**Chapter 12. Chemical Kinetics**

**Reaction Rate**
- Reaction rate = change in reagent concentration per unit of time.
- Rate > 0 increase
- Rate < 0 decrease

The reaction rate changes as the reaction proceeds because the reactant and product concentrations vary.

We often consider the “initial” reaction rate because when the concentration of products is small, the extent of the reverse reaction is negligible.

**Integrated Rate Laws: Concentration v. Time**

**General Rate Law**

\[ aA + bB \rightarrow C \] products

Initial reaction rate = 

\[ \frac{\Delta[A]}{\Delta t} = k[A]^m[B]^n[C]^p \]

- \( k = \) rate constant
- \( A, B = \) concentration of reactants
- \( C = \) concentration of catalyst
- \( m = \) order of rxn for \( A \)
- \( n = \) order of rxn for \( B \)
- \( p = \) order of rxn for \( C \)

Total rxn order = \( m + n + p \)

They are not necessarily related to the balanced rxn equation.

**Rate Laws are Determined Empirically**

\[ A + B \rightarrow \text{products} \]

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Initial [A] mol/L</th>
<th>Initial [B] mol/L</th>
<th>Initial rate mol/(L·min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.20</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>0.10</td>
<td>150</td>
</tr>
</tbody>
</table>

Rate = \( k[A]^m[B]^n \) determine \( m \) and \( n \)

Compare #1 and #2 \( A \) constant, \( B \) doubles, rate quadruples

so rate \( B^2 \) i.e. \( n = 2 \)

Compare #1 and #3 \( B \) constant, \( A \) triples, rate triples

so rate \( A \) i.e. \( m = 1 \)

Rate = \( k[A][B]^2 \) 3rd order

**Half Life - \( t_{1/2} \)**

\( t_{1/2} \) = length of time for reactant concentration to decrease by half

Therefore, at \( t = t_{1/2} \) \( [A] = [A]_0/2 \)

\[ \ln\left(\frac{[A]}{[A]_0}\right) = \ln\left(\frac{1}{2}\right) = \ln(0.5) = -k t_{1/2} \]

\[ t_{1/2} = \frac{\ln(0.5)}{-k} \]

1st order kinetics

Independent of \([A]_0\)
**Mechanism Example**

CHCl₃ (g) + Cl₂ (g) → CCl₄ (g) + HCl (g)

Mechanism:
- step 1: Cl₂ (g) → 2 Cl (g) fast, reversible
- step 2: CHCl₃ (g) + Cl (g) → CCl₄ (g) + HCl (g) slow
- step 3: CCl₃ (g) + Cl (g) → CCl₄ (g) fast

Cl₂, CCl₃, and Cl₂ are called reaction intermediates. Produced in one step and consumed in another. They do not appear in the net rxn equation.

- When only one step is slow and the others are fast, the slow step is called the rate limiting step (step 2 above).
- The overall rxn can go no faster than the rate limiting step.
- Rate of rxn = rate of rate limiting step

**Rate Laws of Elementary Steps**

Unlike net rxn equations, elementary steps have specific associated rate laws.

<table>
<thead>
<tr>
<th>step</th>
<th>molecularity</th>
<th>law</th>
</tr>
</thead>
<tbody>
<tr>
<td>A → A products</td>
<td>unimolecular</td>
<td>rate = ( k[A] )</td>
</tr>
<tr>
<td>2A → A + B products</td>
<td>bimolecular</td>
<td>rate = ( k[A]^2 )</td>
</tr>
<tr>
<td>3A → A + B + C products</td>
<td>termolecular</td>
<td>rate = ( k[A]^3 )</td>
</tr>
</tbody>
</table>

Note: order of rate law = molecularity of step

- Collisions are necessary for a rxn to occur.
- Probability of A colliding with B is proportional to \([A] \) and \([B] \).
- Elementary steps with molecularity \( \geq 3 \) are extremely rare and would require a simultaneous collision between 4 or more molecules.
Chap 12: Chemical Kinetics

**Transition State Theory**

- In the middle of a reaction, there is a "transition state" that is energetically unfavorable.
- For example, a molecule must often be deformed in order to react, or an existing bond might have to be weakened prior to forming a new bond.
- The transition state is an energy "barrier" to overcome.
- Reactants need to be "activated" with some additional energy to get over the barrier.

**Molecular Collision Model of Rxn Rate**

- Molecules must collide
- The collision must be "effective" (appropriate orientation, etc.)
- The collision must be with sufficient energy to form an activated complex

Kinetic molecular theory: Molecules have greater thermal kinetic energy at higher temperatures. Therefore, as temperature increases, collisions are more likely to form an activated complex and proceed to products.

**Energy Diagram**

- Transition state: "activated complex"
- Reaction energy: $E = E_{\text{transition state}} - E_{\text{reactants}}$
- Energy of reaction: $\Delta E = E_{\text{products}} - E_{\text{reactants}}$

In the case pictured above, $\Delta E < 0$ (exothermic reaction)

**Quantify Molecular Model**

Rate constant: $k = p \frac{Z e^{[E_0/kT]}}{RT}$

- $p = "steric\ factor"$ \text{fraction of collisions with effective orientations}
- $Z = \text{constant related to collision frequency}$
- $e^{[E_0/kT]} = \text{fraction of collisions with sufficient energy}$

Also written: $k = A e^{[E_0/kT]}$ \text{Arrhenius equation}

$A = "frequency\ factor"$

Alternate form: $\ln k = \ln A + \frac{E_0}{RT}$

**Catalysis**

**Types of Catalysis**

**Homogeneous**: Catalyst is in the same phase as the reactants. Typically a molecule dissolved into a fluid reaction mixture. Examples: acids, enzymes

**Heterogeneous**: Catalyst is in a different phase than the reactants. Typically a solid catalyst. The reaction occurs when the reactant molecules adsorb on the catalyst surface. Examples: Pt, catalytic converter

How to increase the reaction rate:
- Increase reactant concentration
- Raise $T$
- Lower energy barrier – catalyst!

- Catalysis alter the reaction mechanism to lower the activation barrier
- Catalysts are not consumed or produced in the reaction, so they do not appear in the overall balance reaction equation.
- Since the catalyst may appear in the rate limiting step, the catalyst concentration may appear in the rate law.