Reaction Mechanism

- A step-by-step description of the sequence of bonding changes that actually happen in the course of a chemical reaction.

\[
\begin{align*}
2 \text{N}_3 & \quad + \quad 6 \text{I}^\cdot \\
\text{N}_2 & \quad + \quad 3 \text{I}_2 \\
\Delta U & = -444 \text{ kJ/mol}
\end{align*}
\]

- Each step (called an elementary step) must be balanced, and has its own rate law.

- Since an elementary step (ES) is a literal description of what atoms/molecules are colliding with each other at some point in a reaction, the stoichiometric coefficients in an elementary step are equal to the reaction orders.

- Terminology…

<table>
<thead>
<tr>
<th>Number of Reactants</th>
<th>Molecularity</th>
<th>ES is said to be…</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Unimolecular</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>Bimolecular</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>Termolecular</td>
</tr>
</tbody>
</table>

- The elementary steps of a mechanism must add up to the overall reaction.

- The mechanism’s overall rate law must agree with that observed for the overall reaction. However, one does not simply add up rate laws for individual elementary steps to obtain the overall rate law.
Mechanism Examples

\[
H_2(g) + Br_2(g) \rightarrow 2 HBr(g) \quad \frac{d[HBr]}{dr} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2]^2 + k'[HBr]} \quad (23.4)
\]

The following mechanism has been proposed to account for this rate law (Fig. 23.1):

**Initiation:** \( Br_2 + M \rightarrow Br_+ + Br_+ + M \quad v = k_1[Br_2][M] \)

where M is either \( Br_2 \) or \( H_2 \). This step is an example of a **thermolysis**, a reaction initiated by heat, which stimulates vigorous intermolecular collisions.

**Propagation:** \( Br_+ + H_2 \rightarrow HBr + H_+ \quad v = k_4[Br_+][H_2] \)
\( H_+ + Br_2 \rightarrow HBr + Br_+ \quad v = k'_4[H_+][Br_2] \)

**Retardation:** \( H_+ + HBr \rightarrow H_2 + Br_+ \quad v = k_1[H_+][HBr] \)

**Termination:** \( Br_+ + Br_+ + M \rightarrow Br_2 + M^* \quad v = k_1[Br_+]^2[M] \)