

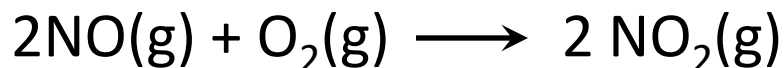
Chemical Kinetics

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The study of the rates and
mechanisms of chemical reactions

The rate of a chemical reaction

For a chemical reaction like:



we define the instantaneous rate of the reaction as $v(t)$:

$$v(t) = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

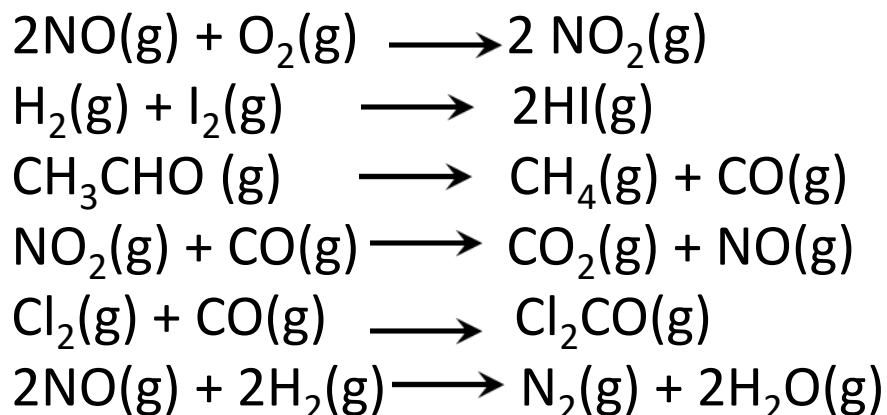
$v(t)$ is the rate of decrease of reactants or rate of increase in products, and it changes as the reaction proceeds. It can be approximated by finite differences:

$$v(t) \approx -\frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}$$

Chemical Reaction Rates

follow a Rate Law

Reaction:



Rate Law:

$$\begin{aligned}v(t) &= k [\text{NO}]^2[\text{O}_2] \\ v(t) &= k [\text{H}_2][\text{I}_2] \\ v(t) &= k [\text{CH}_3\text{CHO}]^{3/2} \\ v(t) &= k [\text{NO}_2]^2 \\ v(t) &= k [\text{Cl}_2]^{3/2}[\text{CO}] \\ v(t) &= k [\text{NO}]^2[\text{H}_2]\end{aligned}$$

k is called the rate constant for the reaction.

IN ALL CASES, the rate law must be determined by experiments.

NOTE: when $v(t)$ can be written as $v(t) = k[\text{A}]^n[\text{B}]^m$, the superscripts n and m are called the order of the reaction with respect to the reactants A and B, respectively. The overall order of the reaction is $m+n$.

Experimental determination of a rate law

By systematically varying the reactant concentrations, and measuring the rate of reaction, the rate law and the rate constant can be determined.

Example: $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \longrightarrow 2\text{NO}_2\text{F}(\text{g})$

Run:	$[\text{NO}_2]_0$	$[\text{F}_2]_0$	v_0 (These are initial values)
1	1.15 mol/L	1.15 mol/L	$6.12 \times 10^{-4} \text{ M}\cdot\text{s}^{-1}$
2	1.72 mol/L	1.15 mol/L	$1.36 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$
3	1.15 mol/L	2.30 mol/L	$1.22 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$

Note that in runs 1 and 2, $[\text{F}_2]_0$ is the same, and in runs 1 and 3, $[\text{NO}_2]_0$ is the same. This helps greatly in the data analysis.

Experimental determination of a rate law

Continuing the example: $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \longrightarrow 2\text{NO}_2\text{F}(\text{g})$

Run:	$[\text{NO}_2]_0$	$[\text{F}_2]_0$	v_0 (These are initial values)
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3	1.15 mol/L	2.30 mol/L	$1.22 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$

If we assume a rate law of the form $v(t) = k[\text{NO}_2]^n[\text{F}_2]^m$, we can compare the initial rates of runs 1 and 2 by dividing the rate law expressions for these two cases:

$$\frac{v_0(\text{run } 1)}{v_0(\text{run } 2)} = \frac{k[1.15 \text{ M}]^n[1.15 \text{ M}]^m}{k[1.72 \text{ M}]^n[1.15 \text{ M}]^m} = \frac{6.12 \times 10^{-4} \text{ M}\cdot\text{s}^{-1}}{1.36 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}} = 0.450$$

$$\frac{[1.15 \text{ M}]^n}{[1.72 \text{ M}]^n} = \left(\frac{1.15}{1.72}\right)^n = (0.6686)^n = 0.450$$

Taking logarithms, $n(\ln 0.6686) = \ln 0.450$, or $n = \frac{\ln 0.450}{\ln 0.6686} = 1.984$

This is close to 2, so **the reaction order with respect to $[\text{NO}_2]$ is 2, within error limits.**

Experimental determination of a rate law

Continuing the example: $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \longrightarrow 2\text{NO}_2\text{F}(\text{g})$

Run:	$[\text{NO}_2]_0$	$[\text{F}_2]_0$	v_0 (These are initial values)
1	1.15 mol/L	1.15 mol/L	$6.12 \times 10^{-4} \text{ M}\cdot\text{s}^{-1}$
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3	1.15 mol/L	2.30 mol/L	$1.22 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$

Likewise, we can take the ratio of the reaction rates in runs 1 and 3 to deduce the reaction order with respect to $[\text{F}_2]$:

$$\frac{v_0(\text{run } 1)}{v_0(\text{run } 3)} = \frac{k[1.15 \text{ M}]^n[1.15 \text{ M}]^m}{k[1.15 \text{ M}]^n[2.30 \text{ M}]^m} = \frac{6.12 \times 10^{-4} \text{ M}\cdot\text{s}^{-1}}{1.22 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}} = 0.5016$$

$$\frac{[1.15 \text{ M}]^m}{[2.30 \text{ M}]^m} = \left(\frac{1.15}{2.30}\right)^m = (0.500)^n = 0.5016$$

$$\text{Taking logarithms, } n(\ln 0.500) = \ln 0.5016, \text{ or } n = \frac{\ln 0.5016}{\ln 0.500} = 0.9954$$

This is close to 1, so the reaction order with respect to $[\text{F}_2]$ is 1, within the error limits.

Experimental determination of a rate law

Continuing the example: $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \longrightarrow 2\text{NO}_2\text{F}(\text{g})$

Run:	$[\text{NO}_2]_0$	$[\text{F}_2]_0$	v_0 (These are initial values)
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Now we know that the rate expression is $v(t) = k[\text{NO}_2]^2[\text{F}_2]$, so we can solve for k in the three runs. First, solving the rate expression for k gives:

$$k = \frac{v}{[\text{NO}_2]^2[\text{F}_2]}$$

Using the initial concentrations and initial rates in the three runs we get:

$$\text{Run 1: } k = \frac{6.12 \times 10^{-4} \text{ M}\cdot\text{s}^{-1}}{[1.15 \text{ M}]^2[1.15 \text{ M}]} = 4.02 \times 10^{-4} \text{ M}^{-2}\text{s}^{-1}$$

$$\text{Run 2: } k = \frac{1.36 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}}{[1.72 \text{ M}]^2[1.15 \text{ M}]} = 4.00 \times 10^{-4} \text{ M}^{-2}\text{s}^{-1}$$

$$\text{Run 3: } k = \frac{1.22 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}}{[1.15 \text{ M}]^2[2.30 \text{ M}]} = 4.01 \times 10^{-4} \text{ M}^{-2}\text{s}^{-1}$$

We can report a rate constant of $k = (4.01 \pm 0.01) \times 10^{-4} \text{ M}^{-2}\text{s}^{-1}$.

The units of the rate constant

Because the rate law expression can be different for different reactions, the units of k will vary from one rate law to another as well.

For an overall reaction order of N , the rate expression has units of:

$$v(\text{in } \text{M}\cdot\text{s}^{-1}) = k \times (\text{concentration, in } \text{M})^N$$

Solving for the units of k , we get

$$k = v(\text{in } \text{M}\cdot\text{s}^{-1}) / (\text{concentration, in } \text{M})^N$$

$$\text{or } k = \text{M}\cdot\text{s}^{-1} / \text{M}^N = \text{M}^{(1-N)}\cdot\text{s}^{-1}$$

Here are some examples:

Rate Law	Overall Order	Units of k
$v = k$	0	$\text{M}\cdot\text{s}^{-1}$
$v = k [A]$	1	s^{-1}
$v = k [A]^2$	2	$\text{M}^{-1}\cdot\text{s}^{-1}$
$v = k [A][B]$	2 (1 in A, 1 in B, 2 overall)	$\text{M}^{-1}\cdot\text{s}^{-1}$
$v = k [A]^{1/2}$	$\frac{1}{2}$	$\text{M}^{1/2}\cdot\text{s}^{-1}$
$v = k [A][B]^{1/2}$	$3/2$ (1 in A, $\frac{1}{2}$ in B)	$\text{M}^{-1/2}\cdot\text{s}^{-1}$

The units of k are whatever they need to be for the expression to make sense.

Integrated Rate Laws

Instantaneous reaction rates, like $\frac{d[A]}{dt}$ are hard to measure. To get around this, we need integrated forms of the rate laws.

First order reaction: $\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$ $v(t) = -\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$

We can solve the rate law for $[\text{N}_2\text{O}_5]_t$ by first rewriting it as:

$$\frac{d[\text{N}_2\text{O}_5]}{[\text{N}_2\text{O}_5]} = -k dt, \quad \text{then integrating both sides from time } t=0 \text{ to } t.$$

$$\int_0^t \frac{d[\text{N}_2\text{O}_5]}{[\text{N}_2\text{O}_5]} = -k \int_0^t dt \quad \text{Integration then gives:}$$

$$\ln \frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0} = -kt \quad \text{Exponentiating both sides and multiplying by } [\text{N}_2\text{O}_5]_0$$

gives the final form of the solution:
$$[\text{N}_2\text{O}_5]_t = [\text{N}_2\text{O}_5]_0 e^{-kt}$$

First order reactions show an exponential decay of the reactant over time.

Other examples:

- fluorescence or phosphorescence – after excitation $[A^*]_t = [A^*]_0 e^{-kt} = [A^*]_0 e^{-t/\tau}$

The intensity of emitted light also decays exponentially $I(t) = I_0 e^{-t/\tau}$

- radioactive decay of a nucleus – written to base 2, instead of e, for example

$$[^{14}\text{C}]_t = [^{14}\text{C}]_0 2^{-t/\tau_{1/2}}, \text{ where } \tau_{1/2} \text{ is the half-life, given by}$$

$$\tau_{1/2} = (\ln 2)/k = 0.693/k \quad (\tau_{1/2} = 5730 \text{ y for } ^{14}\text{C}).$$

Integrated Rate Laws

Second order reaction: $\text{NOBr(g)} \longrightarrow \text{NO} + \frac{1}{2} \text{Br}_2$ $v(t) = -\frac{d[\text{NOBr}]}{dt} = k[\text{NOBr}]^2$

We can solve the rate law for $[\text{NOBr}]_t$ by first rewriting it as:

$$\frac{d[\text{NOBr}]}{[\text{NOBr}]^2} = -k dt \quad \text{then integrating from 0 to } t$$

$$\int_0^t \frac{d[\text{NOBr}]}{[\text{NOBr}]^2} = \int_0^t [\text{NOBr}]^{-2} d[\text{NOBr}] = -k \int_0^t dt \quad \text{Integration then gives:}$$

$$-\frac{1}{[\text{NOBr}]_t} + \frac{1}{[\text{NOBr}]_0} = -kt \quad \text{or} \quad \boxed{\frac{1}{[\text{NOBr}]_t} = \frac{1}{[\text{NOBr}]_0} + kt}$$

Compare first-order reactions with second-order reactions:

First order:

$$\boxed{[\text{N}_2\text{O}_5]_t = [\text{N}_2\text{O}_5]_0 e^{-kt}}$$

A plot of the $\ln \frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0}$ vs. t
is linear, with a slope of $-k$.

Second order:

$$\boxed{\frac{1}{[\text{NOBr}]_t} = \frac{1}{[\text{NOBr}]_0} + kt}$$

A plot of $\frac{1}{[\text{NOBr}]_t}$ vs. t
is linear, with a slope of $+k$.

This is a way to distinguish between these two cases, and to determine k .

Determining Rate Laws: The Method of Isolation

Example: The reaction $\text{CS}_2(\text{g}) + 2\text{O}_3(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{SO}_2(\text{g})$

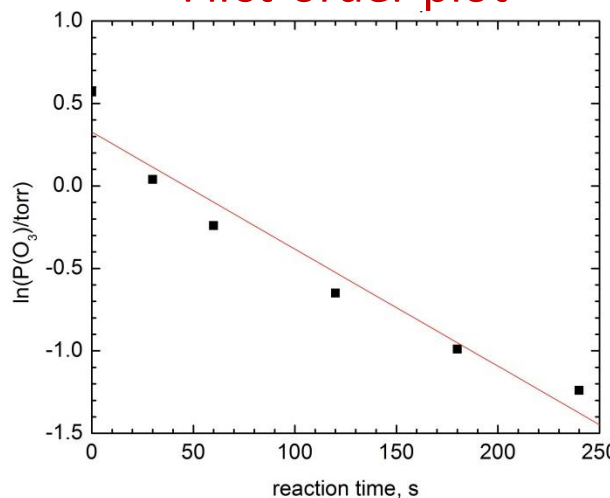
Assume a rate law: $v(t) = -\frac{d[\text{CS}_2]}{dt} = k[\text{CS}_2]^m[\text{O}_3]^n$

With a large excess of CS_2 , we get the data below. But if CS_2 is in large excess, its concentration is nearly constant. We can test for the order with respect to O_3 by plotting the drop in O_3 partial pressure as a function of time, assuming either first order or second order kinetics in O_3 :

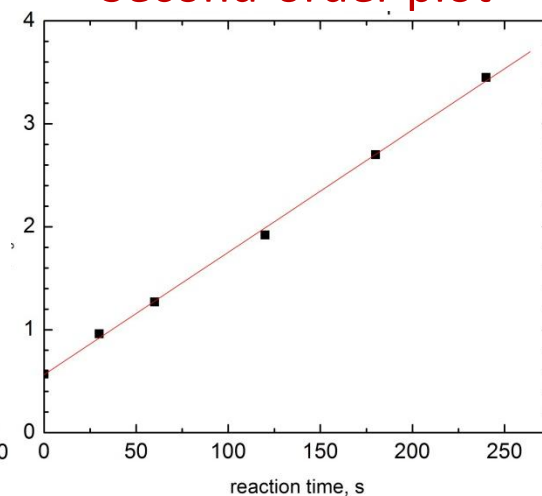
Data:

<u>Time(s)</u>	<u>O₃ pressure(torr)</u>
0	1.76
30	1.04
60	0.79
120	0.52
180	0.37
240	0.29

First-order plot



Second-order plot

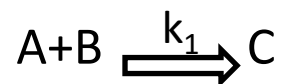


Looks pretty definite that the reaction
is second order in O_3 !

Reaction Mechanisms

A reaction mechanism is the sequence of elementary reactions that carry the system from reactants to products.

Each elementary reaction follows a rate law that makes sense from the stoichiometry, so for example the elementary reaction



follows the rate law $\frac{d[A]}{dt} = -k_1[A][B]$.

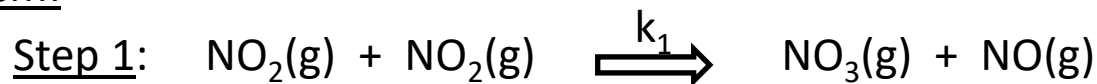
Here I'll use the symbol $\xRightarrow{\hspace{1cm}}$ to indicate a reaction that is an elementary step, to distinguish it from an overall reaction, which is indicated by \longrightarrow .

The Rate-Determining Step

For some reactions, one step is much slower than the others, becoming the rate determining step. Subsequent steps need not be considered – products will be formed as fast as the rate-determining step can proceed.

An example: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \longrightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$

Mechanism:



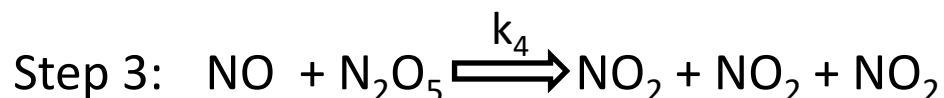
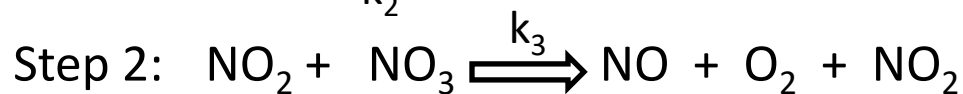
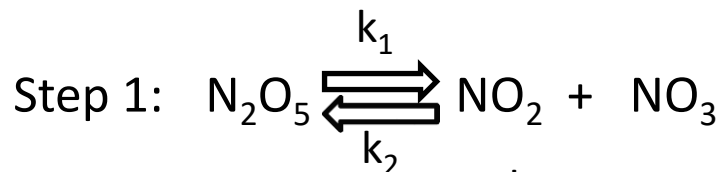
In this mechanism, $k_1 \gg k_2$, so step 1 is the rate determining step. The rate law is simply:

$$v = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{NO}]}{dt} = \frac{d[\text{CO}_2]}{dt} = k_1 [\text{NO}_2]^2$$

This breaks down when the CO concentration is so low that the rate of step 2 is slower than step 1, but for a broad range of CO concentrations, the reaction follows this rate law.

Mechanisms

A Plausible Mechanism for $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$:



Each elementary reaction contributes to the production or destruction of a molecule, so:

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -k_1[\text{N}_2\text{O}_5] + k_2[\text{NO}_2][\text{NO}_3] - k_4[\text{NO}][\text{N}_2\text{O}_5]$$

$$\frac{d[\text{NO}_2]}{dt} = k_1[\text{N}_2\text{O}_5] - k_2[\text{NO}_2][\text{NO}_3] + 3k_4[\text{NO}][\text{N}_2\text{O}_5]$$

$$\frac{d[\text{NO}_3]}{dt} = k_1[\text{N}_2\text{O}_5] - k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}_2][\text{NO}_3] = k_1[\text{N}_2\text{O}_5] - (k_2 + k_3)[\text{NO}_2][\text{NO}_3]$$

$$\frac{d[\text{NO}]}{dt} = k_3[\text{NO}_2][\text{NO}_3] - k_4[\text{NO}][\text{N}_2\text{O}_5]$$

and

$$\frac{d[\text{O}_2]}{dt} = k_3[\text{NO}_2][\text{NO}_3]$$

A Plausible Mechanism for $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$

Looking at all the reactants and product species, we end up with FIVE coupled nonlinear differential equations! **YIKES!!**

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -k_1[\text{N}_2\text{O}_5] + k_2[\text{NO}_2][\text{NO}_3] - k_4[\text{NO}][\text{N}_2\text{O}_5]$$

$$\frac{d[\text{NO}_2]}{dt} = k_1[\text{N}_2\text{O}_5] - k_2[\text{NO}_2][\text{NO}_3] + 3k_4[\text{NO}][\text{N}_2\text{O}_5]$$

$$\frac{d[\text{NO}_3]}{dt} = k_1[\text{N}_2\text{O}_5] - (k_2 + k_3)[\text{NO}_2][\text{NO}_3]$$

$$\frac{d[\text{NO}]}{dt} = k_3[\text{NO}_2][\text{NO}_3] - k_4[\text{NO}][\text{N}_2\text{O}_5]$$

$$\text{and } \frac{d[\text{O}_2]}{dt} = k_3[\text{NO}_2][\text{NO}_3]$$

How can we solve this messy problem?

Key simplifying approximation: Reactive intermediates are consumed almost as quickly as they are produced, so their concentration is small and doesn't change much. We can set their time derivatives to zero. [This is the steady-state approximation.]

In the environment of the N_2O_5 decomposition, the reactive intermediates are NO_3 and NO . Therefore, we can set the rates $\frac{d[\text{NO}_3]}{dt} = 0$ and $\frac{d[\text{NO}]}{dt} = 0$. This gives

$$k_1[\text{N}_2\text{O}_5] - (k_2 + k_3)[\text{NO}_2][\text{NO}_3] = 0 \quad \text{from } \frac{d[\text{NO}_3]}{dt} = 0$$

$$\text{and } k_3[\text{NO}_2][\text{NO}_3] - k_4[\text{NO}][\text{N}_2\text{O}_5] = 0 \quad \text{from } \frac{d[\text{NO}]}{dt} = 0$$

The Steady-State Approximation Simplifies Things!

We have the net rate of change in N_2O_5 concentration:

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -k_1[\text{N}_2\text{O}_5] + k_2[\text{NO}_2][\text{NO}_3] - k_4[\text{NO}][\text{N}_2\text{O}_5]$$

And the steady-state approximations:

1. For $[\text{NO}_3]$: $k_1[\text{N}_2\text{O}_5] - (k_2 + k_3)[\text{NO}_2][\text{NO}_3] = 0$

2. For $[\text{NO}]$: $k_3[\text{NO}_2][\text{NO}_3] - k_4[\text{NO}][\text{N}_2\text{O}_5] = 0$

We can solve these equations for $[\text{NO}_2][\text{NO}_3]$ and $[\text{NO}][\text{N}_2\text{O}_5]$:

From 1: $[\text{NO}_2][\text{NO}_3] = \frac{k_1}{(k_2 + k_3)} [\text{N}_2\text{O}_5]$

From 2: $[\text{NO}][\text{N}_2\text{O}_5] = \frac{k_3}{k_4} [\text{NO}_2][\text{NO}_3]$
 $= \frac{k_1 k_3}{(k_2 + k_3) k_4} [\text{N}_2\text{O}_5]$

Putting these two expressions into the expression for $\frac{d[\text{N}_2\text{O}_5]}{dt}$, we get a net first-order rate equation for the decomposition of N_2O_5 :

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -k_1[\text{N}_2\text{O}_5] + k_2 \frac{k_1}{(k_2 + k_3)} [\text{N}_2\text{O}_5] - k_4 \frac{k_1 k_3}{(k_2 + k_3) k_4} [\text{N}_2\text{O}_5]$$

Simplifying, this gives: $\frac{d[\text{N}_2\text{O}_5]}{dt} = \left(-k_1 + \frac{k_1 k_2}{(k_2 + k_3)} - \frac{k_1 k_3}{(k_2 + k_3)} \right) [\text{N}_2\text{O}_5] = -\frac{2k_1 k_3}{(k_2 + k_3)} [\text{N}_2\text{O}_5]$

The experimental rate law was $\frac{d[\text{N}_2\text{O}_5]}{dt} = -k[\text{N}_2\text{O}_5]$, so this mechanism is consistent with

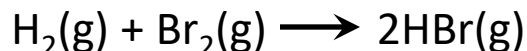
the measured rate constant, k , which is given in terms of elementary steps by $k = \frac{2k_1 k_3}{(k_2 + k_3)}$

Important Things to Note:

1. Elementary steps follow straightforward rate laws given by $k[A]^n[B]^m$, etc. where n molecules of A react with m molecules of B. The total number of molecules involved in one elementary step (n+m+...) is called the molecularity of that step.

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1. Elementary steps follow straightforward rate laws given by $k[A]^n[B]^m$, etc. where n molecules of A react with m molecules of B. The total number of molecules involved in one elementary step (n+m+...) is called the molecularity of that step.
2. The overall reaction follows a rate law often does not follow the stoichiometry of the reaction. For reactions that proceed by a complicated series of elementary steps, the rate law can be very complicated. For example, in the reaction

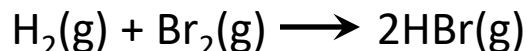


the rate law would be NOT $\frac{d[\text{H}_2]}{dt} = \frac{d[\text{Br}_2]}{dt} = -k[\text{H}_2][\text{Br}_2]$, which would be true if the equation written above were an elementary step.

The measured rate law is $\frac{d[\text{H}_2]}{dt} = \frac{d[\text{Br}_2]}{dt} = -\frac{k'[\text{H}_2][\text{Br}_2]^{1/2}}{1+k''[\text{HBr}]/[\text{Br}_2]}$, which shows that there is much more to this reaction than just a single elementary step!

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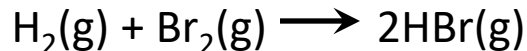
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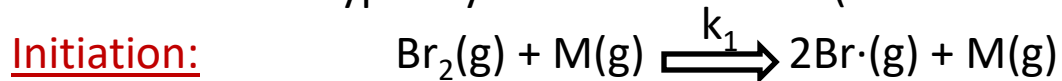
3. Just because a mechanism can be found that gives the proper, experimentally-measured rate law does not mean that mechanism is correct! Often, more than one mechanism can be written that agrees with the overall experimentally-measured rate law.

Chain Reactions:

An example of a chain reaction is the reaction



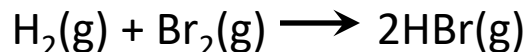
Chain reactions typically involve at least 3 (and sometimes 4) types of elementary steps:



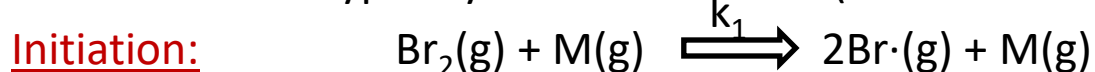
[Here M is any molecule in the gas, which energizes the Br_2 by colliding with it.]

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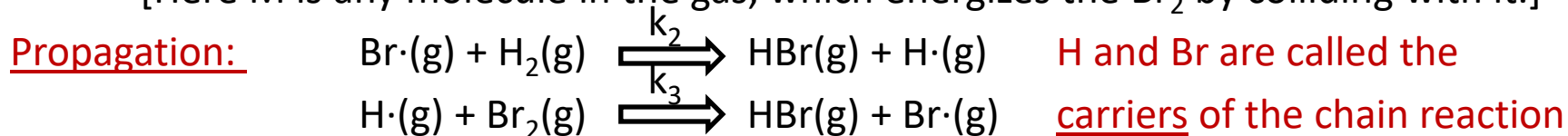
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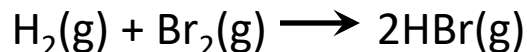
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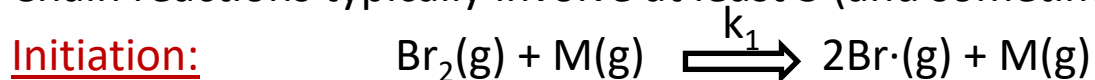
The propagation steps consume chain carriers just as quickly as they regenerate them.

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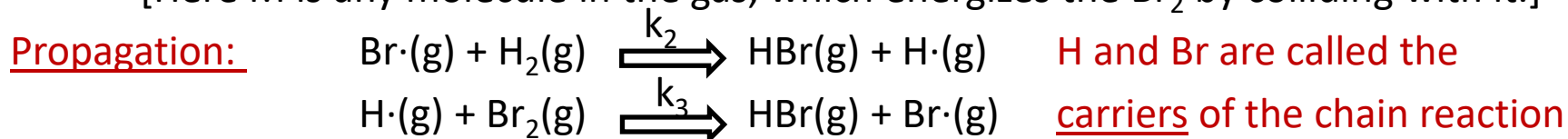
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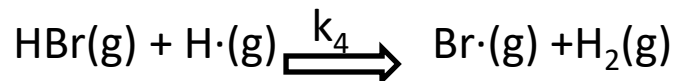


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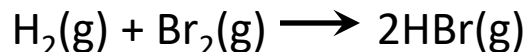
Inhibition: This step is not always present, so some chain reactions are very fast.



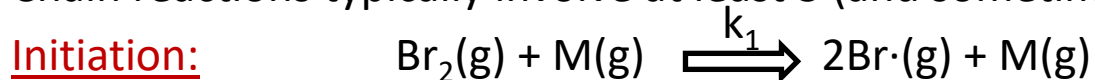
Here, the inhibition reaction re-forms a reactant, so it slows the net rate of reaction.

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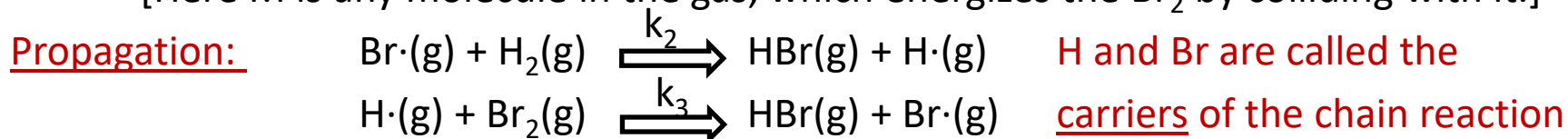
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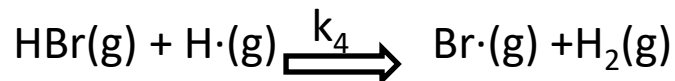


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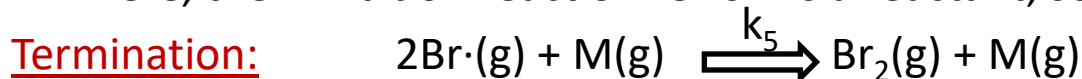


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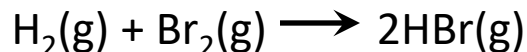


The termination reaction destroys two chain carriers, and forms a reactant molecule.

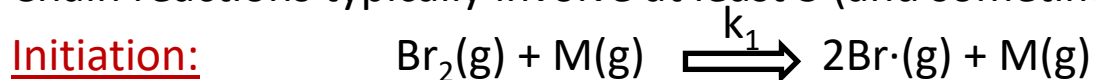
In this system, the Br and H atoms that are the chain carriers are radicals (atoms or molecules with unpaired electrons), which are highly reactive. Chain reactions typically involve radicals as the chain carriers.

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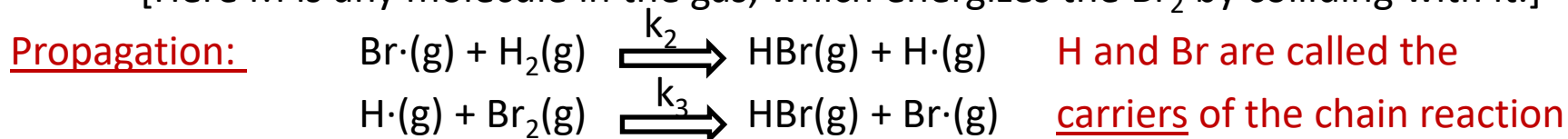
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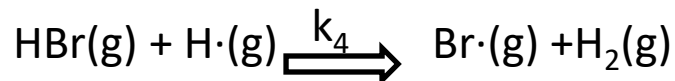


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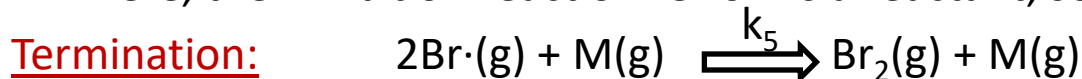


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In this system, the Br and H atoms that are the chain carriers are radicals (atoms or molecules with unpaired electrons), which are highly reactive. Chain reactions typically involve radicals as the chain carriers.

The **steady-state approximation** can be used to work out the kinetics of this system, giving the correct, experimentally observed rate law.

Branching Chain Reactions:

A branching chain reaction has steps that increase the number of chain carriers. These reactions really take off, usually explosively!

Example:

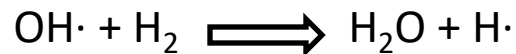
1. Initiation Step:



2. Chain Propagation:



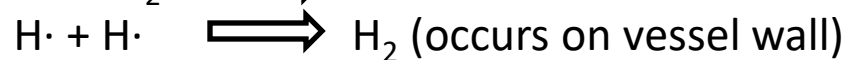
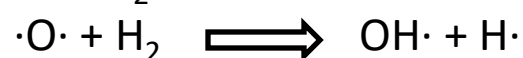
3. Chain Branching:



4. Chain Branching:



5. Termination



Steps 3 and 4 together give $\text{H}\cdot + \text{O}_2 + \text{H}_2 \longrightarrow 2\text{OH}\cdot + \text{H}\cdot$

These two steps multiply the number of chain carriers by a factor of three! **BANG!**

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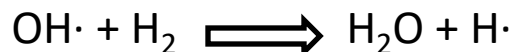
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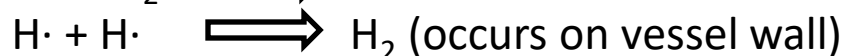
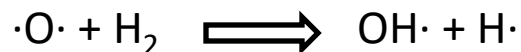
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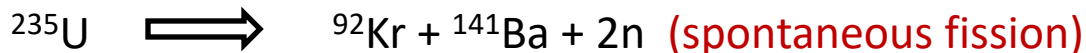


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Example 2: (SIMPLIFIED) $^{235}\text{U} \longrightarrow ^{92}\text{Kr} + ^{141}\text{Ba} + 2\text{n}$, chain carriers are **n**

1. Initiation Step:



2. Chain Branching:



(triples the number of chain carriers)



<https://www.youtube.com/watch?v=11e8XyUBqRQ>



AtomCentral.com

Branching Chain Reactions:



<https://www.youtube.com/watch?v=-zX-gz1IRt0>

Enzyme Kinetics:

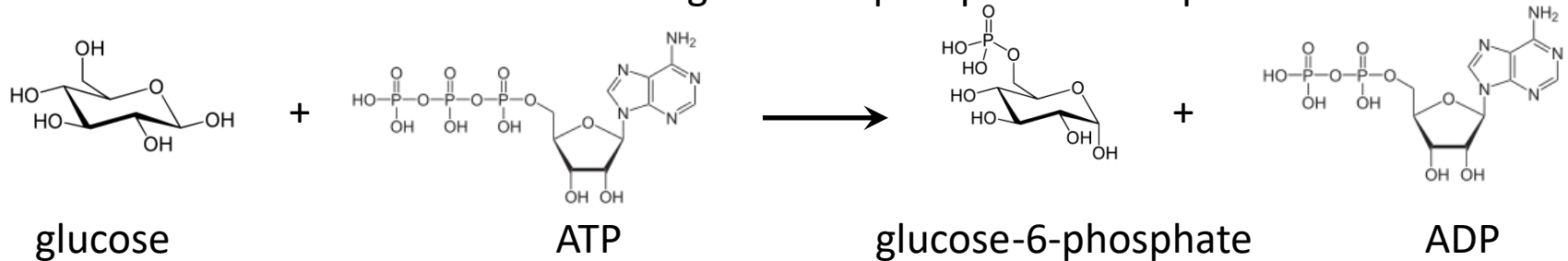
Enzymes - Proteins that convert **substrates** to products

The overall reaction may be written as

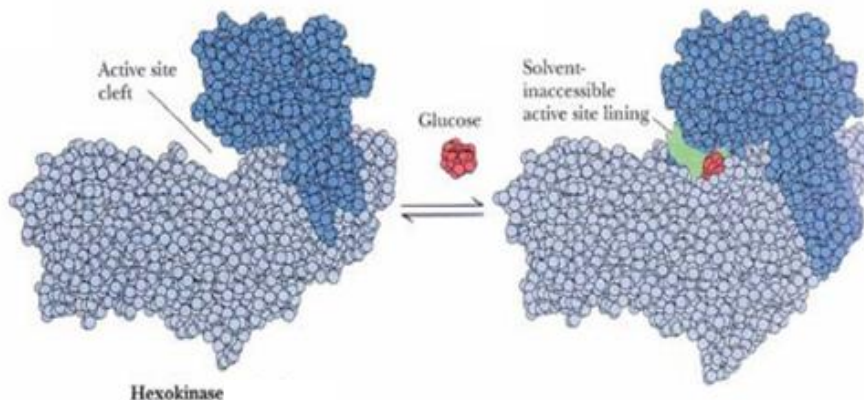


Example: Phosphorylation of glucose to glucose-6-phosphate, catalyzed by hexokinase.

Glucose is the substrate and glucose-6-phosphate is the product.



Hexokinase accepts glucose into its active site, where the presence of the correct amino acid side groups greatly accelerates the reaction:



Enzyme Kinetics:

Many enzyme-catalyzed reactions (including this one) follow a rate law of the form

$$-\frac{d[S]}{dt} = \frac{k[S]}{K + [S]} [E]_0 ,$$

where [S] is the concentration of the substrate,
[E]₀ is the total concentration of enzyme, and
k and K are constants.

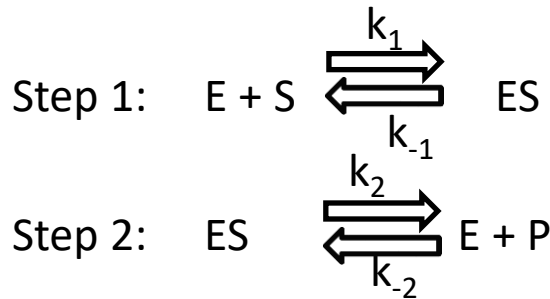
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This is explained by the **Michaelis-Menten reaction mechanism** (1913):



ES is the enzyme with the substrate bound in the active site.

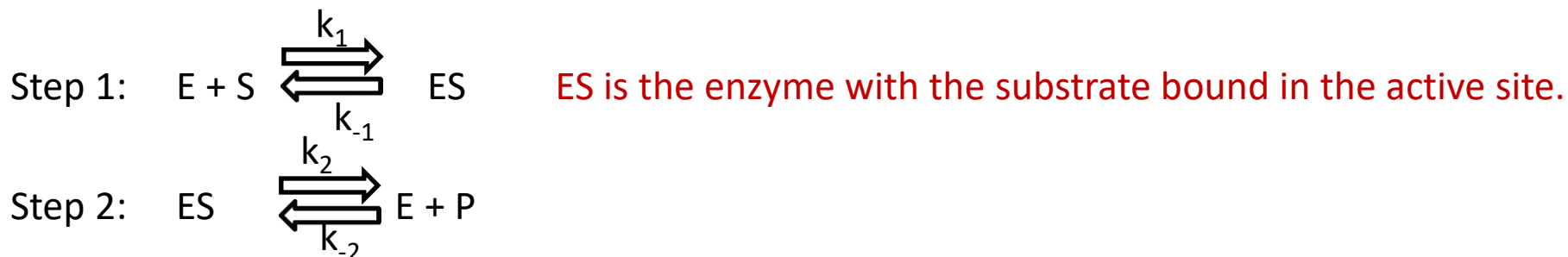
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This gives rate expressions for $[S]$, $[ES]$, and $[P]$.

$$\frac{d[S]}{dt} = -k_1[E][S] + k_{-1}[ES]$$

$$\begin{aligned} \frac{d[ES]}{dt} &= k_1[E][S] - k_{-1}[ES] - k_2[ES] + k_{-2}[E][P] \\ &= k_1[E][S] - (k_{-1} + k_2)[ES] + k_{-2}[E][P] \end{aligned}$$

$$\frac{d[P]}{dt} = k_2[ES] - k_{-2}[E][P]$$

Enzyme Kinetics:

Three coupled differential equations: How can we solve them?

$$1. \frac{d[S]}{dt} = -k_1[E][S] + k_{-1}[ES]$$

$$2. \frac{d[ES]}{dt} = k_1[E][S] - (k_{-1} + k_2)[ES] + k_{-2}[E][P]$$

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The enzyme is not consumed in the reaction, so $[E] + [ES]$ is conserved, defined as $[E]_0$:

$$[E]_0 \equiv [ES] + [E] \quad \text{or} \quad [E] = [E]_0 - [ES]$$

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$$\begin{aligned} \frac{d[ES]}{dt} &= k_1([E]_0 - [ES])[S] - (k_{-1} + k_2)[ES] + k_{-2}([E]_0 - [ES])[P] \\ &= -(k_{-1} + k_2 + k_{-2}[P] - k_1[S])[ES] + k_1([E]_0)[S] + k_{-2}([E]_0)[P] \end{aligned}$$

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We can apply the **steady-state approximation** to $[ES]$:

$$\frac{d[ES]}{dt} = -(k_{-1} + k_2 + k_{-2}[P] + k_1[S])[ES] + k_1([E]_0)[S] + k_{-2}([E]_0)[P] = 0.$$

Solving for $[ES]$ gives:

$$[ES] = \frac{k_1[S] + k_{-2}[P]}{k_1[S] + k_{-2}[P] + k_{-1} + k_2} [E]_0$$

Enzyme Kinetics:

The steady-state expression:
$$[ES] = \frac{k_1[S] + k_{-2}[P]}{k_1[S] + k_{-2}[P] + k_{-1} + k_2} [E]_0$$

can be substituted into $\frac{d[S]}{dt} = -k_1[E][S] + k_{-1}[ES]$, to give the reaction rate:

$$v = -\frac{d[S]}{dt} = k_1[E][S] - k_{-1} \frac{k_1[S] + k_{-2}[P]}{k_1[S] + k_{-2}[P] + k_{-1} + k_2} [E]_0$$

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Again using $[E] = [E]_0 - [ES]$ and the steady-state approximation for $[ES]$ (above), this gives

$$-\frac{d[S]}{dt} = k_1 \left([E]_0 - \frac{k_1[S] + k_{-2}[P]}{k_1[S] + k_{-2}[P] + k_{-1} + k_2} [E]_0 \right) [S] - k_{-1} \frac{k_1[S] + k_{-2}[P]}{k_1[S] + k_{-2}[P] + k_{-1} + k_2} [E]_0$$

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If the experimental measurements are only made during the initial period, when only 1-3% of substrate is converted to products, we may approximate $[S] = [S]_0$ and $[P] = 0$, to obtain:

$$-\frac{d[S]}{dt} = \frac{k_1 k_2 [S]_0}{k_1 [S]_0 + k_{-1} + k_2} [E]_0$$

or
$$-\frac{d[S]}{dt} = \frac{k_2 [S]_0}{[S]_0 + (k_{-1} + k_2)/k_1} [E]_0$$

Michaelis-Menten equation

Enzyme Kinetics:

The Michaelis-Menten equation

$$-\frac{d[S]}{dt} = \frac{k_2[S]_0}{[S]_0 + (k_{-1} + k_2)/k_1} [E]_0$$

shows that when $[S]_0 \gg (k_{-1} + k_2)/k_1$, the rate becomes $-\frac{d[S]}{dt} = k_2[E]_0$
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Small values of K_M correspond to enzymes that tightly bind the substrate (k_1 is the reaction that binds substrate to the enzyme, k_{-1} and k_2 release substrate or product from the enzyme).

Enzyme Kinetics:

The Michaelis-Menten equation

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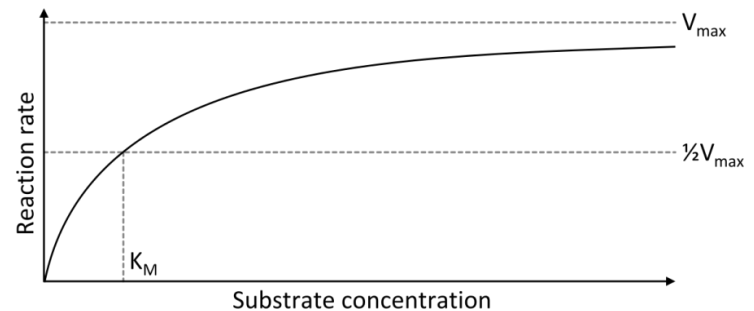
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The rate constant, k_2 (units of s^{-1}), gives the maximum rate of product molecule production per enzyme molecule, and is called the turnover number.

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Small values of K_M correspond to enzymes that tightly bind the substrate (k_1 is the reaction that binds substrate to the enzyme, k_{-1} and k_2 release substrate or product from the enzyme).

Studies of enzyme kinetics are performed very frequently in the pharmaceutical industry, where molecules are sought that can block or reduce enzyme activity to treat a particular disease or condition.



Temperature Dependence of Reaction Rates:

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Here's an example: The decomposition of N_2O_5 follows the first-order integrated rate law

$$[N_2O_5]_t = [N_2O_5]_0 e^{-kt}$$

and k is measured at various temperatures as:

T(K)	k(s ⁻¹)
298	1.74×10^{-5}
308	6.61×10^{-5}
318	2.51×10^{-4}
328	7.59×10^{-4}
338	2.40×10^{-3}

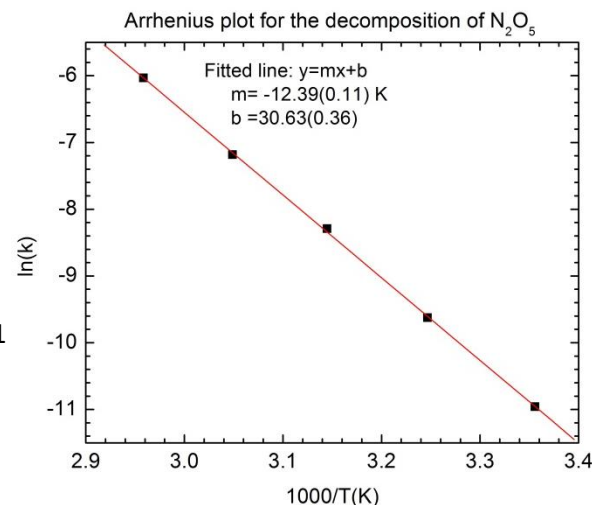
This gives the Arrhenius plot of $\ln(k)$ vs. $1/T$:

$$-\frac{E_a}{RT} = \frac{-12.39(0.11)K \times 1000}{T}$$

$$E_a = (12,390 \pm 110)K \cdot R$$

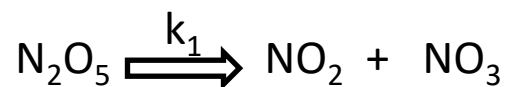
$$E_a = (12,390 \pm 110)K \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$E_a = 103 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$$

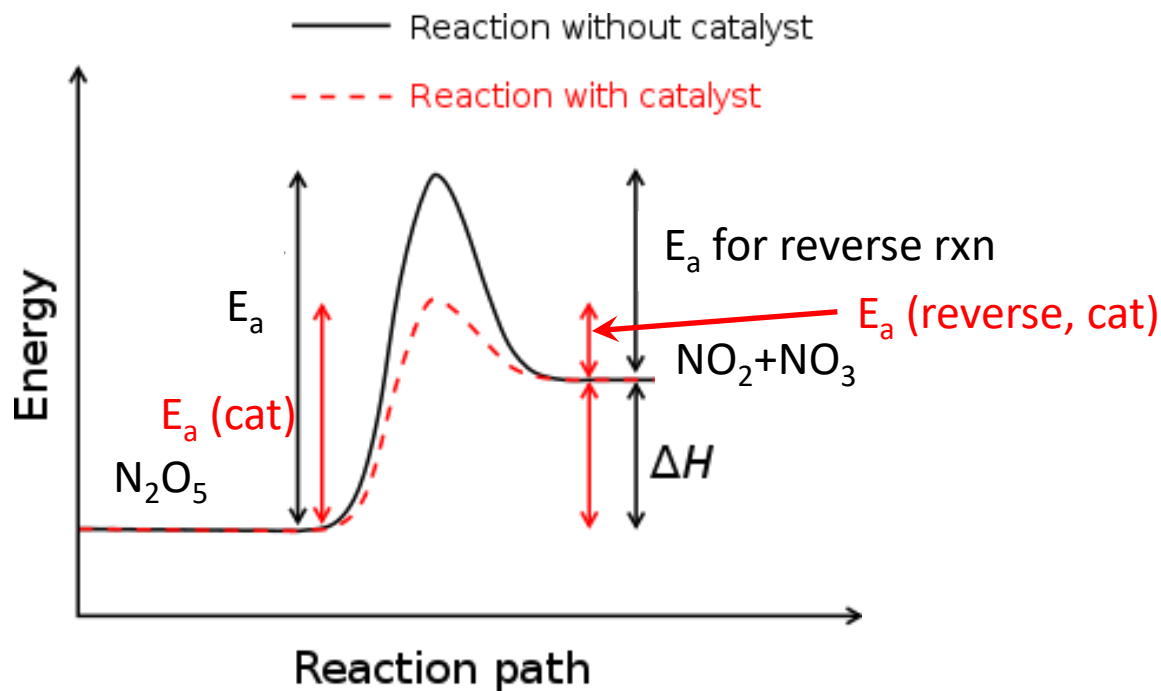


Activation Energy:

The activation energy is interpreted as the amount of energy needed to initiate the reaction. The idea is that the reaction, energy must be added to the reactants to distort them in a manner that can allow products to form. In reality, there is a separate activation energy for each step in the reaction mechanism, although we often lump these together to get an overall activation energy. For a single fundamental step, such as the reaction

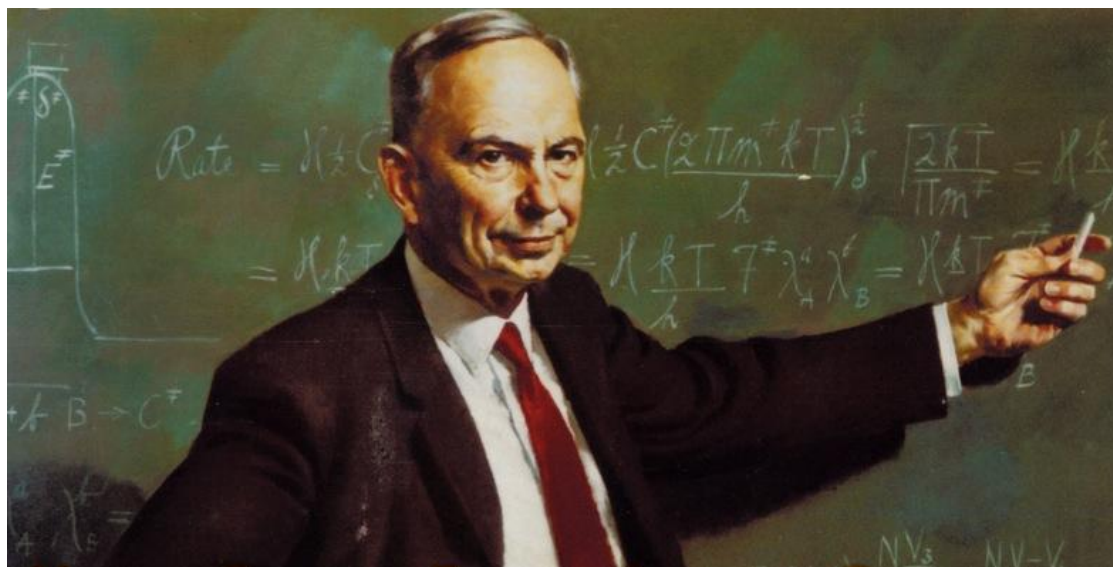


the N_2O_5 molecule must first be deformed to a point where it is downhill in energy to form products.



Transition State Theory:

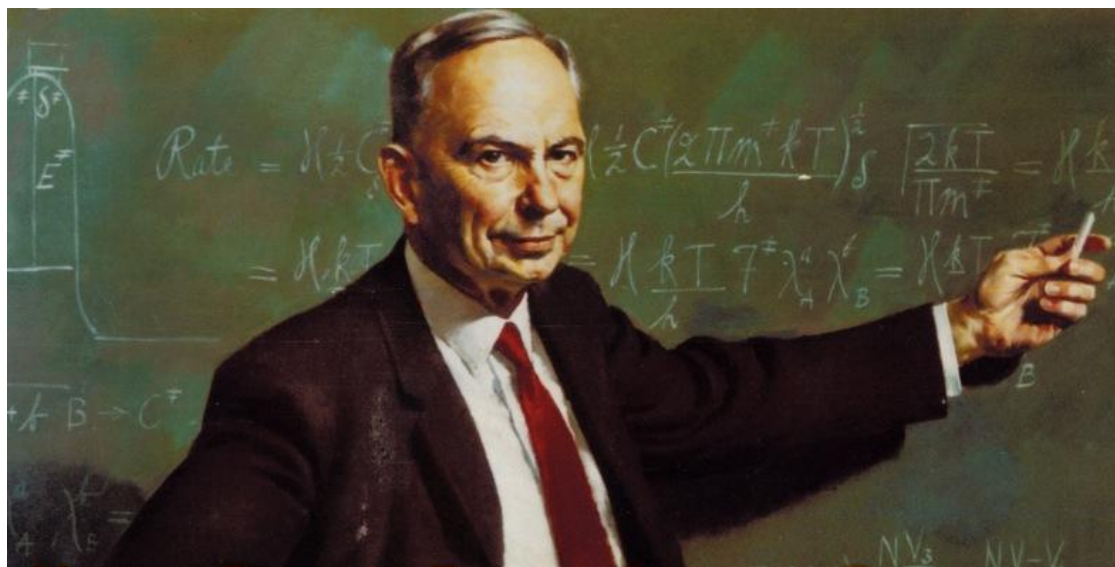
Our own Henry Eyring, who founded the graduate school at the University of Utah,



developed a more fundamental theory of reaction processes that is now known as transition state theory. This theory uses statistics to calculate the probability that the reactants reach the top of the reaction barrier, and then assumes there is an equal probability of dropping back down to starting materials or going forward to products.

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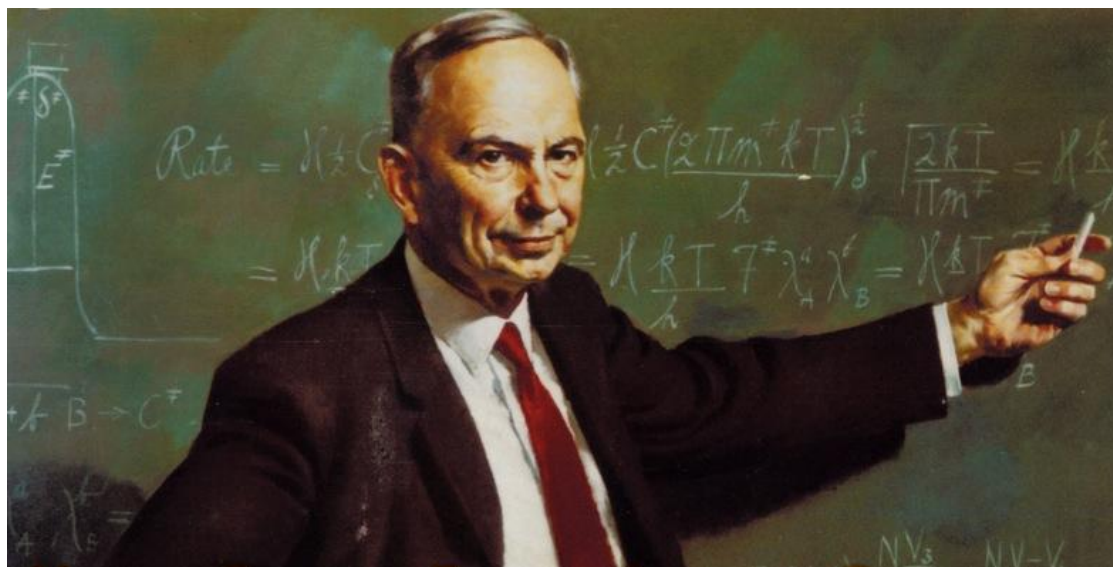
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The final expression for the rate constant that is obtained is:

$$k(T) = \frac{k_B T}{h c^\circ} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$
 Here ΔH^\ddagger and ΔS^\ddagger refer to the enthalpy and entropy change in forming the transition state, k_B is Boltzmann's constant, and c° is the standard state concentration (using 1 M).

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Thanks for your attention!

For your pleasure: A reaction with a really complicated reaction mechanism:

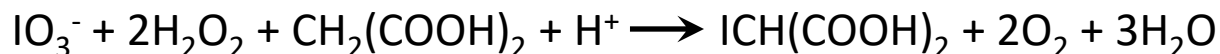
The Briggs-Rauscher oscilating chemical reaction



<https://www.youtube.com/watch?v=weQz8lf55jM>

https://www.youtube.com/watch?v=WasYuiOk5xQ&ebc=ANyPxKrHgX3dg eQi5IAFukyGwOB7mXDgYkF3Z7OHuSiVbS0EW-UFucUCiVIDzUpFE61nvcsV9NpW1_6K703_pmSeXHDfvj6MKw

This example is the Briggs-Rauscher reaction, which has the overall reaction:



There are many steps, some of which produce intermediates that slow down the reaction. The reaction is catalyzed by the Mn^{2+} ion. The color change is due to the production of I_2 , which is detected using the blue color of an I_2 -starch complex.