Chapter 14
Chemical Kinetics

Learning goals and key skills:
- Understand the factors that affect the rate of chemical reactions
- Determine the rate of reaction given time and concentration
- Relate the rate of formation of products and the rate of disappearance of reactants given the balanced chemical equation for the reaction.
- Understand the form and meaning of a rate law including the ideas of reaction order and rate constant.
- Determine the rate law and rate constant for a reaction from a series of experiments given the measured rates for various concentrations of reactants.
- Use the integrated form of a rate law to determine the concentration of a reactant at a given time.
- Explain how the activation energy affects a rate and be able to use the Arrhenius Equation.
- Predict a rate law for a reaction having multistep mechanism given the individual steps in the mechanism.
- Explain how a catalyst works.

\[ \Delta G^{\circ}_{\text{rxn}} = -2.84 \text{ kJ} \quad \text{spontaneous!} \]

\[ \Delta G^{\circ}_{\text{rxn}} = -394.4 \text{ kJ} \quad \text{spontaneous!} \]
Chemical kinetics is the study of how fast chemical reactions occur.

Factors that affect rates of reactions:
1) physical state of the reactants.
2) concentration of the reactants.
3) temperature of the reaction.
4) presence or absence of a catalyst.

1) Physical State of the Reactants
- The more readily the reactants collide, the more rapidly they react.
  - Homogeneous reactions are often faster.
  - Heterogeneous reactions that involve solids are faster if the surface area is increased; i.e., a fine powder reacts faster than a pellet.

2) Concentration
- Increasing reactant concentration generally increases reaction rate since there are more molecules/vol., more collisions occur.

3) Temperature
- Reaction rate generally increases with increased temperature.
- Kinetic energy of molecules is related to temperature.
- At higher temperatures, molecules move more quickly, increasing numbers of collisions and the energy the molecules possess during the collisions.

4) Catalysts
- Catalysts affect rate without being in overall balanced equation.
- Catalysts affect the kinds of collisions, changing the mechanism (individual reactions that are part of the pathway from reactants to products).
**Reaction Rates**

Rate is a change in concentration over a time period: \( \Delta [\text{ }] / \Delta t \).

\( \Delta \) means “change in.”

[ ] means molar concentration.

\( t \) represents time.

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**Reaction rates**

Measured from the change in concentration of reactants or products per unit time.

- average rate
- instantaneous rate
- initial rate

For the reaction: \( A \rightarrow B \)

Average rate of appearance of \( B \) = \( \frac{\text{change in concentration of } B}{\text{change in time}} \)
Average Reaction Rates

\[ C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq) \]

- Note that the average rate decreases as the reaction proceeds.
- This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

### TABLE 14.1 Rate Data for Reaction of \( C_4H_9Cl \) with Water

<table>
<thead>
<tr>
<th>Time, ts</th>
<th>([C_4H_9Cl] ) (M)</th>
<th>Average Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.1000</td>
<td>( 1.9 \times 10^{-4} )</td>
</tr>
<tr>
<td>50.0</td>
<td>0.0906</td>
<td>( 1.7 \times 10^{-4} )</td>
</tr>
<tr>
<td>100.0</td>
<td>0.0820</td>
<td>( 1.6 \times 10^{-4} )</td>
</tr>
<tr>
<td>150.0</td>
<td>0.0741</td>
<td>( 1.4 \times 10^{-4} )</td>
</tr>
<tr>
<td>200.0</td>
<td>0.0677</td>
<td>( 1.22 \times 10^{-4} )</td>
</tr>
<tr>
<td>300.0</td>
<td>0.0540</td>
<td>( 1.01 \times 10^{-4} )</td>
</tr>
<tr>
<td>400.0</td>
<td>0.0448</td>
<td>( 8.80 \times 10^{-5} )</td>
</tr>
<tr>
<td>500.0</td>
<td>0.0368</td>
<td>( 8.00 \times 10^{-5} )</td>
</tr>
<tr>
<td>600.0</td>
<td>0.0290</td>
<td>( 7.20 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

### Reaction Rates as a function of time

- A plot of concentration versus time.
- The slope of a line tangent to the curve at any point is the **instantaneous rate** at that time.
- The instantaneous rate at time zero is called the **initial rate**; this is often the rate of interest to chemists.

\[
\text{Rate} = -\frac{\Delta [C_4H_9Cl]}{\Delta t} = \frac{\Delta [C_4H_9OH]}{\Delta t}
\]
Reaction rates

rate = change in conc. / change in time

$$aA + bB \rightarrow cC + dD$$

$$Rate = R = -\frac{\Delta[A]}{a \cdot \Delta t} = -\frac{\Delta[B]}{b \cdot \Delta t} = \frac{\Delta[C]}{c \cdot \Delta t} = \frac{\Delta[D]}{d \cdot \Delta t}$$

The rate can be related to the concentration of the reactants or products. 
**Reactants have a negative sign.**
**Don’t forget to use the stoichiometric coefficients.**

**Example**

Ammonia reacts with oxygen to form nitrogen monoxide and steam. Relate the reactant and product reaction rates.
Rate laws
\[ aA + bB \rightleftharpoons cC + dD \]
rate equation:
\[ \text{Rate} = R = k \, [A]^x \, [B]^y \]
x and y are experimentally determined. **They are not the stoichiometric coefficients!**

How to determine? Keep every concentration constant except for one reactant and see what happens to the rate. Then, change a different reactant. Do this until it is determined how the concentration of each reactant has affected the rate.

Rate laws and reaction orders
\[ \text{Rate} = R = k \, [A]^x \, [B]^y \]
k is the rate constant for this reaction.

\[ x = \text{order of the reaction with respect to the concentration of reactant A} \]

\[ y = \text{order of the reaction with respect to the concentration of reactant B} \]

\[ x+y = \text{overall reaction order or (total) order of the reaction.} \]

If exponent is 1, first order; 2 is second order.
Experiments 1–3 show how \([\text{NH}_4^+]\) affects rate. Experiments 4–6 show how \([\text{NO}_2^-]\) affects rate.

Some rates depend *only* on one reactant to the first power. These are *first order* reactions.

- The rate law becomes: Rate = \(k [A]\)
- rate = \(-\Delta [A] / \Delta t\)
- So: \(k [A] = -\Delta [A] / \Delta t\)
- Rearrange to: \(\Delta [A] / [A] = -k \Delta t\)
- Integrate: \(\ln ([A]_t / [A]_o) = -k t\)
- Rearrange: \(\ln [A]_t = -k t + \ln [A]_o\)
- Note: this follows the equation of a line:
  \[ y = mx + b \]
- A plot of \(\ln [A]\) vs. \(t\) is linear.

**TABLE 14.2  Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C**

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial (\text{NH}_4^+) Concentration (M)</th>
<th>Initial (\text{NO}_2^-) Concentration (M)</th>
<th>Observed Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0100</td>
<td>0.200</td>
<td>(5.4 \times 10^{-7})</td>
</tr>
<tr>
<td>2</td>
<td>0.0200</td>
<td>0.200</td>
<td>(10.8 \times 10^{-7})</td>
</tr>
<tr>
<td>3</td>
<td>0.0400</td>
<td>0.200</td>
<td>(21.5 \times 10^{-7})</td>
</tr>
<tr>
<td>4</td>
<td>0.200</td>
<td>0.0202</td>
<td>(10.8 \times 10^{-7})</td>
</tr>
<tr>
<td>5</td>
<td>0.200</td>
<td>0.0404</td>
<td>(21.6 \times 10^{-7})</td>
</tr>
<tr>
<td>6</td>
<td>0.200</td>
<td>0.0808</td>
<td>(43.3 \times 10^{-7})</td>
</tr>
</tbody>
</table>
Some rates depend only on a reactant to the second power. These are **second order** reactions.

- The rate law becomes: \( \text{Rate} = k [A]^2 \)
- \( \text{rate} = k [A]^2 \)
- \( \text{rate} = -\Delta [A] / \Delta t \)
- So, \( k [A]^2 = -\Delta [A] / \Delta t \)
- Rearranging: \( \Delta [A] / [A]^2 = -k \Delta t \)
- Using calculus: \( 1/[A]_t = k t + 1/[A]_0 \)
- Note: this follows the equation of a line: \( y = mx + b \)
- A plot of \( 1/[A] \) vs. \( t \) is linear.

Some rates do not depend on reactant concentration. These are **zero order** reactions.

- The rate law is: \( \text{Rate} = k \)
- These reactions are linear in concentration.

\[
\begin{align*}
[A]_t &= -kt + [A]_0 \\
y &= mx + b
\end{align*}
\]
**Half-life, \( t_{1/2} \)**

The half-life, \( t_{1/2} \) is the time needed for the concentration of a reactant to decrease to half of its initial value.

\[
[A]_{t_{1/2}} = \frac{1}{2}[A]_0
\]

For a 1\(^{\text{st}}\) order,

\[
\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt
\]

\[
t_{1/2} = -\frac{\ln \left( \frac{[A]_t}{[A]_0} \right)}{k} = -\frac{\ln \frac{\frac{1}{2}[A]_0}{[A]_0}}{k} = -\frac{\ln \frac{1}{2}}{k} = \ln 2 \approx 0.693
\]

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**Using Graphs**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>H(_2)O(_2) (M)</th>
<th>ln (H(_2)O(_2))</th>
<th>1/(H(_2)O(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.02</td>
<td>-3.91202</td>
<td>50</td>
</tr>
<tr>
<td>200</td>
<td>0.016</td>
<td>-4.13517</td>
<td>62.5</td>
</tr>
<tr>
<td>400</td>
<td>0.0131</td>
<td>-4.33514</td>
<td>76.33588</td>
</tr>
<tr>
<td>600</td>
<td>0.0106</td>
<td>-4.5469</td>
<td>94.33962</td>
</tr>
<tr>
<td>800</td>
<td>0.0086</td>
<td>-4.75599</td>
<td>116.2791</td>
</tr>
<tr>
<td>1000</td>
<td>0.0069</td>
<td>-4.97623</td>
<td>144.9275</td>
</tr>
<tr>
<td>1200</td>
<td>0.0056</td>
<td>-5.18499</td>
<td>178.5714</td>
</tr>
<tr>
<td>1600</td>
<td>0.0037</td>
<td>-5.59942</td>
<td>270.2703</td>
</tr>
<tr>
<td>2000</td>
<td>0.0024</td>
<td>-6.03229</td>
<td>416.6667</td>
</tr>
</tbody>
</table>
Example

Fluorine combines with chlorine dioxide.

\[ \text{F}_2 (g) + 2 \text{ClO}_2 (g) \rightarrow 2 \text{FCIO}_2 (g) \]

<table>
<thead>
<tr>
<th>exp</th>
<th>init[F(_2)] (M)</th>
<th>init[ClO(_2)] (M)</th>
<th>init rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.010</td>
<td>0.0012</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.040</td>
<td>0.0048</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.010</td>
<td>0.0024</td>
</tr>
</tbody>
</table>

Prove that

\[ \text{rate} = k \ [\text{F}_2][\text{ClO}_2] \]

where \( k = 1.2 \text{ M}^{-1} \text{s}^{-1} \)
Example

The decomposition of SO$_2$Cl$_2$ is first order in SO$_2$Cl$_2$ and has a rate constant of 1.42 × 10$^{-4}$ s$^{-1}$.

a) If the initial concentration of SO$_2$Cl$_2$ is 1.00 M, how long will it take for the concentration to decrease to 0.78 M?

b) If the initial concentration of SO$_2$Cl$_2$ is 0.150 M, what is the concentration of SO$_2$Cl$_2$ after 5.00 × 10$^2$ s?

Example

The 1$^{st}$ order rate constant for the decomposition of N$_2$O$_5$ to NO$_2$ and O$_2$ at 70 °C is 6.82 × 10$^{-3}$ s$^{-1}$. What is the half-life of this reaction at 70 °C?
Temperature and Rate

- Generally, as temperature increases, so does the reaction rate.
- Rate constant $k$ is temperature dependent.

Collision model, based on kinetic molecular theory

for a reaction to proceed,
- contact is necessary between reactants
- contact must lead to breaking of bonds (need sufficient energy)
- the reactants must have proper orientation (orientation factor)
**E_a, Activation energy**

- There is a minimum amount of energy required for reaction: the activation energy, $E_a$.
- Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.

- Graph shows the energy possessed by the particles as the reaction proceeds.
- At the highest energy state, the transition state is formed.
- Reactions can be endothermic or exothermic.
- Rate constant ($k$) depends on the magnitude of $E_a$. 
Energy Distributions

At any temperature there is a wide distribution of kinetic energies.

\[ f = e^{\frac{-E_a}{RT}} \]

Arrhenius Equation

Arrhenius developed a mathematical relationship between \( k \) and \( E_a \):

\[ k = A e^{-\frac{E_a}{RT}} \]

where \( A \) is the frequency factor, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

\[ \ln k = -\frac{E_a}{RT} + \ln A \]

\[ \ln \left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

many data points  two data points
Example

For the reaction \( \text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO} \)
\( k = 0.220 \text{ M}^{-1} \text{ s}^{-1} \) at 650. K and \( k = 1.30 \text{ M}^{-1} \text{ s}^{-1} \) at 700. K. Calculate the activation energy for this reaction.
A mechanism is a series of stepwise reactions that show how reactants become products.

- Reactions may occur all at once or through several discrete steps.
- Each of these processes is known as an elementary reaction or elementary process.
- The **molecularity** of an elementary step is equal to the number of reactant molecules in the elementary reaction.

**TABLE 14.3  Elementary Reactions and Their Rate Laws**

<table>
<thead>
<tr>
<th>Molecularity</th>
<th>Elementary Reaction</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimolecular</td>
<td>(A \longrightarrow \text{products})</td>
<td>(\text{Rate} = k[A])</td>
</tr>
<tr>
<td>Bimolecular</td>
<td>(A + A \longrightarrow \text{products})</td>
<td>(\text{Rate} = k[A]^2)</td>
</tr>
<tr>
<td>Bimolecular</td>
<td>(A + B \longrightarrow \text{products})</td>
<td>(\text{Rate} = k[A][B])</td>
</tr>
<tr>
<td>Termolecular</td>
<td>(A + A + A \longrightarrow \text{products})</td>
<td>(\text{Rate} = k[A]^3)</td>
</tr>
<tr>
<td>Termolecular</td>
<td>(A + A + B \longrightarrow \text{products})</td>
<td>(\text{Rate} = k[A]^2[B])</td>
</tr>
<tr>
<td>Termolecular</td>
<td>(A + B + C \longrightarrow \text{products})</td>
<td>(\text{Rate} = k[A][B][C])</td>
</tr>
</tbody>
</table>

**Rate Determining Steps**

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, **rate-determining step**.
Mechanisms

Most reactions have more than one elementary step. The net reaction is the sum of all the elementary steps.

<table>
<thead>
<tr>
<th>Step 1</th>
<th>Unimolecular</th>
<th>( \text{O}_2(g) \rightarrow \text{O}_2(g) + \text{O}(g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 2</td>
<td>Bimolecular</td>
<td>( \text{O}_2(g) + \text{O}(g) \rightarrow 2 \text{O}_2(g) )</td>
</tr>
<tr>
<td>Overall reaction</td>
<td></td>
<td>( 2 \text{O}_2(g) \rightarrow 3 \text{O}_2(g) )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Step 1</th>
<th>Bimolecular</th>
<th>( \text{NH}_3 + \text{OCl}^- \rightarrow \text{NH}_2\text{Cl} + \text{OH}^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 2</td>
<td>Bimolecular</td>
<td>( \text{NH}_2\text{Cl} + \text{NH}_3 \rightarrow \text{N}_2\text{H}_5^+ + \text{Cl}^- )</td>
</tr>
<tr>
<td>Step 3</td>
<td>Bimolecular</td>
<td>( \text{N}_2\text{H}_5^+ + \text{OH}^- \rightarrow \text{N}_2\text{H}_4 + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Overall reaction</td>
<td></td>
<td>( 2 \text{NH}_3 + \text{OCl}^- \rightarrow \text{N}_2\text{H}_4 + \text{H}_2\text{O} + \text{Cl}^- )</td>
</tr>
</tbody>
</table>

**NOTE**
1. Rate law is determined from experiment.
2. Order and stoichiometric coefficients are not necessarily the same!
3. Rate law reflects all chemistry down to and including the slowest step in multistep reaction.
Slow Initial Step

\[
\text{NO}_2 (g) + \text{CO} (g) \longrightarrow \text{NO} (g) + \text{CO}_2 (g)
\]

- The rate law for this reaction is found experimentally to be
  \[
  \text{Rate} = k [\text{NO}_2]^2
  \]
- CO is necessary for this reaction to occur, but the rate of the reaction does not depend on its concentration. This suggests the reaction occurs in two steps.

\[
\text{NO}_2 (g) + \text{CO} (g) \longrightarrow \text{NO} (g) + \text{CO}_2 (g)
\]

Slow Initial Step

- A proposed mechanism for this reaction is
  Step 1:  \( \text{NO}_2 + \text{NO}_2 \longrightarrow \text{NO}_3 + \text{NO} \) (slow)
  Step 2:  \( \text{NO}_3 + \text{CO} \longrightarrow \text{NO}_2 + \text{CO}_2 \) (fast)
- \( \text{NO}_3 \) intermediate, not observed in the overall reaction, is consumed in the second step.
- As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.
- Add individual steps to obtain overall reaction.
  \[
  \text{NO}_2 (g) + \text{CO} (g) \longrightarrow \text{NO} (g) + \text{CO}_2 (g)
  \]
The rate law for this reaction is found to be
\[ \text{Rate} = k [\text{NO}]^2 [\text{Br}_2] \]
Termolecular processes are rare, this rate law suggests a two-step mechanism.

A proposed mechanism is:

**Step 1:** $\text{NO} + \text{Br}_2 \xrightleftharpoons[k_i]{k_{-1}} \text{NOBr}_2 \quad \text{(fast)}$

**Step 2:** $\text{NOBr}_2 + \text{NO} \xrightarrow{k_2} 2 \text{NOBr} \quad \text{(slow)}$

Step 1 includes the forward and reverse reactions.

The rate of the overall reaction depends upon the rate of the slow step.

The rate law of an elementary step is determined by its molecularity.

The rate law for that (slow) step would be
\[ \text{Rate} = k_2 [\text{NOBr}_2] [\text{NO}] \]
But how can we find $[\text{NOBr}_2]$?

$\text{NOBr}_2$ can react two ways:
- With NO to form NOBr (step 2)
- By decomposition to reform NO and Br$_2$ (step 1)

The reactants and products of the first step are in equilibrium with each other.

Therefore,
\[ \text{Rate}_r = \text{Rate}_r \]
Fast Initial Step

- Because Rate_f = Rate_r,
  \[ k_1 \text{[NO]} \text{[Br}_2\text{]} = k_{-1} \text{[NOBr}_2\text{]} \]
- Solving for [NOBr_2] gives us
  \[ \frac{k_1}{k_{-1}} \text{[NO]} \text{[Br}_2\text{]} = \text{[NOBr}_2\text{]} \]

Substituting this expression for [NOBr_2] in the rate law for the rate-determining step gives

\[
\text{Rate} = \frac{k_2 k_1}{k_{-1}} \text{[NO]} \text{[Br}_2\text{]} \text{[NO]} = k \text{[NO]}^2 \text{[Br}_2\text{]}
\]

Example

\[ 2 \text{I}^- + \text{H}_2\text{O}_2 + 2 \text{H}^+ \rightarrow \text{I}_2 + 2 \text{H}_2\text{O} \]
\[ \text{Rate} = k \text{[I}^-\text{][H}_2\text{O}_2] \]

Proposed Mechanism

Step 1 — slow
\[ \text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{HOI} + \text{OH}^- \]

Step 2 — fast
\[ \text{HOI} + \text{I}^- \rightarrow \text{I}_2 + \text{OH}^- \]

Step 3 — fast
\[ 2 \text{OH}^- + 2 \text{H}^+ \rightarrow 2 \text{H}_2\text{O} \]

Rate of the reaction is controlled by the slow step — the rate-determining step (rds) or rate-limiting step. Elementary Step 1 is bimolecular and involves I^- and H_2O_2. Therefore, this predicts the rate law should be

\[ \text{Rate} \propto [\text{I}^-][\text{H}_2\text{O}_2] \] — as observed

The species HOI and OH^- are reaction intermediates.
Homogeneous Catalysts

- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.
- Catalysts change the mechanism by which the process occurs.

Heterogeneous Catalysts

1. $\text{H}_2$ and $\text{C}_2\text{H}_4$ adsorb on metal surface.
2. One free H attaches to $\text{C}_2\text{H}_4$ to form $\text{C}_2\text{H}_5$ (ethyl group) intermediate.
3. Second free H is about to attach to $\text{C}_2\text{H}_5$ intermediate to form $\text{C}_2\text{H}_6$.
4. Ethane, $\text{C}_2\text{H}_6$, desorbs from metal surface.

- In heterogeneous catalysis, the catalyst is present as a solid phase and the reaction takes place on the surface of the catalyst.
Enzymes

catalysts in biological systems
The **substrate** fits into the active site of the **enzyme** much like a key fits into a lock.
Enzymes are efficient catalysts.

**Turnover number**, number of individual catalytic events occurring at an active site per unit time is typically $10^3$-$10^7$ per second.