Chapter 7 Chemical Reactions: Energy, Rates, and Equilibrium

Introduction
This chapter considers three factors:

a) **Thermodynamics** (Energies of Reactions)
   ______ a reaction will occur

b) **Kinetics** (Rates of Reactions)
   _____________ a reaction will occur.

c) **Equilibrium**
   _________________ a reaction will occur.

7.1 Energy and Chemical Bonds
There are two fundamental kinds of energy.

- **Potential energy** is _____________ energy.
  – The water in a reservoir behind a dam
  – An automobile poised to coast downhill
  – A coiled spring

- **Kinetic energy** is the energy of _____________.
  – Water falls over a dam and turns a turbine.
  – The car rolls downhill.
  – The spring uncoils and makes the hands on a clock move.

- The attractive forces between ions or atoms are a form of _____________ energy.
• When these forces result in the formation of ionic or covalent bonds, the potential energy is often converted into ___________.
  – **Breaking bonds** requires an input of energy and __________________ heat.
  – **Forming bonds** releases energy and __________________ heat.

In reactions,
• some bonds break
  – (energy ____)
• and new bonds can form
  – (energy ____).
• If the products have are ______________ in potential energy than the reactants, the products are __________ stable than the reactants.

### 7.2 Heat Changes During Chemical Reactions

In order for a chemical reaction to take place,

Bonds within reactant molecules must be broken.  
  Breaking bonds requires energy

Bonds within product molecules must be formed.  
  Forming bonds releases energy.

• The **greater** the bond dissociation energy, the more __________ the chemical bond.
• The more stable a molecule, the ________ reactive it is.

\[
: \text{N}::\text{N}:: \xrightarrow{226 \text{ kcal/mol}} :\text{N}^\cdot + \cdot\text{N}^\cdot \quad \text{N}_2 \text{ bond dissociation energy} = 226 \text{ kcal/mol}
\]

\[
: \text{Cl}::\text{Cl}:: \xrightarrow{58 \text{ kcal/mol}} :\text{Cl}^\cdot + \cdot\text{Cl}^\cdot \quad \text{Cl}_2 \text{ bond dissociation energy} = 58 \text{ kcal/mol}
\]

The greater stability of the triple bond explains why N\(_2\) is less reactive than Cl\(_2\).
Law of Conservation of Energy
(aka First Law of Thermodynamics)

Energy can be neither __________________________ in any chemical or physical change.

- In a chemical reaction, the difference between
  the heat absorbed in breaking bonds and
  the heat released in forming bonds is the
  __________________________ .

Heat of Reaction (when measured at constant pressure.) =

\[ \Delta \text{H} = \sum (\text{bond dissociation energies})_{\text{reactants}} - \sum (\text{bond dissociation energies})_{\text{products}} \]

The book has examples of calculations using this formula. I will not require this calculation. You just need to understand the concept.
7.3 Endothermic and Exothermic Reactions

<table>
<thead>
<tr>
<th>Energy In</th>
<th>Energy Out</th>
<th>ΔH</th>
<th>called</th>
<th>heat flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>If</td>
<td>Energy to break bonds</td>
<td>&lt;</td>
<td>Energy from formed bonds</td>
<td></td>
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All combustion reactions are ________________(give off energy).
That is why we use them to run our cars!

For **exothermic** reactions, heat is a ____________.

*An exothermic reaction—negative ΔH*

CH$_4$(g) + 2 O$_2$(g) → CO$_2$(g) + 2 H$_2$O(l) + 213 kcal

CH$_4$(g) + 2 O$_2$(g) → CO$_2$(g) + 2 H$_2$O(l) \[ ΔH = -213 \text{ kcal} \]

For **endothermic** reactions, heat is a ____________.

*An endothermic reaction—positive ΔH*

N$_2$(g) + O$_2$(g) → 2 NO(g) + 43 kcal

N$_2$(g) + O$_2$(g) → 2 NO(g) \[ ΔH = +43 \text{ kcal/mol} \]

**Rules for Calculating ΔH**

ΔH depends on the amounts of chemicals present.

**Rule 1.**
If you multiply the coefficients by 2, you multiply the value of ΔH by ____.

*Doubling the above reaction gives double the heat.*

\[ 2 \text{ N}_2(\text{g}) + 2 \text{ O}_2(\text{g}) \rightarrow 4 \text{ NO}_2(\text{g}) \quad \Delta H = \text{__________________________} \]
Rule 2. If you reverse a reaction, the magnitude (size) of ΔH is the same, but you must change the __________.
Reversing the above reaction gives:

\[ \text{2 NO}_\text{g} \rightarrow \text{N}_2\text{g} + \text{O}_2\text{g} \quad \Delta H = \text{________________________} \]

**Problem:** For the reaction \( \text{C(s) + O}_2\text{g} \rightarrow \text{CO}_2\text{g} + 394 \text{kJ} \)

a) What is the value of ΔH for the reaction?

b) Is the reaction exothermic or endothermic?

**Problem:** In photosynthesis, green plants convert carbon dioxide and water into glucose (\( \text{C}_6\text{H}_{12}\text{O}_6 \)) according to the following equation:

\[ \text{6 CO}_\text{g} + 6 \text{ H}_2\text{O}_\text{l} + 678 \text{ kcal} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6\text{aq} + 6 \text{ O}_2\text{g} \]

a) Is the reaction exothermic or endothermic?

b) What is the value of ΔH for the reaction?

c) What is the value of ΔH for the reaction

\[ 3 \text{ C}_6\text{H}_{12}\text{O}_6 + 18 \text{ O}_2 \rightarrow 18 \text{ CO}_2 + 18 \text{ H}_2\text{O} \]

d) How many kcal are needed to use up 3.50 moles of carbon dioxide?

e) If 800. kcal is available, how many grams of oxygen can be produced.
**Problem:** The following equation shows the conversion of aluminum oxide to aluminum:

\[ 2 \text{Al}_2\text{O}_3(s) \rightarrow 4 \text{Al}(s) + 3 \text{O}_2(g) \] \[ \Delta H = +801 \text{ kcal} \]

a) *Is the reaction exothermic or endothermic?*

b) *How many kilocalories are required to produce 1.00 mol of Al?*

*Hint: Rewrite the equation including the heat and then apply normal stoichiometry.*

Note:

It could be \(801/2 = 400. \text{ kcal/mol Al}_2\text{O}_3\) decomposed or \(801/4 = 200. \text{ kcal/mol Al} \) produced or \(801/3 = 267 \text{ kcal/mol O}_2 \) produced

c) *How many kilocalories are required to produce 10.0 g of Al?*

**Problem:** How much heat is absorbed during the production of 145 g of NO by the combustion of nitrogen and oxygen according to the reaction:

\[ \text{N}_2(g) + \text{O}_2(g) \rightarrow 2 \text{NO}(g) \] \[ \Delta H = +43 \text{ kcal} \]

*Heat can be treated as a reactant (if +) or as a product (if -).*

Rewriting the equation:
7.4 Why Do Chemical Reactions Occur?

Free Energy

**Spontaneous and Non-spontaneous Changes**

A **spontaneous process** is one that, ____________, proceeds on its own without any external influence.

- Events that lead to lower energy tend to happen spontaneously.

A **non-spontaneous** process requires that something be done in order for it to occur.

![Spontaneous and Non-spontaneous Changes](image)

**Most** (but not all) _________________ reactions are spontaneous.

**Most** (but not all) _________________ reactions are **non-spontaneous**.

**Question:** is the melting of ice an **endothermic** or **exothermic** process.

**Question:** Does ice melt spontaneously?

So _________________ makes a difference.

Let’s look at what makes this true.

**Question:** Is water more or less disorganized than ice?

**Entropy(S):** A measure of the amount of molecular disorder in a system.

(Measured in calories/(mol·K) or J/(mol·K)).

The world naturally tends towards a random state, which is lower in energy.
Increases in entropy result in a positive _____ value for $\Delta S$.

Decreases in entropy result in a negative _____ value for $\Delta S$.

All spontaneous endothermic processes have an __________ in molecular disorder, or randomness. __________

**Problem:** Does entropy increase or decrease in the following processes?

a) Gasoline fumes escape as the fuel is pumped into your car.

b) $\text{Mg}(s) + \text{Cl}_2(g) \rightarrow \text{MgCl}_2(s)$

For 2 reasons: (1) _____

(2) _____

**Gibbs Free Energy Change**

Two factors favor spontaneity.

A __________________________

An __________ in molecular disorder ________.

- When enthalpy and entropy are **both favorable**
  
  ($-\Delta H$, $+\Delta S$), a process is __________ spontaneous.

- When **both are unfavorable**, 
  
  ($+\Delta H$, $-\Delta S$ negative) a process is ________ spontaneous.

When one factor favors spontaneity but the other doesn’t we need to take temperature into account.

- To take both into account, a quantity called the **Gibbs free-energy change** ($\Delta G$) is used.
Spontaneity also depends on temperature ($T$).

- At **low** temperature, 
  - $T\Delta S$ is small, 
  - ______ is the dominant factor.

- At **high** enough temperature, 
  - the value of $T\Delta S$ becomes larger than $\Delta H$ and 
  - ______ becomes the deciding factor.

An endothermic process that is nonspontaneous at low temperature can become spontaneous at a higher temperature.

**The sign of $\Delta G$** tells us a lot about the reaction:

- $\Delta G > 0$ (+) then reaction is ________________________.
- $\Delta G < 0$ (-) then reaction is ________________________.
- $\Delta G = 0$ reaction is ________________________.
- An ________________________ reaction is
  spontaneous
  releases free energy
  has a negative $\Delta G$.
- An ________________________ reaction is
  nonspontaneous
  absorbs free energy
  has a positive $\Delta G$.
Spontaneity Chart for $\Delta G = \Delta H - T\Delta S$

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-) favors</td>
<td>(+) favors</td>
<td>Always (-) always spontaneous</td>
</tr>
<tr>
<td>(+) disfavors</td>
<td>(-) disfavors</td>
<td>Always (+) always non-spontaneous</td>
</tr>
<tr>
<td>(-) favors</td>
<td>(+) disfavors</td>
<td>(-) spontaneous at _______ Temp (+) / non-spontaneous at _______ Temp</td>
</tr>
<tr>
<td>(+) disfavors</td>
<td>(-) favors</td>
<td>(+) / non-spontaneous at _______ Temp (-) / spontaneous at _______ Temp</td>
</tr>
</tbody>
</table>

When one factor favors spontaneity and the other one doesn’t
_______ wins out at low temperatures
_______ wins out at high temperatures

(when $T\Delta S$ exceed $\Delta H$)

**Problem:** Lime, (CaO) is prepared by the decomposition of limestone (CaCO₃) according to the reaction:

\[
\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \quad \Delta G = +31 \text{ kcal/mol at } 25 \, ^\circ\text{C}
\]

a) Does the reaction occur spontaneously at 25 °C?

b) Is the reaction exergonic or endergonic?

c) Does entropy increase or decrease in this reaction?

d) What could we say about the sign of $\Delta H$? (+)
**Problem:** The melting of ice to form liquid water has $\Delta H = +1.44 \text{ kcal/mol}$ and $\Delta S = +5.26 \text{ cal/(mol} \cdot \text{K)}$

a) What is the value of $\Delta G$ for the melting process at -10°C (263 K)?

Hint: Be careful to have $T$ and $S$ in the same units!

b) Is the melting of ice spontaneous at this temperature?

c) If we were to recalculate with a temp 10°C would we expect the reaction to be spontaneous or non-spontaneous?

d) Would the sign of $\Delta G$ be positive or negative?

If we change the direction of the reaction?

- The sign of $\Delta G$ changes
- It switches spontaneity

The value of $\Delta G$ tells us only whether a reaction _______ occur; it says nothing about how _______ the reaction will occur.

**Kinetics** measures the time required for a reaction to occur, as well as the mechanism for the how the reaction occurs.
7.5-7.6 Reaction Rates (Kinetics)

This is the study of reactions as a function of time.

**Effective Collisions**

Not all collisions between reactants result in products.

For reactants to make products:

1) Particles must ____________________.

2) In the ____________________.

For ozone to react with NO to produce NO₂ and oxygen, the nitrogen end of the NO must be the part that hit the ozone molecule.

3) With sufficient ________________ to break reactant bonds.

   Heat causes particles to move faster. This is why it is often necessary to heat a reaction to get it to proceed.
   (If it is already spontaneous, heating it will make it go faster.)

**Activation Energy**

**Activation Energy** (Eₐ): The energy barrier that must be climbed or the amount of energy required to initiate a chemical reaction. It determines the rate of reaction.

Eₐ affects the _________ of the reaction.

The _____________ the activation energy, the _____________ the reaction.
The energy changes that happen during a reaction can be shown in diagrams.

Left Side:
- Exergonic Reaction
- Products lower in energy than reactants
- ____ value of \( \Delta G \)

Right Side:
- Endergonic Reaction
- Products higher in energy than reactants
- ____ value of \( \Delta G \)

These reactions are sometimes shown with \( \Delta H \) instead of \( \Delta G \).

_______ reaction
Spontaneous only at _______ temp.

_______ Reaction
Spontaneous at _______ temps.
When the activation energy is high, we may need to add energy to get the reaction to start.

**Example:** Burning of charcoal in our BBQs

Simplified Rxn: \[ C + O_{2(g)} \rightarrow CO_2 + \text{heat} \] (exothermic rxn)

Does the charcoal self ignite?

Do we need to keep adding more energy to keep the reaction going?

Why don’t we need to take the same precautions with normal air, which also contains oxygen?

Let’s continue and find out!

**Factors That Influence Reaction Rates**

**Temperature**

Rule of Thumb: A ________ increase in temperature will double the rate of a reaction.