Chapter 13
CHEMICAL KINETICS
The Rates of Chemical Reactions

Hill, Petrucci, McCreary & Perry 4th Ed.
Rates of Reaction

Definitions of Reaction Rate:

The Increase in Molar Concentration of a Product per unit of time.

The Decrease in Molar Concentration of a Reactant per unit of time.

Rates are always Positive!
General Reaction:

\[ A \rightarrow B \]

rate \( \equiv \frac{\Delta[B]}{\Delta t} \equiv -\frac{\Delta[A]}{\Delta t} \)

Where:
\( \Delta t \equiv t_{\text{final}} - t_{\text{initial}} \)

\( \Delta[B] \equiv [B]_{\text{final}} - [B]_{\text{initial}} \)

more - less \( \Rightarrow \) positive

\( \Delta[A] \equiv [A]_{\text{final}} - [A]_{\text{initial}} \)

less - more \( \Rightarrow \) negative
Rates are Related by the Reaction Stoichiometry

\[2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})\]

rate = ?

\[
\frac{\Delta [\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta [\text{NO}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta [\text{N}_2\text{O}_5]}{\Delta t}
\]

\[4 \text{ times larger than } \text{O}_2 \text{ rate}\]

\[\text{neg & 2 times larger than } \text{O}_2 \text{ rate}\]
To Determine a Reaction Rate the experimentalist must determine the concentration of a *reactant* or a *product* over the course of a reaction.

**Average Rate for:** \[ \text{A} \rightarrow \text{B} \]

\[
\text{rate} = \frac{\Delta[B]}{\Delta t} = \frac{[B]_{\text{final}} - [B]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}
\]

Experimentalist needs two \([B]\) at two different times to get an average change in \([B]\) over time.
Experimentally Measuring the Rate of a Chemical Reaction

\[ \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2} \text{O}_2(\text{g}) \]

What can we measure?

Easiest: Evolution of Oxygen!

Others, the concentration changes of Hydrogen peroxide or water can be obtained by stoichiometry!
Measuring Reaction Rates

• In general, the greater the reactant concentration the *faster* the reaction.

• The *average rate* is the rate of reaction over the duration of the whole experiment.

• An *instantaneous rate* is equal to the *tangent to the curve* at a given point. Think of this like a speedometer reading at any point in a trip from A to B, while the average rate was for the whole journey.
### Decomposition of $\text{H}_2\text{O}_2$

$$\text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(l) + \frac{1}{2} \text{O}_2(g)$$

<table>
<thead>
<tr>
<th>Time, s</th>
<th>Mass $\text{O}_2$, g</th>
<th>$[\text{H}_2\text{O}_2]$, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.882</td>
</tr>
<tr>
<td>60</td>
<td>2.960</td>
<td>0.697</td>
</tr>
<tr>
<td>120</td>
<td>5.056</td>
<td>0.566</td>
</tr>
<tr>
<td>180</td>
<td>6.784</td>
<td>0.458</td>
</tr>
<tr>
<td>240</td>
<td>8.160</td>
<td>0.372</td>
</tr>
<tr>
<td>300</td>
<td>9.344</td>
<td>0.298</td>
</tr>
<tr>
<td>360</td>
<td>10.336</td>
<td>0.236</td>
</tr>
<tr>
<td>420</td>
<td>11.104</td>
<td>0.188</td>
</tr>
<tr>
<td>480</td>
<td>11.680</td>
<td>0.152</td>
</tr>
<tr>
<td>540</td>
<td>12.192</td>
<td>0.120</td>
</tr>
<tr>
<td>600</td>
<td>12.608</td>
<td>0.094</td>
</tr>
</tbody>
</table>
Mathematical Determination of [H₂O₂]

\[ \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2} \text{O}_2(\text{g}) \]

1.00 L, 0.882 M -- To calculate [H₂O₂] at 60 sec from .

**Number of moles of O₂ produced at 60 s:**

\[ \frac{2.960 \text{ g O}_2}{32.00 \text{ g O}_2} \times \frac{1 \text{ mol O}_2}{1 \text{ mol O}_2} = 0.09250 \text{ mol O}_2 \]

**Number of moles of H₂O₂ consumed at 60 s:**

\[ 0.09250 \text{ mol O}_2 \times \frac{2 \text{ mol H}_2\text{O}_2}{1 \text{ mol O}_2} = 0.1850 \text{ mol H}_2\text{O}_2 \]

**Number of moles of H₂O₂ present at 0 s:**

\[ 1.00 \text{ L} \times 0.882 \text{ M H}_2\text{O}_2 = 0.882 \text{ mol H}_2\text{O}_2 \]

**Number of moles of H₂O₂ remaining at 60 s:**

\[ 0.882 \text{ mol H}_2\text{O}_2 - 0.185 \text{ mol H}_2\text{O}_2 \text{ consumed} = 0.697 \text{ mol H}_2\text{O}_2 \]

\[ \frac{0.697 \text{ mol H}_2\text{O}_2}{1.00 \text{ L}} = 0.697 \text{ M H}_2\text{O}_2 \text{ at 60 sec.} \]
The General Rate Law

\[ a \text{A} + b \text{B} \xrightarrow{C} d \text{D} + e \text{E} \]

Rate = \( k [A]^m [B]^n [C]^p \)

Where:
- \( k \) = rate constant
- \( m \) = order in \([A]\)
- \( n \) = order in \([B]\)
- \( p \) = order in \([C]\)

Note: \( m, n, p \) do not appear in the equation. They must be determined by experiment! Usually they are small whole numbers and may coincidentally be the same as \( a \) or \( b \).

\( m + n + p = \text{overall reaction order} \)
Determination of Reaction Order

The Initial Rate Method!

• Conduct multiple experiments in which one reactant concentration is “doubled” and all the other reactant concentrations and the catalyst concentration is held constant.

• The rate is measured before and after the concentration “doubling” and the effect on the rate of reaction is measured.

• This process is repeated for each reactant being “doubled”. The others remaining constant.
Effect on Reaction Rate for Different Orders!

\[ a \, A + b \, B \xrightarrow{C} d \, D + e \, E \]

Rate = \( k \, [A]^m \, [B]^n \, [C]^p \)

Expt. 1: \( k, [B], [C] \) are constant

If \([A] \) is doubled and:

<table>
<thead>
<tr>
<th>m is:</th>
<th>rate is:</th>
<th>order is:</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>halved</td>
<td>-1</td>
</tr>
<tr>
<td>0</td>
<td>unchanged</td>
<td>zero</td>
</tr>
<tr>
<td>1</td>
<td>doubled</td>
<td>first</td>
</tr>
<tr>
<td>2</td>
<td>quadrupled</td>
<td>second</td>
</tr>
</tbody>
</table>
**Reaction Order from Initial Rates**

**Example Problem:**

\[
\text{H}_2\text{O}_2(\text{aq}) + 3\text{I}^- (\text{aq}) + 2\text{H}^+ (\text{aq}) \rightarrow \text{I}_3^- (\text{aq}) + 2\text{H}_2\text{O}(\text{l})
\]

<table>
<thead>
<tr>
<th>Expt:</th>
<th>(\text{H}_2\text{O}_2)</th>
<th>(\text{I}^-)</th>
<th>(\text{H}^+)</th>
<th>Initial Rate (\text{mol}/(\text{L} \times \text{s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.010</td>
<td>0.010</td>
<td>0.00050</td>
<td>1.15 (\times) 10^{-6}</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>0.010</td>
<td>0.00050</td>
<td>2.30 (\times) 10^{-6}</td>
</tr>
</tbody>
</table>

*Initial Concentrations, M*

When the rate doubles on doubling concentration: \(n = 1\)!

3  0.010  0.020  0.00050  2.30 \(\times\) 10^{-6}

Now compare Expt 1 & 3 for \([\text{I}^-]\)! \(m = _____\)?

4  0.010  0.010  0.00100  1.15 \(\times\) 10^{-6}

Now compare Expt 1 & 4 for \([\text{H}^+]\)! \(p = _____\)?

<table>
<thead>
<tr>
<th>Initial Rate</th>
<th>mol/(L x s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15 (\times) 10^{-6}</td>
<td>doubled</td>
</tr>
<tr>
<td>2.30 (\times) 10^{-6}</td>
<td>doubled</td>
</tr>
</tbody>
</table>
Calculation of Order by Initial Rates

Eqn. \( \text{H}_2\text{O}_2(\text{aq}) + 3\text{I}^- (\text{aq}) + 2\text{H}^+ (\text{aq}) \rightarrow \text{products} \)

Compare Expt 1 with Expt 2

\[
\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k [\text{H}_2\text{O}_2]^m [\text{I}^-]^n [\text{H}^+]^p}{k [\text{H}_2\text{O}_2]^m [\text{I}^-]^n [\text{H}^+]^p} = \frac{[0.020]^m [0.010]^n [0.0005]^p}{[0.010]^m [0.010]^n [0.0005]^p}
\]

\[
\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{0.020}{0.010} = \frac{2.30 \times 10^{-6}}{1.15 \times 10^{-6}} = 2
\]

\[ [2]^m = 2 \]

\[ m = 1 \]

Then compare Expt 1 with Expt 3 & then Expt 4
Example Reactions and Orders

\[
\begin{align*}
\text{H}_2\text{C} &\quad \xrightarrow{\Delta} \quad \text{CH}_3\text{CH} &= \text{CH}_2 \\
\text{Rate} &= k [\text{cC}_3\text{H}_6]^1 \\
2 \text{NO}(g) + 2 \text{H}_2(g) &\quad \rightarrow \quad \text{N}_2(g) + 2 \text{H}_2\text{O}(g) \\
\text{Rate} &= k [\text{NO}]^2[\text{H}_2]^1 \\
\text{CH}_3\text{COCH}_3(aq) + \text{I}_2(aq) &\quad \xrightarrow{\text{H}^+} \quad \text{CH}_3\text{COCH}_2\text{I}(aq) + \text{HI}(aq) \\
\text{Rate} &= k [\text{CH}_3\text{COCH}_3]^1[\text{I}_2]^0[\text{H}^+]^1 \\
\text{Rate} &= k [\text{CH}_3\text{COCH}_3][\text{H}^+] \\
\end{align*}
\]
Change of Concentration with Time

First Order of type: \[ a \xrightarrow{} A \rightarrow \text{products} \]

\[ \frac{\delta[A]}{\delta t} = \text{Rate} = k [A]^1 \]

Can’t be used to calculate an elapsed time or a concentration change.

The Integrated Rate Equation:

\[ \ln \left( \frac{[A]_t}{[A]_0} \right) = -kt \quad \text{or} \quad \log \left( \frac{[A]_t}{[A]_0} \right) = \frac{-kt}{2.303} \]

\[ \ln [A]_t = -k t + \ln [A]_0 \]

\[ y = m X + b \quad \text{equation straight line} \]
Half-life & the Integrated Rate Equation

Half-life = Elapsed Time necessary to reduce $[A]_t$ to one-half of $[A]_0$.

$$\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt \quad \text{but} \quad [A]_t = \frac{1}{2}[A]_0$$

$$\ln \left( \frac{\frac{1}{2}[A]_0}{[A]_0} \right) = -kt = \ln \left( \frac{1}{2} \right) \quad \text{or} \quad \ln 2 = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

For a first order reaction: $A \rightarrow \text{products}$

The half-life is a constant!
Relating Half-life to the Rate Constant

EXAMPLE: \( \text{SO}_2\text{Cl}_2(g) \rightarrow \text{SO}_2(g) + \text{Cl}_2(g) \)

Experimental Data: At 320 °C \( k = 2.20 \times 10^{-5} \text{ s}^{-1} \)
The reaction is determined to be first order.

Calculating half life: \[ t_{\frac{1}{2}} = \frac{0.693}{2.20 \times 10^{-5} \text{ s}^{-1}} \]

Half-Lives: \[ t_{\frac{1}{2}} = 3.15 \times 10^4 \text{ s} \text{ or } 8.75 \text{ h} \]

Fraction Remaining:

\[
\begin{align*}
0 & \quad 1 & \quad 2 & \quad 3 & \quad 4 & \quad 5 & \quad 6 & \quad 7 & \quad 8 \\
1 & \quad \frac{1}{2} & \quad \frac{1}{4} & \quad \frac{1}{8} & \quad \frac{1}{16} & \quad \frac{1}{32} & \quad \frac{1}{64} & \quad \frac{1}{128} & \quad \frac{1}{256}
\end{align*}
\]

Percent Remaining: [Percent Reacted:]

\[
\begin{align*}
100 & \quad 50 & \quad 25 & \quad 12.5 & \quad 6.25 & \quad 3.125 \\
\quad 0 & \quad 50 & \quad 75 & \quad 87.5 & \quad 93.75 & \quad 96.875 
\end{align*}
\]
First Order Reactions:

• If the half-life, $t_{1/2}$, is known then the rate constant, $k$, is known.

• The half-life, $t_{1/2}$, does \textit{NOT} depend on the \textit{initial concentration of the reactant}!

• All Radioactive Decays are First Order!

• The half-life, $t_{1/2}$, is a \textit{constant} which is commonly tabulated and used to characterize radioactive nuclides.
Effect of Temperature on Reaction Rate
Arrhenius Equation

Rate constant, \( k = A e^{-E_a/RT} \)

Rates of reaction *double* or *triple* with every 10K increase in temperature. The precise amount depends on \( E_a \), the *activation energy* for the reaction.
Reaction Mechanism

A series of *elementary reactions* leading from reactants to products. The sum of these elementary reactions = *net chemical equation*.

Example: \[ \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \]

Rate Law: \[ \text{rate} = k[\text{NO}_2]^2 \]

Mechanism:

\[ \begin{align*}
\text{NO}_2(g) + \text{NO}_2(g) & \rightarrow \text{NO}(g) + \text{NO}_3(g) \\
\text{NO}_3(g) + \text{CO}(g) & \rightarrow \text{NO}_2(g) + \text{CO}_2(g)
\end{align*} \]

Note: A reaction intermediate may be detected but cannot be isolated.
Molecularity & Reaction Order

Unimolecular

\[ \text{Cl}_2 \quad \rightarrow \quad \text{Cl}\cdot + \text{Cl}\cdot \]

Bimolecular

\[ \text{Cl}\cdot + \text{CHCl}_3 \quad \rightarrow \quad \text{HCl} + \text{CCl}_3 \]

Bimolecular

\[ \text{Cl}\cdot + \text{CCl}_3 \quad \rightarrow \quad \text{CCl}_4 \]

Termolecular

\[ \text{Br}\cdot + \text{Br}\cdot + \text{Ar} \quad \rightarrow \quad \text{Br}_2 + \text{Ar}^* \]

The Asterisk means that the Argon atom carries away energy, otherwise the two bromine atoms would simply separate again.
Rate Equations for Elementary Reactions

Unimolecular: \[ A \rightarrow B + C \]
\[ \text{rate} = k [A] \]

Bimolecular: \[ A + B \rightarrow C + D \]
\[ \text{rate} = k [A][B] \]

Termolecular: \[ A + B + C \rightarrow D + E \]
\[ \text{rate} = k [A][B][C] \]

The rate law can be written directly from the elementary reaction.
Kinetics and the Reaction Mechanism

The Experimental Rate Law is an important clue to the Chemical Reaction Mechanism! This is why kinetics is so important to chemistry!

The Experimental Rate Law is directly related to the Rate Determining Step, the RDS, of the reaction.

The Rate Determining Step is the Slowest! Step in a chemical reaction mechanism.
Kinetics and the Reaction Mechanism

Net Chemical Eqn: \[ 2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g) \]

Experimental Rate Law: \[ \text{Rate} = k [\text{NO}_2][\text{F}_2] \]

Reaction Mechanism:

RDS: \[ 2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g) \]

\[ \text{RDS} \quad k_2 > k_1 \]

\[ \text{NO}_2(g) + \text{F}_2(g) \quad \text{slow} \quad k_1 \rightarrow \text{NO}_2\text{F}(g) + \cdot\text{F}(g) \]

\[ \text{NO}_2(g) + \cdot\text{F}(g) \quad \text{fast} \quad k_2 \rightarrow \text{NO}_2\text{F}(g) \]

\[ \text{Rate} = k_1 [\text{NO}_2][\text{F}_2] \]
Mechanisms Involving a Fast Equilibrium Step

Chemical Reaction: \[ 2 \text{N}_2\text{O}_5(g) \rightarrow 4 \text{NO}_2(g) + \text{O}_2(g) \]

Expt. Rate Law: \[ \text{Rate} = k [\text{N}_2\text{O}_5] \]

Mechanism:
\[ \text{N}_2\text{O}_5 \xrightarrow{k_1 \text{ fast}} \text{NO}_2 + \text{NO}_3 \]
\[ \text{fast} \quad \text{fast} \quad \text{fast} \]

RDS: \[ \text{NO}_2 + \text{NO}_3 \xrightarrow{k_2 \text{ slow}} \text{NO} + \text{NO}_2 + \text{O}_2 \]

\[ \text{NO} + \text{NO}_3 \xrightarrow{k_3 \text{ fast}} \text{NO}_2 + \text{NO}_2 \]
Experimental *versus* Theoretical Rate Law

- Experimental and Theoretical Rate Laws *must be equivalent!* From the previous reaction:

**Expt. Rate Law:** \( \text{Rate} = k [N_2O_5] \)

**Theor. Rate Law:** \( \text{Rate} = k_2[NO_2][NO_3] \Leftrightarrow \text{RDS} \)

- The Meaning of Chemical Equilibrium:

  \[
  \text{Forward Rate} = \text{Reverse Rate} \\
  \text{Rate}_1 = \text{Rate}_{-1} \\
  \text{Rate}_1 = k_1[N_2O_5] = k_{-1}[NO_2][NO_3] = \text{Rate}_{-1} .
  \]
Reconciliation of the Theor. & Expt. Rate Laws

From the Equilibrium:

\[
\text{[NO}_3\text{]} = \frac{k_1\text{[N}_2\text{O}_5\text{]}}{k_{-1}\text{[NO}_2\text{]}}
\]

Theoretical Rate Law:

\[
\text{Rate} = k_2 \text{[NO}_2\text{]}\text{[NO}_3\text{]}
\]

\[
\text{Rate} = k_2 \frac{k_1\text{[N}_2\text{O}_5\text{]}}{k_{-1}\text{[NO}_2\text{]}}
\]

\[
\text{Rate} = \frac{k_2 k_1}{k_{-1}} \text{[N}_2\text{O}_5\text{]}
\]

\[
\Rightarrow k_{\text{expt}} = \frac{k_2 k_1}{k_{-1}}
\]

\[
\text{Rate} = k_{\text{expt}}\text{[N}_2\text{O}_5\text{]}
\]
Mechanisms Involving a Fast Equilibrium Step:

Derive the theoretical rate equation and show it is equivalent to the Experimental Rate Law:

Chemical Reaction: \[ 2 \text{NO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g) \]

Rate = \( k [\text{NO}]^2[\text{O}_2] \)

Mechanism:

\[ \text{NO} + \text{O}_2 \xrightleftharpoons{\text{fast}}^{k_1} \text{NO}_3 \]

\[ \text{NO} + \text{NO}_3 \xrightarrow{\text{slow}}^{k_2} \text{NO}_2 + \text{NO}_2 \]

RDS

\[ \text{NO} + \text{NO}_3 \xrightarrow{\text{slow}}^{k_2} \text{NO}_2 + \text{NO}_2 \]
Catalysis

• A Catalyst increases the Rate of a chemical reaction but is not consumed in the reaction.

• A Catalyst changes the Mechanism of a chemical reaction. This change results in a lower Energy of Activation.

• A Catalyst can be present in trace or in stoichiometric amounts depending on its activity and mode of action.
Catalysis: Points to Note

• Catalysis can be homogeneous (same phase) of heterogeneous (not same phase).

• *Inhibitors* are molecules which *block an available mechanism* forcing a reaction to use a mechanism with a higher energy of activation. Inhibitors slow or prevent reactions from occurring and are useful as food preservatives, stabilizers, *etc.* Sometimes inhibitors deactivate natural catalysts formed in a system.
Ozone Decomposition

Chemical Reaction: \[ 2 \text{O}_3(g) \rightarrow 3 \text{O}_2(g) \]

Mechanism:

\[
\begin{align*}
\text{O}_3 & \quad \overset{k_1}{\underset{k_-1}{\rightleftharpoons}} \quad \text{O} + \text{O}_2 \\
\text{RDS} & \quad \text{O} + \text{O}_3 \quad \overset{k_2}{\text{slow}} \quad 2 \text{O}_2
\end{align*}
\]

*concentrations are very low in air.

equilibrium shifted by LeChatelier's P.

Catalysed Mechanism:

\[
\begin{align*}
\text{O}_3 + \text{Cl}^- & \quad \overset{\text{fast}}{\rightarrow} \quad \text{ClO}^- + \text{O}_2 \\
\text{ClO}^- + \text{O}_3 & \quad \overset{\text{fast}}{\rightarrow} \quad \text{Cl}^- + 2 \text{O}_2
\end{align*}
\]
Heterogeneous Adsorption Catalysis

• Reactant molecules are *adsorbed* on catalyst surface.

• Reactant molecules diffuse along the surface.

• Reactant molecules react to form *product* molecules.

• *Product* molecules are *desorbed* from the surface.