CHAPTER 13. CHEMICAL KINETICS

Kinetics - Study of factors that affect how fast a reaction occurs and the step-by-step processes involved in chemical reactions.

Factors that Affect Reaction Rate
A. Concentration of reactants - higher reactant concentrations increase the rate of reaction.
B. Catalyst – substance that accelerates the reaction rate without being transformed.
C. Temperature - higher temperatures usually increase the rate of reaction.
D. Surface area of solid - smaller particles have more surface area so the rate increases.

13.1. THE RATE OF A REACTION

Rate of reaction: The change in the amount of a reactant or product per unit time. (Analogy: speed of an automobile = \( \frac{\Delta \text{Distance}}{\Delta \text{time}} \).)

\[
\text{Average Rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}}
\]

E.g. For a reaction \( A \rightarrow B \)

Average Rate for B = \[ \ldots \] ; Average Rate for A = \[ \ldots \]

- The reaction rate is a measure of how fast a reaction occurs.
- Rate can be expressed as the rate of formation of products or the rate of disappearance of reactants.
- Reaction rate is always positive, so a (-) sign is used for reactant rate expressions. (Because the concentration of reactants decreases with time, \( \Delta [\text{Reactants}] \) is a negative quantity.)
- Reaction rate decreases with time ⇒ slope of curve decreases as reaction progresses.

Experimental Determination of Rate
We can find the rate of reaction by measuring the concentration of a reactant or product during the course of the reaction. Concentration can be obtained by different methods including titration, spectroscopy, and by taking manometer pressure readings.

Spectrometer Measurements
E.g. \( \text{Br}_2 + \text{HCO}_2\text{H} \rightarrow 2\text{Br}^- + 2\text{H}^+ + \text{CO}_2 \)

A colored species, \( \text{Br}_2 \), is consumed during this reaction, so we can use a spectrophotometer to measure the absorbance of light over a series of time intervals. (The absorbance is proportional to the concentration of \( \text{Br}_2 \).) The concentration of \( \text{Br}_2 \) vs. time can then be plotted as shown in Figure 13.5.

Example. Calculate the average rate from \( t = 50.0 \text{ s} \) to \( 100.0 \text{ s} \)

Instantaneous rate: Rate at a specific point in time. Analogy: the speed a car is traveling when a photo radar camera snaps the picture.
To calculate instantaneous rate - draw a line tangent to the curve at a given instant in time & find the slope of the line.

Example. Instantaneous Rate at t = 200.0 s:

*Due to estimating the values used in determining the slope of the line, the value that you obtain for the instantaneous rate may differ from the instantaneous rates given in your text book.

**Gas Phase Reactions**

If one of the substances in the reaction mixture is a gas, manometer readings can be taken to monitor the pressure of the gas.

e.g. \( 2\text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \)

The rate of oxygen evolution can be measured with a manometer. The pressure of oxygen can then be converted to concentration by using the ideal gas law:

\[
P \cdot V = n \cdot R \cdot T
\]

Concentration can be expressed as:

\[
\frac{n}{V} = \frac{\text{moles}}{\text{L}} = M
\]

By substitution: \( P = MRT \) or \( M = \frac{P}{RT} \)

**Reaction Rates & Stoichiometry**

Consider the reaction: \( 2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2 \)

- For this reaction, the rate of disappearance of \( \text{N}_2\text{O}_5 \) is twice the rate of formation of \( \text{O}_2 \).
- To make the rates equal, divide rates by their stoichiometric coefficients:

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

Example. For the reaction, \( 3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3 \), write the rate expressions in terms of the disappearance of the reactants and the appearance of the products.

Example. For the reaction, \( 2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2 \), if the rate of decomposition of \( \text{N}_2\text{O}_5 \) is \( 4.2 \times 10^{-7} \text{ mol}/(\text{L} \cdot \text{s}) \), what is the rate of appearance of (a) \( \text{NO}_2 \); (b) \( \text{O}_2 \)?

**13.2. THE RATE LAW**

**Rate law:** gives relationship of the reaction rate to the rate constant and the concentrations of the reactants.

E.g. \( 2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2 \) \hspace{1cm} \text{Rate} = k[\text{N}_2\text{O}_5]

\( k = \text{Rate Constant} \): \( k \) is a numerical constant for a reaction at a given temperature.

- \( k \) is not affected by \([\text{Reactants}]\), but reaction rate is affected by \([\text{Reactants}]\).
For a reaction \[ aA + bB \rightarrow xX \]
\[ \text{Rate} = k[A]^x[B]^y \]

**Reaction Order:** Exponent of a reactant in the rate equation.

**Overall Reaction Order:** Sum of all exponents in the rate equation.

- Exponents cannot be obtained by looking at the equation; they are experimentally determined values.
- Exponents are usually + whole #’s (0, 1, 2), but can be negative #’s or fractions.
- \(k\) units: \(M^{-(\text{overall order} - 1)} \text{time}^{-1}\)

Example. For the following reaction: \[ 2\text{ClO}_2 + F_2 \rightarrow 2\text{FCIO}_2 \]
\[ \text{Rate} = k[\text{ClO}_2][F_2] \]
order of ClO\(_2\) = ___; order of F\(_2\) = ___; Overall order = ___

**Determination of Rate Law from Initial Rates Data**
To determine the rate law, we observe the effect of changing the initial concentrations of the reactants on the initial rate of reaction.

Experimental Data: Initial rates (\(\Delta[\text{Products}]/\Delta t\) after 1-2% of limiting reactant has been consumed) are usually given; there is less chance of error from competing side reactions & reversible reactions.

E.g. A reactant is 1\(^{st}\) order if doubling [Reactant] causes the rate to double (For a first order reaction, rate is directly proportional to [Reactant]).

E.g. A reactant is 2\(^{nd}\) Order if doubling [Reactant] causes the rate to quadruple.

- To find the order, \(x\), for a specific reactant, examine what happens to the rate as the concentration of only that particular reactant changes:

\[ \left( \frac{\text{conc}_2}{\text{conc}_1} \right)^x = \frac{\text{Rate}_2}{\text{Rate}_1} \]

- Repeat this process to find the orders for all of the reactants.

Example.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.020</td>
<td>0.010</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.040</td>
<td>0.010</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>0.040</td>
<td>0.020</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Order for A: ____ Order for B: ____

**Rate Law:**

### 13.3 RELATION BETWEEN REACTANT CONCENTRATION AND TIME

**First Order Reactions**
For a reaction, \(A \rightarrow \text{Products}\)

\[ \text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A] \]

Integrated Rate law:

\[ \ln \left( \frac{[A]_t}{[A]_0} \right) = -kt \]
\([A]_0 = \text{ initial concentration; } [A]_t = \text{ concentration at time } t\)
\[\Rightarrow \text{ Units for } A \text{ can be g, moles, M, torr, etc}\]
\[\Rightarrow A_t \text{ is always less than } A_0\]
\[\text{Rearrange: } \ln [A]_t - \ln [A]_0 = -kt \text{ to match straight line form of } y = mx + b\]
\[\ln [A]_t = -kt + \ln [A]_0\]
\[\text{• y intercept } = \ln [A]_0; \text{ slope } = -k \Rightarrow k = -\frac{\Delta \ln [A]_t}{\Delta t}\]
\[\text{Note: Only for 1st order reactions will you get a straight line when plotting } \ln [A]_t \text{ vs. time!}\]

**Second Order Reactions**

For a reaction, \(A \rightarrow \text{ Products}\)
\[\text{Rate } = -\frac{\Delta [A]}{\Delta t} = k[A]^2\]

Integrated 2nd order Equation:
\[\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \Rightarrow \frac{1}{[A]_t} = kt + \frac{1}{[A]_0}\]
\[\text{• For 2nd order plot: slope } = k; \text{ y-intercept } = \frac{1}{[A]_0}\]
\[\text{Note: Only for 2nd order reactions will you get a straight line when plotting } \frac{1}{[A]_t} \text{ vs. time.}\]

**Zero Order Reactions**

For a reaction, \(A \rightarrow \text{ Products}\): \[\text{Rate } = -\frac{\Delta [A]}{\Delta t} = k[A]^0 = k\]

Integrated 0 order law: \([A]_0 - [A]_t = kt \Rightarrow [A]_t = -kt + [A]_0\]
\[\text{• For Zero order plot: slope } = -k; \text{ y-intercept } = [A]_0\]
\[\text{Note: Only for 0 order reactions will you get a straight line when plotting } [A] \text{ vs. time.}\]

**Half-Life for 1st Order Reactions**

\(t_{1/2} = \text{Half-life}: \text{ Time that it takes for } [A] \text{ to drop to 1/2 of its initial value}. \ [A]_t = \frac{1}{2} [A]_0\)

Plug into the 1st order law:
\[\ln \frac{1}{2} [A]_0 \Rightarrow \ln \frac{1}{2} = -kt_{1/2} \Rightarrow k \cdot t_{1/2} = 0.693\]
\[\text{• } t_{1/2} \text{ does not depend on the initial } [A] \text{ only for 1st order reactions.}\]
Characteristics of zero, first and second order reactions

<table>
<thead>
<tr>
<th>Order</th>
<th>Rate Law</th>
<th>Integrated Law</th>
<th>Linear graph</th>
<th>slope</th>
<th>Half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Rate = k</td>
<td>([A]_t = -kt + [A]_0)</td>
<td>[A] vs. t</td>
<td>-k</td>
<td>(t_{1/2} = \frac{[A]_0}{2k})</td>
</tr>
<tr>
<td>1</td>
<td>Rate = k[A]</td>
<td>(\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt)</td>
<td>ln [A] vs. t</td>
<td>-k</td>
<td>(t_{1/2} = \frac{0.693}{k})</td>
</tr>
<tr>
<td>2</td>
<td>Rate = k[A]^2</td>
<td>(\frac{1}{[A]_t} = kt + \frac{1}{[A]_0})</td>
<td>(\frac{1}{[A]_t}) vs. t</td>
<td>+k</td>
<td>(t_{1/2} = \frac{1}{k[A]_0})</td>
</tr>
</tbody>
</table>

**Graphical Method of Determining Rate Law**

1) Make 3 plots: [A] vs time; ln [A] vs. time; and \(\frac{1}{[A]}\) vs. time.

2) The most linear plot gives the correct order for A; the other 2 graphs should be curves.

**13.4 ACTIVATION ENERGY AND TEMPERATURE DEPENDENCE OF RATE CONSTANTS**

Collision Theory: Molecules must collide with each other in order to react!

Collision frequency affects the reaction rate:
- An increase in [Reactant] results in more collisions, so the rate of reaction is faster.
- ↑T causes molecules to move faster and collide more frequently, increasing the rate.

**Transition State Theory**

However, only a small fraction of colliding molecules will react because:

1) the molecules must possess enough Kinetic Energy to
   A. overcome e-cloud - e-cloud repulsions
   B. transfer translational KE to vibrational energy to weaken/break reactant bonds

Molecules at a given Temperature possess a KE distribution:

**E_a, Activation Energy** - Energy barrier that molecules have to surmount in order to react.

Energy is needed to break reactant bonds (endothermic process).

analogy: putting a golf ball over a hill or getting started on an unpleasant task

- Only a small fraction of molecules have high enough KE to initiate a reaction.
- \(E_a\) is different for each reaction – for reactions with low \(E_a\), the reaction rate is faster and k is larger because more molecules can overcome \(E_a\).
- At higher temperatures, a larger fraction of molecules have enough KE to surmount \(E_a\). (This is the primary reason that the reaction rate increases rapidly as temperature rises.)

2) molecules must be properly oriented to have an effective collision.

**Figure 13.17:** \(K + CH_3I \rightarrow KI + CH_3\)

- K must collide with I in order for the reaction to occur.
**Activated Complex (transition state)** – a highly unstable species formed by the collision of the reactant molecules; arrangement of atoms at the top of the energy barrier.

E.g. \( O=N + Cl-Cl \rightarrow O=N--Cl--Cl \rightarrow O=N-Cl + Cl \)

Reactants \hspace{1cm} \text{Activated Complex} \hspace{1cm} \text{Products}

**Potential energy diagram for endothermic reaction:**

\[
\Delta H = \text{Heat of reaction}; \text{ this is } \Delta H(\text{products}) - \Delta H(\text{reactants}).
\]

The \( E_a \) shown above is the activation energy for the forward reaction, \( E_a(\text{forward}) \). This is the difference in energy between the activated complex and the reactants.

There is also an activation energy associated with the reverse process, \( E_a(\text{reverse}) \). This is the difference in energy between the activated complex and the products.

**Potential energy diagram for exothermic reaction:**

**Arrhenius Equation**

The Arrhenius equation gives the relationship between the rate constant and the temperature:

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

\( e = \ln^{-1} \) or inv \( \ln \)

\( R = \text{gas constant} = 8.314 \text{ J/K-mol} \)

\( e^{-E_a/RT} = \text{fraction of molecules that have enough KE to react} \)

\( A = \text{frequency factor} \) (relates to \# of collisions that are properly oriented)

By taking the natural log of both sides and rearranging, we obtain:

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

- plot of \( \ln k \) vs \( 1/T \) yields a straight line \( \Rightarrow \) \( \ln k \)
  \( 1/T \)

  slope = \( -\frac{E_a}{R} \); y intercept = \( \ln A \)

**Non-graphical method:**

If you have 2 sets of conditions, solve for \( k_1, k_2, T_1, T_2 \) or \( E_a \) using:

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

Many chemical reactions occur by a sequence of 2 or more steps – the specific sequence of steps is referred to as the reaction mechanism.

Each individual event in the overall reaction is called an **elementary step**.

**Molecularity:** number of molecules that react in an elementary step

- **Unimolecular:** 1 molecule $A \rightarrow \text{products}$
- **Bimolecular:** 2 molecules $2A \rightarrow \text{products}$ or $A + B \rightarrow \text{products}$
- **Termolecular (uncommon):** $3A \rightarrow \text{products}$ or $2A + B \rightarrow P$ or $A + B + C \rightarrow P$

**Example.** The 2 step mechanism for the overall reaction $\text{Br}_2 + 2\text{NO} \rightarrow 2\text{BrNO}$ is:

- **Step 1:** $\text{Br}_2 + \text{NO} \rightarrow \text{Br}_2\text{NO}$ (Bimolecular step)
- **Step 2:** $\text{Br}_2\text{NO} + \text{NO} \rightarrow 2\text{BrNO}$ (Bimolecular step)

**Intermediates** are short lived species that are formed during the reaction, then are subsequently consumed. Intermediates do not appear in the overall balanced equation. e.g. $\text{Br}_2\text{NO}$ for the example above

$\Rightarrow$ For an elementary step, the rate law can be written using the stoichiometric coefficients of the reactants (molecularity = order).

E.g. Step 1 in the reaction above: $\text{Rate} = \ldots$

**Rate determining step:** the slowest step in the reaction is the rate determining step; this step limits how fast products can form. Analogy: freeway during rush hour

$\Rightarrow$ The rate law for the overall reaction is determined by the rate of this step.

**Mechanisms with an Initial Slow Step**

Example. The mechanism for the overall reaction $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$ is proposed to be:

- **Step 1:** $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$ (slow)
- **Step 2:** $\text{F} + \text{NO}_2 \rightarrow \text{NO}_2\text{F}$ (fast)

What is the Rate Law for this reaction? $\text{Rate} = \ldots$

$\Rightarrow$ The reactants for the slow step (step 1) give us the rate law for the overall reaction.

**Mechanisms with an Initial Fast Equilibrium Step**

Many chemical reactions involve mechanisms with equilibrium steps:

Example. The mechanism for the reaction $\text{Br}_2 + 2\text{NO} \rightarrow 2\text{BrNO}$ occurs via two steps:

- **Step 1:** $\text{Br}_2 + \text{NO} \leftrightharpoons \text{Br}_2\text{NO}$ (fast equilibrium)
- **Step 2:** $\text{Br}_2\text{NO} + \text{NO} \rightarrow 2\text{BrNO}$ (slow)

What is the Rate Law predicted by this mechanism?

$\Rightarrow$ From the slow step: $\text{Rate} = \ldots$

$\Rightarrow$ However, it is not possible to accurately measure the concentration of an intermediate so an intermediate cannot be part of an experimental rate law.

$\Rightarrow$ Since most of $\text{Br}_2\text{NO}$ decomposes during the equilibrium reaction established in step 1, we can set up an equilibrium expression based on the rates of the forward and reverse reactions:
Rate of forward reaction = Rate of reverse reaction

⇒ Solve for [intermediate]:

⇒ Substitute in Rate law:

Experimentally you should observe the rate law: Rate = $k[\text{NO}]^2[\text{Br}_2]$ where $k = \frac{k_f}{k_r}$ (k is the experimentally obtained rate constant)

### 13.6 CATALYSIS

**Catalyst**: A substance that increases the rate of reaction, but is not part of the overall reaction.

- A catalyst lowers the $E_a$ ⇒ usually a catalyst helps weaken or break reactant bonds.
- A catalyst alters the reaction mechanism, but does not change the overall reaction.
- A catalyst may appear in the experimental rate law ⇒ a reaction may have more than one rate law.

Catalyzed reaction: $E_a$ is lower, but $\Delta H = \Delta H$ (products) - $\Delta H$ (reactants) is the same:

![Reaction path](image)

**Heterogeneous** – The catalyst is in a different phase than the reactants. Typically, a metal is used to provide a surface upon which reactants can adsorb and react.

E.g. Catalytic converters contain platinum metal mixed with rhodium. Pt catalyzes the oxidation of CO and unburned hydrocarbons to CO$_2$ and H$_2$O. Rh converts NO to N$_2$ and O$_2$.

**Homogeneous** – The catalyst is in the same phase as the reactants. The catalyst is consumed, then regenerated in a subsequent step. Homogeneous catalyst may appear in rate law.

Example. Homogeneous catalyzed decomposition of hydrogen peroxide: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

Step 1 $\quad \text{H}_2\text{O}_2 + I^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$ \hspace{1cm} Slow

Step 2 $\quad \text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + I^-$ \hspace{1cm} Fast

![Reaction Path](image)

**Enzymes** - Large protein molecules with one or more active sites that serve as biological catalysts in living organisms. The enzymes are compatible with specific substrate molecules.