Reaction Rate

- Change in concentration of a reactant or product per unit time.

\[
\text{Rate} = \frac{\text{concentration of } A \text{ at time } t_2 - \text{concentration of } A \text{ at time } t_1}{t_2 - t_1}
\]

\[
= \frac{\Delta[A]}{\Delta t}
\]

[A] means concentration of A in mol/L; A is the reactant or product being considered.
The Decomposition of Nitrogen Dioxide
Instantaneous Rate

- Value of the rate at a particular time.
- Can be obtained by computing the slope of a line tangent to the curve at that point.
Tidbits

- Reactant rates are negative.
- Product rates are positive.

- Rate is not constant
- Typically it decreases with time
Consider the reaction

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

- NO is produced at the same rate as NO\(_2\) is consumed
- Rate of NO production is twice the rate of O\(_2\) production

Is the rate of NO positive or negative?
Section 12.2
Rate Laws: An Introduction

Rate Law

- Shows how the rate depends on the concentrations of reactants.
- For the decomposition of nitrogen dioxide:
  \[ 2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g) \]

Rate \( = k[\text{NO}_2]^n: \)
  - \( k \) = rate constant
  - \( n \) = order of the reactant
Rate Law

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

- The concentrations of the products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.
- The value of the exponent \( n \) must be determined by experiment; it cannot be written from the balanced equation.
Rate Constant

- Definition of reaction rate in terms of the consumption of NO₂

\[
\text{Rate} = -\frac{\Delta [\text{NO}_2]}{\Delta t} = k \ [\text{NO}_2]^n
\]

- Definition of the reaction rate in terms of production of O₂

\[
\text{Rate}' = \frac{\Delta [\text{O}_2]}{\Delta t} = k' \ [\text{NO}_2]^n
\]
As two moles of NO\(_2\) molecules are consumed for every O\(_2\) molecule produced,

\[
\text{Rate} = 2 \times \text{rate}'
\]

Or

\[
k[\text{NO}_2]^n = 2k'[\text{NO}_2]^n
\]

and

\[
k = 2 \times k'
\]

Value of the rate constant depends on how the rate is defined
Section 12.2
Rate Laws: An Introduction

Types of Rate Laws

- Differential Rate Law (rate law) – shows how the rate of a reaction depends on concentrations.

- Integrated Rate Law – shows how the concentrations of species in the reaction depend on time.

- The type of rate law used depends on what types of data are easiest to collect.
Rate Laws: A Summary

- Because we typically consider reactions only under conditions where the reverse reaction is unimportant, our rate laws will involve only concentrations of reactants.

- Because the differential and integrated rate laws for a given reaction are related in a well-defined way, the experimental determination of either of the rate laws is sufficient.
Experimental convenience usually dictates which type of rate law is determined experimentally.

Knowing the rate law for a reaction is important mainly because we can usually infer the individual steps involved in the reaction from the specific form of the rate law.
Determine experimentally the power to which each reactant concentration must be raised in the rate law.
Method of Initial Rates

- The initial rate is determined for each experiment as close to $t = 0$ as possible.
- Several experiments are carried out using different initial concentrations of each of the reactants, and the initial rate is determined for each run.
- The results are then compared to see how the initial rate depends on the initial concentrations of each of the reactants.
Overall Reaction Order

- The sum of the exponents in the reaction rate equation.

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

Overall reaction order = \( n + m \)

\( k = \) rate constant

\( [A] = \) concentration of reactant A

\( [B] = \) concentration of reactant B
How do exponents (orders) in rate laws compare to coefficients in balanced equations?

Why?
Interactive Example 12.1 - Determining a Rate Law

- The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the following equation:

\[ \text{BrO}_3^- (aq) + 5\text{Br}^- (aq) + 6\text{H}^+ (aq) \rightarrow 3\text{Br}_2 (l) + 3\text{H}_2\text{O}(l) \]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial Concentration of BrO$_3^-$ (mol/L)</th>
<th>Initial Concentration of Br$^-$ (mol/L)</th>
<th>Initial Concentration of H$^+$ (mol/L)</th>
<th>Measured Initial Rate (mol/L · s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>$8.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>0.10</td>
<td>0.10</td>
<td>$1.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.20</td>
<td>0.10</td>
<td>$3.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>0.10</td>
<td>0.20</td>
<td>$3.2 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Interactive Example 12.1 - Determining a Rate Law (Continued)

- Determine the orders for all three reactants, the overall reaction order, and the value of the rate constant
Interactive Example 12.1 - Solution

- **General form of the rate law**
  \[
  \text{Rate} = k \left[ \text{BrO}_3^- \right]^n \left[ \text{Br}^- \right]^m \left[ \text{H}^+ \right]^p
  \]

- **Step 1 - Determine the value of } n\]
  - Use the results from Experiments 1 and 2

  \[
  \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{1.6 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}} = \frac{k(0.20 \text{ mol/L})^n (0.10 \text{ mol/L})^m (0.10 \text{ mol/L})^p}{k(0.10 \text{ mol/L})^n (0.10 \text{ mol/L})^m (0.10 \text{ mol/L})^p}
  \]

  \[
  2.0 = \left( \frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}} \right)^n = (2.0)^n
  \]

  - Thus, } n = 1\]
Interactive Example 12.1 - Solution (Continued 1)

- Step 2 - Determine the value of $m$
  - Use the results from Experiments 2 and 3

\[
\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{3.2 \times 10^{-3} \text{ mol/L s}}{1.6 \times 10^{-3} \text{ mol/L s}} = \frac{k(0.20 \text{ mol/L})^n (0.20 \text{ mol/L})^m (0.10 \text{ mol/L})^p}{k(0.20 \text{ mol/L})^n (0.10 \text{ mol/L})^m (0.10 \text{ mol/L})^p}
\]

\[
2.0 = \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^m = (2.0)^m
\]

- Thus, $m = 1$
Interactive Example 12.1 - Solution (Continued 2)

- Step 3 - Determine the value of $p$
  - Use the results from Experiments 1 and 4

\[
\frac{\text{Rate 4}}{\text{Rate 1}} = \frac{3.2 \times 10^{-3} \text{ mol} / \text{L} \cdot \text{s}}{8.0 \times 10^{-4} \text{ mol} / \text{L} \cdot \text{s}} = \frac{k(0.10 \text{ mol} / \text{L})^n (0.10 \text{ mol} / \text{L})^m (0.20 \text{ mol} / \text{L})^p}{k(0.10 \text{ mol} / \text{L})^n (0.10 \text{ mol} / \text{L})^m (0.10 \text{ mol} / \text{L})^p}
\]

\[
4.0 = \left( \frac{0.20 \text{ mol} / \text{L}}{0.10 \text{ mol} / \text{L}} \right)^p
\]

\[
4.0 = (2.0)^p = (2.0)^2
\]

- Thus, $p = 2$
- The overall reaction order is $n + m + p = 4$
The rate law for the reaction
\[ \text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2 \]

The value of the rate constant \( k \) can be calculated from the results of any of the four experiments.

For Experiment 1, the initial rate is \( 8.0 \times 10^{-4} \) mol/L·s

\[ [\text{BrO}_3^-] = 0.100 \ M, [\text{Br}^-] = 0.10 \ M, \text{ and } [\text{H}^+] = 0.10 \ M \]
Interactive Example 12.1 - Solution (Continued 4)

- Using the values from the initial rate in the rate law

  \[ 8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s} = k(0.10 \text{ mol/L})(0.10 \text{ mol/L})(0.10 \text{ mol/L})^2 \]

  \[ 8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s} = k(1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4) \]

  \[ k = \frac{8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}}{1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4} = 8.0 \text{ L}^3/\text{mol}^3 \cdot \text{s} \]

- Reality Check
  - Verify that the same value of \( k \) can be obtained from the results of the other experiments
Section 12.4
The Integrated Rate Law

First-Order

- Rate = $k[A]$
- Integrated:
  $$\ln[A] = -kt + \ln[A]_o$$

$[A] = \text{concentration of A at time } t$

$k = \text{rate constant}$

$t = \text{time}$

$[A]_o = \text{initial concentration of A}$
Integrated First-Order Rate Law - Key Points

- The equation expresses the influence of time on the concentration of A
  - The initial concentration of A and the rate constant $k$ can be used to calculate the concentration of A at any time
- The equation is of the form $y = mx + b$
  - $y = \ln[A]$, $x = t$, $m = -k$, and $b = \ln[A]_0$
  - For a first-order reaction, a plot of $\ln[A]$ versus $t$ is always a straight line
The equation can be expressed in terms of a ratio of $[A]$ and $[A]_0$

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$
Section 12.4

The Integrated Rate Law

Plot of $\ln[N_2O_5]$ vs Time

<table>
<thead>
<tr>
<th>$\ln[N_2O_5]$</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-2.303$</td>
<td>0</td>
</tr>
<tr>
<td>$-2.649$</td>
<td>50</td>
</tr>
<tr>
<td>$-2.996$</td>
<td>100</td>
</tr>
<tr>
<td>$-3.689$</td>
<td>200</td>
</tr>
<tr>
<td>$-4.382$</td>
<td>300</td>
</tr>
<tr>
<td>$-5.075$</td>
<td>400</td>
</tr>
</tbody>
</table>
Calculate $[\text{N}_2\text{O}_5]$ at 150 s after the start of the following reaction:

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

Use the following information:

<table>
<thead>
<tr>
<th>$[\text{N}_2\text{O}_5]$ (mol/L)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1000</td>
<td>0</td>
</tr>
<tr>
<td>0.0707</td>
<td>50</td>
</tr>
<tr>
<td>0.0500</td>
<td>100</td>
</tr>
<tr>
<td>0.0250</td>
<td>200</td>
</tr>
<tr>
<td>0.0125</td>
<td>300</td>
</tr>
<tr>
<td>0.00625</td>
<td>400</td>
</tr>
</tbody>
</table>
Interactive Example 12.3 - Solution

- **Information available**
  - \([N_2O_5] = 0.0500 \text{ mol/L at 100 s}\)
  - \([N_2O_5] = 0.0250 \text{ mol/L at 200 s}\)

- **Formula required to calculate \([N_2O_5]\) after 150 s**

  \[
  \ln [N_2O_5] = -kt + \ln [N_2O_5]_0
  \]

  Where \(t = 150 \text{ s}, k = 6.93 \times 10^{-3} \text{ s}^{-1}\), and \([N_2O_5]_0 = 0.1000 \text{ mol/L}\)
Interactive Example 12.3 - Solution (Continued)

\[
\ln ([N_2O_5]_{t=150}) = -(6.93 \times 10^{-3} \text{ s}^{-1}) (150 \text{ s}) + \ln(0.100) \\
= -1.040 - 2.303 = -3.343 \\
([N_2O_5]_{t=150}) = \text{antilog} (-3.343) = 0.0353 \text{ mol/L}
\]

- Note that this value of \([N_2O_5]\) is not halfway between 0.0500 and 0.0250 mol/L
Section 12.4
The Integrated Rate Law

First-Order

- Time required for a reactant to reach half its original concentration
- Half–Life:

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

\(k = \text{rate constant}\)

- Half–life does not depend on the concentration of reactants.
Section 12.4
The Integrated Rate Law

**Figure 12.4** - A Plot of $[\text{N}_2\text{O}_5]$ versus Time for the Decomposition of $\text{N}_2\text{O}_5$
Interactive Example 12.4 - Half-Life for a First-Order Reaction

- A certain first-order reaction has a half-life of 20.0 minutes
  
  a. Calculate the rate constant for this reaction
  
  b. How much time is required for this reaction to be 75% complete?
Interactive Example 12.4 - Solution (a)

- Solving equation (12.3) for \( k \) gives

\[
k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20.0 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}
\]
Interactive Example 12.4 - Solution (b)

- We use the integrated rate law in the form

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

- If the reaction is 75% complete, 75% of the reactant has been consumed, leaving 25% in the original form

\[ \frac{[A]}{[A]_0} \times 100\% = 25\% \]
Interactive Example 12.4 - Solution (b) (Continued 1)

\[
\frac{[A]}{[A]_0} = 0.25 \text{ or } \frac{[A]_0}{[A]} = \frac{1}{0.25} = 4.0
\]

\[
\ln \left( \frac{[A]_0}{[A]} \right) = \ln(4.0) = kt = \left( \frac{3.47 \times 10^{-2}}{\text{min}} \right) t
\]

\[
t = \frac{\ln(4.0)}{3.47 \times 10^{-2} \text{ min}^{-1}} = 40 \text{ min}
\]

- It takes 40 minutes for this particular reaction to reach 75% completion
A first order reaction is 35% complete at the end of 55 minutes. What is the value of $k$?

$$ k = 7.8 \times 10^{-3} \text{ min}^{-1} $$
Section 12.4

The Integrated Rate Law

Second-Order

- Rate = \( k[A]^2 \)
- Integrated:

\[
\frac{1}{[A]} = kt + \frac{1}{[A]_o}
\]

\([A] = \text{concentration of A at time } t\)

\(k = \text{rate constant}\)

\(t = \text{time}\)

\([A]_o = \text{initial concentration of A}\)
Section 12.4
The Integrated Rate Law

Plot of $\ln[C_4H_6]$ vs Time and Plot of $1/[C_4H_6]$ vs Time
Characteristics of Equation (12.5)

- A plot of $1/[A]$ versus $t$ will produce a straight line with a slope equal to $k$.
- The equation shows how $[A]$ depends on time and can be used to calculate $[A]$ at any time $t$, provided $k$ and $[A]_0$ are known.
Section 12.4
The Integrated Rate Law

Second-Order

- Half–Life:
  
  \[ t_{1/2} = \frac{1}{k[A]_0} \]

  \( k = \) rate constant

  \( [A]_0 = \) initial concentration of A

- Half–life gets longer as the reaction progresses and the concentration of reactants decrease.
- Each successive half–life is double the preceding one.
For a reaction \( aA \rightarrow \text{Products} \), \([A]_0 = 5.0\ M\), and the first two half-lives are 25 and 50 minutes, respectively.

a) Write the rate law for this reaction.
   
   \[
   \text{rate} = k[A]^2
   \]

b) Calculate \( k \).
   
   \[
   k = 8.0 \times 10^{-3}\ M^{-1}\min^{-1}
   \]

c) Calculate \([A]\) at \( t = 525\ \text{minutes} \).
   
   \[
   [A] = 0.23\ M
   \]
Example 12.5 - Determining Rate Laws

- Butadiene reacts to form its dimer according to the equation

\[ 2\text{C}_4\text{H}_6(g) \rightarrow \text{C}_8\text{H}_{12}(g) \]

<table>
<thead>
<tr>
<th>[C\textsubscript{4}H\textsubscript{6}] (mol/L)</th>
<th>Time (±1 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01000</td>
<td>0</td>
</tr>
<tr>
<td>0.00625</td>
<td>1000</td>
</tr>
<tr>
<td>0.00476</td>
<td>1800</td>
</tr>
<tr>
<td>0.00370</td>
<td>2800</td>
</tr>
<tr>
<td>0.00313</td>
<td>3600</td>
</tr>
<tr>
<td>0.00270</td>
<td>4400</td>
</tr>
<tr>
<td>0.00241</td>
<td>5200</td>
</tr>
<tr>
<td>0.00208</td>
<td>6200</td>
</tr>
</tbody>
</table>
Example 12.5 - Determining Rate Laws (Continued)

a. Is this reaction a first order or second order?
b. What is the value of the rate constant for the reaction?
c. What is the half-life for the reaction under the initial conditions of this experiment?
Example 12.5 - Solution (a)

- To decide whether the rate law for this reaction is first order or second order, we must see whether the plot of $\ln[C_4H_6]$ versus time is a straight line (first order) or the plot of $1/[C_4H_6]$ versus time is a straight line (second order)
Example 12.5 - Solution (a) (Continued 1)

- The data necessary to make these plots are as follows:

<table>
<thead>
<tr>
<th>$t$ (s)</th>
<th>$\frac{1}{[C_4H_6]}$</th>
<th>$\ln[C_4H_6]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>−4.605</td>
</tr>
<tr>
<td>1000</td>
<td>160</td>
<td>−5.075</td>
</tr>
<tr>
<td>1800</td>
<td>210</td>
<td>−5.348</td>
</tr>
<tr>
<td>2800</td>
<td>270</td>
<td>−5.599</td>
</tr>
<tr>
<td>3600</td>
<td>320</td>
<td>−5.767</td>
</tr>
<tr>
<td>4400</td>
<td>370</td>
<td>−5.915</td>
</tr>
<tr>
<td>5200</td>
<td>415</td>
<td>−6.028</td>
</tr>
<tr>
<td>6200</td>
<td>481</td>
<td>−6.175</td>
</tr>
</tbody>
</table>
Example 12.5 - Solution (a) (Continued 2)

- The reaction is second order
- The rate law for this reaction is:

\[
\text{Rate} = -\frac{\Delta[C_4H_6]}{\Delta t} = k[C_4H_6]^2
\]

A plot of \(\ln[C_4H_6]\) versus \(t\)
A plot of \(1/[C_4H_6]\) versus \(t\)
Example 12.5 - Solution (b)

- For a second-order reaction, a plot of $1/[C_4H_6]$ versus $t$ produces a straight line of slope $k$
  - In terms of the standard equation for a straight line, $y = mx + b$, we have $y = 1/[C_4H_6]$ and $x = t$
  - Slope of the line can be expressed as follows:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{\Delta \left( \frac{1}{[C_4H_6]} \right)}{\Delta t}$$
Example 12.5 - Solution (b) (Continued)

- Using the points at $t = 0$ and $t = 6200$, we can find the rate constant for the reaction

$$k = \text{slope} = \frac{(481 - 100) \text{ L}/\text{mol}}{(6200 - 0) \text{ s}} = \frac{381}{6200} \text{ L}/\text{mol} \cdot \text{s}$$

$$= 6.14 \times 10^{-2} \text{ L}/\text{mol} \cdot \text{s}$$
Example 12.5 - Solution (c)

- The expression for the half-life of a second-order reaction is

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

- In this case \( k = 6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s} \) (from part b) and \( [A]_0 = [C_4H_6]_0 = 0.01000 \text{ M} \) (the concentration at \( t = 0 \))

\[ t_{1/2} = \frac{1}{(6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s})(1.000 \times 10^{-2} \text{ mol/L})} = 1.63 \times 10^3 \text{s} \]

- The initial concentration of \( C_4H_6 \) is halved in 1630 s
Half-Life for a First-Order Reaction versus Half-Life of a Second-Order Reaction

- $t_{1/2}$
  - First-order reaction - $t_{1/2}$ depends on $k$
  - Second-order reaction - $t_{1/2}$ depends on $k$ and $[A]_0$

- Half-life
  - First-order reaction - A constant time is required to reduce the concentration of the reactant by half
  - Second-order reaction - Each successive half-life is double the preceding one
Section 12.4
The Integrated Rate Law

Zero-Order

- Rate = $k[A]^0 = k$
- Integrated:
  
  $$[A] = -kt + [A]_o$$

[A] = concentration of A at time $t$

$k$ = rate constant

$t$ = time

$[A]_o$ = initial concentration of A
Section 12.4
The Integrated Rate Law

Plot of \([A]\) vs Time

\[
\text{Slope} = \frac{\Delta[A]}{\Delta t} = -k
\]
Zero-Order

- Half-Life:

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

\( k = \text{rate constant} \)
\( [A]_0 = \text{initial concentration of A} \)

- Half-life gets shorter as the reaction progresses and the concentration of reactants decrease.
How can you tell the difference among 0\textsuperscript{th}, 1\textsuperscript{st}, and 2\textsuperscript{nd} order rate laws from their graphs?
Section 12.4
The Integrated Rate Law

Rate Laws

To play movie you must be in Slide Show Mode
PC Users: Please wait for content to load, then click to play
Mac Users: CLICK HERE
Section 12.4
The Integrated Rate Law

Summary of the Rate Laws

Table 12.6 | Summary of the Kinetics for Reactions of the Type \(aA \rightarrow \) Products That Are Zero, First, or Second Order in \([A]\)

<table>
<thead>
<tr>
<th></th>
<th>Zero</th>
<th>First</th>
<th>Second</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>Integrated rate law</td>
<td>([A] = -kt + [A]_0)</td>
<td>(\ln[A] = -kt + \ln[A]_0)</td>
<td>(\frac{1}{[A]} = kt + \frac{1}{[A]_0})</td>
</tr>
<tr>
<td>Plot needed to give a straight line</td>
<td>([A]) versus (t)</td>
<td>(\ln[A]) versus (t)</td>
<td>(\frac{1}{[A]}) versus (t)</td>
</tr>
<tr>
<td>Relationship of rate constant to the slope of straight line</td>
<td>Slope = (-k)</td>
<td>Slope = (-k)</td>
<td>Slope = (k)</td>
</tr>
<tr>
<td>Half-Life</td>
<td>(t_{1/2} = \frac{[A]_0}{2k})</td>
<td>(t_{1/2} = \frac{0.693}{k})</td>
<td>(t_{1/2} = \frac{1}{k[A]_0})</td>
</tr>
</tbody>
</table>
Consider the reaction $aA \rightarrow \text{Products}$. 
$[A]_0 = 5.0 \, M$ and $k = 1.0 \times 10^{-2}$ (assume the units are appropriate for each case). Calculate $[A]$ after 30.0 seconds have passed, assuming the reaction is:

a) Zero order $\quad 4.7 \, M$

b) First order $\quad 3.7 \, M$

c) Second order $\quad 2.0 \, M$
Most chemical reactions occur by a series of steps.

Example - The reaction between nitrogen dioxide and carbon monoxide involves the following steps:

\[
\begin{align*}
\text{NO}_2(g) + \text{NO}_2(g) & \xrightarrow{k_1} \text{NO}_3(g) + \text{NO}(g) \\
\text{NO}_3(g) + \text{CO}(g) & \xrightarrow{k_2} \text{NO}_2(g) + \text{CO}_2(g)
\end{align*}
\]

Where \( k_1 \) and \( k_2 \) are the rate constants of the individual reactions.
In the reaction, NO$_3$ is an intermediate

- **Intermediate**: Species that is formed and consumed during the reaction but is neither a reactant nor a product

Each of the reactions is called an elementary step

- **Elementary step**: A reaction whose rate law can be written from its molecularity
A Molecular Representation of the Elementary Steps in the Reaction of NO₂ and CO

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

- **Unimolecular** – reaction involving one molecule; first order.
- **Bimolecular** – reaction involving the collision of two species; second order.
- **Termolecular** – reaction involving the collision of three species; third order. Very rare.
Rate-Determining Step

- A reaction is only as fast as its slowest step.
- The rate-determining step (slowest step) determines the rate law and the molecularity of the overall reaction.
Reaction Mechanism Requirements

- The sum of the elementary steps must give the overall balanced equation for the reaction.
- The mechanism must agree with the experimentally determined rate law.
## Table 12.7 - Examples of Elementary Steps

<table>
<thead>
<tr>
<th>Elementary Step</th>
<th>Molecularity</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>A → products</td>
<td>Unimolecular</td>
<td>Rate = $k[A]$</td>
</tr>
<tr>
<td>A + A → products (2A → products)</td>
<td>Bimolecular</td>
<td>Rate = $k[A]^2$</td>
</tr>
<tr>
<td>A + B → products</td>
<td>Bimolecular</td>
<td>Rate = $k[A][B]$</td>
</tr>
<tr>
<td>A + A + B → products (2A + B → products)</td>
<td>Termolecular</td>
<td>Rate = $k[A]^2[B]$</td>
</tr>
<tr>
<td>A + B + C → products</td>
<td>Termolecular</td>
<td>Rate = $k[A][B][C]$</td>
</tr>
</tbody>
</table>
Example 12.6 - Reaction Mechanisms

- The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is
  \[2\text{NO}_2 (g) + \text{F}_2 (g) \rightarrow 2\text{NO}_2\text{F}(g)\]
- Experimentally determined rate law is
  \[\text{Rate} = k[\text{NO}_2][\text{F}_2]\]
Example 12.6 - Reaction Mechanisms (Continued)

- Suggested mechanism for this reaction is

\[ \text{NO}_2 + F_2 \xrightleftharpoons[k_1]{k_2} \text{NO}_2 F + F \quad \text{(slow)} \]
\[ F + \text{NO}_2 \rightarrow \text{NO}_2 F \quad \text{(fast)} \]

- Is this an acceptable mechanism?
  - Does it satisfy the two requirements?
Example 12.6 - Solution

- First requirement for an acceptable mechanism
  - The sum of the steps should give the balanced equation

\[
\begin{align*}
NO_2 + F_2 &\rightarrow NO_2F + F \\
F + NO_2 &\rightarrow NO_2F \\
\underline{2NO_2 + F_2 + F} &\rightarrow \underline{2NO_2F + F}
\end{align*}
\]

Overall reaction: \(2NO_2 + F_2 \rightarrow 2NO_2F\)

- The first requirement is met
Second requirement

The mechanism must agree with the experimentally determined rate law

- The overall reaction rate must be that of the first step
- The first step is bimolecular, so the rate law is

\[ \text{Rate} = k_1 [\text{NO}_2][\text{F}_2] \]

- The second requirement is met

The mechanism is acceptable as both requirements are satisfied
Decomposition of $\text{N}_2\text{O}_5$
Decomposition of $N_2O_5$

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

Step 1: $2(N_2O_5 \rightleftharpoons NO_2 + NO_3)$ (fast)

Step 2: $NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$ (slow)

Step 3: $NO_3 + NO \rightarrow 2NO_2$ (fast)
The reaction $A + 2B \rightarrow C$ has the following proposed mechanism:

$$\begin{align*}
A + B & \rightleftharpoons D & \text{(fast equilibrium)} \\
D + B & \rightarrow C & \text{(slow)}
\end{align*}$$

Write the rate law for this mechanism.

$$\text{rate} = k[A][B]^2$$
Collision Model

- Molecules must collide to react.
- Main Factors:
  - Activation energy, $E_a$. Energy that must be overcome to produce a chemical reaction.
  - Temperature
  - Molecular orientations
- Kinetic energy is changed into potential energy as the molecules are distorted during a collision to break bonds and rearrange the atoms into product molecules
Transition States and Activation Energy

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Section 12.6
A Model for Chemical Kinetics

Change in Potential Energy
Relation between Effective Collisions and Temperature

- The fraction of effective collisions increases exponentially with temperature.
For Reactants to Form Products

- Collision must involve enough energy to produce the reaction (must equal or exceed the activation energy).
- Relative orientation of the reactants must allow formation of any new bonds necessary to produce products.
The Gas Phase Reaction of NO and Cl\textsubscript{2}
Arrhenius Equation

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

- \( A \) = frequency factor
- \( E_a \) = activation energy
- \( R \) = gas constant (8.3145 J/K·mol)
- \( T \) = temperature (in K)
Linear Form of Arrhenius Equation

\[
\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A)
\]
Linear Form of Arrhenius Equation

\[ \text{Slope} = \frac{\Delta \ln(k)}{\Delta(1/T)} = -1.2 \times 10^4 \text{ K} \]

\[ \ln(k) \]

\[ 1/T (\text{K}) \]

\[ 3.00 \times 10^{-3} \quad 3.25 \times 10^{-3} \quad 3.50 \times 10^{-3} \]
Based on the plot

\[
\text{Slope} = \frac{\Delta \ln(k)}{\Delta \left(\frac{1}{T}\right)} = -1.2 \times 10^4 \text{ K}
\]

Determine the value of $E_a$ by solving the following equation

\[
\text{Slope} = \frac{-E_a}{R}
\]
Chemists commonly use a rule of thumb that an increase of 10 K in temperature doubles the rate of a reaction. What must the activation energy be for this statement to be true for a temperature increase from 25°C to 35°C?

\[ E_a = 53 \text{ kJ} \]
Catalyst

- A substance that speeds up a reaction without being consumed itself.
- Provides a new pathway for the reaction with a lower activation energy.
Energy Plots for a Catalyzed and an Uncatalyzed Pathway for a Given Reaction
Section 12.7

Catalysis

Effect of a Catalyst on the Number of Reaction-Producing Collisions

![Diagram showing the effect of a catalyst on the number of reaction-producing collisions](image-url)
Heterogeneous Catalyst

- Most often involves gaseous reactants being adsorbed on the surface of a solid catalyst.
- Adsorption – collection of one substance on the surface of another substance.
Heterogeneous Catalysis
Section 12.7
*Catalysis*

Heterogeneous Catalyst

1. Adsorption and activation of the reactants.
2. Migration of the adsorbed reactants on the surface.
3. Reaction of the adsorbed substances.
4. Escape, or desorption, of the products.
Homogeneous Catalyst

- Exists in the same phase as the reacting molecules.
- Enzymes are nature’s catalysts.
Section 12.7
Catalysis

Homogeneous Catalysis

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