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Chemical Kinetics

An Introduction

$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO$

$H_2O_2(aq) \rightarrow H_2O(l) + O_2(g)$

$S_2O_8^{2-} + 2\,I^- \rightarrow I_2 + 2\,SO_4^{2-}$

Kinetics

- Studies the rate at which a chemical process occurs.

- Besides information about the speed at which reactions occur, kinetics also sheds light on the reaction mechanism (exactly *how* the reaction occurs).

Outline: Kinetics

Reaction Rates	How we measure rates.
Rate Laws	How the rate depends on amounts of reactants.
Integrated Rate Laws	How to calculate the amount left or time to reach a given amount.
Half-life	How long it takes to react 50% of initial concentration reactants.
Arrhenius Equation	How rate constant changes with Temperature.
Mechanisms	Link between rate and molecular scale processes.

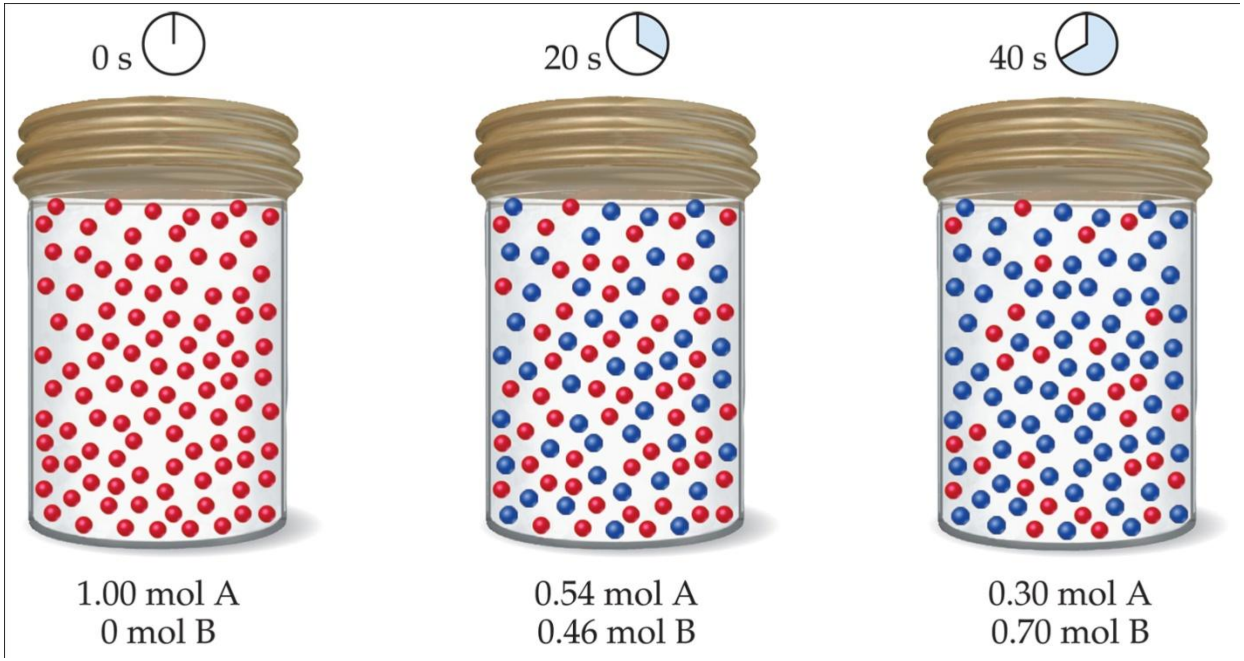
Factors That Affect Reaction Rates

- **Concentration of Reactants**
  - As the concentration of reactants increases, so does the likelihood that reactant molecules will collide more frequently.

- **Temperature**
  - At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.

- **Catalysts**
  - Enhances the speed by changing mechanism.

Reaction Rates



Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time.

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$

Time, t(s)	[C_4H_9Cl] M (M)
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0

In this reaction, the concentration of butyl chloride, **C_4H_9Cl**, was measured at various times, **t**.

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$

Time, t(s)	$[C_4H_9Cl]$ (M)	Average Rate, M/s
0.0	0.1000	
		1.9×10^{-4}
50.0	0.0905	
		1.7×10^{-4}
100.0	0.0820	
		1.6×10^{-4}
150.0	0.0741	
		1.4×10^{-4}
200.0	0.0671	
		1.22×10^{-4}
300.0	0.0549	
		1.01×10^{-4}
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

The **average rate** of the reaction over each interval is the change in concentration divided by the change in time:

$$average\ rate = \frac{\Delta [C_4H_9]}{\Delta t}$$

$$average\ rate = \frac{\Delta [C_4H_9]}{\Delta t} = \frac{0.1000 - 0.0905\ M}{50.0 - 0.0\ s}$$

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$

Time, t(s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
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		1.6×10^{-4}
150.0	0.0741	
		1.4×10^{-4}
200.0	0.0671	
		1.22×10^{-4}
300.0	0.0549	
		1.01×10^{-4}
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

- Note that the average rate decreases as the reaction proceeds.
- This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

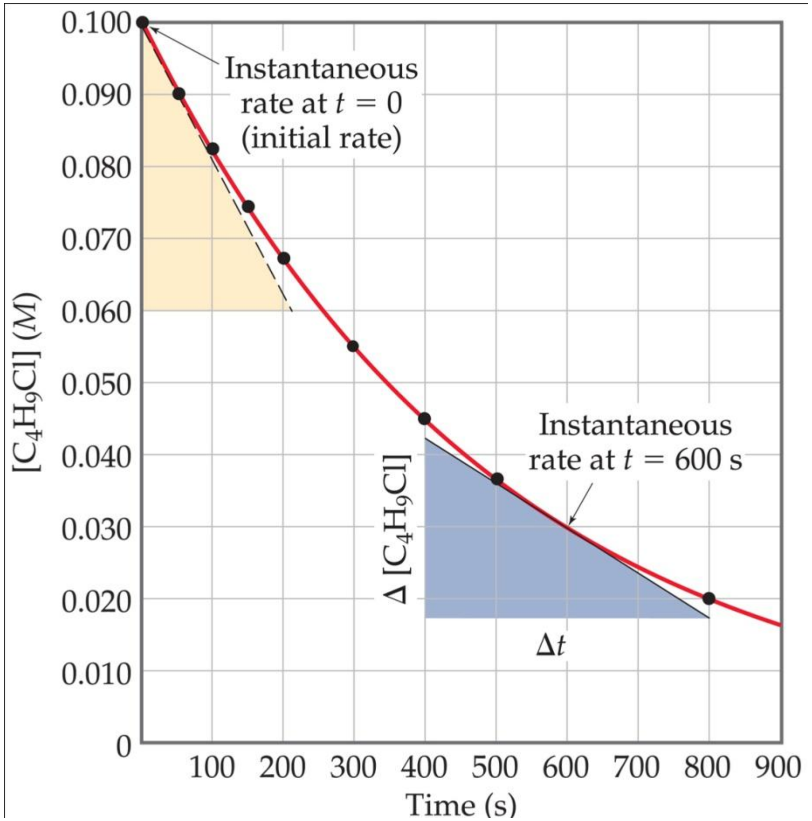
Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$

- A plot of concentration vs. time for this reaction yields a curve like this.

- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.

$$\frac{\Delta [A]}{\Delta t} \Rightarrow \frac{d[A]}{dt}$$

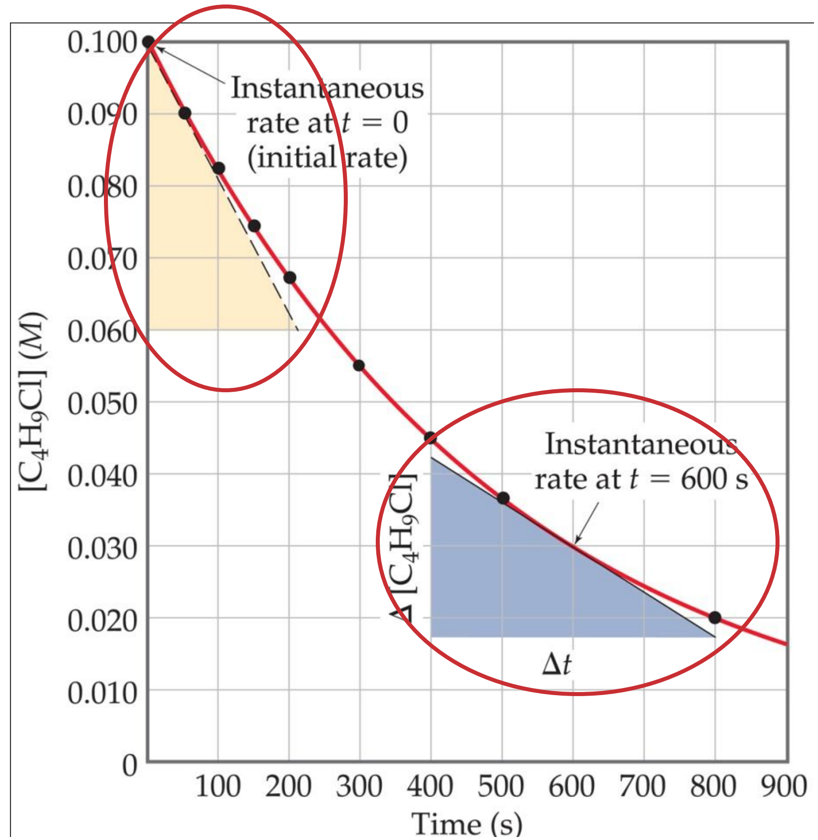


Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$

- The reaction slows down with time because the concentration of the reactants decreases.

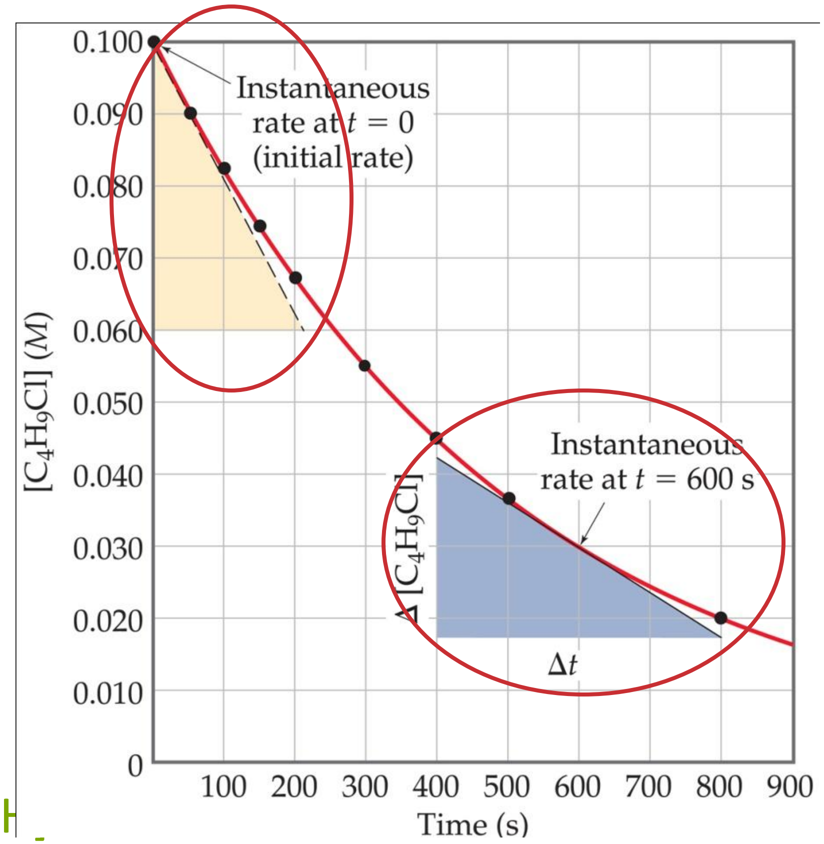
$$\frac{\Delta [A]}{\Delta t} \Rightarrow \frac{d[A]}{dt}$$



Reaction Rates and Stoichiometry

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$

- In this reaction, the ratio of C_4H_9Cl to C_4H_9OH is 1:1.
- Thus, the rate of *disappearance* of C_4H_9Cl is the same as the rate of *appearance* of C_4H_9OH.



$$\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Reaction Rates and Stoichiometry

- What if the ratio is *not* 1:1?

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

- Only 1/2 HI is made for each H_2 used.

$$rate = -\frac{\Delta [H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta [HI]}{\Delta t}$$

Reaction Rates and Stoichiometry

- To generalize, for the reaction

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

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

Reactants (decrease) Products (increase)

Concentration and Rate

"Each reaction has its own equation that gives its rate as a function of reactant concentrations".-

this is called its **Rate Law**

To determine the rate law we measure the rate at different starting concentrations.

Concentration and Rate

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$$NH_4^+(aq) + NO_2^- \rightarrow N_2(g) + 2H_2O(l)$$

Compare Experiments 1 and 2:

when $[NH_4^+]$ doubles, the initial rate doubles.

Concentration and Rate

Experiment Number	Initial NH_4^+ Concentration (*M*)	Initial NO_2^- Concentration (*M*)	Observed Initial Rate (*M*/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$$NH_4^+(aq) + NO_2^- \rightarrow N_2(g) + 2H_2O(l)$$

Likewise, compare Experiments 5 and 6:
when $[NO_2^-]$ doubles, the initial rate doubles.

Concentration and Rate

$$rate \propto [NH_4^+]$$

$$rate \propto [NO_2^-]$$

$$rate \propto [NH_4^+]\,[NO_2^-]$$

$$rate = k\,[NH_4^+]\,[NO_2^-]$$

This equation is called the rate law, and *k* is the rate constant.

$$NH_4^+(aq) + NO_2^- \rightarrow N_2(g) + 2H_2O(l)$$

Rate Laws

- A rate law shows the relationship between the reaction rate and the concentrations of reactants.
  - For gas-phase reactants use P_A instead of [A].

- k is a constant that has a specific value for each reaction.

- The value of k is determined experimentally.

$$rate = k\left[NH_4^+\right]\left[NO_2^-\right]$$

Rate Laws

- Exponents tell the order of the reaction with respect to each reactant.
- This reaction is

  First-order in $[NH_4^+]$

  First-order in $[NO_2^-]$
- The overall reaction order can be found by adding the exponents on the reactants in the rate law.
- This reaction is *second-order overall*.

$$rate = k\left[NH_4^+\right]^1\left[NO_2^-\right]^1$$

Integrated Rate Laws

Consider a simple 1st order rxn: $A \rightleftharpoons B$

$$rate = k[A]$$

Differential form: $$-\frac{d[A]}{dt} = k[A]$$

How much A is left after time *t*? Integrate:

$$-d[A] = k[A]\,dt$$

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

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

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

Integrated Rate Laws

The integrated form of first order rate law:

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

Can be rearranged to give:

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

$[A]_0$ is the initial concentration of A (t = 0).
$[A]_t$ is the concentration of A at some time, t, during the course of the reaction.

Integrated Rate Laws

Manipulating this equation produces…

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

$$ln\,[A]_t - ln\,[A]_0 = -kt$$

$$ln\,[A]_t = -kt + ln\,[A]_0$$

…which is in the form $y \quad = mx + \; b$

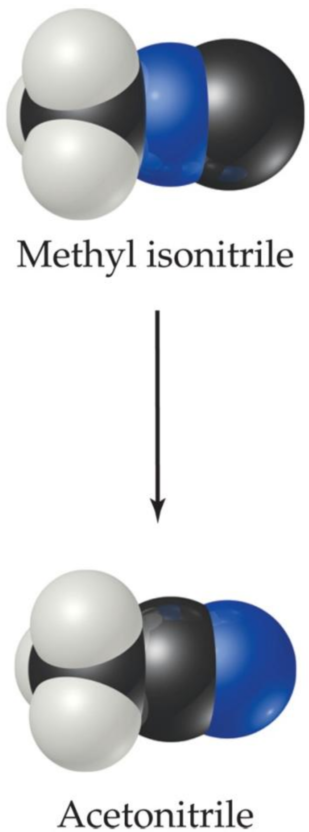
First-Order Processes

$$ln\,[A]_t = -kt + ln\,[A]_0$$

If a reaction is first-order, a plot of ln $[A]_t$ vs. t will yield a straight line with a slope of $-k$.

So, use graphs to determine rxn order.

First-Order Processes



Consider the process in which methyl isonitrile is converted to acetonitrile.

$$CH_3NC \longrightarrow CH_3CN$$

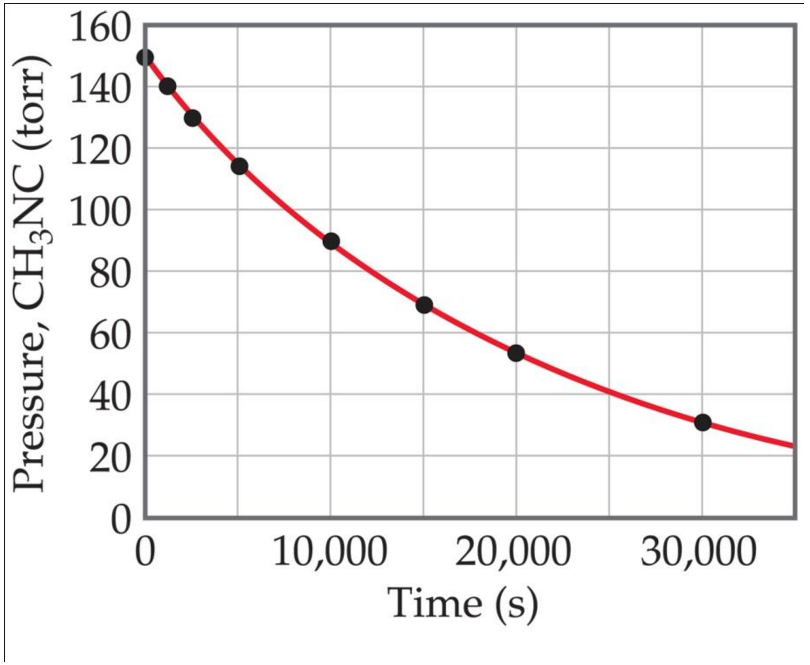
How do we know this is a first order rxn?

First-Order Processes

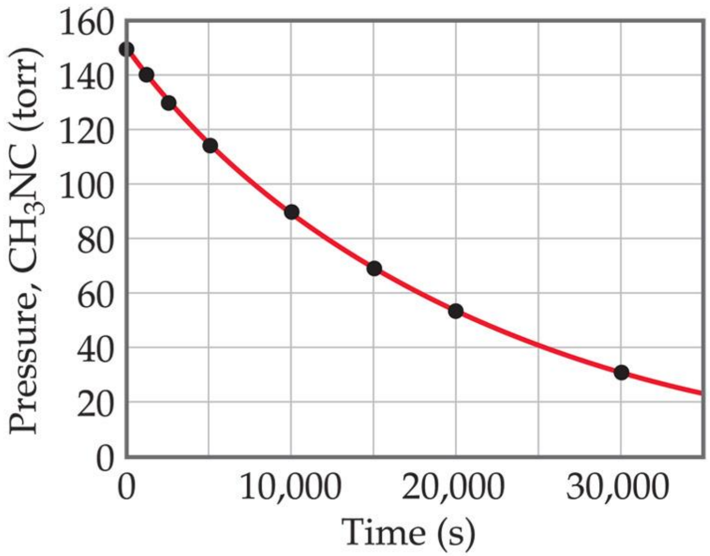
$CH_3NC \longrightarrow CH_3CN$

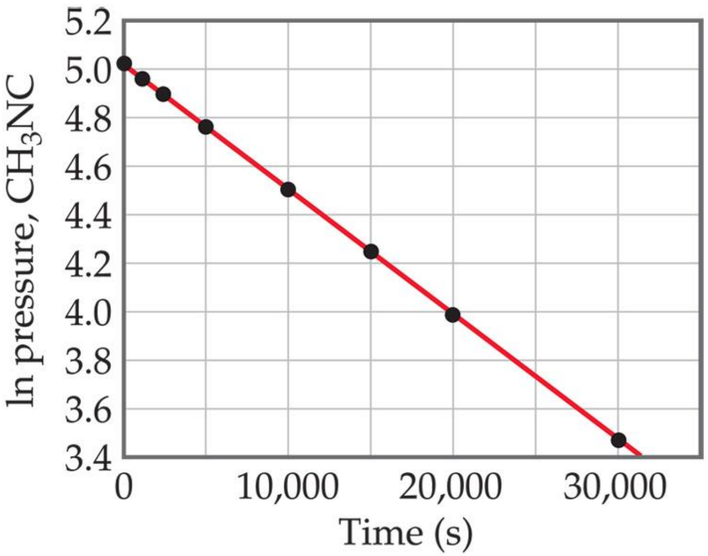
This data was collected for this reaction at 198.9°C.

Does rate=k[CH_3NC] for all time intervals?



First-Order Processes





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

$$ln\,[A]_t = -kt + ln\,[A]_0$$

- When ln*P* is plotted as a function of time, a straight line results.
  - **The process is first-order.**
  - ***k* is the negative slope: 5.1 × 10^{-5} s^{-1}.**

Second-Order Processes

Similarly, integrating the rate law for a process that is second-order in reactant A:

$$rate = -\frac{d[A]}{dt} = k[A]^2$$

Rearrange, integrate: $\frac{1}{[A]_t} = -kt + \frac{1}{[A]_0}$

also in the form $y = \text{mx} + b$

Second-Order Processes

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

So if a process is second-order in A, a plot of 1/[A] vs. t will yield a straight line with a slope of k.

$$ln\,[A]_t = -kt + ln\,[A]_0$$

First order:

If a reaction is first-order, a plot of ln $[A]_t$ vs. t will yield a straight line with a slope of $-k$.

Determining rxn order

The decomposition of NO_2 at 300°C is described by the equation

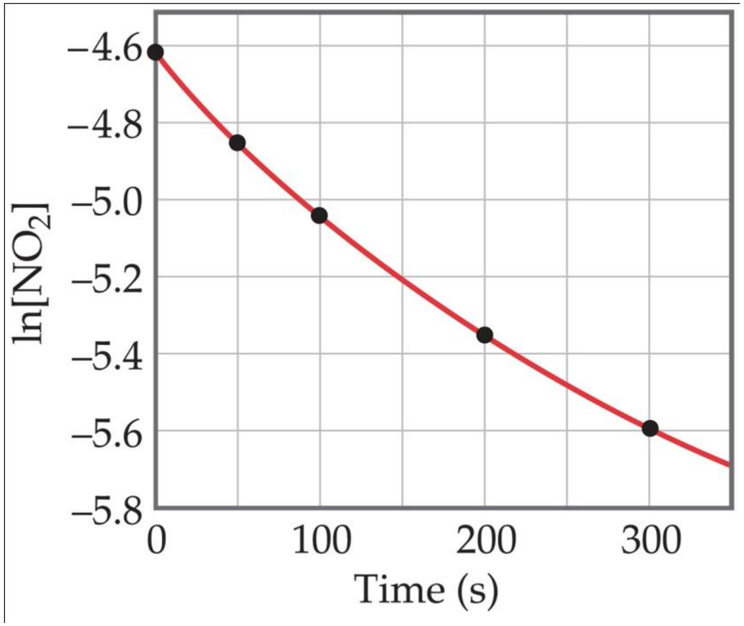
$$NO_2\ (g) \longrightarrow NO\ (g) + 1/2\ O_2\ (g)$$

and yields these data:

Time (*s*)	$[NO_2]$, *M*
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Determining rxn order

Graphing ln $[NO_2]$ vs. *t* yields:



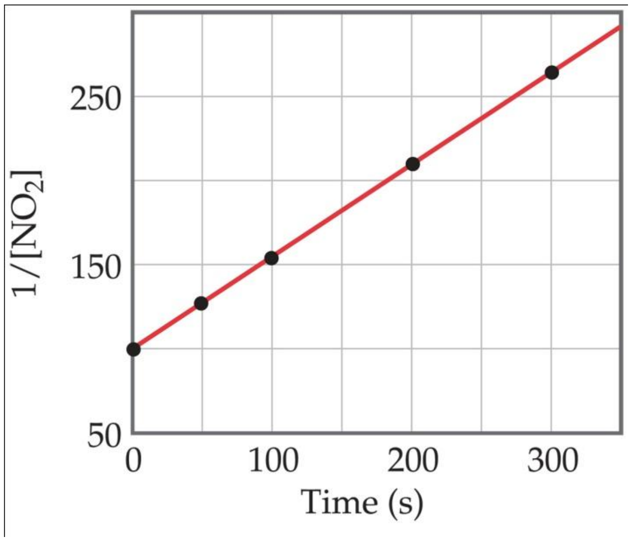
- The plot is *not* a straight line, so the process is *not* first-order in [A].

Time (s)	$[NO_2]$, *M*	ln $[NO_2]$
0.0	0.01000	-4.610
50.0	0.00787	-4.845
100.0	0.00649	-5.038
200.0	0.00481	-5.337
300.0	0.00380	-5.573

Does not fit:

$$ln\,[A]_t = -kt + ln\,[A]_0$$

Second-Order Processes



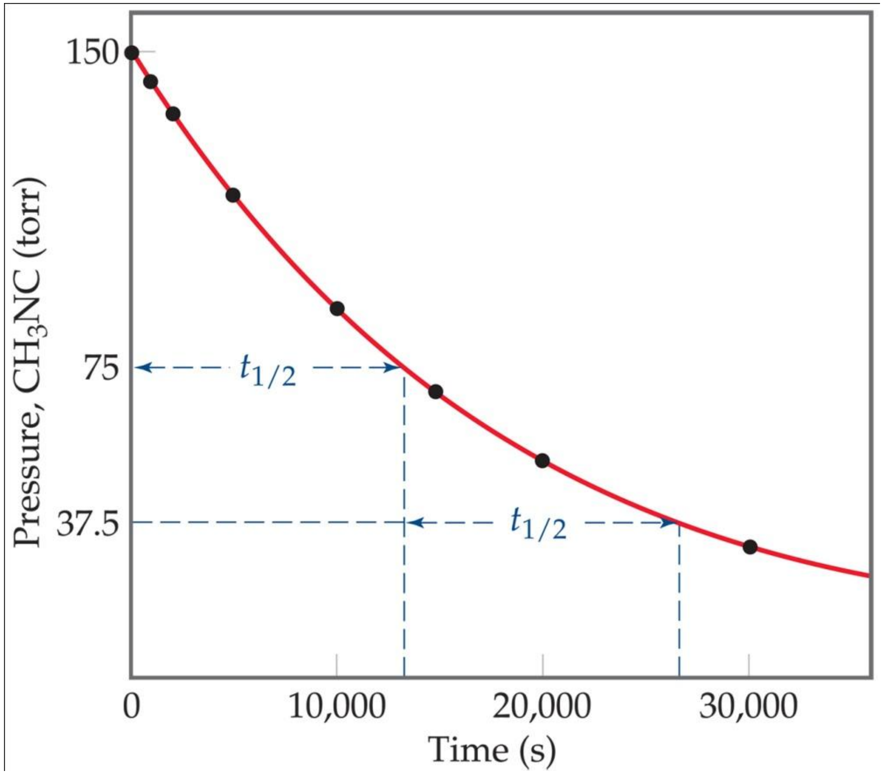
A graph of $1/[NO_2]$ vs. *t* gives this plot.

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

Time (*s*)	$[NO_2]$, *M*	$1/[NO_2]$
0.0	0.01000	100
50.0	0.00787	127
100.0	0.00649	154
200.0	0.00481	208
300.0	0.00380	263

- This *is* a straight line. Therefore, the process is second-order in $[NO_2]$.

Half-Life



- Half-life is defined as the time required for one-half of a reactant to react.
- Because [A] at $t_{1/2}$ is one-half of the original [A],

$$[A]_t = 0.5\ [A]_0.$$

Half-Life

For a first-order process, set $[A]_t$=0.5 $[A]_0$ in integrated rate equation:

$$ln\frac{0.5\,[A]_0}{[A]_0} = -kt_{\frac{1}{2}}$$

$$ln(0.5) = -kt_{\frac{1}{2}}$$

$$ln(2) = 0.693 = -kt_{\frac{1}{2}}$$

$$\frac{0.693}{k} = t_{\frac{1}{2}}$$

NOTE: For a first-order process, the half-life does not depend on $[A]_0$.

Half-Life- 2nd order

For a second-order process, set
$[A]_t = 0.5\ [A]_0$ in 2nd order equation.

$$\frac{1}{0.5\,[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

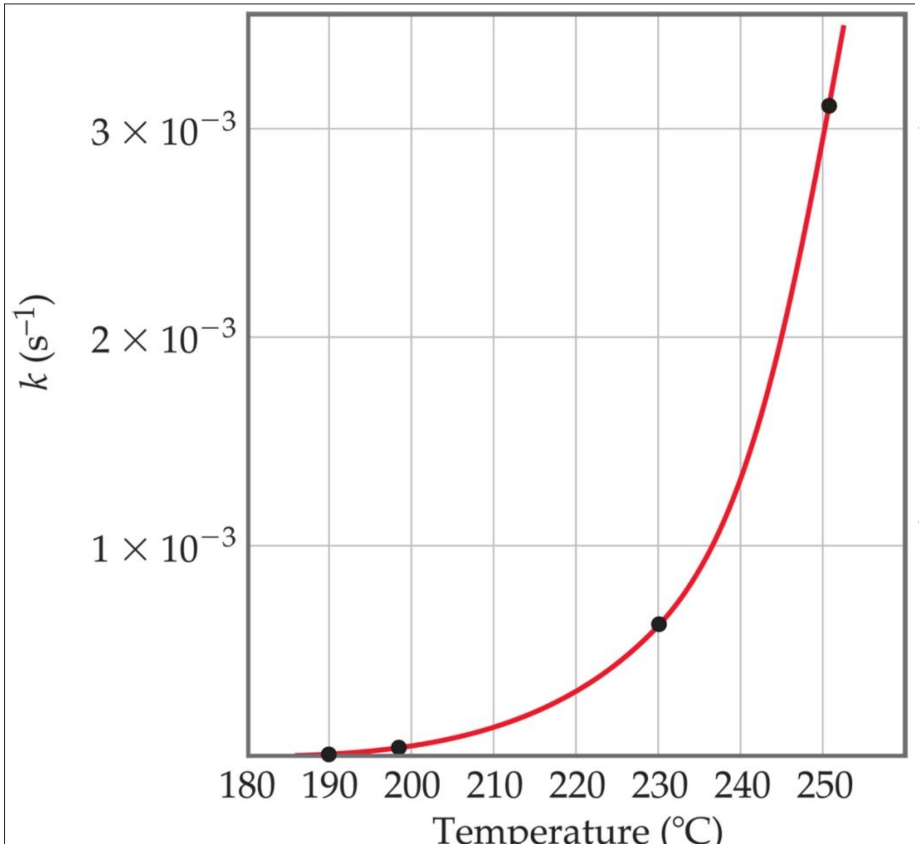
$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{\frac{1}{2}}$$

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

Outline: Kinetics

	First order	Second order (same reactant)	Second order (different reactant)
Rate Laws	$rate = -k\left[A\right]$	$rate = -k\left[A\right]^2$	$rate = -k\left[A\right]\left[B\right]$
Integrated Rate Laws	$ln\frac{[A]_t}{[A]_0} = -kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	complicated
Half-life	$\frac{0.693}{k} = t_{\frac{1}{2}}$	$\frac{1}{k\left[A\right]_0} = t_{\frac{1}{2}}$	complicated

Temperature and Rate



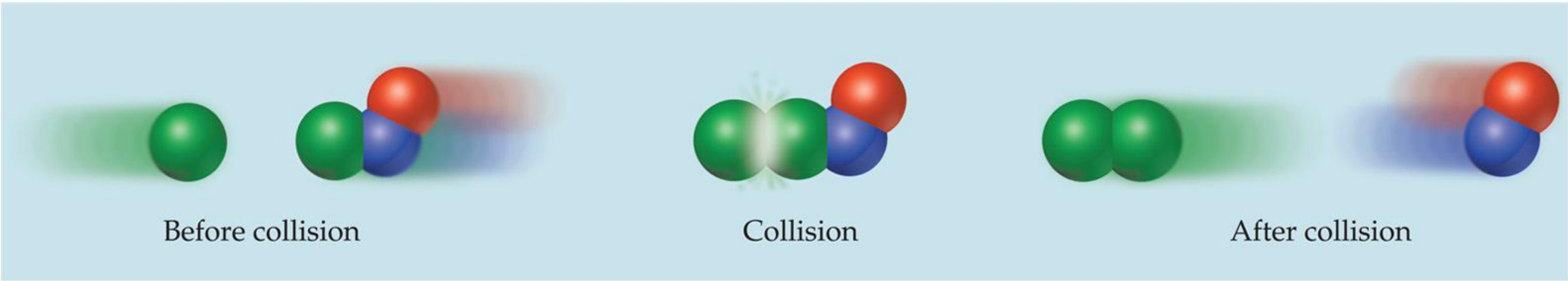
- Generally, as temperature increases, reaction rate a;so increases.
- This is because *k* is temperature dependent.

The Collision Model

- In a chemical reaction, bonds are broken and new bonds are formed.
- Molecules can only react if they collide with each other with appropriate energy and orientation as well.

The Collision Model

Furthermore, molecules must collide with the correct orientation and with enough energy to cause bond breakage and formation.



A + ABC ⟶ A--A--BC ⟶ A_2 + BC

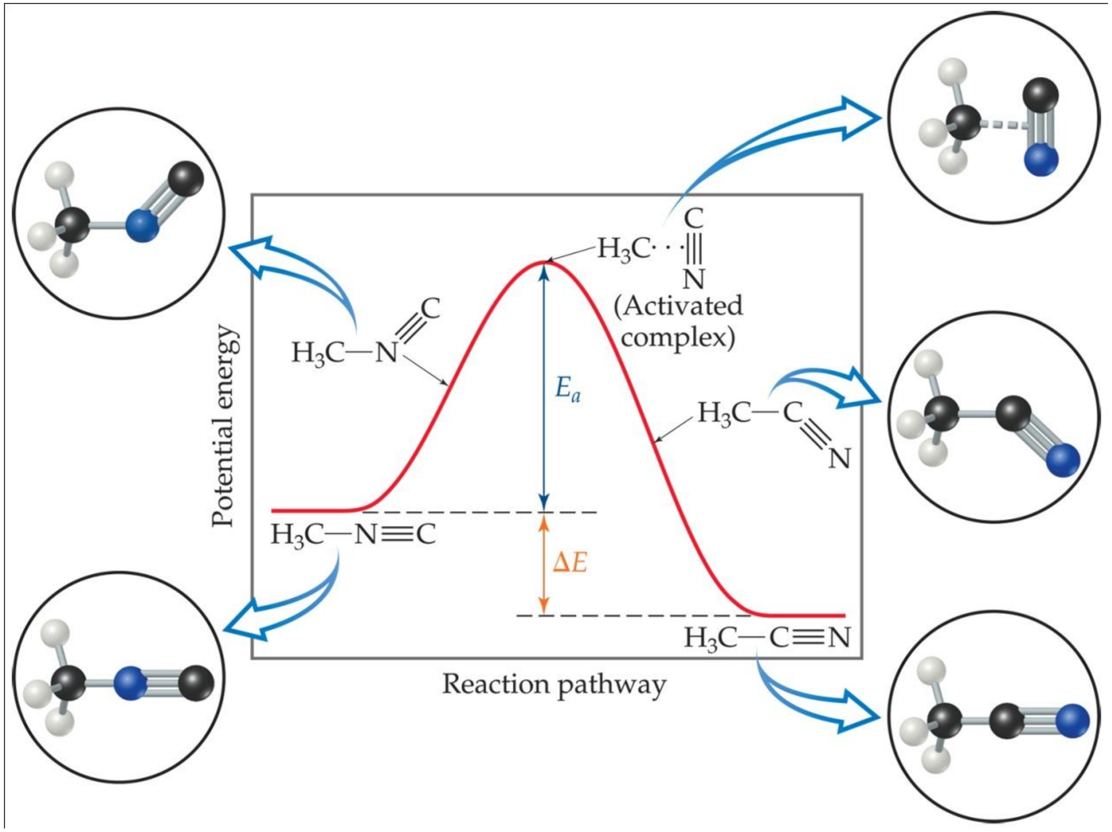
Reactant Transition State Product

Activation Energy

- In other words, there is a minimum amount of energy required for reaction: the activation energy, E_a.
- Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.

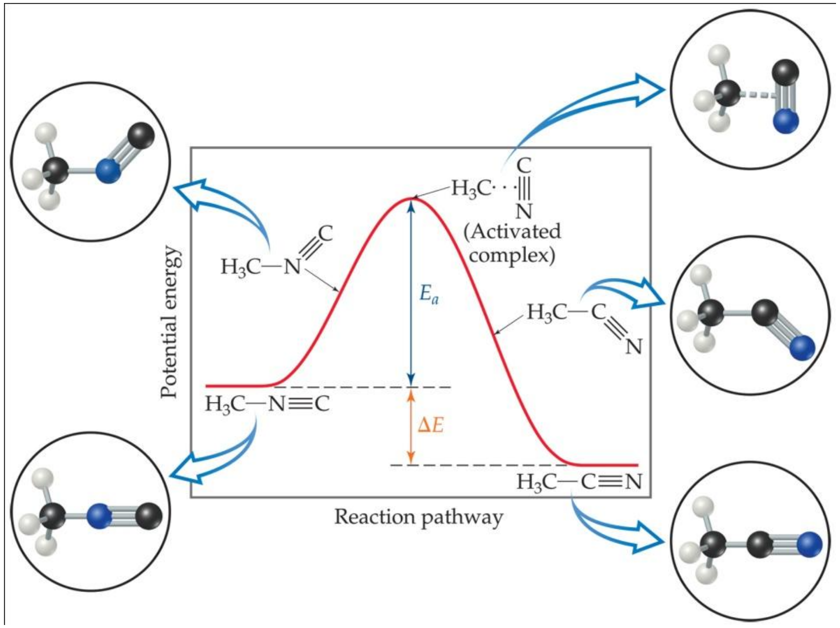
Reaction Coordinate Diagrams

It is helpful to visualize energy changes throughout a process on a reaction coordinate diagram like this one for the rearrangement of methyl isonitrile.



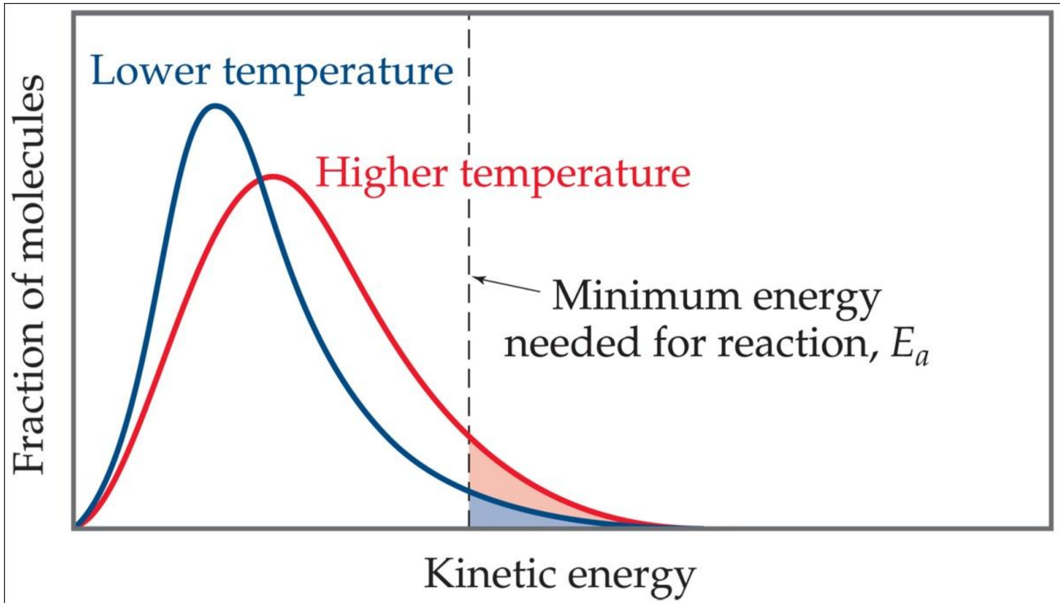
Reaction Coordinate Diagrams

- It shows the energy of the reactants and products (and, therefore, Δ*E*).
- The high point on the diagram is the transition state.



- The species present at the transition state is called the activated complex.
- The energy gap between the reactants and the activated complex is the activation energy barrier.

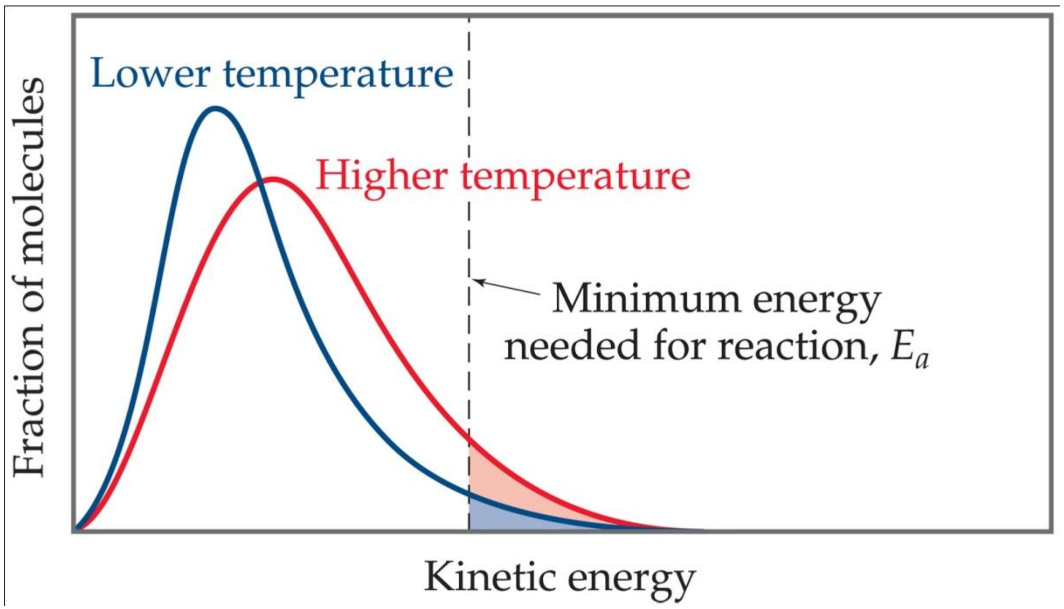
Maxwell–Boltzmann Distributions



- Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.

- At any temperature there is a wide distribution of kinetic energies.

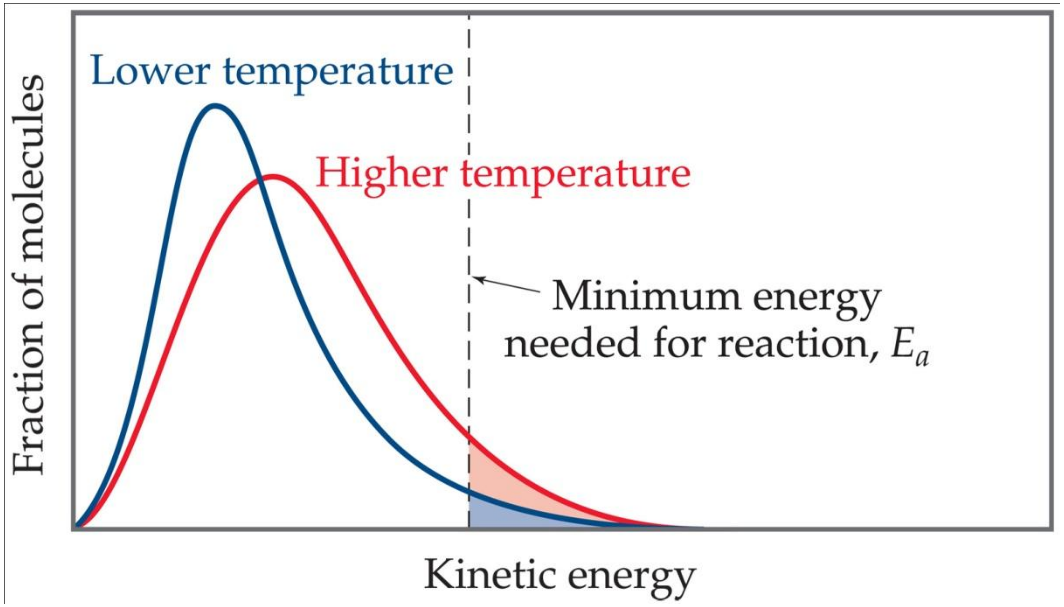
Maxwell–Boltzmann Distributions



- As the temperature increases, the curve flattens and broadens.
- Thus at higher temperatures, a larger population of molecules has higher energy.

Maxwell–Boltzmann Distributions

- If the dotted line represents the activation energy, as the temperature increases, so does the fraction of molecules that can overcome the activation energy barrier.



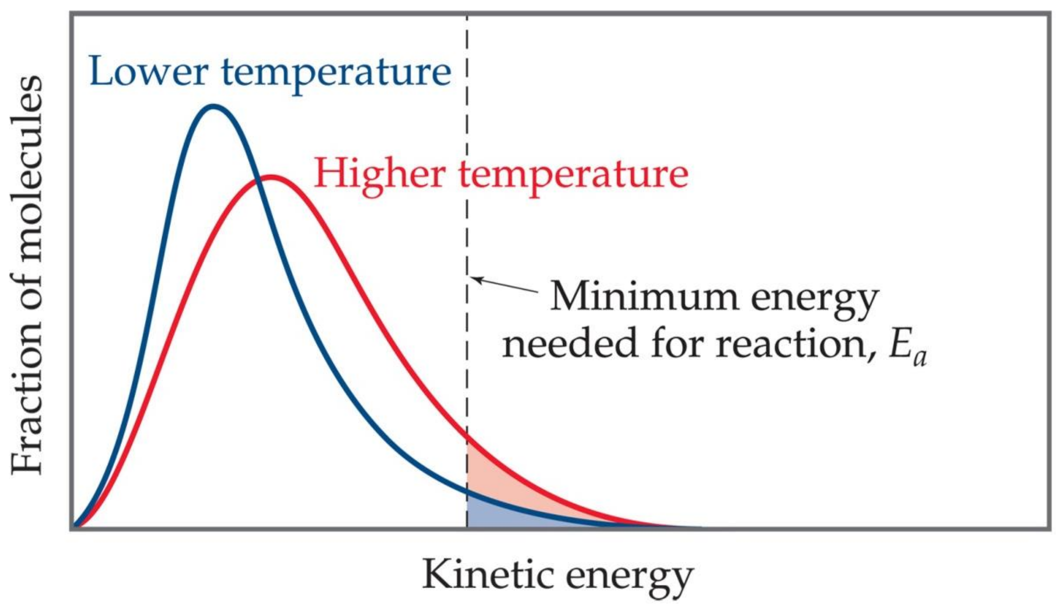
- As a result, the reaction rate increases.

Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression:

$$f = e^{-\frac{E_a}{RT}}$$

where *R* is the gas constant and *T* is the temperature in Kelvin .



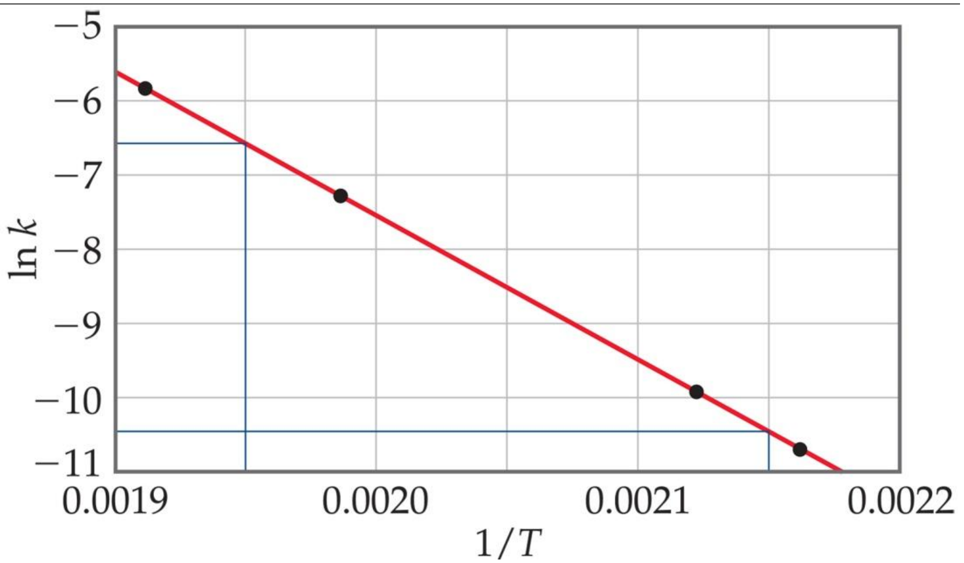
Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between k and E_a:

$$k = Ae^{-\frac{E_a}{RT}}$$

where A is the frequency factor, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Arrhenius Equation



Taking the natural logarithm of both sides, the equation becomes

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

$y \quad = \quad mx + b$

When k is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of ln k vs. $1/T$.

Outline: Kinetics

	First order	Second order	Second order
Rate Laws	$rate = -k\left[A\right]$	$rate = -k\left[A\right]^2$	$rate = -k\left[A\right]\left[B\right]$
Integrated Rate Laws	$ln\frac{[A]_t}{[A]_0} = -kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	complicated
Half-life	$\frac{0.693}{k} = t_{\frac{1}{2}}$	$\frac{1}{k\left[A\right]_0} = t_{\frac{1}{2}}$	complicated
k(T)	$ln(k) = -\frac{E_a}{RT} + lnA$		

Reaction Mechanisms

The sequence of events that describes the actual process by which reactants become products is called the reaction mechanism.

- Reactions may occur all at once or through several discrete steps.
- Each of these processes is known as an elementary reaction or elementary process.

Reaction Mechanisms

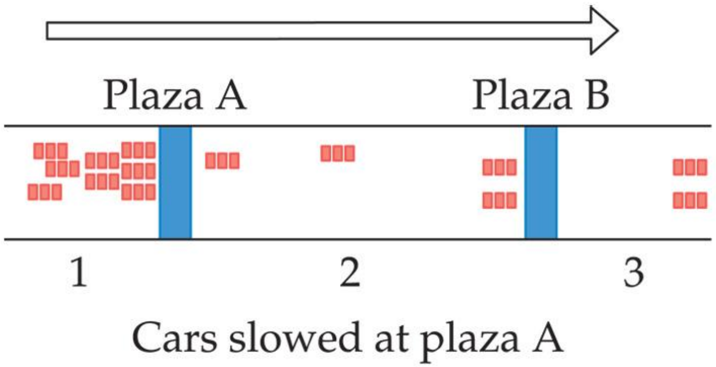
Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

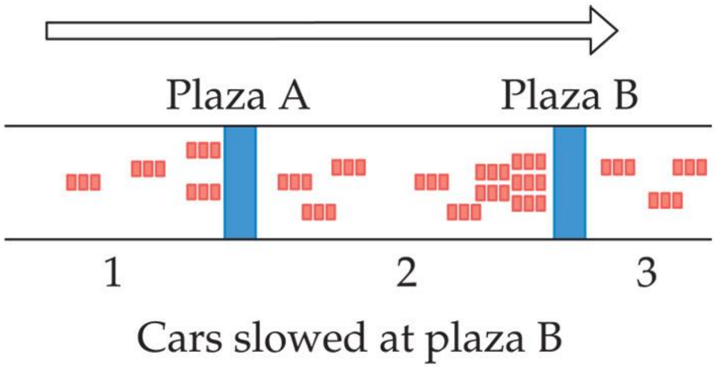
- The molecularity of a process tells how many molecules are involved in the process.

- The rate law for an elementary step is written directly from that step.

Multistep Mechanisms

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, rate-determining step.





Slow Initial Step

$$NO_2\,(g) + CO\,(g) \rightleftharpoons NO\,(g) + CO_2\,(g)$$

- The rate law for this reaction is found experimentally to be

$$\text{Rate} = k\,[NO_2]^2$$

- CO is necessary for this reaction to occur, but the *rate* of the reaction does not depend on its concentration.
- This suggests the reaction occurs in two steps.

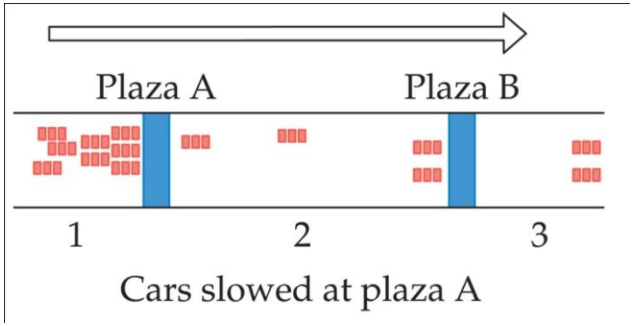
Slow Initial Step

- A proposed mechanism for this reaction is

Step 1: $NO_2 + NO_2 \rightleftharpoons NO_3 + NO$ (slow)

Step 2: $NO_3 + CO \rightleftharpoons NO_2 + CO_2$ (fast)

- The NO_3 intermediate is consumed in the second step.
- As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.



Fast Initial Step

$$2\ NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

- The rate law for this reaction is found (experimentally) to be

$$rate = k\,[NO]^2\,[Br_2]$$

- Because termolecular (= trimolecular) processes are rare, this rate law suggests a two-step mechanism.

Fast Initial Step

- A proposed mechanism is

$$Step\ 1:\ \ NO + Br_2 \rightleftharpoons NOBr_2\ \ \ (fast)$$

$$Step\ 2:\ \ NOBr_2 + NO \rightarrow 2NOBr\ \ \ (slow)$$

Step 1 is an *equilibrium*-

it includes the forward *and* reverse reactions.

Fast Initial Step

$$Step\ 1:\ \ NO + Br_2 \rightleftharpoons NOBr_2\ \ \ (fast)$$

$$Step\ 2:\ \ NOBr_2 + NO \rightarrow 2NOBr\ \ \ (slow)$$

- The rate of the overall reaction depends upon the rate of the slow step.
- The rate law for that step would be

$$rate_2 = k_2\,[NOBr_2]\,[NO]$$

- But how can we find $[NOBr_2]$?

Fast Initial Step

$$Step\ 1:\ NO + Br_2 \rightleftharpoons NOBr_2 \quad (fast)$$

$$Step\ 2:\ NOBr_2 + NO \rightarrow 2NOBr \quad (slow)$$

- NOB
  - With NO to form NOBr
  - By decomposition to reform NO and Br_2
- The reactants and products of the first step are in equilibrium with each other.
- Therefore,

$$Rate_f = Rate_r$$

Fast Initial Step

$$Step\ 1:\ NO + Br_2 \rightleftharpoons NOBr_2\ \ (fast)$$

$$Step\ 2:\ NOBr_2 + NO \rightarrow 2NOBr\ \ (slow)$$

- Because $Rate_f = Rate_r$,

$$k_1\,[NO]\,[Br_2] = k_{-1}\,[NOBr_2]$$

Solving for $[NOBr_2]$ gives us

$$\frac{k_1}{k_{-1}}\,[NO]\,[Br_2] = [NOBr_2]$$

Fast Initial Step

$$Step\ 1:\ \ NO + Br_2 \rightleftharpoons NOBr_2 \quad (fast)$$

$$Step\ 2:\ \ NOBr_2 + NO \rightarrow 2NOBr \quad (slow)$$

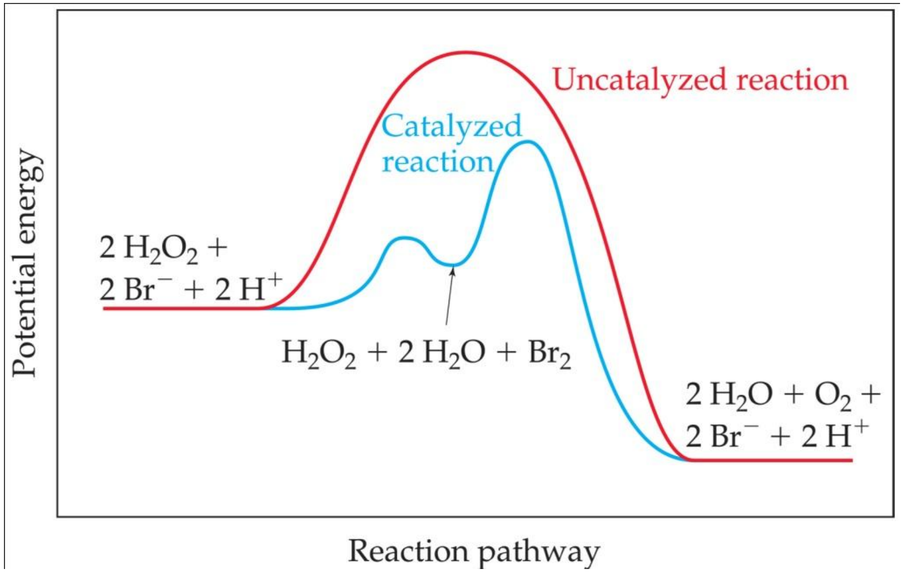
Substituting this expression for $[NOBr_2]$ in the rate law for the rate-determining step gives

$$rate = \frac{k_2 k_1}{k_{-1}} [NO][Br_2][NO]$$

$$= \frac{k_2 k_1}{k_{-1}} [NO]^2 [Br_2]$$

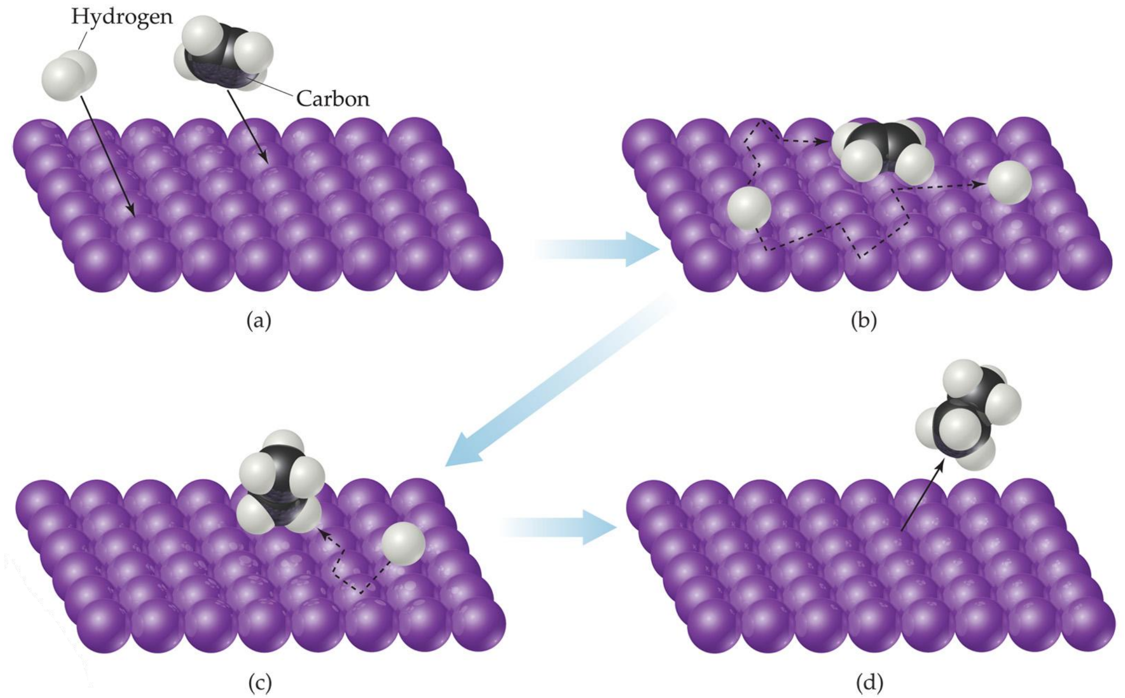
Catalysts

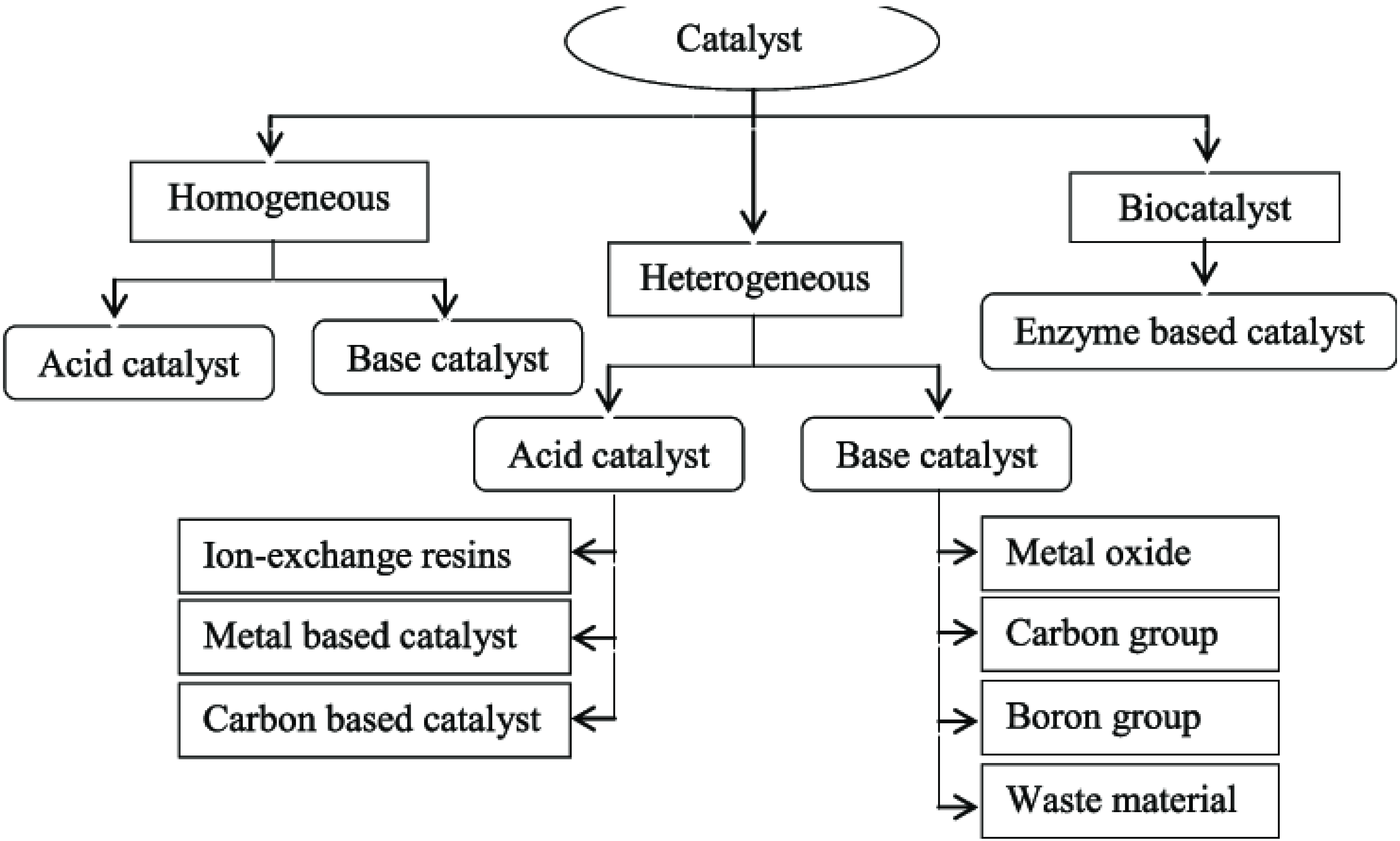
- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.
- Catalysts change the mechanism by which the process occurs.



Catalysts

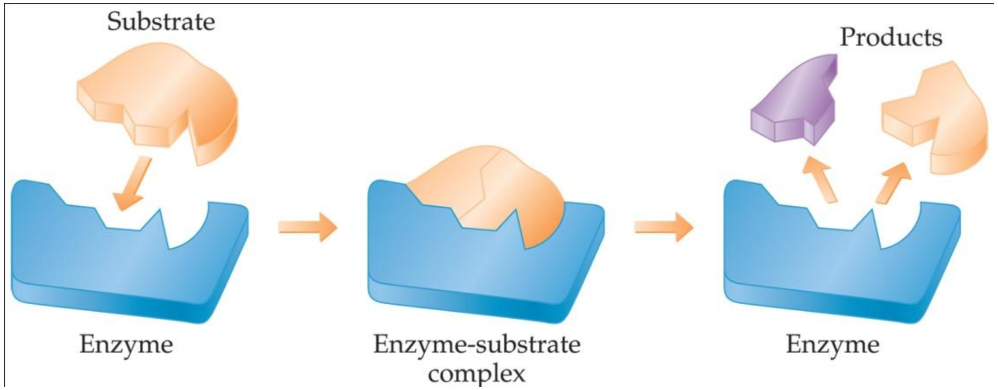
One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.




Catalyst
Homogeneous
Heterogeneous
Biocatalyst
Acid catalyst
Base catalyst
Enzyme based catalyst
Acid catalyst
Base catalyst
Ion-exchange resins
Metal based catalyst
Carbon based catalyst
Metal oxide
Carbon group
Boron group
Waste material

Enzymes

- Enzymes are catalysts in biological systems.
- The substrate fits into the active site of the enzyme much like a key fits into a lock.



Thank you for your time and attention