Delta H - T\Delta S \]

- If \( \Delta H = + \) and \( \Delta S = - \) never spontaneous
  \[ \Delta G = + \]
- If \( \Delta H = - \) and \( \Delta S = + \) always spontaneous
  \[ \Delta G = - \]
- If \( \Delta H = + \) and \( \Delta S = + \) or if \( \Delta H = - \) and \( \Delta S = - \) temperature determines spontaneity
  - At \( T \) where \( \Delta G = - \) reaction is spontaneous
  - At \( T \) where \( \Delta G = + \) reaction is nonspontaneous
Residential: 21%
Commercial: 18%
Industrial: 32%
Transportation: 29%
Energy Consumption by Source

- Petroleum
- Natural gas
- Coal
- Nuclear electric power
- Hydroelectric power
- Wood, waste, alcohol

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