Chemical Kinetics

Reaction Rates:

**Reaction Rate:** The change in the concentration of a reactant or a product with time (M/s).

Reactant → Products

A → B

Average rate = \frac{\text{change in number of moles of B}}{\text{change in time}}

\[ \frac{\Delta \text{(moles of B)}}{\Delta t} = \frac{\Delta [B]}{\Delta t} \]

Since reactants go away with time:  \[ \text{Rate} = -\frac{\Delta [A]}{\Delta t} \]
Consider the decomposition of $\text{N}_2\text{O}_5$ to give $\text{NO}_2$ and $\text{O}_2$:

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

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>$\text{N}_2\text{O}_5$ (M)</th>
<th>$\text{NO}_2$ (M)</th>
<th>$\text{O}_2$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>0.0169</td>
<td>0.0063</td>
<td>0.0016</td>
</tr>
<tr>
<td>200</td>
<td>0.0142</td>
<td>0.0115</td>
<td>0.0029</td>
</tr>
<tr>
<td>300</td>
<td>0.0120</td>
<td>0.0160</td>
<td>0.0040</td>
</tr>
<tr>
<td>400</td>
<td>0.0101</td>
<td>0.0197</td>
<td>0.0049</td>
</tr>
<tr>
<td>500</td>
<td>0.0086</td>
<td>0.0229</td>
<td>0.0057</td>
</tr>
<tr>
<td>600</td>
<td>0.0072</td>
<td>0.0256</td>
<td>0.0064</td>
</tr>
<tr>
<td>700</td>
<td>0.0061</td>
<td>0.0278</td>
<td>0.0070</td>
</tr>
</tbody>
</table>

Reactants decrease with time, products increase with time.
From the graph looking at $t = 300$ to $400$ s

Rate $O_2 = \frac{0.009M}{100s} = 9 \times 10^{-6} \text{Ms}^{-1}$

Rate $NO_2 = \frac{0.0037M}{100s} = 3.7 \times 10^{-5} \text{Ms}^{-1}$

Rate $N_2O_5 = \frac{0.0019M}{100s} = 1.9 \times 10^{-5} \text{Ms}^{-1}$

Why do they differ?

Recall:

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

To compare the rates one must account for the stoichiometry.

Rate $O_2 = \frac{1}{1} \times 9 \times 10^{-6} \text{Ms}^{-1} = 9 \times 10^{-6} \text{Ms}^{-1}$

Rate $NO_2 = \frac{1}{4} \times 3.7 \times 10^{-5} \text{Ms}^{-1} = 9.2 \times 10^{-6} \text{Ms}^{-1}$

Rate $N_2O_5 = \frac{1}{2} \times 1.9 \times 10^{-5} \text{Ms}^{-1} = 9.5 \times 10^{-6} \text{Ms}^{-1}$

Now they agree!

Reaction Rate and Stoichiometry

In general for the reaction:

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

$$\text{Rate} = \frac{1}{a} \frac{\Delta[A]}{\Delta t} = \frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$
The reaction rate law expression relates the rate of a reaction to the concentrations of the reactants. Each concentration is expressed with an order (exponent). The rate constant converts the concentration expression into the correct units of rate (M s\(^{-1}\)). (It also has deeper significance, which will be discussed later)

For the general reaction: \( aA + bB \rightarrow cC + dD \)

Rate = \( k [A]^x [B]^y \)

\( x \) and \( y \) are the reactant orders determined from experiment. \( x \) and \( y \) are NOT the stoichiometric coefficients.

<table>
<thead>
<tr>
<th>Rate Law</th>
<th>Order</th>
<th>Units of ( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate = ( k )</td>
<td>Zero</td>
<td>M s(^{-1})</td>
</tr>
<tr>
<td>Rate = ( k[A] )</td>
<td>First order with respect to A&lt;br&gt;First order overall</td>
<td>s(^{-1})</td>
</tr>
<tr>
<td>Rate = ( k[A]^2 )</td>
<td>Second order with respect to A&lt;br&gt;Second order overall</td>
<td>M(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>Rate = ( k[A][B] )</td>
<td>First order with respect to A&lt;br&gt;First order with respect to B&lt;br&gt;Second order overall</td>
<td>M(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>Rate = ( k[A][B][C] )</td>
<td>First order with respect to A&lt;br&gt;First order with respect to B&lt;br&gt;First order with respect to C&lt;br&gt;Third order overall</td>
<td>M(^{-2}) s(^{-1})</td>
</tr>
</tbody>
</table>

*In the units of \( k \), M represents mol L\(^{-1}\) or moles per liter.*
The **Overall Order** of a reaction is the sum of the individual orders:

\[
\text{Rate (Ms}^{-1}\text{)} = k[A][B]^{1/2}[C]^2
\]

**Overall order:** \(1 + \frac{1}{2} + 2 = 3.5 = \frac{7}{2}\)

or **seven−halves order**

*note:* when the order of a reaction is 1 (first order) no exponent is written.

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**Units for the rate constant:**

The units of a rate constant will change depending upon the overall order.

The units of rate are always M/s or Ms\(^{-1}\)

To find the units of a rate constant for a particular rate law, simply divide the units of rate by the units of molarity in the concentration term of the rate law.

\[
\text{Rate (Ms}^{-1}\text{)} = k[A] \quad 1\text{st order}
\]

\[
k(\text{units}) = \frac{\text{Ms}^{-1}}{\text{M}} = \text{s}^{-1}
\]
Reaction Rates

Instantaneous rate (tangent line)

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

Rules of logarithms

\[
\begin{align*}
\log (1) &= 0 & \ln (1) &= 0 \\
\log (10) &= 1 & \ln (e) &= 1 \\
\log (100) &= 2 & \ln (e^x) &= x \\
\log (10^x) &= x \\
\log A^x &= x \log A & \ln A^x &= x \ln A \\
\log \left( \frac{A^x}{B^y} \right) &= \log \left( \frac{A}{B} \right)^x = x \log \left( \frac{A}{B} \right) \\
\log(AB) &= \log A + \log B & \log \left( \frac{A}{B} \right) &= \log A - \log B
\end{align*}
\]
The reaction of nitric oxide with hydrogen at 1280°C is:

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

From the following data, determine the rate law and rate constant.

<table>
<thead>
<tr>
<th>Run</th>
<th>([\text{NO}]_0) (M)</th>
<th>([\text{H}_2]_0) (M)</th>
<th>Initial Rate (M/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0100</td>
<td>0.0100</td>
<td>0.00600</td>
</tr>
<tr>
<td>2</td>
<td>0.0200</td>
<td>0.0300</td>
<td>0.144</td>
</tr>
<tr>
<td>3</td>
<td>0.0100</td>
<td>0.0200</td>
<td>0.0120</td>
</tr>
</tbody>
</table>

The rate law for the reaction is given by:

\[ \text{Rate}(\text{M/min}) = k \left[ \text{NO} \right]^x \left[ \text{H}_2 \right]^y \]

Taking the ratio of the rates of runs 3 and 1 one finds:

\[
\frac{\text{Rate}(3)}{\text{Rate}(1)} = \frac{k \left[ \text{NO} \right]_0^x \left[ \text{H}_2 \right]_0^y}{k \left[ \text{NO} \right]_0^x \left[ \text{H}_2 \right]_0^y} = \frac{\left[ \text{NO} \right]_0^x \left[ \text{H}_2 \right]_0^y}{\left[ \text{NO} \right]_0^x \left[ \text{H}_2 \right]_0^y}
\]

\[
\frac{0.0120\text{M/min}}{0.00600\text{M/min}} = 2 = \frac{\left[0.0200\right]^y}{\left[0.0100\right]^y} = \frac{0.0200^y}{0.0100^y}
\]

\[
\frac{0.0200^y}{0.0100^y} = \left[ \frac{0.0200}{0.0100} \right]^y
\]
\[
\log \left( \frac{0.0200}{0.0100} \right)^y = 2 \\
\log \left( \frac{0.0200}{0.0100} \right) = \log 2 \\
y \log (2) = \log 2 \\
y = 1
\]

Now that “y” is known, we may solve for x in a similar manner:

\[
\frac{1}{24} = \left( \frac{1}{2} \right) \times \left( \frac{1}{3} \right) \\
\left( \frac{1}{2} \right)^x = \frac{1}{8} \\
x \log \left( \frac{1}{2} \right) = \log \left( \frac{1}{8} \right) \\
x = 3
\]

\textbf{The Rate Law is:}

\[
\text{Rate(M/min)} = k \ [\text{NO}]^3 [\text{H}_2]
\]

To find the rate constant, choose one set of data and solve:

\[
0.0120 \frac{M}{\text{min}} = k (0.0100M)^3 (0.0200M) \\
k = \frac{0.0120 \frac{M}{\text{min}}}{(0.0100M)^3 (0.0200M)} = \frac{0.0120 \frac{M}{\text{min}}}{(0.0100)^3 (0.0200)^4} \\
k = 6.00 \times 10^4 \frac{M^{-3}}{\text{min}}
\]
**Integrated Rate Laws: time dependence of concentration**

For a first order process, the rate law can be written: \[ A \rightarrow \text{products} \]

\[
\text{Rate (Ms}^{-1}) = -\frac{\Delta [A]}{\Delta t} = k[A]
\]

This is the “**average rate**”

If one considers the infinitesimal changes in concentration and time the rate law equation becomes:

\[
\text{Rate (Ms}^{-1}) = -\frac{d[A]}{dt} = k[A]
\]

This is the “**instantaneous rate**”

Integrating in terms of \(d[A]\) and \(dt\):

\[
\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt
\]

where \([A] = [A]_0\) at time \(t = 0\) and \([A] = [A]\) at time \(t = t\)

\[
\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt \quad \rightarrow \quad \ln \left( \frac{[A]}{[A]_0} \right) = -kt
\]

Taking the exponent to each side of the equation:

\[
\frac{[A]}{[A]_0} = e^{-kt} \quad \text{or} \quad [A] = [A]_0 e^{-kt}
\]

**Conclusion:** The concentration of a reactant governed by first order kinetics falls off from an initial concentration exponentially with time.
Recognizing a first order process: \( A \rightarrow \text{products} \)

Whenever the conc. of a reactant falls off exponentially, the kinetics follow first order.

\[
[A] = [A]_0 e^{-kt}
\]

A plot of \( \ln[A] \) versus time (t) is a straight line with slope \(-k\) and intercept \( \ln[A]_0 \).

Determining the Rate constant for a first order process

Taking the log of the integrated rate law for a first order process we find:

\[
\ln([A] = [A]_0 e^{-kt}) \quad \rightarrow \quad \ln[A] = \ln[A]_0 - k \times t
\]

A plot of \( \ln[A] \) versus time (t) is a straight line with slope \(-k\) and intercept \( \ln[A]_0 \).
**Example:** The rate of decomposition of azomethane ($\text{C}_2\text{H}_6\text{N}_2$) was studied by monitoring the partial pressure of the reactant as a function of time. Determine if the data below support a first order reaction. Calculate the rate constant for the reaction.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>$P$ (mmHg)</th>
<th>$\ln(P)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>284</td>
<td>5.66</td>
</tr>
<tr>
<td>100</td>
<td>220</td>
<td>5.39</td>
</tr>
<tr>
<td>150</td>
<td>193</td>
<td>5.26</td>
</tr>
<tr>
<td>200</td>
<td>170</td>
<td>5.14</td>
</tr>
<tr>
<td>250</td>
<td>150</td>
<td>5.01</td>
</tr>
</tbody>
</table>

$k = 2.6 \times 10^{-3} \text{ s}^{-1}$

![Plot of $\ln(P)$ vs. time](image)

$y = -0.0026x + 5.6485$

$R^2 = 1$

**Reaction Half-Life**

![Concentration of A vs. time](image)
**Reaction Half-life:**

Half-life is the time taken for the concentration of a reactant to drop to half its original value.

\[ [A] = \frac{[A]_0}{2} \]

For a first order process the half life \( (t_{1/2}) \) is found mathematically from:

1. \( \ln[A] = -kt + \ln[A]_0 \)
2. \( \ln[A] = \ln[A]_0 - kt \)
3. \( \ln\left(\frac{[A]}{[A]_0}\right) = -kt \)
4. \( \ln\left(\frac{[A]_0}{[A]}\right) = kt \)

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

A certain reaction proceeds through first order kinetics. The half-life of the reaction is 180 s. What percent of the initial concentration remains after 900 s?

Step 1: Determine the magnitude of the rate constant, \( k \).

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

\[ k = \frac{\ln 2}{180 s} = 0.00385 s^{-1} \]

Using the integrated rate law, substituting in the value of \( k \) and 900 s we find:

\[ \frac{[A]}{[A]_0} = e^{-kt} \rightarrow \frac{[A]}{[A]_0} = e^{-0.00385 s^{-1} \times 900 s} = 0.0312 \]

Since the ratio of \([A]\) to \([A]_0\) represents the fraction of \([A]_0\) that remains, the % is given by:

\[ 100 \times 0.0312 = 3.12\% \]
For a Second Order Process:

A $\rightarrow$ Products

Rate $= k[A]^2$

$$\text{Rate (Ms}^{-1}) = -\frac{d[A]}{dt} = k[A]^2$$

Integrating as before we find:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

A plot of $1/[A]$ versus $t$ is a straight line with slope $k$ and intercept $1/[A]_0$.

For a second order reaction, a plot of $\ln[A]$ vs. $t$ is **not linear**.
**Half-life for a second-order reaction**

Unlike a first order reaction, the rate constant for a second order process depends on and the initial concentration of a reactant.

\[
\frac{1}{[A]}_t = kt + \frac{1}{[A]_0}
\]

at the half–life, \( [A]_t = \frac{1}{2} [A]_0 \)

Substituting and solving, \( t_{1/2} = \frac{1}{k[A]_0} \)

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**EXAMPLE:** The reaction

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

is a second order reaction with respect to NOBr.

\( k = 0.810 \text{ M}^{-1} \cdot \text{s}^{-1} \) at 10\(^\circ\) C.

If \([\text{NOBr}]_0 = 7.5 \times 10^{-3} \text{ M}\), how much NOBr will be left after a reaction time of 10 minutes?

Determine the half-life of this reaction.
**SOLUTION:** One can solve for the amount of NOBr after 10 minutes by substituting the given data into the integrated rate law for a second-order reaction.

\[
\frac{1}{[\text{NOBr}]_t} = kt + \frac{1}{[\text{NOBr}]_0} \quad \text{(Second Order)}
\]

\[
\frac{1}{[\text{NOBr}]_t} = (0.810 \text{ M}^{-1} \cdot \text{s}^{-1}) \times (600 \text{ s}) + \frac{1}{7.5 \times 10^{-3} \text{ M}}
\]

\[
\frac{1}{[\text{NOBr}]_t} = 6.19 \times 10^2 \text{ M}^{-1}
\]

\[
[\text{NOBr}]_t = 1.6 \times 10^{-3} \text{ M}
\]

To determine the half-life for this reaction, we substitute the initial concentration of NOBr and the rate constant for the reaction into the equation for the half-life of a second-order reaction.

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

\[
t_{1/2} = \frac{1}{0.810 \text{ M}^{-1} \cdot \text{s}^{-1} \times (7.5 \times 10^{-3} \text{ M})} = 160 \text{ s}
\]
The Arrhenius Equation:

Temperature dependence of the Rate Constant

Most reactions speed up as temperature increases. (example: food spoils when not refrigerated.)

\[ k = f(T) \]

Where “f” is some function.

Therefore one can conclude that:

\[ k(T) \propto e^{f(T)} \]

The magnitude of a first order rate constant is seen to increase exponentially with an increase in temperature.
Why would $k$ (along with the rate) increase with temperature? Let’s go back to *Kinetic Molecular Theory* to understand…

**The Collision Model:** In order for molecules to react they must collide.

As temperature increases, the molecules move faster and the collision frequency increases.

Therefore, the greater the number of collisions the faster the rate. Thus reaction rate should increase with an increase in temperature.

Also, the more molecules present, the greater the probability of collision and the faster the rate. Thus reaction rate should increase with an increase in the concentration of reactant molecules.

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**Activation Energy**

*Arrhenius*: Molecules must posses a minimum amount of energy to react. Why?

(1) In order to form products, bonds must be broken in the reactants.
(2) Bond breakage requires energy.
(3) Molecules moving too slowly, with too little kinetic energy, don’t react when they collide.

The **Activation energy**, $E_a$, is the minimum energy required to initiate a chemical reaction. $E_a$ is specific to a particular reaction.
Consider the reaction:

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

The progress of a reaction can be described by a **Reaction Coordinate**

Recall for KMT that the temperature for a system of particles is described by a distribution.

At higher temps, more particles have enough energy to go over the barrier.
**Orientation factors into the equation**

The orientation of a molecule during collision can have a profound effect on whether or not a reaction occurs.

Some collisions do not lead to reaction even if there is sufficient energy.

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**The Arrhenius Equation**

Arhenius discovered that most reaction-rate data obeyed an equation based on three factors:

1. The number of collisions per unit time.
2. The fraction of collisions that occur with the correct orientation.
3. The fraction of the colliding molecules that have an energy greater than or equal to $E_a$.

From these observations Arrhenius developed the aptly named *Arrhenius equation*. 
**Arrhenius equation**

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

- \( k \) is the rate constant
- \( T \) is the temperature in K
- \( E_a \) is the activation energy
- \( R \) is the ideal-gas constant (8.314 J/Kmol)
- \( A \) is known as the *frequency or pre-exponential factor*

Both \( A \) and \( E_a \) are *specific to a given reaction*.

### Determining the Activation Energy

\( E_a \) may be determined experimentally.

First take natural log of both sides of the Arrhenius equation:

\[ \ln k = \ln A + \frac{-E_a}{RT} \]

\( \ln k = -\frac{E_a}{RT} + \ln A \)

*Golly-gee, what do we have once again…*

A plot of \( \ln k \) vs \( 1/T \) will have a slope of \( -E_a/R \) and a y-intercept of \( \ln A \).
Determining the Activation Energy

One can determine the activation energy of a reaction by measuring the rate constant at two temperatures:

Writing the Arrhenius equation for each temperature:

\[ \ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A \]

If one takes the natural log of the ratio of \( k_2 \) over \( k_1 \) we find that:

\[ \ln \left( \frac{k_2}{k_1} \right) = \ln k_2 - \ln k_1 \]

Substituting in the values for \( E_a \) into the equation:

\[ \ln k_2 - \ln k_1 = \left( -\frac{E_a}{RT_2} + \ln A \right) - \left( -\frac{E_a}{RT_1} + \ln A \right) \]

**Lookie what happens…**

Knowing the rate at two temps yields the rate constant.

or

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

Knowing the \( E_a \) and the rate constant at one temp allows one to find \( k(T_2) \)
**Example:** The activation energy of a first order reaction is 50.2 kJ/mol at 25°C. At what temperature will the rate constant double?

(1) \( k_2 = 2k_1 \)

(2) \( \ln \left( \frac{k_2}{k_1} \right) = \ln \left( \frac{2k_1}{k_1} \right) = \ln(2) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \)

(3) \( \frac{E_a}{R} = \frac{50.2 \text{ kJ/mol} \times \frac{10^3 \text{ J}}{1 \text{ kJ}}}{8.314 \frac{\text{ J}}{\text{ mol} \cdot \text{ K}}} = 6.04 \times 10^3 \text{ K} \)

(4) \( \ln(2) = 0.693 = 6.04 \times 10^3 \text{ K} \times \left( \frac{1}{298 \text{ K}} - \frac{1}{T_2} \right) \)

(5) \( \frac{1}{T_2} = 3.24 \times 10^{-3} \text{ K}^{-1} \quad \Rightarrow \quad T_2 = 308 \text{ K} \)

*An 10°C change of temperature doubles the rate!*