Factors That Influence Reaction Rate

- Particles must collide in order to react.
- The higher the **concentration** of reactants, the greater the reaction rate.
  - A higher concentration of reactant particles allows a greater number of collisions.
- The **physical state** of the reactants influences reaction rate.
  - Substances must mix in order for particles to collide.
- The higher the **temperature**, the greater the reaction rate.
  - At higher temperatures particles have more energy and therefore collide more often and more effectively.
Figure 14.3  The effect of surface area on reaction rate.

A hot steel nail glows feebly when placed in $\text{O}_2$. The same mass of steel wool bursts into flame.

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Figure 14.4  Sufficient collision energy is required for a reaction to occur.
Expressing the Reaction Rate

Reaction rate is measured in terms of the changes in concentrations of reactants or products per unit time.

For the general reaction \( A \rightarrow B \), we measure the concentration of \( A \) at \( t_1 \) and at \( t_2 \):

\[
\text{Rate} = \frac{\text{change in concentration of } A}{\text{change in time}} = \frac{\text{conc } A_2 - \text{conc } A_1}{t_2 - t_1} = \frac{\Delta(\text{conc } A)}{\Delta t}
\]

Square brackets indicate a concentration in moles per liter.

The \textit{negative} sign is used because the concentration of \( A \) is \textit{decreasing}. This gives the \textit{rate} a \textit{positive} value.
**Table 14.1** Concentration of O\(_3\) at Various Times in its Reaction with C\(_2\)H\(_4\) at 303 K

\[
\text{C}_2\text{H}_4 (g) + \text{O}_3 (g) \rightleftharpoons \text{C}_2\text{H}_4\text{O} (g) + \text{O}_2 (g)
\]

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Concentration of O(_3) (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3.20x10(^{-5})</td>
</tr>
<tr>
<td>10.0</td>
<td>2.42x10(^{-5})</td>
</tr>
<tr>
<td>20.0</td>
<td>1.95x10(^{-5})</td>
</tr>
<tr>
<td>30.0</td>
<td>1.63x10(^{-5})</td>
</tr>
<tr>
<td>40.0</td>
<td>1.40x10(^{-5})</td>
</tr>
<tr>
<td>50.0</td>
<td>1.23x10(^{-5})</td>
</tr>
<tr>
<td>60.0</td>
<td>1.10x10(^{-5})</td>
</tr>
</tbody>
</table>

\[
\text{rate} = - \frac{\Delta [\text{C}_2\text{H}_4]}{\Delta t} = - \frac{\Delta [\text{O}_3]}{\Delta t}
\]
Figure 14.5  Three types of reaction rates for the reaction of O$_3$ and C$_2$H$_4$.

\[ \text{C}_2\text{H}_4 \ (g) + \text{O}_3 \ (g) \rightleftharpoons \text{C}_2\text{H}_4\text{O} \ (g) + \text{O}_2 \ (g) \]
Figure 14.6A  Plots of [reactant] and [product] vs. time.

\[ \text{C}_2\text{H}_4 + \text{O}_3 \rightarrow \text{C}_2\text{H}_4\text{O} + \text{O}_2 \]

[O\textsubscript{2}] increases just as fast as [C\textsubscript{2}H\textsubscript{4}] decreases.

\[
\text{Rate} = -\frac{\Delta\text{[C}_2\text{H}_4]}{\Delta t} = -\frac{\Delta\text{[O}_3]}{\Delta t} = \frac{\Delta\text{[C}_2\text{H}_4\text{O}]}{\Delta t} = \frac{\Delta\text{[O}_2]}{\Delta t}
\]
Figure 14.6B  Plots of [reactant] and [product] vs. time.

\[ \text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} \]

[HI] increases twice as fast as [H\textsubscript{2}] decreases.

\[
\text{Rate} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}
\]

\[
\text{Rate} = \frac{\Delta[\text{IH}]}{\Delta t} = -2 \frac{\Delta[\text{H}_2]}{\Delta t} = -2 \frac{\Delta[\text{I}_2]}{\Delta t}
\]

The expression for the rate of a reaction and its numerical value depend on which substance serves as the reference.
In general, for the reaction

\[ aA + bB \rightarrow cC + dD \]

where \( a, b, c, \) and \( d \) are the coefficients for the balanced equation, the rate is expressed as:

\[
\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}
\]
Sample Problem 14.1  Expressing Rate in Terms of Changes in Concentration with Time

PROBLEM: Hydrogen gas has a nonpolluting combustion product (water vapor). $H_2$ is used as a fuel aboard the space shuttle and in earthbound cars with prototype engines:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

(a) Express the rate in terms of changes in $[H_2]$, $[O_2]$, and $[H_2O]$ with time.

(b) When $[O_2]$ is decreasing at 0.23 mol/L·s, at what rate is $[H_2O]$ increasing?

PLAN: We choose $O_2$ as the reference because its coefficient is 1. For every molecule of $O_2$ that disappears, two molecules of $H_2$ disappear, so the rate of $[O_2]$ decrease is ½ the rate of $[H_2]$ decrease. Similarly, the rate at which $[O_2]$ decreases is ½ the rate at which $[H_2O]$ increases.
Sample Problem 14.1

SOLUTION:

(a) \[ \text{Rate} = - \frac{\Delta [O_2]}{\Delta t} = - \frac{1}{2} \frac{\Delta [H_2]}{\Delta t} = \frac{1}{2} \frac{\Delta [H_2O]}{\Delta t} \]

(b) Calculating the rate of change of \([H_2O]\):

\[ \frac{1}{2} \frac{\Delta [H_2O]}{\Delta t} = - \frac{\Delta [O_2]}{\Delta t} = -(-0.23 \text{ mol/L} \cdot \text{s}) \]

\[ \frac{\Delta [H_2O]}{\Delta t} = 2(0.23 \text{ mol/L} \cdot \text{s}) = 0.46 \text{ mol/L} \cdot \text{s} \]
For any general reaction occurring at a fixed temperature

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

The term $k$ is the **rate constant**, which is specific for a given reaction at a given temperature.

The exponents $m$ and $n$ are **reaction orders** and are determined **by experiment**.

The values of $m$ and $n$ are **not** necessarily related in any way to the coefficients $a$ and $b$. 
Reaction Orders

A reaction has an *individual order* “with respect to” or “in” each reactant.

For the simple reaction A → products:

If the rate doubles when [A] doubles, the rate depends on [A]¹ and the reaction is *first order* with respect to A.

If the rate quadruples when [A] doubles, the rate depends on [A]² and the reaction is *second order* with respect to [A].

If the rate does not change when [A] doubles, the rate does not depend on [A], and the reaction is *zero order* with respect to A.
Figure 14.7  Plots of reactant concentration, [A], vs. time for first-, second-, and zero-order reactions.
Figure 14.8  Plots of rate vs. reactant concentration, [A], for first-, second-, and zero-order reactions.

- **Zero-order reaction**
  \[ \text{Rate} = k[A]^0 \]

- **First-order reaction**
  \[ \text{Rate} = k[A]^1 \]

- **Second-order reaction**
  \[ \text{Rate} = k[A]^2 \]
Individual and Overall Reaction Orders

For the reaction $2\text{NO}(g) + 2\text{H}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)$:

The rate law is $\text{rate} = k[\text{NO}]^2[\text{H}_2]$.

The reaction is second order with respect to NO, first order with respect to H$_2$ and third order overall.

Note that the reaction is first order with respect to H$_2$ even though the coefficient for H$_2$ in the balanced equation is 2.

Reaction orders must be determined from experimental data and cannot be deduced from the balanced equation.
Sample Problem 14.2

Determining Reaction Orders from Rate Laws

PROBLEM: For each of the following reactions, use the given rate law to determine the reaction order with respect to each reactant and the overall order.

(a) $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$; rate $= k[\text{NO}]^2[\text{O}_2]$

(b) $\text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_4(g) + \text{CO}(g)$; rate $= k[\text{CH}_3\text{CHO}]^{3/2}$

(c) $\text{H}_2\text{O}_2(aq) + 3\text{I}^-(aq) + 2\text{H}^+(aq) \rightarrow \text{I}_3^-(aq) + 2\text{H}_2\text{O}(l)$; rate $= k[\text{H}_2\text{O}_2][\text{I}^-]$

PLAN: We inspect the exponents in the rate law, not the coefficients of the balanced equation, to find the individual orders. We add the individual orders to get the overall reaction order.

SOLUTION:

(a) The exponent of $[\text{NO}]$ is 2 and the exponent of $[\text{O}_2]$ is 1, so the reaction is second order with respect to $\text{NO}$, first order with respect to $\text{O}_2$ and third order overall.
Sample Problem 14.2

(b) The reaction is \( \frac{3}{2} \) order in \( \text{CH}_3\text{CHO} \) and \( \frac{3}{2} \) order overall.

(c) The reaction is first order in \( \text{H}_2\text{O}_2 \), first order in \( \text{I}^- \), and second order overall. The reactant \( \text{H}^+ \) does not appear in the rate law, so the reaction is zero order with respect to \( \text{H}^+ \).

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Determining Reaction Orders

For the general reaction $A + 2B \rightarrow C + D$, the rate law will have the form

$$\text{Rate} = k[A]^m[B]^n$$

To determine the values of $m$ and $n$, we run a series of experiments in which one reactant concentration changes while the other is kept constant, and we measure the effect on the initial rate in each case.
Table 14.2  Initial Rates for the Reaction between A and B

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial Rate (mol/L·s)</th>
<th>Initial [A] (mol/L)</th>
<th>Initial [B] (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.75x10^{-3}</td>
<td>2.50x10^{-2}</td>
<td>3.00x10^{-2}</td>
</tr>
<tr>
<td>2</td>
<td>3.50x10^{-3}</td>
<td>5.00x10^{-2}</td>
<td>3.00x10^{-2}</td>
</tr>
<tr>
<td>3</td>
<td>3.50x10^{-3}</td>
<td>2.50x10^{-2}</td>
<td>6.00x10^{-2}</td>
</tr>
<tr>
<td>4</td>
<td>7.00x10^{-3}</td>
<td>5.00x10^{-2}</td>
<td>6.00x10^{-2}</td>
</tr>
</tbody>
</table>

[B] is kept constant for experiments 1 and 2, while [A] is doubled. Then [A] is kept constant while [B] is doubled.
Finding $m$, the order with respect to A:

We compare experiments 1 and 2, where [B] is kept constant but [A] doubles:

\[
\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[A]^m[B]^n}{k[A]^m[B]^n} = \frac{[A]^m}{[A]^m} = \left(\frac{[A]_2}{[A]_1}\right)^m
\]

\[
\frac{3.50 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{1.75 \times 10^{-3} \text{ mol/L} \cdot \text{s}} = \left(\frac{5.00 \times 10^{-2} \text{ mol/L}}{2.50 \times 10^{-2} \text{ mol/L}}\right)^m
\]

Dividing, we get $2.00 = (2.00)^m$ so $m = 1$
Finding $n$, the order with respect to B:

We compare experiments 3 and 1, where [A] is kept constant but [B] doubles:

\[
\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[A]^m[B]^n}{k[A]^m[B]^n} = \frac{[B]^n}{[B]^n} = \left(\frac{[B]^3}{[B]^1}\right)^n
\]

\[
\frac{3.50 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{1.75 \times 10^{-3} \text{ mol/L} \cdot \text{s}} = \left(\frac{6.00 \times 10^{-2} \text{ mol/L}}{3.00 \times 10^{-2} \text{ mol/L}}\right)^m
\]

Dividing, we get $2.00 = (2.00)^n$ so $n = 1$
Table 14.3 Initial Rates for the Reaction between $O_2$ and NO

$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$

Rate = $k[O_2]^m[NO]^n$

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial Rate (mol/L·s)</th>
<th>$[O_2]$</th>
<th>$[NO]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.21x10^{-3}</td>
<td>1.10x10^{-2}</td>
<td>1.30x10^{-2}</td>
</tr>
<tr>
<td>2</td>
<td>6.40x10^{-3}</td>
<td>2.20x10^{-2}</td>
<td>1.30x10^{-2}</td>
</tr>
<tr>
<td>3</td>
<td>12.48x10^{-3}</td>
<td>1.10x10^{-2}</td>
<td>2.60x10^{-2}</td>
</tr>
<tr>
<td>4</td>
<td>9.60x10^{-3}</td>
<td>3.30x10^{-2}</td>
<td>1.30x10^{-2}</td>
</tr>
<tr>
<td>5</td>
<td>28.8x10^{-3}</td>
<td>1.10x10^{-2}</td>
<td>3.90x10^{-2}</td>
</tr>
</tbody>
</table>
Finding $m$, the order with respect to $O_2$:

We compare experiments 1 and 2, where $[\text{NO}]$ is kept constant but $[O_2]$ doubles:

\[
\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[O_2]^m[\text{NO}]^n}{k[O_2]^m[\text{NO}]^n} = \frac{[O_2]^m}{[O_2]^m} = \left(\frac{[O_2]_2}{[O_2]_1}\right)^m
\]

\[
\frac{6.40 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{3.21 \times 10^{-3} \text{ mol/L} \cdot \text{s}} = \left(\frac{2.20 \times 10^{-2} \text{ mol/L}}{1.10 \times 10^{-2} \text{ mol/L}}\right)^m
\]

Dividing, we get $1.99 = (2.00)^m$ or $2 = 2^m$, so $m = 1$

The reaction is first order with respect to $O_2$. 

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Sometimes the exponent is not easy to find by inspection. In those cases, we solve for \( m \) with an equation of the form \( a = b^m \):

\[
m = \frac{\log a}{\log b} = \frac{\log 1.99}{\log 2.00} = 0.993
\]

This confirms that the reaction is first order with respect to \( \text{O}_2 \).

Reaction orders may be positive integers, zero, negative integers, or fractions.
Finding \( n \), the order with respect to NO:

We compare experiments 1 and 3, where \([\text{O}_2]\) is kept constant but \([\text{NO}]\) doubles:

\[
\frac{\text{Rate}_3}{\text{Rate}_1} = \left( \frac{[\text{NO}]_3}{[\text{NO}]_1} \right)^n = \frac{12.8 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{3.21 \times 10^{-3} \text{ mol/L} \cdot \text{s}} = \frac{2.60 \times 10^{-2} \text{ mol/L}}{1.30 \times 10^{-2} \text{ mol/L}}
\]

Dividing, we get \( 3.99 = (2.00)^n \) or \( 4 = 2^n \), so \( n = 2 \).

Alternatively:

\[
\frac{\log a}{\log b} = \frac{\log 3.99}{\log 2.00} = 2.00
\]

The reaction is second order with respect to NO.

The rate law is given by: \( \text{rate} = k[\text{O}_2][\text{NO}]^2 \)
PROBLEM: Many gaseous reactions occur in a car engine and exhaust system. One of these reactions is

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

rate = \( k[\text{NO}_2]^m[\text{CO}]^n \)

Use the following data to determine the individual and overall reaction orders:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial Rate (mol/L·s)</th>
<th>Initial [NO(_2)] (mol/L)</th>
<th>Initial [CO] (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0050</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>2</td>
<td>0.080</td>
<td>0.40</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>0.0050</td>
<td>0.10</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Sample Problem 14.3

PLAN: We need to solve the general rate law for \( m \) and for \( n \) and then add those orders to get the overall order. We proceed by taking the ratio of the rate laws for two experiments in which only the reactant in question changes concentration.

SOLUTION:

To calculate \( m \), the order with respect to NO\(_2\), we compare experiments 1 and 2:

\[
\frac{\text{rate 2}}{\text{rate 1}} = \frac{k [\text{NO}_2]^m [\text{CO}]^n}{k [\text{NO}_2]^1 [\text{CO}]^1} = \left(\frac{[\text{NO}_2]^2}{[\text{NO}_2]^1}\right)^m = \left(\frac{0.080}{0.0050}\right)^m = \left(\frac{0.40}{0.10}\right)^m
\]

\[16 = (4.0)^m \quad \text{so} \quad m = 2\]

The reaction is second order in NO\(_2\).
Sample Problem 14.3

To calculate \( n \), the order with respect to CO, we compare experiments 1 and 3:

\[
\frac{\text{rate 3}}{\text{rate 1}} = \frac{k [\text{NO}_2]^m_3 [\text{CO}]^n_3}{k [\text{NO}_2]^m_1 [\text{CO}]^n_1} = \left( \frac{[\text{CO}]_3}{[\text{CO}]_1} \right)^n = \frac{0.0050}{0.0050} = \left( \frac{0.20}{0.10} \right)^n
\]

\[1.0 = (2.0)^n \text{ so } n = 0\]

The reaction is zero order in CO.

\[
\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0 \text{ or rate} = k[\text{NO}_2]^2
\]
Sample Problem 14.4

Determining Reaction Orders from Molecular Scenes

**PROBLEM:** At a particular temperature and volume, two gases, A (red) and B (blue), react. The following molecular scenes represent starting mixtures for four experiments:

(a) What is the reaction order with respect to A? With respect to B? The overall order?
(b) Write the rate law for the reaction.
(c) Predict the initial rate of experiment 4.

**PLAN:** We find the individual reaction orders by seeing how a change in each reactant changes the rate. Instead of using concentrations we count the number of particles.
Sample Problem 14.4

SOLUTION:

(a) For reactant A (red):
Experiments 1 and 2 have the same number of particles of B, but the number of particles of A doubles. The rate doubles. Thus the order with respect to A is 1.

For reactant B (blue):
Experiments 1 and 3 show that when the number of particles of B doubles (while A remains constant), the rate quadruples. The order with respect to B is 2.

The overall order is $1 + 2 = 3$.

(b) Rate = $k[A][B]^2$

(c) Between experiments 3 and 4, the number of particles of A doubles while the number of particles of B does not change. The rate should double, so rate = $2 \times 2.0 \times 10^{-4} = 4.0 \times 10^{-4}$ mol/L·s
Figure 14.9 Information sequence to determine the kinetic parameters of a reaction.

- **Series of plots of concentration vs. time**
- **Initial rates**
- **Determine slope of tangent at \( t_0 \) for each plot.**
- **Compare initial rates when \([A]\) changes and \([B]\) is held constant (and vice versa).**
- **Reaction orders**
- **Substitute initial rates, orders, and concentrations into rate = \( k[A]^m[B]^n \), and solve for \( k \).**
- **Rate constant (\( k \)) and actual rate law**
An integrated rate law includes \textit{time} as a variable.

\textbf{First-order rate equation:}
\[
\text{rate} = - \frac{\Delta[A]}{\Delta t} = k \ [A]
\]
\[
\ln \frac{[A]_0}{[A]_t} = kt
\]

\textbf{Second-order rate equation:}
\[
\text{rate} = - \frac{\Delta[A]}{\Delta t} = k \ [A]^2
\]
\[
\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt
\]

\textbf{Zero-order rate equation:}
\[
\text{rate} = - \frac{\Delta[A]}{\Delta t} = k \ [A]^0
\]
\[
[A]_t - [A]_0 = -kt
\]
Sample Problem 14.5 Determining the Reactant Concentration after a Given Time

PROBLEM: At 1000°C, cyclobutane \((\text{C}_4\text{H}_8)\) decomposes in a first-order reaction, with the very high rate constant of 87 s\(^{-1}\), to two molecules of ethylene \((\text{C}_2\text{H}_4)\).

(a) If the initial \(\text{C}_4\text{H}_8\) concentration is 2.00 M, what is the concentration after 0.010 s?

(b) What fraction of \(\text{C}_4\text{H}_8\) has decomposed in this time?

PLAN: We must find the concentration of cyclobutane at time \(t\), \([\text{C}_4\text{H}_8]_t\). The problem tells us the reaction is first-order, so we use the integrated first-order rate law:

\[
\ln \frac{[\text{C}_4\text{H}_8]_0}{[\text{C}_4\text{H}_8]_t} = kt
\]
Sample Problem 14.5

SOLUTION:

(a) \[ \ln \frac{[C_4H_8]_0}{[C_4H_8]_t} = kt \]

\[ \ln \frac{2.00 \text{ mol/L}}{[C_4H_8]_t} = (87 \text{ s}^{-1})(0.010 \text{ s}) = 0.87 \]

\[ \frac{2.00 \text{ mol/L}}{[C_4H_8]_t} = e^{0.87} = 2.4 \]

\[ [C_2H_4] = \frac{2.00 \text{ mol/L}}{2.4} = 0.83 \text{ mol/L} \]

(b) Finding the fraction that has decomposed after 0.010 s:

\[ \frac{[C_4H_8]_0 - [C_4H_8]_t}{[C_4H_8]_0} = \frac{2.00 \text{ M} - 0.87 \text{ M}}{2.00 \text{ M}} = 0.58 \]
Figure 14.10A  Graphical method for finding the reaction order from the integrated rate law.

First-order reaction

integrated rate law
\[ \ln \frac{[A]_0}{[A]_t} = kt \]

straight-line form
\[ \ln[A]_t = -kt + \ln[A]_0 \]

A plot of \( \ln [A] \) vs. time gives a straight line for a first-order reaction.
Figure 14.10B  Graphical method for finding the reaction order from the integrated rate law.

Second-order reaction

integrated rate law
\[ \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \]

straight-line form
\[ \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \]

A plot of \( \frac{1}{[A]} \) vs. time gives a straight line for a second-order reaction.
Figure 14.10C  Graphical method for finding the reaction order from the integrated rate law.

Zero-order reaction

A plot of $[A]$ vs. time gives a straight line for a first-order reaction.

integrated rate law

$[A]_t - [A]_0 = -kt$

straight-line form

$[A]_t = -kt + [A]_0$
Figure 14.11 Graphical determination of the reaction order for the decomposition of N\textsubscript{2}O\textsubscript{5}.

The concentration data is used to construct three different plots. Since the plot of \( \ln \text{[N}_2\text{O}_5] \) vs. time gives a straight line, the reaction is first order.
Integrated Rate Laws

An integrated rate law includes \textit{time} as a variable.

\textbf{First-order rate equation:}
\[
\text{rate} = - \frac{\Delta [A]}{\Delta t} = k [A]
\]
\[
\ln \frac{[A]_0}{[A]_t} = kt
\]

\textbf{Second-order rate equation:}
\[
\text{rate} = - \frac{\Delta [A]}{\Delta t} = k [A]^2
\]
\[
\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt
\]

\textbf{Zero-order rate equation:}
\[
\text{rate} = - \frac{\Delta [A]}{\Delta t} = k [A]^0
\]
\[
[A]_t - [A]_0 = - kt
\]
The half-life \( t_{1/2} \) for a reaction is the time taken for the concentration of a reactant to drop to half its initial value.

For a first-order reaction, \( t_{1/2} \) does not depend on the starting concentration.

\[
t_{1/2} = \frac{\ln 2}{k} = 0.693 \frac{k}{k}
\]

The half-life for a first-order reaction is a constant. Radioactive decay is a first-order process. The half-life for a radioactive nucleus is a useful indicator of its stability.
Figure 14.12  A plot of $[\text{N}_2\text{O}_5]$ vs. time for three reaction half-lives.

for a first-order process

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$
Sample Problem 14.6 Using Molecular Scenes to Find Quantities at Various Times

PROBLEM: Substance A (green) decomposes to two other substances, B (blue) and C (yellow), in a first-order gaseous reaction. The molecular scenes below show a portion of the reaction mixture at two different times (0 sec and 30 sec):

(a) Draw a similar molecular scene of the reaction mixture at \( t = 60.0 \) s.
(b) Find the rate constant of the reaction.
(c) If the total pressure (\( P_{\text{total}} \)) of the mixture is 5.00 atm at 90.0 s, what is the partial pressure of substance B (\( P_B \))?
Sample Problem 14.6

SOLUTION:

(a) After 30.0 s, the number of particles of A has decreased from 8 to 4; since [A] has halved in this time, 30.0 s is the half-life of the reaction. After 60.0 s another half-life will have passed, and the number of A particles will have halved again. Each A particle forms one B and one C particle.

\[ t = 60.0 \text{ s} \]
Sample Problem 14.6

(b) The rate constant $k$ is determined using the formula for $t_{1/2}$ of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \quad \text{so} \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30.0 \text{ s}} = 0.023 \times 10^{-2} \text{ s}^{-1}$$

(c) After 90.0 s, three half-lives will have passed. The number of A particles will have halved once again, and each A will produced one B and one C. There will be 1 A, 7 B and 7 C particles.

mole fraction of B, $X_B = \frac{7}{1 + 7 + 7} = 0.467$

$$P_B = X_B \times P_{\text{total}} = 0.467 \times 5.00 \text{ bar} = 2.33 \text{ bar}$$
Determining the Half-Life of a First-Order Reaction

PROBLEM: Cyclopropane is the smallest cyclic hydrocarbon. Because its 60° bond angles allow poor orbital overlap, its bonds are weak. As a result, it is thermally unstable and rearranges to propene at 1000°C via the following first-order reaction:

\[
\begin{align*}
H_2C\equiv CH_2 (g) & \rightarrow CH_3-O-CH\equiv CH_2 (g) \\
\end{align*}
\]

The rate constant is 9.2 s\(^{-1}\), (a) What is the half-life of the reaction? (b) How long does it take for the concentration of cyclopropane to reach one-quarter of the initial value?

PLAN: The reaction is first order, so we find \( t_{1/2} \) using the half-life equation for a first order reaction. Once we know \( t_{1/2} \) we can calculate the time taken for the concentration to drop to 0.25 of its initial value.
Sample Problem 14.7

SOLUTION:

(a) \[ t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{9.2 \text{ s}^{-1}} = 0.075 \text{ s} \]

(b) For the initial concentration to drop to one-quarter of its value requires 2 half-lives to pass.

\[ \text{Time} = 2(0.075 \text{ s}) = 0.15 \text{ s} \]
Half-life Equations

For a **first-order** reaction, $t_{1/2}$ does not depend on the initial concentration.

For a **second-order** reaction, $t_{1/2}$ is *inversely* proportional to the initial concentration:

$$t_{1/2} = \frac{1}{k[A]^0} \quad \text{(second order process; rate = } k[A]^2)$$

For a **zero-order** reaction, $t_{1/2}$ is *directly* proportional to the initial concentration:

$$t_{1/2} = \frac{[A]^0}{2k^0} \quad \text{(zero order process; rate = } k)$$
Table 14.5  An Overview of Zero-Order, First-Order, and Simple Second-Order Reactions

<table>
<thead>
<tr>
<th></th>
<th>Zero Order</th>
<th>First Order</th>
<th>Second Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate law</td>
<td>rate = $k$</td>
<td>rate = $k[A]$</td>
<td>rate = $k[A]^2$</td>
</tr>
<tr>
<td>Units for $k$</td>
<td>mol/L·s</td>
<td>1/s</td>
<td>L/mol·s</td>
</tr>
<tr>
<td>Half-life</td>
<td>$\frac{[A]_0}{2k}$</td>
<td>$\ln 2$</td>
<td>$\frac{1}{k[A]_0}$</td>
</tr>
<tr>
<td>Integrated rate law</td>
<td>$[A]_t = -kt + [A]_0$</td>
<td>$\ln[A]_t = -kt + \ln[A]_0$</td>
<td>$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$</td>
</tr>
<tr>
<td>Plot for straight line</td>
<td>$[A]_t$ vs. $t$</td>
<td>$\ln[A]_t$ vs. $t$</td>
<td>$\frac{1}{[A]_t}$ vs. $t$</td>
</tr>
<tr>
<td>Slope, y intercept</td>
<td>$-k$, $[A]_0$</td>
<td>$-k$, $\ln[A]_0$</td>
<td>$k$, $\frac{1}{[A]_0}$</td>
</tr>
<tr>
<td>Graph</td>
<td><img src="image1.png" alt="Graph" /></td>
<td><img src="image2.png" alt="Graph" /></td>
<td><img src="image3.png" alt="Graph" /></td>
</tr>
</tbody>
</table>
The basic principle of **collision theory** is that particles must collide in order to react.

An increase in the concentration of a reactant leads to a larger number of collisions, hence increasing reaction rate.

The number of collisions depends on the **product** of the numbers of reactant particles, not their sum. Concentrations are multiplied in the rate law, not added.
Figure 14.13  The number of possible collisions is the product, not the sum, of reactant concentrations.
Temperature and the Rate Constant

Temperature has a dramatic effect on reaction rate. For many reactions, an increase of 10°C will double or triple the rate.

Experimental data shows that *k increases exponentially as T increases*. This is expressed in the **Arrhenius equation**:

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

- \( k \) = rate constant
- \( A \) = frequency factor
- \( E_a \) = activation energy

**Higher \( T \) \rightarrow larger \( k \) \rightarrow increased rate**
Figure 14.14  Increase of the rate constant with temperature for the hydrolysis of an ester

The rate constant $k$ increases exponentially with $T$.

<table>
<thead>
<tr>
<th>Expt</th>
<th>[Ester]</th>
<th>[H₂O]</th>
<th>$T$ (K)</th>
<th>Rate (mol/L·s)</th>
<th>$k$ (L/mol·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100</td>
<td>0.200</td>
<td>288</td>
<td>1.04x10⁻³</td>
<td>0.0521</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
<td>0.200</td>
<td>298</td>
<td>2.20x10⁻³</td>
<td>0.101</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.200</td>
<td>308</td>
<td>3.68x10⁻³</td>
<td>0.184</td>
</tr>
<tr>
<td>4</td>
<td>0.100</td>
<td>0.200</td>
<td>318</td>
<td>6.64x10⁻³</td>
<td>0.332</td>
</tr>
</tbody>
</table>

Reaction rate and $k$ increase exponentially as $T$ increases.
In order to be **effective**, collisions between particles must exceed a certain energy **threshold**.

When particles collide effectively, they reach an **activated state**. The energy difference between the reactants and the activated state is the **activation energy** \( (E_a) \) for the reaction.

The **lower** the activation energy, the **faster** the reaction.

Smaller \( E_a \) $\rightarrow$ larger \( f \) $\rightarrow$ larger \( k \) $\rightarrow$ increased rate
Collisions must occur with sufficient energy to reach an **activated state**.

This particular reaction is reversible and is **exothermic** in the forward direction.
Temperature and Collision Energy

An increase in temperature causes an increase in the kinetic energy of the particles. This leads to more frequent collisions and reaction rate increases.

At a higher temperature, the fraction of collisions with sufficient energy equal to or greater than $E_a$ increases. Reaction rate therefore increases.
Figure 14.16  The effect of temperature on the distribution of collision energies.

At \( T_2 \), with \( T_2 > T_1 \), a larger fraction of collisions have enough energy to exceed \( E_a \).
Table 14.6  The Effect of $E_a$ and $T$ on the Fraction ($f$) of Collisions with Sufficient Energy to Allow Reaction

<table>
<thead>
<tr>
<th>$E_a$ (kJ/mol)</th>
<th>$f$ (at $T = 298$ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.70x10^{-9}</td>
</tr>
<tr>
<td>75</td>
<td>7.03x10^{-14}</td>
</tr>
<tr>
<td>100</td>
<td>2.90x10^{-18}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T$</th>
<th>$f$ (at $E_a = 50$ kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C (298 K)</td>
<td>1.70x10^{-9}</td>
</tr>
<tr>
<td>35°C (308 K)</td>
<td>3.29x10^{-9}</td>
</tr>
<tr>
<td>45°C (318 K)</td>
<td>6.12x10^{-9}</td>
</tr>
</tbody>
</table>
Calculating Activation Energy

$E_a$ can be calculated from the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

so

$$\ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right)$$

straight-line form

If data is available at two different temperatures:

$$\ln \frac{k_2}{k_1} = - \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$
Figure 14.17  Graphical determination of the activation energy.

\[ \ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right) \]
Sample Problem 14.8 Determining the Energy of Activation

PROBLEM: The decomposition of hydrogen iodide is shown here, $2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)$, The reaction has rate constants of $9.51 \times 10^{-9}$ L/mol·s at 500. K and $1.10 \times 10^{-5}$ L/mol·s at 600. K. Find $E_a$.

PLAN: We are given two rate constants and two temperatures, so we can use the Arrhenius equation to solve for $E_a$.

SOLUTION:

$$\ln \frac{k_2}{k_1} = - \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$ so $E_a = -R \left( \ln \frac{k_2}{k_1} \right) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)^{-1}$

$$E_a = -(8.314 \text{ J/mol·K}) \ln \left( \frac{1.10 \times 10^{-5} \text{ L/mol·s}}{9.51 \times 10^{-9} \text{ L/mol·s}} \right) \left( \frac{1}{600. \text{ K}} - \frac{1}{500. \text{ K}} \right)^{-1}$$

$$= 1.76 \times 10^5 \text{ J/mol} = 1.76 \times 10^2 \text{ kJ/mol}$$
Molecular Structure and Reaction Rate

For a collision between particles to be effective, it must have both sufficient energy and the appropriate relative orientation between the reacting particles.

The term $A$ in the Arrhenius equation is the frequency factor for the reaction.

$$k = Ae^{-E_a/RT} \quad A = \rho Z$$

$\rho = \text{orientation probability factor}$

$Z = \text{collision frequency}$

The term $\rho$ is specific for each reaction and is related to the structural complexity of the reactants.
Figure 14.18  The importance of molecular orientation to an effective collision.

\[ \text{NO}(g) + \text{NO}_3(g) \rightarrow 2\text{NO}_2(g) \]

There is only one relative orientation of these two molecules that leads to an effective collision.
Transition State Theory

An effective collision between particles leads to the formation of a *transition state* or *activated complex*.

The transition state is an unstable species that contains *partial bonds*. It is a transitional species partway between reactants and products. Transition states cannot be isolated.

The transition state exists at the point of maximum potential energy. The energy required to form the transition state is the activation energy.
Figure 14.19  The transition state of the reaction between BrCH$_3$ and OH$^-$. 

\[ \text{BrCH}_3 + \text{OH}^- \rightarrow \text{Br}^- + \text{CH}_3\text{OH} \]

The transition state contains partial bonds (dashed) between C and Br and between C and O. It has a trigonal bipyramidal shape.
Figure 14.20  Depicting the reaction between BrCH$_3$ and OH$^-$. 

Before reaction, C is bonded to Br, not O.

After reaction, C is bonded to O, not Br.

Reactants

<table>
<thead>
<tr>
<th>BrC(\cdot)H + OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br(\cdot)C(\cdots)OH</td>
</tr>
<tr>
<td>Br(\cdots)C(\cdots)OH</td>
</tr>
<tr>
<td>Br(\cdots)C(\cdots)OH</td>
</tr>
<tr>
<td>Br(^-) + H(\cdot)C(\cdots)OH</td>
</tr>
</tbody>
</table>

Before transition state

Transition state

After transition state

Products

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Figure 14.21  Reaction energy diagrams and possible transition states for two reactions.
Sample Problem 14.9

Drawing Reaction Energy Diagrams and Transition States

PROBLEM: The following reaction is a key reaction in the upper atmosphere:

\[ O_3(g) + O(g) \rightarrow 2O_2(g) \]

The \( E_{a(fwd)} \) is 19 kJ, and the \( \Delta H_{rxn} \) for the reaction as written is -392 kJ. Draw a reaction energy diagram, predict a structure for the transition state, and calculate \( E_{a(rev)} \).

PLAN: The reaction is highly exothermic (\( \Delta H_{rxn} = -392 \) kJ), so the products are much lower in energy than the reactants. The small \( E_{a(fwd)} \) (19 kJ) means that the energy of the reactants lies only slightly below that of the transition state. We calculate the value of \( E_{a(rev)} \) from the value of \( \Delta H \) and \( E_{a(fwd)} \).

To predict the transition state structure, we note that one O-O bond of \( O_3 \) breaks and a new O-O bond forms.
**Sample Problem 14.9**

**SOLUTION:**

\[ \Delta H_{\text{rxn}} = E_{a(\text{fwd})} - E_{a(\text{rev})} \]

So \( E_{a(\text{rev})} = + E_{a(\text{fwd})} - \Delta H_{\text{rxn}} = 19 \text{ kJ} - (-392 \text{ kJ}) = 411 \text{ kJ} \)
The mechanism of a reaction is the sequence of single reaction steps that make up the overall equation.

The individual steps of the reaction mechanism are called elementary steps because each one describes a single molecular event.

Each elementary step is characterized by its molecularity, the number of particles involved in the reaction.

The rate law for an elementary step can be deduced from the reaction stoichiometry – reaction order equals molecularity for an elementary step only.
Table 14.7  Rate Laws for General Elementary Steps

<table>
<thead>
<tr>
<th>Elementary Step</th>
<th>Molecularity</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>A → product</td>
<td>Unimolecular</td>
<td>Rate = [A]</td>
</tr>
<tr>
<td>2A → product</td>
<td>Bimolecular</td>
<td>Rate = $k[A]^2$</td>
</tr>
<tr>
<td>A + B → product</td>
<td>Bimolecular</td>
<td>Rate = $k[A][B]$</td>
</tr>
<tr>
<td>2A + B → product</td>
<td>Termolecular</td>
<td>Rate = $k[A]^2[B]$</td>
</tr>
</tbody>
</table>
Sample Problem 14.10  Determining Molecularity and Rate Laws for Elementary Steps

PROBLEM: The following elementary steps are proposed for a reaction mechanism:

(1) \( \text{NO}_2\text{Cl}(g) \rightarrow \text{NO}_2(g) + \text{Cl}(g) \)
(2) \( \text{NO}_2\text{Cl}(g) + \text{Cl}(g) \rightarrow \text{NO}_2(g) + \text{Cl}_2(g) \)

(a) Write the overall balanced equation.
(b) Determine the molecularity of each step.
(c) Write the rate law for each step.

PLAN: We find the overall equation from the sum of the elementary steps. The molecularity of each step equals the total number of reactant particles. We write the rate law for each step using the molecularities as reaction orders.
Sample Problem 14.10

SOLUTION:

(a) Writing the overall balanced equation:

\[
\begin{align*}
(1) & \quad \text{NO}_2\text{Cl}(g) \rightarrow \text{NO}_2(g) + \text{Cl}(g) \\
(2) & \quad \text{NO}_2\text{Cl}(g) + \text{Cl}(g) \rightarrow \text{NO}_2(g) + \text{Cl}_2(g)
\end{align*}
\]

\[2\text{NO}_2\text{Cl}(g) \rightarrow 2\text{NO}_2(g) + \text{Cl}_2(g)\]

(b) Step(1) is unimolecular. Step(2) is bimolecular.

(c) \[\text{rate}_1 = k_1[\text{NO}_2\text{Cl}]\]
\[\text{rate}_2 = k_2[\text{NO}_2\text{Cl}][\text{Cl}]\]
The Rate-Determining Step of a Reaction

The *slowest* step in a reaction is the *rate-determining* or *rate-limiting* step.

The reaction \( \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \) has been proposed to occur by a two-step mechanism:

1. \( \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \) [slow; rate-determining]
2. \( \text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \) [fast]

Observed rate law: \( \text{rate} = k[\text{NO}_2]^2 \)

The rate law for the rate-determining step becomes the rate law for the overall reaction.
Correlating Mechanism with the Rate Law

A valid mechanism must meet three criteria:

The elementary steps must add up to the overall balanced equation.

The elementary steps must be reasonable.

The mechanism must correlate with the observed rate law.

A mechanism is a hypothesis—we cannot prove it is correct, but if it is consistent with the data, and can be used to predict results accurately, it is a useful model for the reaction.
Mechanisms with a Slow Initial Step

The overall reaction \(2\text{NO}_2(g) + \text{F}_2(g) \rightarrow 2\text{NO}_2\text{F}(g)\) has an experimental rate law \(\text{Rate} = k[\text{NO}_2][\text{F}_2]\).

The accepted mechanism is

1. \(\text{NO}_2(g) + \text{F}_2(g) \rightarrow \text{NO}_2\text{F}(g) + \text{F}(g)\) [slow; rate determining]
2. \(\text{NO}_2(g) + \text{F}(g) \rightarrow \text{NO}_2\text{F}(g)\) [fast]

The elementary steps sum to the overall balanced equation:

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

Step 1 is the slow step, and rate\(_1\) correlates with the \text{observed} rate law.

The mechanism is therefore reasonable.
Mechanisms with a Fast Initial Step

The overall reaction $2\text{NO} \, (g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ has an experimental rate law \( \text{Rate} = k[\text{NO}]^2[\text{O}_2] \).

A proposed mechanism is

(1) $\text{NO} \, (g) + \text{O}_2(g) \rightleftharpoons \text{NO}_3(g)$ \hspace{1cm} [fast]
(2) $\text{NO}_3(g) + \text{NO}(g) \rightarrow 2\text{NO}_2(g)$ \hspace{1cm} [slow; rate determining]

\[ 2\text{NO} \, (g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \]

The elementary steps sum to the overall balanced equation:

Both steps are bimolecular and are therefore reasonable.

\[
\begin{align*}
\text{rate}_{1(\text{fwd})} &= k_1[\text{NO}][\text{O}_2] \\
\text{rate}_{1(\text{rev})} &= k_{-1}[\text{NO}_3] \\
\text{rate}_2 &= k_2[\text{NO}_3][\text{NO}]
\end{align*}
\]

When equilibrium (1) has been established

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

\[ \text{rate}_2 = k_2[\text{NO}_3]\text{[NO]} = k_2 \left( \frac{k_1}{k_{-1}} \text{[NO][O}_2] \right) \text{[NO]} \]

The ratio of rate constants is itself a constant, equal to the overall rate constant for the reaction, so

\[ \text{rate}_2 = k[\text{NO}]^2[\text{O}_2] \] which is consistent with the observed rate law.

For any mechanism, only reactants involved up to and including the slow (rate-determining) step appear in the overall rate law.
Each step in a multi-step reaction has its own transition state, which occurs at the energy maximum for that step.
A catalyst is a substance that increases the reaction rate without itself being consumed in the reaction.

In general, a catalyst provides an alternative reaction pathway that has a lower total activation energy than the uncatalyzed reaction.

A catalyst will speed up both the forward and the reverse reactions.

A catalyst does not affect either $\Delta H$ or the overall yield for a reaction.
Figure 14.23  Reaction energy diagram for a catalyzed (*green*) and uncatalyzed (*red*) process.
Figure 14.24  The catalyzed decomposition of H$_2$O$_2$.
A *homogeneous* catalyst is in the same phase as the reaction mixture.

A small amount of NaBr is added to a solution of H$_2$O$_2$. Oxygen gas forms quickly as Br$^-$(aq) catalyzes the H$_2$O$_2$ decomposition; the intermediate Br$_2$ turns the solution orange.
Figure 14.25 The metal-catalyzed hydrogenation of ethene.

A *heterogeneous* catalyst is in a different phase than the reaction mixture.
Figure 14.26A  Two models of enzyme action.

A  Lock-and-key model: fixed shape of active site matches shape of substrate(s).

The lock-and-key model visualizes the enzyme active site having a fixed shape. This shape matches the shape of its substrate(s). The active site is therefore specific to its substrate.