Chapter 6

Chemical Reactivity and Reaction Mechanisms
Chemical Reactivity
Enthalpy
A simple chemical reaction can be broken down into bond creating and bond breaking components:

\[
A-B + Y-Z \rightarrow A-Y + B-Z
\]

\[
A-B \rightarrow A\cdot + B\cdot \quad \Delta H^\circ = +\text{BDE}
\]

\[
Y-Z \rightarrow Y\cdot + Z\cdot \quad \Delta H^\circ = +\text{BDE}
\]

\[
A\cdot + Y\cdot \rightarrow A-Y \quad \Delta H^\circ = -\text{BDE}
\]

\[
B\cdot + Z\cdot \rightarrow B-Z \quad \Delta H^\circ = -\text{BDE}
\]

\[
\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{bonds broken}} - \sum \Delta H^\circ_{\text{bonds formed}}
\]

BDE = Bond dissociation energy
### Homolytic Bond Dissociation Energies ($\Delta H^\circ$): $Y-Z \rightarrow Y\cdot + Z\cdot$

<table>
<thead>
<tr>
<th>Bond</th>
<th>kcal/mol</th>
<th>kJ/mol</th>
<th>Bond</th>
<th>kcal/mol</th>
<th>kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3-\text{H}$</td>
<td>105</td>
<td>439</td>
<td>$\text{H}-\text{H}$</td>
<td>104</td>
<td>435</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2-\text{H}$</td>
<td>101</td>
<td>423</td>
<td>$\text{F}-\text{F}$</td>
<td>38</td>
<td>159</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2\text{CH}_2-\text{H}$</td>
<td>101</td>
<td>423</td>
<td>$\text{Cl}-\text{Cl}$</td>
<td>58</td>
<td>242</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{CH}-\text{H}$</td>
<td>99</td>
<td>414</td>
<td>$\text{Br}-\text{Br}$</td>
<td>46</td>
<td>192</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{C}-\text{H}$</td>
<td>97</td>
<td>406</td>
<td>$\text{I}-\text{I}$</td>
<td>36</td>
<td>150</td>
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<tr>
<td>$\text{CH}_3-\text{CH}_3$</td>
<td>88</td>
<td>368</td>
<td>$\text{H}-\text{Cl}$</td>
<td>103</td>
<td>432</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2-\text{CH}_3$</td>
<td>85</td>
<td>355</td>
<td>$\text{H}-\text{Br}$</td>
<td>87</td>
<td>366</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{CH}-\text{CH}_3$</td>
<td>84</td>
<td>351</td>
<td>$\text{H}-\text{I}$</td>
<td>71</td>
<td>298</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{C}-\text{CH}_3$</td>
<td>80</td>
<td>334</td>
<td>$\text{CH}_3-\text{F}$</td>
<td>108</td>
<td>451</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}=\text{CH}_2$</td>
<td>174</td>
<td>728</td>
<td>$\text{CH}_3-\text{Cl}$</td>
<td>84</td>
<td>350</td>
</tr>
<tr>
<td>$\text{HC}=\text{CH}$</td>
<td>231</td>
<td>966</td>
<td>$\text{CH}_3\text{CH}_2-\text{Cl}$</td>
<td>82</td>
<td>343</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$(\text{CH}_3)_2\text{CH}-\text{Cl}$</td>
<td>81</td>
<td>338</td>
</tr>
<tr>
<td>$\text{HO}-\text{H}$</td>
<td>119</td>
<td>497</td>
<td>$(\text{CH}_3)_3\text{C}-\text{Cl}$</td>
<td>79</td>
<td>330</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O}-\text{H}$</td>
<td>104</td>
<td>435</td>
<td>$\text{CH}_3-\text{Br}$</td>
<td>70</td>
<td>294</td>
</tr>
<tr>
<td>$\text{CH}_3-\text{OH}$</td>
<td>92</td>
<td>387</td>
<td>$\text{CH}_3\text{CH}_2-\text{Br}$</td>
<td>69</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(\text{CH}_3)_2\text{CH}-\text{Br}$</td>
<td>68</td>
<td>285</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(\text{CH}_3)_3\text{C}-\text{Br}$</td>
<td>63</td>
<td>264</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\text{CH}_3-\text{I}$</td>
<td>57</td>
<td>239</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\text{CH}_3\text{CH}_2-\text{I}$</td>
<td>55</td>
<td>230</td>
</tr>
</tbody>
</table>

For the process:

\[ \text{A-B + Y-Z} \rightarrow \text{A-Y + B-Z} \]

\[ \Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{bonds broken}} - \sum \Delta H^\circ_{\text{bonds formed}} \]

\[ \begin{array}{c}
\text{H}_3\text{C} - \text{C} - \text{H} + \text{Br} - \text{Br} \rightarrow \text{H}_3\text{C} - \text{C} - \text{Br} + \text{H} - \text{Br}
\end{array} \]

423 kJ/mol \hspace{1cm} 192 kJ/mol \hspace{1cm} 294 kJ/mol \hspace{1cm} 366 kJ/mol

Bond Dissociation Energies
\[ \Delta H^o_{\text{rxn}} = \sum \Delta H^o_{\text{bonds broken}} - \sum \Delta H^o_{\text{bonds formed}} \]

\[ \text{H}_3\text{C} - \text{C} - \text{H} + \text{Br} - \text{Br} \rightarrow \text{H}_3\text{C} - \text{C} - \text{Br} + \text{H} - \text{Br} \]

423 kJ/mol  192 kJ/mol  294 kJ/mol  366 kJ/mol

\[ \Delta H^o_{\text{rxn}} = 423 + 192 - 294 - 366 \]

\[ = -45 \text{ kJ/mol} \]
An Exothermic Reaction

\[ \Delta H^0 = -\theta \]

Enthalpy (H)

A + B

C + D

Reaction coordinate
Enthalpy \( (H) \)

**And Endothermic Reaction**

\[
\Delta H^0 = \bigoplus \quad A + B \\
\downarrow \quad \downarrow \quad \downarrow \\
C + D \\
\downarrow \\
\Delta H^0 = \bigoplus
\]

Reaction coordinate
Chemical Reactivity

Entropy
(a measure of the disorder associated with a system)
Entropy

Entropy change is favorable when the result is a more random system.

This is called a Positive Entropy Change.
The Concept of Entropy  
(The Degree of Randomness)

A change in degree of randomness is a change in the number of ways of arranging particles.

More order $\rightarrow$ Less Order

- solid $\rightarrow$ liquid $\rightarrow$ gas
- solid + liquid $\rightarrow$ ions in solution
- solid + solid $\rightarrow$ gases + ions in solution
- fewer particles $\rightarrow$ more particles

Fewer degrees of movement $\rightarrow$ More degrees of movement
Chemical Reactivity

Gibbs Free Energy Change

$$\Delta G = \Delta H - T\Delta S$$

Enthalpy Factor

Entropy Factor
Exergonic (Spontaneous) process

Free energy ($G$)

Reaction coordinate

$\Delta G^0 = \Theta$

$A + B \rightarrow C + D$
Free energy ($G$)

Endergonic (non-Spontaneous) Process

$\Delta G^0 = \oplus$

Reaction coordinate

$A + B \rightarrow C + D$
Chemical Reactivity
Equilibria

\[ m \text{ A} + n \text{ B} \rightleftharpoons s \text{ C} + t \text{ D} \]

\[ K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[\text{C}]^s [\text{D}]^t}{[\text{A}]^m [\text{B}]^n} \]

\[ \Delta G^\circ = -RT \ln K \]

Note: As \( K_{eq} \) increases, i.e., \( \Delta G \) becomes more negative and the reaction becomes more favorable.
\[ \Delta G = \Delta H - T \Delta S \]

\( \Delta G < 0 \) for a spontaneous process

\( \Delta G > 0 \) for a nonspontaneous process

\( \Delta G = 0 \) for a process at equilibrium

<table>
<thead>
<tr>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
<th>Low Temperature</th>
<th>High Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>+</td>
<td>Spontaneous</td>
<td>Spontaneous</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>Non-Spontaneous</td>
<td>Non-Spontaneous</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>Spontaneous</td>
<td>Non-Spontaneous</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>Spontaneous</td>
<td>Non-Spontaneous</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>Non-Spontaneous</td>
<td>Spontaneous</td>
</tr>
</tbody>
</table>
# Relationship Between $\Delta G$ and $K_{eq}$

<table>
<thead>
<tr>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$K_{eq}$</th>
<th>% product at equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>-17</td>
<td>1000</td>
<td>99.9%</td>
</tr>
<tr>
<td>-11</td>
<td>100</td>
<td>99%</td>
</tr>
<tr>
<td>-6</td>
<td>10</td>
<td>90%</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>50%</td>
</tr>
<tr>
<td>+6</td>
<td>0.1</td>
<td>10%</td>
</tr>
<tr>
<td>+11</td>
<td>0.01</td>
<td>1%</td>
</tr>
<tr>
<td>+17</td>
<td>0.001</td>
<td>0.1%</td>
</tr>
</tbody>
</table>
Chemical Reactivity

Kinetics and Rates
**Thermodynamics vs. Kinetics**

- **Potential energy**
  - Reactants
  - Products
  - \( E_{activation} \)

**Thermodynamics**
- Initial and final states
- Spontaneity

**Kinetics**
- Intermediate states
- Speed of reaction

**Reaction coordinate**
Rate of a Reaction

rate of a reaction = \left( \frac{\text{number of collisions}}{\text{per unit of time}} \right) \times \left( \frac{\text{fraction with sufficient energy}}{} \right) \times \left( \frac{\text{fraction with proper orientation}}{} \right)

First-Order Kinetics

A → B

rate \propto [A]

rate = k[A]

Second-Order Kinetics

A + B → C + D

rate = k[A][B]

A + A → B

rate = k[A]^2
What Affects the Rate of a Reaction?

Energy of Activation
Temperature
Steric Considerations
Influence of a Catalyst

Reactants $\rightarrow$ Products

Potential energy

Reactants $\rightarrow$ Products

$catalyzed$ $reaction$

$uncatalyzed$ $reaction$

$E_a$ $E_a$
\[
\Delta H^\circ \approx -95 \text{ kJ/mol}
\]

\[
\Delta H^\circ \approx -20 \text{ kJ/mol}
\]
\[ \Delta H^\circ \approx -20 \text{ kJ/mol} \]

\[ \Delta H^\circ \approx -43 \text{ kJ/mol} \]
\[
\begin{align*}
\text{H} & \quad \begin{array}{c}
\text{C} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array} & \quad \text{Br} & \quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array} & \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array} \\
\text{(l)} & \quad \rightarrow & \quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{H} \\
\text{H}
\end{array} & \quad \begin{array}{c}
\text{C} \\
\text{C} \\
\text{H}
\end{array} & \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array} & \quad \text{H} & \quad \text{Br} \\
\text{(g)} & \quad \text{(g)} & \quad \text{(g)}
\end{align*}
\]

\[\Delta H^\circ \approx +86 \text{ kJ/mol}\]

\[
\begin{align*}
\text{H} & \quad \begin{array}{c}
\text{C} \\
\text{C}
\end{array} & \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} & \quad \text{Br} & \quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array} & \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array} \\
\text{(l)} & \quad \rightarrow & \quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array} & \quad \begin{array}{c}
\text{C} \\
\text{C} \\
\text{H}
\end{array} & \quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array} & \quad \text{H} & \quad \text{Br} \\
\text{(g)} & \quad \text{(g)} & \quad \text{(g)}
\end{align*}
\]

\[\Delta H^\circ \approx +98 \text{ kJ/mol}\]
Chemical Reactivity

Transition States vs. Intermediates
Potential energy

Reactant

Transition State

High-energy state
Cannot be isolated
Bonds being broken or formed

Product

Reaction coordinate
Potential energy

Reactant

Transition State

Intermediate

Longer-lived Bonds not being broken or formed

Transition State

Product

Reaction coordinate
Some reactions proceed through a single transition state.
Some reactions proceed through two or more reactive intermediates and transition states.
Effect of a Catalyst

![Diagram showing the effect of a catalyst on reaction energy and progress]

- **Energy**
- **Reaction Progress**
- **E_a (no catalyst)**
- **E_a (with catalyst)**
- **ΔG**
Reaction coordinate

Energy

Reaction 1

Product #1

Intermediate

E_{act}

Reaction 2

Thermodynamic product

Product #2

Kinetic product
In an exergonic reaction, the transition state is closer to the energy and structure of the reactant(s).

Changing the energy of the products does very little to influence the rate of the reaction.
The Hammond Postulate

In an endergonic reaction, the transition state is closer to the energy and structure of the product(s).

Changing the energy of the products lowers the energy of activation and increases the rate of the reaction.
Chemical Reactivity

Nucleophiles and Electrophiles
Nucleophilic Centers

An electron-rich atom which is capable of donating a pair of electrons (i.e., a “Lewis base”)

May or may not have a negative charge:

Must consider electronegativity of atoms:
Electrophilic Centers

An electron-deficient atom which is capable of accepting a pair of electrons (i.e., a “Lewis acid”)

May or may not have a positive charge:

The electrophilic center may be an empty orbital:
Patterns of Chemical Reactions

Nucleophilic Attack
Loss of a Leaving Group
Proton Transfer
Carbocation Rearrangements
Patterns of Chemical Reactions

Nucleophilic Attack

\[
\begin{align*}
\text{Br}^- & \quad \text{+} \quad \text{H}^+ \\
\downarrow & \\
\text{: Br} & \\
\end{align*}
\]
Patterns of Chemical Reactions
Loss of a Leaving Group

\[
\begin{align*}
\text{Br} & \rightarrow \text{Br} \\
\rightarrow & \rightarrow \\
\text{+} & + \text{Br} \\
\rightarrow & \rightarrow \\
\text{O} & \rightarrow \text{Br} \\
\rightarrow & \rightarrow \\
\text{+} & + \text{Br}
\end{align*}
\]
Patterns of Chemical Reactions
Proton Transfer
Patterns of Chemical Reactions
Proton Transfer

\[ \text{Patterns of Chemical Reactions} \]
\[ \text{Proton Transfer} \]

\[ \text{Diagram with molecular structures and reactions} \]
Patterns of Chemical Reactions

Nucleophilic Attack
Loss of a Leaving Group
Proton Transfer
Carbocation Rearrangements
Examples
Patterns of Chemical Reactions
Carbocation Rearrangements

Where do carbocations come from?

\[ \text{C} \quad \text{LG} \quad \rightarrow \quad \text{C}^+ \quad \text{LG}^- \]
Two views of the methyl cation, $\text{CH}_3^+$. The carbon and three hydrogens all lie in the same plane and the carbon is $sp^2$ hybridized.

One unoccupied, unhybridized $p$ orbital remains perpendicular to the plane of the four atoms.

The orbitals of the three $\text{C-H}$ bonds lie perpendicular to the $p$ orbital, resulting in zero overlap and zero stabilization.
Two views of the ethyl cation, $\text{CH}_3\text{CH}_2^+$. The carbon and three hydrogens of the positive carbon all lie in the same plane and the carbon is $sp^2$ hybridized.

One unoccupied, unhybridized $p$ orbital remains perpendicular to the plane of the four atoms. The second carbon has the expected $sp^3$ hybridization.

Electron density flows from the sigma bond toward the electron deficient carbon, resulting in stabilization of the carbocation.

Note: This stabilization is also present in two other conformers as the C-C bond rotates.
Patterns of Chemical Reactions

Carbocation Rearrangements

Increasing Stability

As more adjacent carbons with additional attached groups are added, additional hyperconjugation and stabilization of the resulting carbocation occurs.

Methyl     Primary     Secondary     Tertiary
Carbocations may “rearrange” from $1^\circ \longrightarrow 2^\circ \longrightarrow 3^\circ$ to form more stable structures !!!
Patterns of Chemical Reactions
Carbocation Rearrangements

**Hydride Shift**

2º carbocation → 3º carbocation

2º carbocation

**Methyl Shift**

2º carbocation → 3º carbocation

2º carbocation
Patterns of Chemical Reactions
Carbocation Rearrangements

formation of a more stable resonance structure

$2^\circ$ carbocation

$3^\circ$ carbocation
Examples