Chapter 13 Chemical Kinetics

**Rate** equals change in something with time

$$\frac{\Delta x}{\Delta t} = \text{velocity}$$

velocity

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

reaction rate = A = reactant or product

For the reaction $A \rightarrow B$, measure the rate two ways:

disappearance of reactant $A$ rate $= \frac{-\Delta [A]}{\Delta t}$ or

appearance of product $B$ rate $= \frac{\Delta [B]}{\Delta t}$.

**Average Rate** $= -\frac{\Delta [A]}{\Delta t} = \frac{\Delta [A]_{\text{final}} - \Delta [A]_{\text{initial}}}{\Delta t_{\text{final}} - \Delta t_{\text{initial}}}$

$rate \propto [A]$  
$rate = k[A]$  
k is the rate constant  
$k = \frac{rate}{[A]}$
Reaction with gases

For the reaction: \( 2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \)

\[
P V = n R T \quad P = \frac{n}{V} R T = [\text{O}_2] R T
\]

\[
[\text{O}_2] = \frac{1}{R T} P 
\]

\[
[\text{O}_2] \propto P
\]

\[
\text{rate} = \frac{\Delta [\text{O}_2]}{\Delta t} = \frac{1}{R T} \frac{\Delta P}{\Delta t}
\]

Reaction Rates and Stoichiometry

\[a \, \text{A} + b \, \text{B} \rightarrow c \, \text{C} + d \, \text{D}\]

\[
\text{rate} = -\frac{1}{a} \frac{\Delta [\text{A}]}{\Delta t} = -\frac{1}{b} \frac{\Delta [\text{B}]}{\Delta t} = \frac{1}{c} \frac{\Delta [\text{C}]}{\Delta t} = \frac{1}{d} \frac{\Delta [\text{D}]}{\Delta t}
\]

\[
\frac{\Delta [\text{C}]}{\Delta t} = -\frac{c}{a} \frac{\Delta [\text{A}]}{\Delta t}
\]

Ex: It was found that the rate of formation of \( \text{N}_2(\text{g}) \) in the following reaction

\[4 \, \text{NH}_3(\text{g}) + 3 \, \text{O}_2(\text{g}) \rightarrow 2 \, \text{N}_2(\text{g}) + 6 \, \text{H}_2\text{O}(\text{g})\]

is 0.52 M \( \cdot \) s\(^{-1} \) at a particular point in time. Determine the rate of disappearance of \( \text{NH}_3 \).
Factors that effect rate of chemical reactivity

1. State of subdivision (greater surface area)
2. Temperature (higher T - higher rate

   +10°, rate doubles ~)
3. Concentration
4. Presence of Catalysts

Rate Equations
(keep all Factors constant, but change concentration)

2A → B

slope changes over time, so rate changes over time because rate depends on [A] (in this experiment)

How to find rate dependence on [ ]?
Through experiment
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Experiment: 2A + B → C

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.020</td>
<td>0.030</td>
<td>0.030</td>
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<tr>
<td>0.010</td>
<td>0.010</td>
<td>0.010</td>
<td>0.020</td>
</tr>
<tr>
<td>1.50</td>
<td>3.00</td>
<td>4.50</td>
<td>18.0</td>
</tr>
</tbody>
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Now set up rate expression: rate = [A]^x[\text{B}]^y

The object is to determine the value of x and y.

Compare experiments 1 and 2. [A] doubles and [\text{B}] is held constant.

rate \propto [A]^x[\text{B}]^y

rate = k[A]^x[\text{B}]^y \quad \text{k = "rate constant"}

x, y determined from experiment (important!)

1.50 = k[0.010]^x[\text{B}]^y

3.00 = k[0.020]^x[\text{B}]^y

rate doubles as concentration of A doubles

rate doubles if x = 1

would quadruple if x = 2

4.50 = k[A]^x[0.010]^y

18.0 = k[A]^x[0.020]^y
\[
\frac{18.0}{4.50} = 4 \quad \text{quadruples}
\]
\[
\text{doubles, so } y = 2
\]

\[
4.50 = k[A]^1[0.010]^y
\]
\[
\text{quad} = \text{quad}
\]
\[
18.0 = k[A]^1[0.020]^2
\]

"rate expression" or **rate law**

rate = \( k[A][B]^2 \)

value of \( k \)?

(take values from any of experiments in table)

\[
1.50 \text{ mol/L}\cdot\text{s} = k[0.01][0.010]^2
\]
\[
k = \frac{1.50 \text{ mol/L}\cdot\text{s}}{(0.010 \text{ mol/L})(0.010 \text{ mol/L})^2}
\]
\[
k = 1.50 \times 10^6 \text{ L}^2/\text{mol}^2\text{s}^{-1}
\]
Why bother calculating $k$ and rate expression?

Because rate depends on concentration, which changes over time. The rate expression gives the rate for a particular set of concentrations of each reactant.

"**Order**" ≡ value of exponent

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

first order in $A$

second order in $B$

"Overall order" ≡ sum of exponents

third order overall ($1 + 2$)

**First Order Reactions (Overall)**

\[ \text{slope} = \frac{d[A]}{dt} \]

\[ \text{rate} = \frac{d[A]}{dt} = k[A] \]
Calculus gives:  Integrated Rate Expression

\[ kdt = - \frac{d[A]}{[A]} \]

\[ k(t - t_0) = kt = -\ln([A] - [A]_0) = \ln \frac{[A]_0}{[A]} \]

\[ \ln \frac{[A]_0}{[A]} = kt \quad \text{A}_0 = \text{initial conc.} \]

\[ A = \text{conc. at time } t \]

\[ \ln[A]_0 - \ln[A] = kt \]

**Half Life**, \( t_{1/2} \) = time required for half of the original concentration of the limiting reactant to be consumed.

at \( t_{1/2}, [A] = 1/2 [A]_0 \)

so for first order reactions in A

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

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

**Second Order Reactions**

\[ k[A]^2 = - \frac{d[A]}{dt} \quad kdt = -\frac{1}{[A]^2} d[A] \]

\[ \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad t_{1/2} = \frac{1}{k[A]_0} \]
Effect of Temperature on Rate thought of in terms of Collision Theory

Three requirements for a chemical reaction
1. Molecules must collide
2. Molecules must collide with sufficient energy
3. Molecules must collide with proper orientation

• Factors to get colliding molecules to go on to product molecules

\[
\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2
\]

\[
\begin{array}{c}
\text{O} \\
\text{N} \equiv \text{O} \\
\text{C} \equiv \text{O}
\end{array}
\]

"activated complex"

or

"transition state"

\[
\begin{array}{c}
\text{O} \\
\text{N} \equiv \text{O} \\
\text{C} \equiv \text{O}
\end{array}
\]

or

bounce away from each other without reacting

• Rearrangement of bonds
break bonds - costs energy
form bonds - gain energy

\[\text{Ea} \quad "activation energy"
\]

energy needed to break bonds in going to "transition state" arrangement of nuclei and bonds
**Arrhenius equation**

rate (as k) depends on the above 2 factors

\[ k = Ae^{-\frac{E_a}{RT}} \quad \text{or} \quad \ln k = \ln A - \frac{E_a}{RT} \]

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

\[ y = m \cdot x + b \]

- k rate constant
- A "frequency factor"
- E\textsubscript{a} activation energy
- R gas constant
- \( T \) absolute temperature

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

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

- \( E_a \) depends on pathway that nuclei take to rearrange
- infinite number of ways but only one takes the minimum amount of energy (\( E_a \))
If there is only one Ea (minimum pathway), how does a change in temperature change rate?

1. Temperature average K.E. of particles
2. at any one temp, distribution of speeds (K.E.)
3. distribution changes in 2 ways when T is increased.

**Ex:** The rate constant for the reaction

\[ 2\text{ICl}(g) + \text{H}_2(g) \rightarrow \text{I}_2(s) + 2\text{HCl}(g) \]

is \(0.120 \text{ L mol}^{-1}\text{s}^{-1}\) at \(225^\circ\text{C}\) and

is \(0.350 \text{ L mol}^{-1}\text{s}^{-1}\) at \(245^\circ\text{C}\). Calculate \(E_a\).
The reaction mechanism is the step by step process by which the reaction occurs; a sequence of bond breaking and bond forming steps

Elementary steps the molecularity of an elementary step and its order are the same.

unimolecular: one molecule in elementary step
A → B first order: rate = k[A]

bimolecular: two molecules in elementary step.
A + B → C second order: rate = k[A][B]

termolecular: three molecules in elementary step (rare)
A + B + C → D third order: rate = k[A][B][C]

Rate laws of multistep mechanisms
Most reactions occur by mechanism with more than one elementary step
Often one step is slower than the other.
The slow step limits the overall reaction rate.
This is the rate determining step (rds).
Slow first step:

\[ \mathrm{NO}_2 + \mathrm{CO} \rightarrow \mathrm{NO} + \mathrm{CO}_2 \]

step (a): \[ \mathrm{NO}_2 + \mathrm{NO}_2 \xrightarrow{k_1} \mathrm{NO}_3 + \mathrm{NO} \] slow step

step (b): \[ \mathrm{NO}_3 + \mathrm{CO} \xrightarrow{k_2} \mathrm{NO}_2 + \mathrm{CO}_2 \] fast step

Fast first step

\[ 2\mathrm{NO} + \mathrm{Br}_2 \rightarrow 2\mathrm{NOBr} \]

step (a): \[ \mathrm{NO} + \mathrm{Br}_2 \xrightarrow{k_1} \mathrm{NOBr}_2 \] fast step

step (b): \[ \mathrm{NOBr}_2 + \mathrm{NO} \xrightarrow{k_2} 2\mathrm{NOBr} \] slow step

**Catalyst**

- Changes the rate of a chemical reaction without itself undergoing a permanent chemical change in the process (not consumed in the reaction).
- Increase reaction rate by lowering the activation energy.
heterogeneous

absorption - uptake of molecules into the interior of another substance.

adsorption - binding of reactant molecules to catalyst surface.

Enzymes - biological catalyst
- large protein molecules
- increase rates by $10^6$ to $10^{18}$
- highly specific