Chapter 13 Rates of Reactions

Chemical reactions require varying lengths of time for completion, depending on the characteristics of the reactants and products. The study of the rate, or speed, of a reaction has important applications.

**Chemical kinetics** is the study of reaction rates, how reaction rates change under varying conditions, and what molecular events occur during the overall reaction.

The rate of reaction can be affected by the following factors:

1. Concentration of reactants: Often the rate increases when the concentration of a reactant is increased.

2. Concentration of a catalyst: A catalyst is a substance that increases the rate of reaction without being consumed in the overall reaction.

3. Temperature: Often reactions speed up when the temperature increases.

4. Surface area: Reaction rates increase with an increase in surface area

**Reaction rate** is the increase in molar concentration of product of a reaction per unit time, or the decrease in molar concentration of reactant per unit time.

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

Rate of formation of oxygen = \( \Delta [\text{O}_2] / \Delta t \)
Calculate the average rate of decomposition of \( \text{N}_2\text{O}_5 \), \(-\Delta[\text{N}_2\text{O}_5]/\Delta t\), during the time interval from \( t = 600 \) s to \( t = 1200 \) s using the following data:

<table>
<thead>
<tr>
<th>Time</th>
<th>( [\text{N}_2\text{O}_5] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 s</td>
<td>( 1.24 \times 10^{-2} ) M</td>
</tr>
<tr>
<td>1200 s</td>
<td>( 0.93 \times 10^{-2} ) M</td>
</tr>
</tbody>
</table>

To obtain the rate of reaction, you must determine the concentration of a reactant or product during the course of a reaction. Most convenient are techniques that can continuously follow the progression of a reaction by observing the change in some physical property of the system.

Pressure changes and color changes are good examples.
The rate of reaction is observed to be proportional to the concentration of NO\(_2\) and the concentration of F\(_2\).

A **Rate Law** is an equation that relates the rate of reaction to the concentrations of reactants (and catalyst) raised to various powers.

\[
\text{Rate} = k [NO_2] [F_2]
\]

where \(k\) is a rate constant which is a proportionality constant in the relationship between rate and concentration. It has a fixed value at any given temperature, but it varies with temperature.

\[
k = \frac{\text{rate}}{[NO_2] [F_2]}
\]

As a general example:

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

\[
\text{Rate} = k [A]^x [B]^y
\]

The **reaction order** with respect to a given reactant is the exponent of the concentration of that species in the rate law, as determined experimentally.

The **overall order of reaction** is the sum of the orders of the reactant species in the rate law.

It is tempting to assign \(x = a, y = b\), etc. for the reactant orders, but this is generally not a valid assumption. Reaction order often does not correlate to reactant coefficient. **Rate measurements** are needed to determine the values of \(x\) and \(y\). The reactions is described as being first, second, etc. order in A and first, second etc. order in B. The overall reaction order is the sum of \(x + y + \times \times \times \). Reactant orders are typically 0, 1, 2, 3, or sometimes 0.5.

A zero order reactant means that the rate of the reaction is not influenced by the concentration of that particular reactant.
The rate law will have the concentration of reactant raised to a power of \( x \)

\[
\text{Rate} = k[N_2O_5]^x
\]

The rate of \( x \) must be determined from experimental data. When the concentration is doubles then there is a new rate

\[
\text{Rate'} = k(2[N_2O_5])^x = 2^x k[N_2O_5]^x
\]

The initial concentration is doubled and the rate is multiplied by 4, when \( x = 2 \)

Determining the rate constant \( k \) by substituting values of the rate and the \( N_2O_5 \) concentration

\[
\text{Example: An experimental determination of the order of the reaction between fluorine and chlorine dioxide gas was done by measuring the initial reaction rate for different starting concentrations of fluorine and chlorine dioxide.}
\]

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

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

The units of rate are typically concentration/time, in most cases, M/s.

For carrying out calculations, it is useful to know the value of \( k \), which is invariant when temperature is constant.

\[
k = \text{rate}/([\text{ClO}_2] \ [\text{F}_2])
\]
In the case of a second order reaction, the units of k are M/s divided by $M^2 = M^{-1} \cdot s^{-1}$. In a first order reaction, k has units $M/s \cdot M = s^{-1}$. Higher order reactions have more complicated k units.

If the reaction was elementary, then the rate law would be:

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

where the Rate = $1.50 \times 10^{-2} \text{M/s}$ and the concentration of A an B were 1.00 M. The reaction would be first order in A, first order in B and second order overall. The rate constant can then be determined from initial rate information easily:

$$k = \frac{1.50 \times 10^{-2} \text{M/s}}{(1.00 \text{ M})^2}$$

$$k = 1.50 \times 10^{-2} \text{ l/mol/s}$$

Remember: The units of the rate constant depend on the overall order of the reaction.

More information about the reaction rate law is needed than a single measurement of an initial rate. In order to determine the rate law experimentally, we must use more than one measurement of rate versus concentration

**The Method of Initial Rates**

Consider a reaction $A + B \rightarrow \text{Products}$

In an experiment, you prepare several reaction mixtures and determines the initial reaction rates under these different conditions. The data obtained for several experimental runs is:

<table>
<thead>
<tr>
<th>Run #</th>
<th>Initial [A] ([A]₀)</th>
<th>Initial [B] ([B]₀)</th>
<th>Initial Rate (v₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00 M</td>
<td>1.00 M</td>
<td>$1.50 \times 10^{-2}$ M/s</td>
</tr>
<tr>
<td>2</td>
<td>1.00 M</td>
<td>2.00 M</td>
<td>$3.0 \times 10^{-2}$ M/s</td>
</tr>
<tr>
<td>3</td>
<td>2.00 M</td>
<td>2.00 M</td>
<td>$3.0 \times 10^{-2}$ M/s</td>
</tr>
</tbody>
</table>

What is the rate constant for this reaction?
First, you must determine the order of the reactions with respect to every reactant. Find a pair of experimental runs that the concentration of only one reactant changes. This is called the method of isolation and a good experimental design always has one such pair of experimental runs.

Thus the rate law for the reaction is

\[
\text{rate} = k[B]^1[A]^0 = k[B]
\]

Now, the rate constant can be determined from any of the experimental runs. Let's use run # 3

\[
\text{rate} = 3.0 \times 10^{-2} \text{ M/s} = k (2.0 \text{ M})
\]

\[
k = 1.50 \times 10^{-2} \text{ s}^{-1}
\]

Note that the initial rate of any experimental run (any prepared experimental condition) can now be determined (calculated) since we have the rate law and the rate constant.

A More Complicated Example

Consider a reaction \[ \text{A + B + C} \rightarrow \text{Products} \]

Several initial conditions of this reaction are investigated and the following data was obtained:

<table>
<thead>
<tr>
<th>Run #</th>
<th>[A]</th>
<th>[B]</th>
<th>[C]</th>
<th>Initial Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.151 M</td>
<td>0.213 M</td>
<td>0.398 M</td>
<td>0.480 M/s</td>
</tr>
<tr>
<td>2</td>
<td>0.251 M</td>
<td>0.105 M</td>
<td>0.325 M</td>
<td>0.356 M/s</td>
</tr>
<tr>
<td>3</td>
<td>0.151 M</td>
<td>0.213 M</td>
<td>0.525 M</td>
<td>1.102 M/s</td>
</tr>
<tr>
<td>4</td>
<td>0.151 M</td>
<td>0.250 M</td>
<td>0.480 M</td>
<td>0.988 M/s</td>
</tr>
</tbody>
</table>
What is the initial rate of the reaction when all the reactants are at 0.100 M concentrations?

\[ \text{Rate} = k \ [A]^a \ [B]^b \ [C]^c \]

First: Identify the change in one concentration in two different runs. Example, the ratio between Run #1 and Run #3
**First-Order Reactions**

The rate of a first-reaction depends only on the concentration of one reactant, A.

A → products

By definition, rate = - ∆ [A]/Δ t and rate = k[A]

Therefore, - ∆ [A]/Δ t = k[A]

d[A]/dt = -kt (Instantaneous rate of change described by calculus.)

ln([A]_t /[A_o]) = - kt (Calculus solution to the equation by integration)

\[ \ln[A]_t - \ln[A_o] = - kt \text{ or } \ln[A]_t = - kt + \ln[A_o] \]

This is a useful equation for graphing since it is in the form y = mx + b

Example: For a reaction with k = 5.50 x 10^{-3} s^{-1} at 45.0 °C, what will be the concentration of A remaining after 12.0 min if the initial concentration of A is 0.200 M?

\[ \ln[A]_t = - kt + \ln[A_o] = - 5.50 \times 10^{-3} \text{ s}^{-1} (12.0 \text{ min} \times 60 \text{ s/1 min}) + \ln (0.200) \]

\[ \ln[A]_t = - 3.96 + - 1.61 = - 5.57 \]

\[ [A]_t = 3.81 \times 10^{-3} \text{ M} \]

**Second-Order Reactions**

Second order reactions in A can be easily described mathematically. Second order in [A] and [B] and third order reactions will not be covered in this course.

For second order reactions in A:

A → products

rate = - ∆ [A]/Δ t, but now the rate = k[A]^2
The graphable equation becomes:

\[ \frac{1}{[A]} = kt + \frac{1}{[A_0]} \quad \text{again, } y = mx + b \]

Example: The decomposition of NO\(_2\) at a moderately high temperature (between 300 - 400ºC)

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

At 330ºC the rate constant for the decomposition of NO\(_2\) is 0.775 L/(mol·sec)

Suppose the initial concentration is 0.0030 mol/L. What is the concentration of NO\(_2\) after 645 s ?

Zero Order Reactions

A → products which has a zero order rate law of Rate = k[A]\(^0\)

Rate = k

This rate law indicates that the rate of a zero order reaction does not change with concentration, however the reaction does require some minimum reactant concentration for the reaction to behave as zero-order. The relationship between concentration and time for a zero order reaction is

\[ [A]_t = -kt + [A]_0 \]

Example: The decomposition of N\(_2\)O\(_5\) to NO\(_2\) and O\(_2\) is first order with a rate constant of 4.80 x 10\(^{-3}\)/s at 45ºC. If the initial concentration is 1.65 x 10\(^{-2}\) M, what would be the concentration after 6.00 x 10\(^{-2}\) sec. How long would it take for the concentration of N\(_2\)O\(_5\) to decrease 10.0% of its initial value?
The **half life**, \( t_{1/2} \), of a reaction is the time it takes for the reactant concentration to decrease to one half of its initial value.

For a first order reaction, the half life is independent of the initial concentration.

\[
\ln \frac{[A]_t}{[A]_0} = -kt
\]

where \([A]_t = 1/2 [A]_0\)

\[
\ln \frac{1}{2}[A]_0 / [A]_0 = -kt_{1/2}
\]

\[
t_{1/2} = \frac{0.693}{k} \quad \text{for first order}
\]

If then, the rate is second order overall, where \( \text{Rate} = k[A]^2 \). The half life depends on the initial concentration and each subsequent half life becomes larger as time goes on.

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

and finally, for the zero order reactions, the half life is dependent upon the initial concentration of the reactant. As a zero order reaction proceeds, each half life gets shorter

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

<table>
<thead>
<tr>
<th>TABLE 13.2</th>
<th>Relationships for Zero-Order, First-Order, and Second-Order Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Order</strong></td>
<td><strong>Rate Law</strong></td>
</tr>
<tr>
<td>0</td>
<td>( \text{Rate} = k )</td>
</tr>
<tr>
<td>1</td>
<td>( \text{Rate} = k[A] )</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Rate} = k[A]^2 )</td>
</tr>
</tbody>
</table>
Temperature and Rate of Reaction

The rate constant is found to vary with temperature. Most often we see an increase in the rate constant with an increase in temperature.

This correlation can be explained by the collision theory.

The collision theory of reaction rates is the theory that assumes that, for a reaction to occur, reactant molecules must collide with an energy greater than some minimum value and with the proper orientation.

Activation energy \(E_a\) - is the minimum energy of collision required for two molecules to react. The value of \(E_a\) is dependent on the particular reaction.

The rate constant for a reaction is given as a product;

\[
k = Zfp
\]

where \(Z\) = the collision frequency; \(f\) = the fraction of collisions having the energy greater than the \(E_a\); \(p\) = the fraction of collisions that occur with the reactant molecules properly oriented.

\(Z\), collision frequency, is directly proportional to temperature, but that doesn't fully explain why the rate of reaction will triple when the temperature is raised 10ºC in some reactions.

\(f\), the fraction of collisions changes rapidly in most reactions.

\[
f = e^{-Ea/RT}
\]

where \(e = 2.718\)  \(R\) is the gas constant  \(t\) is the temperature in K

\(p\), proper orientation, is independent on temperature change.
Transition State Theory explains the reaction resulting from the collision of two molecules in terms of an activated complex.

An activated complex (transition state) is an unstable grouping of atoms that can break up to form products.

\[ \text{O} = \text{N} + \text{Cl-Cl} \rightarrow [\text{O} = \text{N} \cdots \text{Cl} \cdots \text{Cl}] \rightarrow \text{O} = \text{N-Cl} + \text{Cl} \]

Potential Energy Diagrams

\[ \text{NO} + \text{Cl}_2 \rightarrow \text{NOCL}_2^\dagger \rightarrow \text{NOCl} + \text{Cl} \]

Energy Diagram shows the change in potential energy that occurs during the progress of the reaction.
Arrenhius Equation is the mathematical equation which expresses the dependence of the rate constant, k, to the temperature:

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

where e is the base of the natural logarithms, \( E_a \) is the activation energy, R is the gas constant, and T is the temperature in Kelvin. The symbol A is the frequency factor and is considered a constant. Taking the natural log of both sides gives

\[ \ln k = \ln a + \left( -\frac{E_a}{RT} \right) \]

For a complete set of data for a reaction you can subtract one equation from the other and get

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

The rate constant for the formation of hydrogen iodide from the elements

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

is 2.7 \times 10^{-4} \text{L(mol sec)} at 600K and 3.5 \times 10^{-3} \text{L(mol sec)} at 650K. Find the activation energy then calculate the rate constant at 700K.
Elementary Reaction is a singular molecular event, such as a collision of molecules, resulting in a reaction.

Reaction Mechanism is a set of elementary reactions whose overall effect is given by the net chemical equation.

A Reaction intermediate is a species produced during a reaction that does not appear in the net equation because it reacts in a subsequent step in the mechanism.

Example: CCl\textsubscript{4} is obtained by chlorinating methane or an incompletely chlorinated methane such as chloroform, CCl\textsubscript{3}. The mechanism for the gas phase chlorination of CCl\textsubscript{3} is:

\[
\begin{align*}
\text{Cl}_2 & \rightarrow 2\text{Cl} \\
\text{Cl} + \text{CHCl}_3 & \rightarrow \text{HCl} + \text{CCl}_3 \\
\text{Cl} + \text{CCl}_3 & \rightarrow \text{CCl}_4
\end{align*}
\]

Obtain the net, or overall, chemical equation from this mechanism

For an elementary reaction, the rate law is proportional to the product of the concentration of each reactant molecule.

\[
\begin{align*}
\text{A} & \rightarrow \text{B} + \text{C} \\
\text{Rate} & = k[A] \\
\text{A} + \text{B} & \rightarrow \text{C} + \text{D} \\
\text{Rate} & = k[A][B]
\end{align*}
\]

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

For a reaction that occurs in more than one step we can show the elementary reaction steps

\[
\begin{align*}
\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) & \stackrel{k_1}{\longrightarrow} \text{NOF}_2(\text{g}) + \text{F} \quad \text{(slow step)} \\
\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) & \stackrel{k_2}{\longrightarrow} \text{NO}_2\text{F}_2(\text{g}) \quad \text{(fast step)}
\end{align*}
\]
Rate determining step is the slowest step in the reaction mechanism

Example: Ozone reacts with nitrogen dioxide to produce oxygen and dinitrogen pentaoxide

\[ \text{O}_3(g) + 2\text{NO}_2(g) \rightarrow \text{O}_2(g) + \text{N}_2\text{O}_5(g) \]

The proposed mechanism is

\[ \text{O}_3(g) + \text{NO}_2(g) \rightarrow \text{O}_2(g) + \text{NO}_3(g) \text{ (slow step)} \]
\[ \text{NO}_3(g) + \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_5(g) \text{ (fast step)} \]

What is the rate law predicted for this mechanism?

Nitrogen monoxide can be reduced with hydrogen gas to give nitrogen and water vapor

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

A proposed mechanism is

\[ 2\text{NO} \rightarrow \text{N}_2\text{O}_2 \text{ (fast, equilibrium)} \]
\[ \text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \text{ (slow)} \]
\[ \text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} \text{ (fast)} \]

What rate law is predicted by this mechanism?
Catalysis is the increase in rate of a reaction that results from the addition of a catalyst.

How do we explain how a catalyst can influence a reaction?

\[
\begin{align*}
2\text{SO}_2(g) + \text{O}_2(g) &\xrightarrow{\text{NO}} 2\text{SO}_3(g) \\
2\text{NO} + \text{O}_2 &\rightarrow 2\text{NO}_2 \\
\text{NO}_2 + \text{SO}_2 &\rightarrow \text{NO} + \text{SO}_3
\end{align*}
\]

Homogeneous catalysis a catalysis that is found in the same phase as the reacting species

Heterogeneous catalysis exists in a different phase from the reacting species