

Chemical Kinetics

Factors that Affect Reaction Rates

Chemical kinetics is the study of how fast chemical reactions occur.

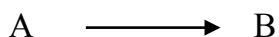
There are several important factors, which affect rate of reactions.

- 1) **Physical state of the reactants**: reactant must come together and collide in order to react.
- 2) **Concentration of the reactants**: most chemical reactions proceed faster if the concentration of one or more reactant increased.
- 3) **Temperature of the reaction**: as T increase, the molecules move faster, they collide more frequently with high energy, leading to increased rate.
- 4) **Presence of catalyst**: catalysts are agents that increase reaction rates without being used up. They affect the kinds of collisions that lead the reaction.

On the molecular level, reaction rate depend on the frequency of collisions between molecules. The greater the collision is, the greater the rate of reaction. In order for a collision to lead to reaction, however, it must occur with sufficient energy to stretch bonds to a critical length and with suitable orientation for new bonds to form in proper locations

Reaction Rates : Rate Describes Change Over Time

The speed of a reaction – is reaction rate_ is the change in the concentration of reactants or products per unit time. thus the units of reaction rate are molarity per second (M/s)-that is , the change in concentration (measured in molarity) divided by time interval (seconds)



There are two ways of measuring rate:

- 1) The average rate with respect to B = Rate of appearance of B

$$\text{Rate} = ([\Delta B]/\Delta t)$$

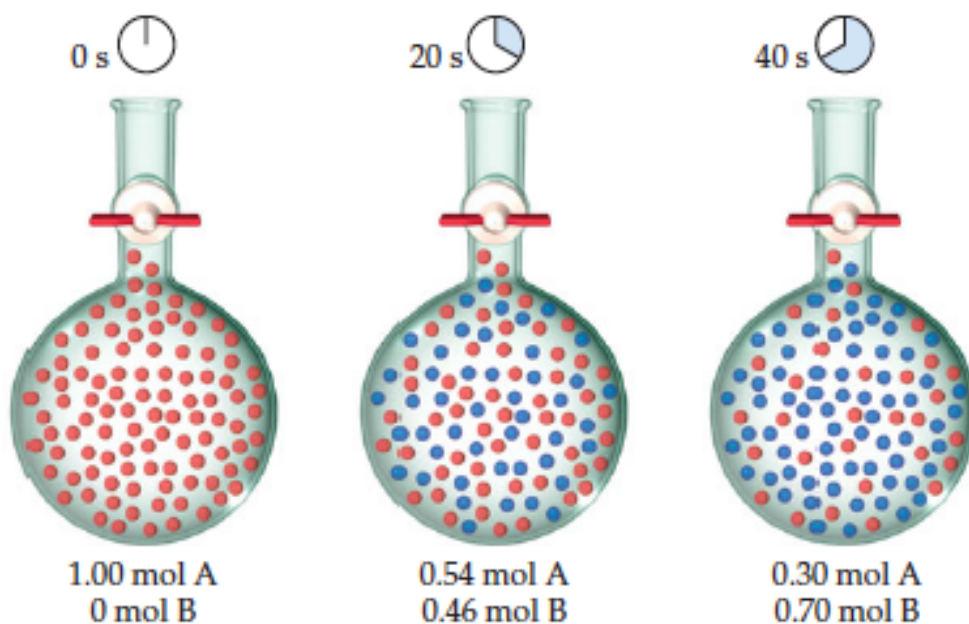
$$\begin{aligned} \text{Average rate of appearance of B} &= \frac{\text{change in concentration of B}}{\text{change in time}} \\ &= \frac{[B] \text{ at } t_2 - [B] \text{ at } t_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t} \end{aligned}$$

- 2) The average rate with respect to A = Rate of disappearance of reactant A

$$\text{Rate} = - [(\Delta A)/\Delta t)$$

$$\begin{aligned} \text{Average rate of disappearance of A} &= - \frac{\text{change in concentration of A}}{\text{change in time}} \\ &= - \frac{\Delta[A]}{\Delta t} \end{aligned}$$

Negative sign = disappearance of a reactant.

Example:

1) Rate of appearance of B:

The average rate of appearance of B over the 20-s interval from the beginning of the reaction ($t_1 = 0$ s to $t_2 = 20$ s) is:

$$\text{Average rate} = \frac{0.46 \text{ M} - 0.00 \text{ M}}{20 \text{ s} - 0 \text{ s}} = 2.3 \times 10^{-2} \text{ M/s}$$

2) Rate of disappearance of A:

The average rate of disappearance of A over the 20-s interval from the beginning of the reaction ($t_1 = 0$ s to $t_2 = 20$ s) is:

$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.54 \text{ M} - 1.00 \text{ M}}{20 \text{ s} - 0 \text{ s}} = 2.3 \times 10^{-2} \text{ M/s}$$

Change of Rate with Time
Reaction Rate Can Be Measured
Concentration Must Be Measured Often

It is typical for rates to decrease as a reaction proceeds because the concentration of reactants decreases.

The reaction of (C₄H₉Cl) and water:



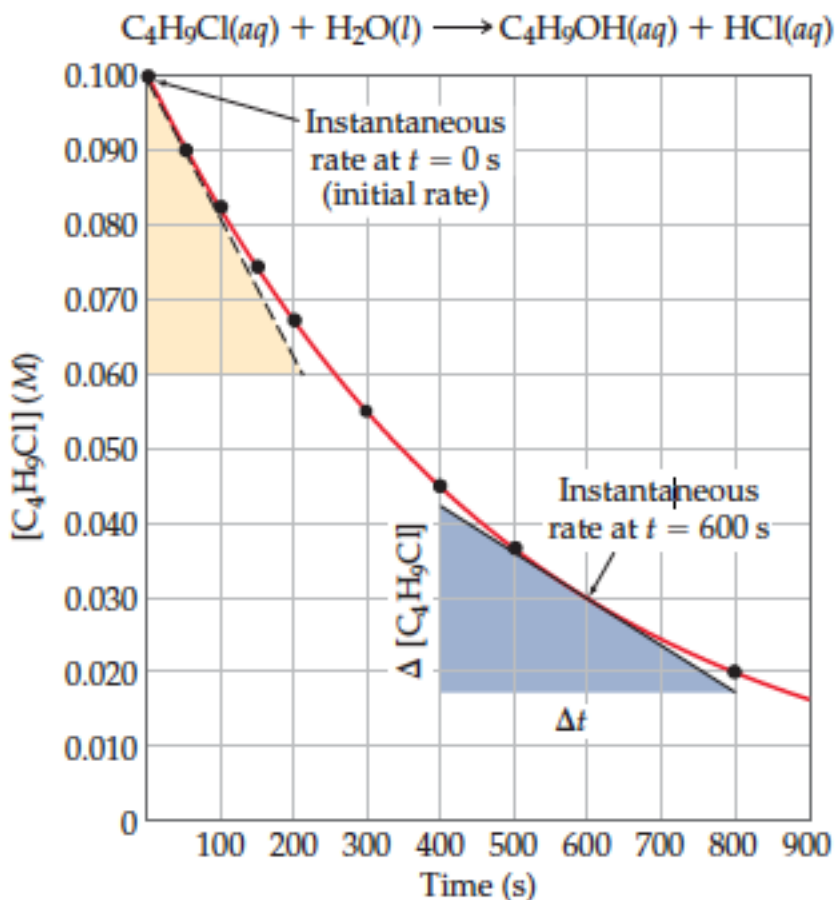
TABLE 14.1 • Rate Data for Reaction of C₄H₉Cl with Water

Time, <i>t</i> (s)	[C ₄ H ₉ Cl](<i>M</i>)	Average Rate (<i>M</i> /s)
0.0	0.1000	
50.0	0.0905	1.9×10^{-4}
100.0	0.0820	1.7×10^{-4}
150.0	0.0741	1.6×10^{-4}
200.0	0.0671	1.4×10^{-4}
300.0	0.0549	1.22×10^{-4}
400.0	0.0448	1.01×10^{-4}
500.0	0.0368	0.80×10^{-4}
800.0	0.0200	0.560×10^{-4}
10,000	0	

Reaction Rate Can Be Represented Graphically:

Instantaneous Rate:

The instantaneous rate is the rate at a particular moment in the reaction. It is determined by the slope (or straight line tangent) of the curve (concentration vs. time) at the point of interest.



The instantaneous rate at $t = 600$ s is:

$$\begin{aligned} \text{Instantaneous rate} &= -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = -\frac{(0.017 - 0.042) \text{ M}}{(800 - 400) \text{ s}} \\ &= 6.3 \times 10^{-5} \text{ M/s} \end{aligned}$$

The instantaneous rate at $t = 0$ s is:

$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = -\frac{(0.060 - 0.100) \text{ M}}{(210 - 0) \text{ s}} = 1.9 \times 10^{-4} \text{ M/s}$$

Balanced Coefficient Appear in the Rate Definition

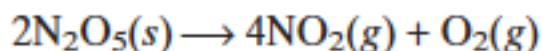
For the reaction: $aA + \dots \longrightarrow bB + cC + dD$

The rate may be expressed as:

$$\text{Rate} = -1/a \left(\frac{\Delta A}{\Delta t} \right) = -1/b \left(\frac{\Delta B}{\Delta t} \right) = 1/c \left(\frac{\Delta C}{\Delta t} \right) = 1/d \left(\frac{\Delta D}{\Delta t} \right)$$

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

Example 1:



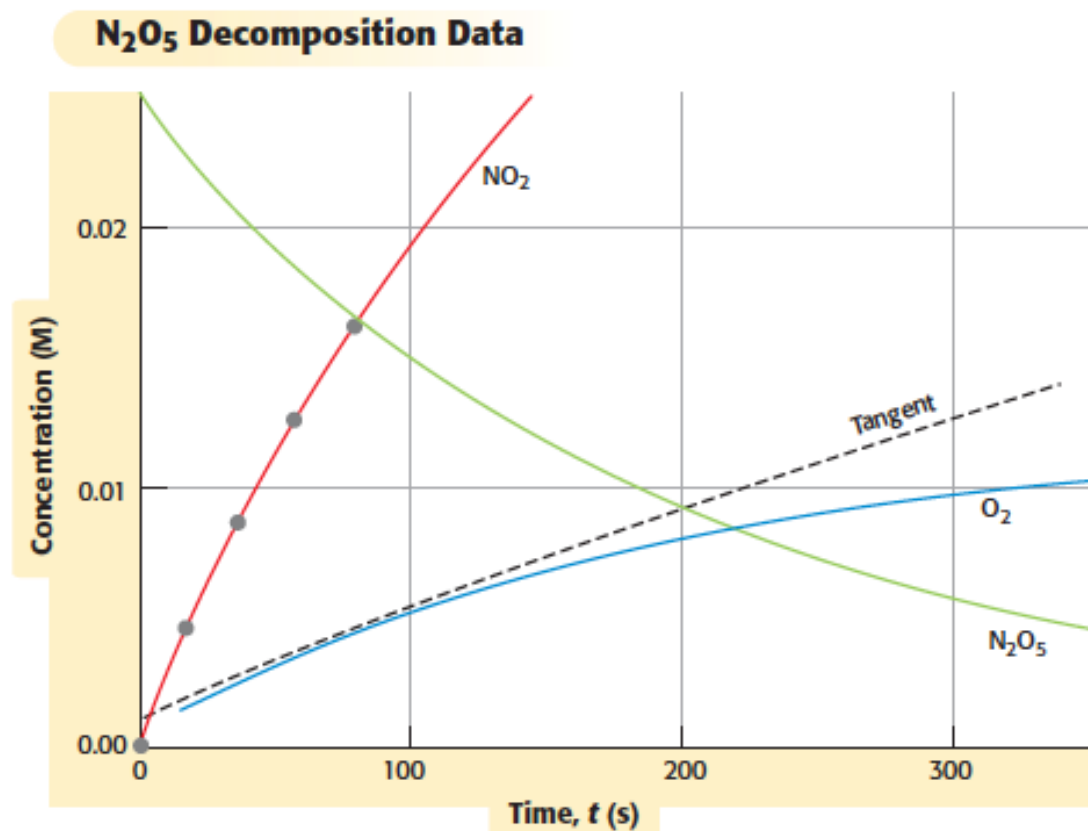
$$\text{rate} = \frac{-\Delta[\text{N}_2\text{O}_5]}{2\Delta t} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

Table 1 Concentration Data and Calculations for the Decomposition of N_2O_5

t (s)	$[\text{NO}_2]$ (M)	$\Delta[\text{NO}_2]$ (M)	Δt (s)	$\Delta[\text{NO}_2]/\Delta t$ (M/s)	Rate (M/s)
0	0	4.68×10^{-3}	20.0	2.34×10^{-4}	5.85×10^{-5}
20.0	0.00468	4.22×10^{-3}	20.0	2.11×10^{-4}	5.28×10^{-5}
40.0	0.00890	3.82×10^{-3}	20.0	1.91×10^{-4}	4.78×10^{-5}
60.0	0.01272	3.44×10^{-3}	20.0	1.72×10^{-4}	4.30×10^{-5}
80.0	0.01616				

$$\text{rate} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = \frac{0.01616 \text{ M} - 0.01272 \text{ M}}{4(80.0 \text{ s} - 60.0 \text{ s})} = 4.30 \times 10^{-5} \text{ M/s}$$

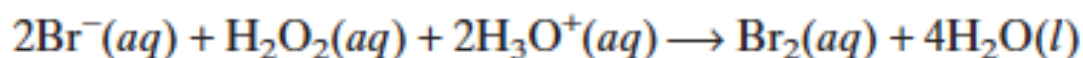
The information can be represented graphically.



$$\text{slope of O}_2 \text{ curve} = \frac{\Delta[\text{O}_2]}{\Delta t} = \text{rate of the reaction}$$

At $t = 70 \text{ s}$, the slope = $4.30 \times 10^{-5} \text{ M/s}$.

This value agrees with the rate calculated in Table 1 at the same instant

Example 2:

Time t (s)	$[\text{H}_3\text{O}^+]$ (M)	$[\text{Br}_2]$ (M)
0	0.0500	0
85	0.0298	0.0101
95	0.0280	0.0110
105	0.0263	0.0118

$$\text{rate} = \frac{-\Delta[\text{H}_3\text{O}^+]}{2\Delta t} = \frac{\Delta[\text{Br}_2]}{\Delta t}$$

$$\Delta[\text{H}_3\text{O}^+] = (0.0263 \text{ M}) - (0.0280 \text{ M}) = -0.0017 \text{ M}$$

$$\Delta[\text{Br}_2] = (0.0118 \text{ M}) - (0.0110) = 0.0008 \text{ M}$$

From the change in hydronium ion concentration,

$$\text{rate} = \frac{-\Delta[\text{H}_3\text{O}^+]}{2\Delta t} = \frac{-(-0.0017 \text{ M})}{2(10 \text{ s})} = 8.5 \times 10^{-5} \text{ M/s}$$

From the change in bromine concentration,

$$\text{rate} = \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{0.0008 \text{ M}}{10 \text{ s}} = 8 \times 10^{-5} \text{ M/s}$$

Concentration and Rate

In general rates:

Increases when reactant concentration is increased.

Decrease as the concentration of reactants is reduced.

The overall concentration dependence of reaction rate is given in a **rate law** or rate expression

For the general reaction: $aA + \dots \longrightarrow bB + cC + dD$

$$\text{Rate} = k [\text{reactant 1}]^m [\text{reactant 2}]^n = k [A]^m [B]^n$$

k: rate constant

The exponent m and n are called **reaction orders**. The overall reaction order is the sum of the reaction orders. The overall order of the reaction is $m + n + \dots$

For the reaction: $\text{NH}_4^+ (aq) + \text{NO}_2^- (aq) \longrightarrow \text{N}_2 (g) + 2 \text{H}_2\text{O} (l)$

$$\text{Rate} = k [\text{NH}_4^+][\text{NO}_2^-]$$

The reaction is said to be first order in $[\text{NH}_4^+]$ first order in $[\text{NO}_2^-]$ and second order overall.

Note that reaction orders must be determined experimentally.

They do **not necessarily** correspond to the **stoichiometric coefficients** in the balanced chemical equation.

We commonly encounter reaction orders of 0, 1, 2.

Even fractional or negative values are possible.

Using Initial Rates to Determine Rate Laws.

To **determine the rate law, we observe the effect of changing initial concentrations.**

If a reaction is zero order in a reactant, changing the initial concentration of that reactant will have no effect on rate.

If a reaction is first order, doubling the concentration will cause the rate to double.

If a reaction is second order, doubling the concentration will result in a 2^2 increase in rate.

Similarly, tripling the concentration results in a 3^2 increase in rate.

A reaction is n th order if doubling the concentration causes a 2^n increase in rate.

Note:

- 1) The **RATE**, not the rate constant, depends on **CONCENTRATION**.
- 2) The **RATE CONSTANT (k)** is affected by **TEMPERATURE** and by the presence of a **CATALYST**.

The Change of Concentration with Time

Goal: Convert the rate Law into a convenient equation that gives concentration as a function of time.

First –Order Reactions

For first order reaction, the **rate doubles** as the concentration of a **reactant doubles**.

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

A plot of $\ln[A]_t$ versus t is a straight line with slope $-k$ and intercept.

$[A]_0$ The concentration of A at the start of the reaction.

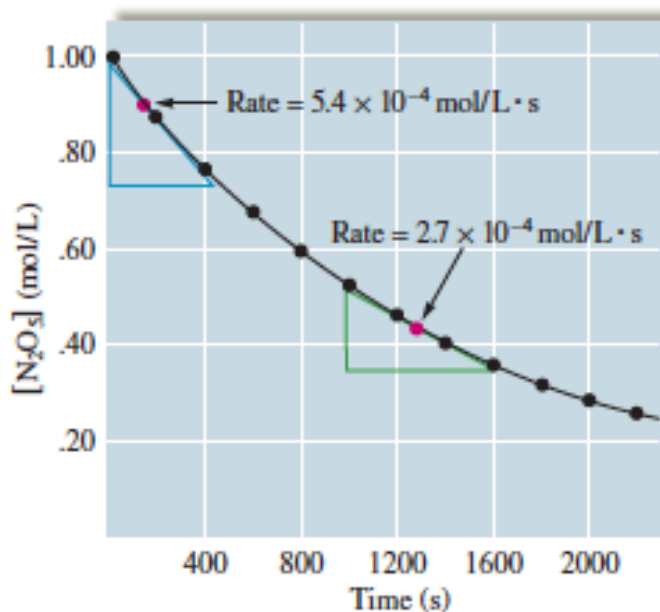
$[A]_t$ The concentration of A at any other time.

Use the natural logarithm, \ln (log to the base e).



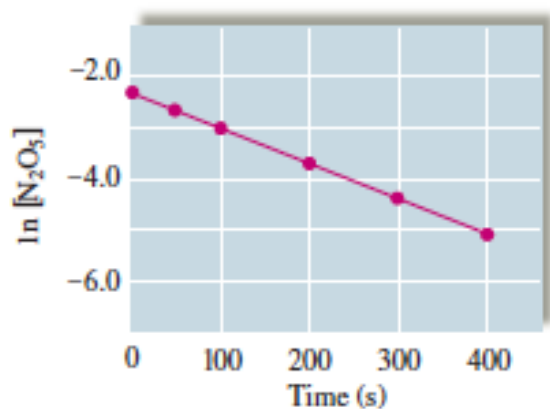
TABLE 12.3 Concentration/Time Data for the Reaction $2\text{N}_2\text{O}_5(\text{soln}) \rightarrow 4\text{NO}_2(\text{soln}) + \text{O}_2(\text{g})$ (at 45°C)

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000



$[\text{N}_2\text{O}_5]$	Rate (mol/L · s)
0.90 M	5.4×10^{-4}
0.45 M	2.7×10^{-4}

Example: $\ln[A]_t$ versus t is a straight line with slope $-k$ and intercept.



$\ln[\text{N}_2\text{O}_5]$	Time (s)
-2.303	0
-2.649	50
-2.996	100
-3.689	200
-4.382	300
-5.075	400

The following results were collected:

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

Half-life for First Order Reaction

Half-life $t_{1/2}$ is the time required for the concentration of a reactant to decrease to half its original value. That is half life $t_{1/2}$ is the time taken for $[A]_0$ to reach $\frac{1}{2} [A]_0$. Mathematically, the half-life of a **first order** reaction is:

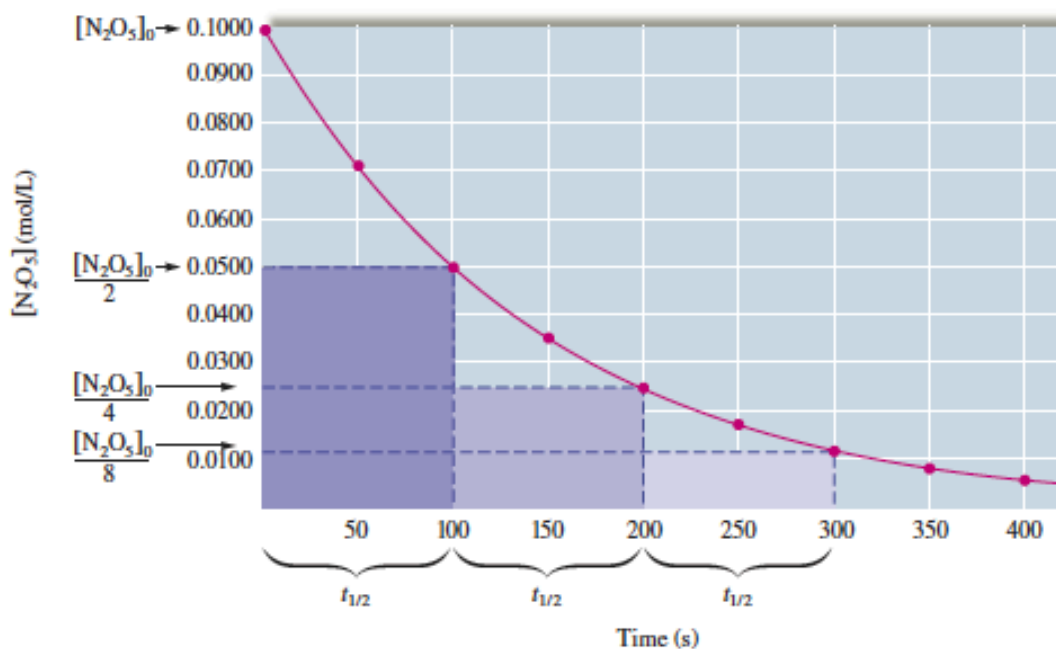
$$t_{1/2} = 0.693/k$$

Below is one example where half life is 100s: **Note that the half-life of a first order reaction is independent of the initial concentration of the reactant.** The concentration of the reactant decreases by $\frac{1}{2}$ in each of a series of regularly spaced time intervals, namely $t_{1/2}$.

$[N_2O_5]$ (mol/L)	Time (s)	$[N_2O_5]$ (mol/L)	t (s)
0.1000	0	0.100	0
0.0707	50	0.0500	100
0.0500	100	0.0250	200
0.0250	200	0.0125	300
0.0125	300	0.0125	300
0.00625	400		

$[N_2O_5]$ (mol/L)	t (s)
0.100	0
0.0500	100
0.0250	200
0.0125	300

$\Delta t = 100 \text{ s}; \frac{[N_2O_5]_{t=100}}{[N_2O_5]_{t=0}} = \frac{0.050}{0.100} = \frac{1}{2}$
 $\Delta t = 100 \text{ s}; \frac{[N_2O_5]_{t=200}}{[N_2O_5]_{t=100}} = \frac{0.025}{0.050} = \frac{1}{2}$
 $\Delta t = 100 \text{ s}; \frac{[N_2O_5]_{t=300}}{[N_2O_5]_{t=200}} = \frac{0.0125}{0.0250} = \frac{1}{2}$



Second-Order Reactions

A second order reaction **is one whose rate depends on the reactant concentration to the second power or on the concentration of two reactants each raised to the first power.** For a second-order reaction:

$$1/[A]_t = kt + 1/[A]_0$$

A plot $1/[A]_t$ of versus t is a straight line with slope k and intercept $1/[A]_0$
For the second order reaction, a plot of versus is not linear. A second order process can have a rate constant expression of the form:

$$\text{Rate} = k [A][B]$$

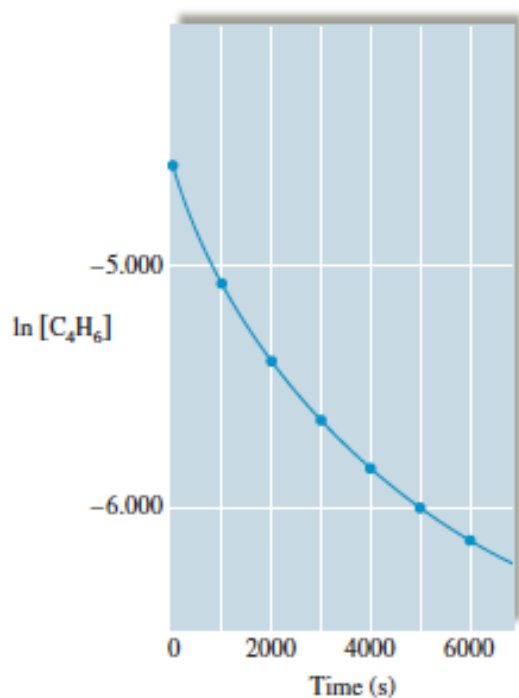
That is, the reaction is second order overall, but has first order dependence on A and B.

Example

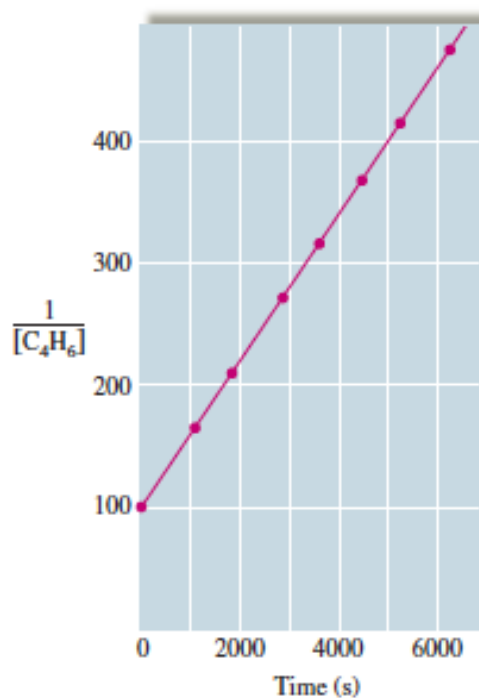


$[\text{C}_4\text{H}_6]$ (mol/L)	Time (± 1 s)
0.01000	0
0.00625	1000
0.00476	1800
0.00370	2800
0.00313	3600
0.00270	4400
0.00241	5200
0.00208	6200

t (s)	$\frac{1}{[\text{C}_4\text{H}_6]}$	$\ln[\text{C}_4\text{H}_6]$
0	100	-4.605
1000	160	-5.075
1800	210	-5.348
2800	270	-5.599
3600	320	-5.767
4400	370	-5.915
5200	415	-6.028
6200	481	-6.175



(a)



(b)

$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_6]}{\Delta t} = k[\text{C}_4\text{H}_6]^2$$

$$k = \text{slope} = \frac{(481 - 100) \text{ L/mol}}{(6200. - 0) \text{ s}} = \frac{381}{6200.} \text{ L/mol} \cdot \text{s} = 6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s}$$

Half-life for Second-Order Reaction

Half-life $t_{1/2}$ is the time required for the concentration of a reactant to decrease to half its original value. That is half life $t_{1/2}$ is the time taken for $[A]_0$ to reach $\frac{1}{2} [A]_0$

In contrast to the behavior of first-order reactions, the half-life for **second order** and other reactions depends on reactant concentrations and therefore changes as the reactions progresses.

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

For the example above:

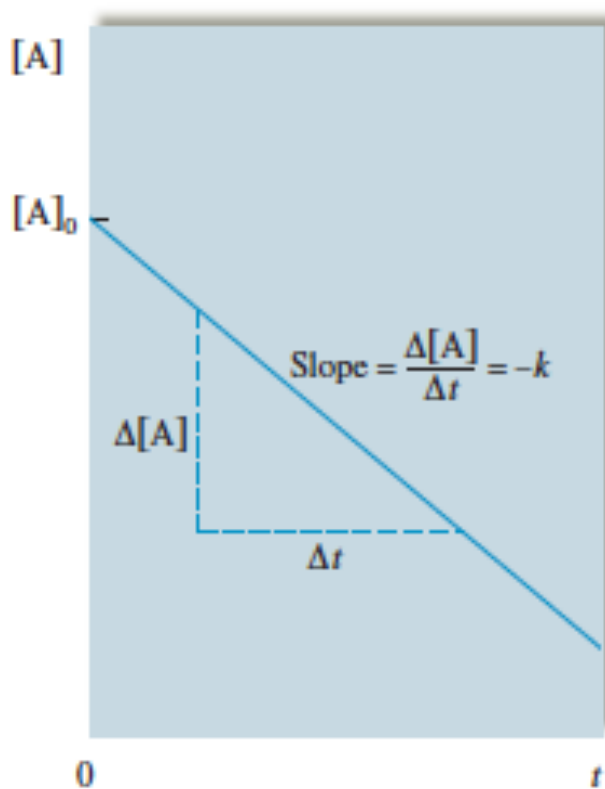
$$t_{1/2} = \frac{1}{(6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s})(1.000 \times 10^{-2} \text{ mol/L})} = 1.63 \times 10^3 \text{ s}$$

Zero-Order Rate Laws

For zero-order reaction, the rate is constant. It does not change with concentration as it does for first-order or second-order. The integrated rate law for zero-order reaction is:

$$[A] = -kt + [A]_0$$

In this case, a plot of $[A]$ versus t is a straight line of slope $-k$.



Half-life for Zero-Order Reaction

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

Summary

TABLE 12.6 Summary of the Kinetics for Reactions of the Type $aA \rightarrow$ Products That Are Zero, First, or Second Order In $[A]$

	Order		
	<i>Zero</i>	<i>First</i>	<i>Second</i>
Rate Law:	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated Rate Law:	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot Needed to Give a Straight Line:	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = k
Half-Life:	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Temperature and Rate

As the temperature increases, the rate increases

The Collision Model

Rates of reactions are affected by concentration and temperature.

We need to develop a model that explains this observation. An explanation is provided by the collision model, based on kinetic-molecular theory.

In order for molecules to react, they must collide. The greater the number of collisions, the faster the react.

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

The higher the temperature, the more energy available to the molecules and the more frequently the molecules collide. Thus rate should increase with an increase in temperature.

However, not all collision lead to products (only small fraction of collision lead to products). Two factors are involved: the orientation factor and the energy factor.

a) The Orientation Factor

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

In order for a reaction to occur, the reactant molecules must collide in the correct orientation and with enough energy to form products.

b) Activation Energy

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

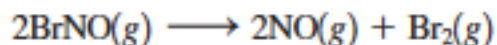
In order for form products, bonds must be broken in the reactants.

Bond breakage requires energy. Molecules moving too slowly, with too little kinetic energy, don't react when they collide.

Activation energy, E_a : is the minimum energy required to initiate a chemical reaction. E_a will vary with the reaction.

The rate depends on the magnitude of the E_a . In general, **the lower the E_a , the faster the rate.**

Example; The decomposition of BrNO in the gas phase.

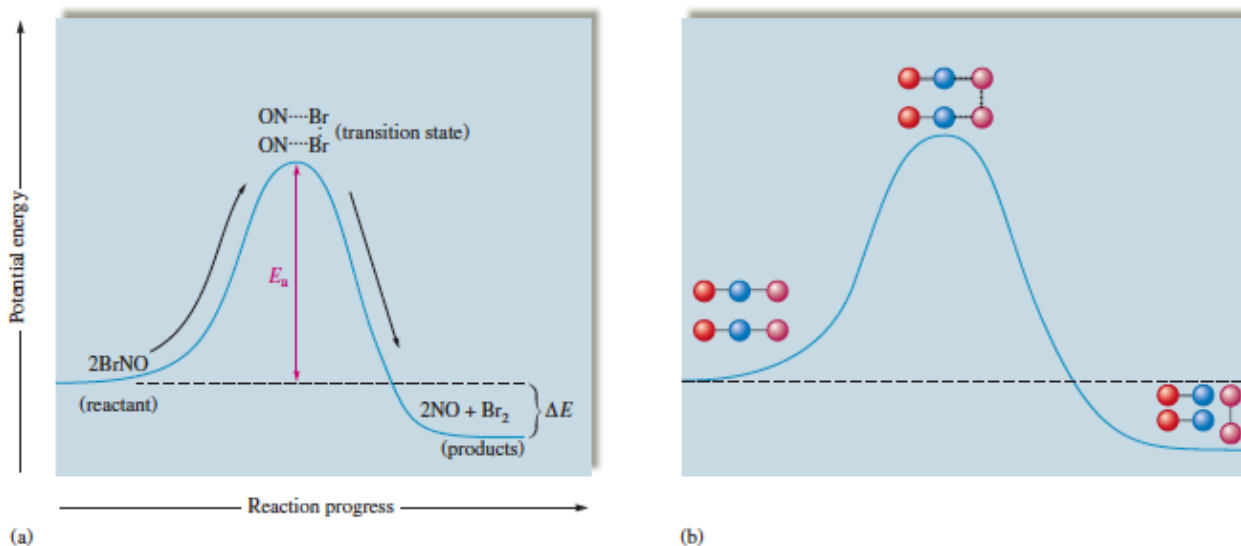


In the reaction, two Br-N must be broken and Br-Br bond must be formed.

The change in the energy for the reaction is the difference in energy between the reactant and the product. E_{rxn} has no effect on reaction rate.

The species at the top barrier is called the **activated complex or transition state**.

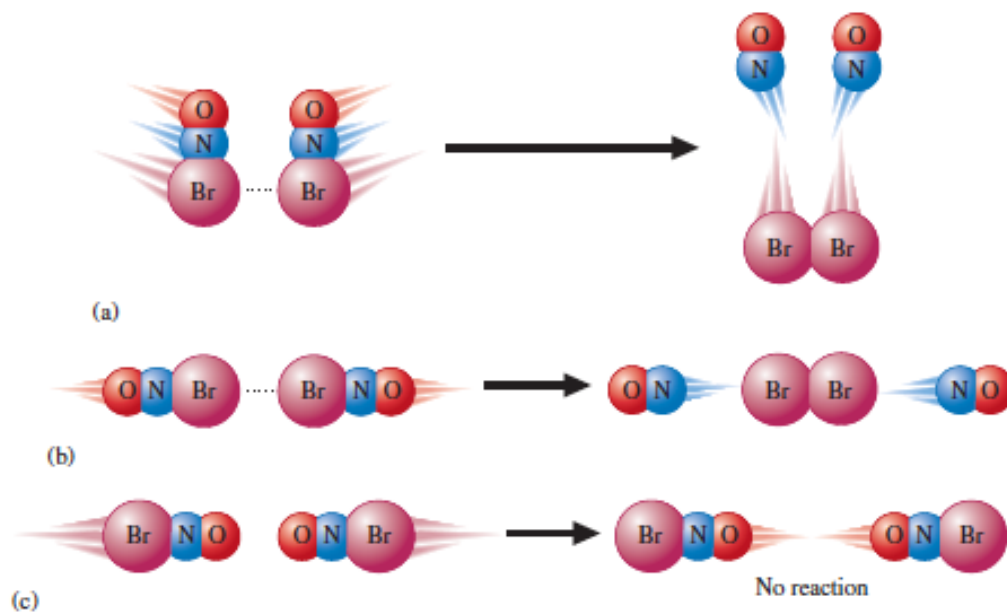
The activation energy is the difference between **reactants and the transition state**.



To summarize, two requirements must be satisfied for reactants to collide successfully (to rearrange to form products):

1. The collision must involve enough energy to produce the reaction; that is, the collision energy must equal or exceed the activation energy.
2. The relative orientation of the reactants must allow formation of any new bonds necessary to produce products.

Example of the molecular orientation during collisions.



Orientation (a) and (b) lead to a reaction, but orientation (c) can not.

How does this relate to temperature?

The fraction of molecules with energy equal to or greater than E_a is given by:

$$f = e^{-E_a/RT}$$

Molecules that have energy equal to or greater than E_a have sufficient energy to react.

As we increase the temperature, the fraction of the population that has an energy equal to or greater than E_a increases. Thus more molecules can react.

The Arrhenius Equation

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

- 1) The number of collision 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 equal to or greater than E_a .

From these observations Arrhenius developed the Arrhenius equation.

$$k = Ae^{-E_a/RT}$$

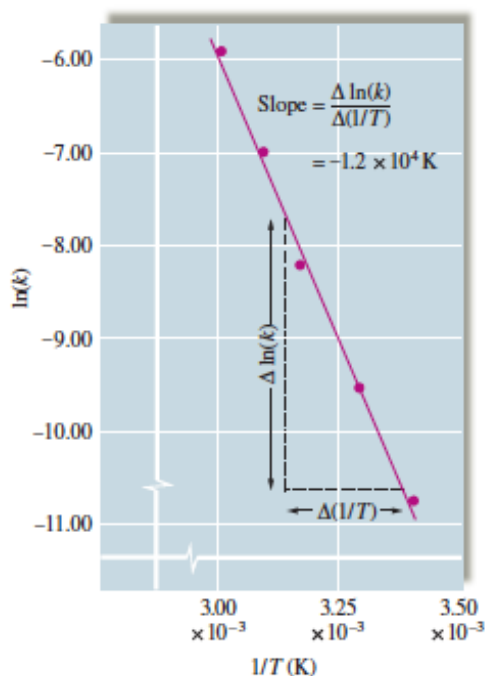
Where k is the rate constant, E_a is the activation energy, R is the ideal gas constant (8.314 J/K.mol) and T is the temperature in K. A is the frequency factor. Both A and E_a are specific to a given reaction.

Determining the Activation Energy (E_a)

E_a may be determined experimentally. Taken the natural log of both sides of the Arrhenius equation:

$$\ln k = -E_a/RT + \ln A$$

A graph of $\ln k$ vs $1/T$ will have a slope of $-E_a/R$ and a y-intercept of $\ln A$. Example below: $-E_a/R = -1.2 \times 10^4 \text{K}$. So, $E_a = -(8.3145 \text{ J/K.mole})(-1.2 \times 10^4 \text{K}) = 1.0 \times 10^5 \text{ J/mole}$



Alternatively we can use:

$$\ln k_1/k_2 = E_a/R (1/T_2 - 1/T_1)$$

Reaction Mechanisms

The balanced chemical equation provides information about substances present at the beginning and end of the reaction.

The reaction mechanism is the process by which the reaction occurs. Mechanisms provide a picture of which bonds are broken and formed during the course of to reaction.

Elementary Steps

Elementary steps are any processes that occur in a single step.

The number of molecules present in an elementary step is the molecularity of that elementary step.

Unimolecular: one molecule in the elementary step.

Bimolecular: Two molecules in the elementary step.

Termolecular: Three molecules in the elementary step (is not common).

Multistep Mechanisms

A multistep mechanism consists of a sequence of elementary steps.

The elementary steps must add to give the balanced chemical equation.

Some multistep mechanisms will include intermediates. These are species that appear in an elementary step but are neither a reactant nor product. They are not found in the balanced equation for the overall reaction.

Rate Laws of Elementary Steps

The rate laws of the elementary steps determine the overall rate law of the reaction.

The rate law of an elementary steps determined by its molecularly.

Unimolecular processes are first order.

Bimolecular processes are second order.

Termolecular processes are third order.

TABLE 12.7 Examples of Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{products}$	<i>Unimolecular</i>	$\text{Rate} = k[A]$
$A + A \rightarrow \text{products}$ ($2A \rightarrow \text{products}$)	<i>Bimolecular</i>	$\text{Rate} = k[A]^2$
$A + B \rightarrow \text{products}$	<i>Bimolecular</i>	$\text{Rate} = k[A][B]$
$A + A + B \rightarrow \text{products}$ ($2A + B \rightarrow \text{products}$)	<i>Termolecular</i>	$\text{Rate} = k[A]^2[B]$
$A + B + C \rightarrow \text{products}$	<i>Termolecular</i>	$\text{Rate} = k[A][B][C]$

Rate Laws for Multistep Mechanisms.

Most reactions occurs by mechanisms with more than one elementary step, often one step is much slower than the others.

The **slow step limit the overall reaction rate**. This is called the **rate-determining step** (rate –limiting step) of the reaction. This step governs the overall rate law for the overall reaction. The theoretical rate law is in agreement with the experimental rate law.

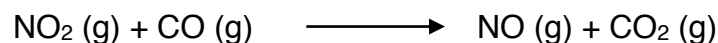
Summary:

We can now define a reaction mechanism more precisely. It is a series of elementary steps that must satisfy two requirements:

1. The sum of the elementary steps must give the overall balanced equation for the reaction.
2. The mechanism must agree with the experimentally determined rate law.

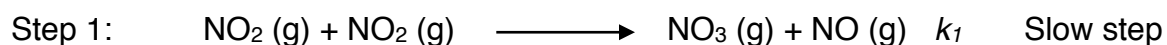
Example:

Consider this reaction:



The experimentally derived rate law is : $\text{Rate} = K [\text{NO}_2]^2$

We propose a mechanism for the reaction:



Note that NO_3 is an intermediate

If $k_2 \gg k_1$, then the overall reaction will depend on the first step (the rate determining step)

$$\text{Rate} = k_1 [\text{NO}_2]^2$$

This theoretical rate is in agreement with the experimental rate law.

Catalysis

A catalyst is a substance that changes the rate of a chemical reaction without itself undergoing a permanent chemical change in the process.

There are two types of catalyst: homogeneous, heterogeneous. Catalysts are common in the body, in the environment, and in the chemistry lab.

A homogeneous catalyst is one that is present in the same phase as the reacting molecules.

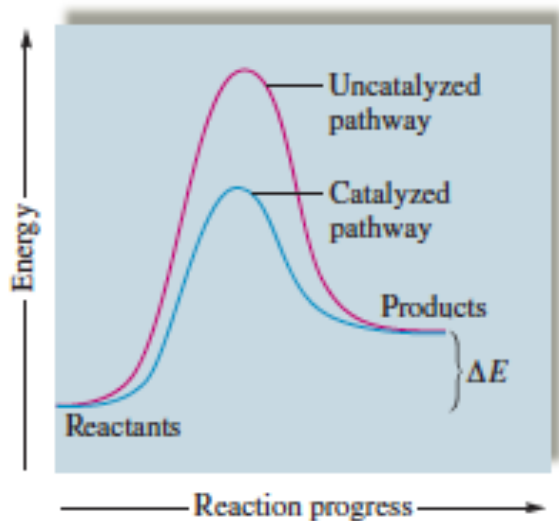
How do catalysts increase reaction rates?

In general, catalysts operate by **lowering the overall activation energy** for a reaction.

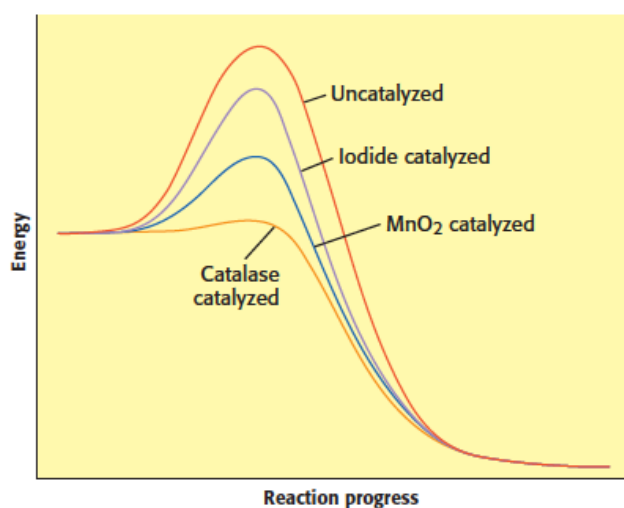
However, catalysts can also operate by increasing the number of effective collisions.

A catalyst usually provides a completely different mechanism for the reaction.

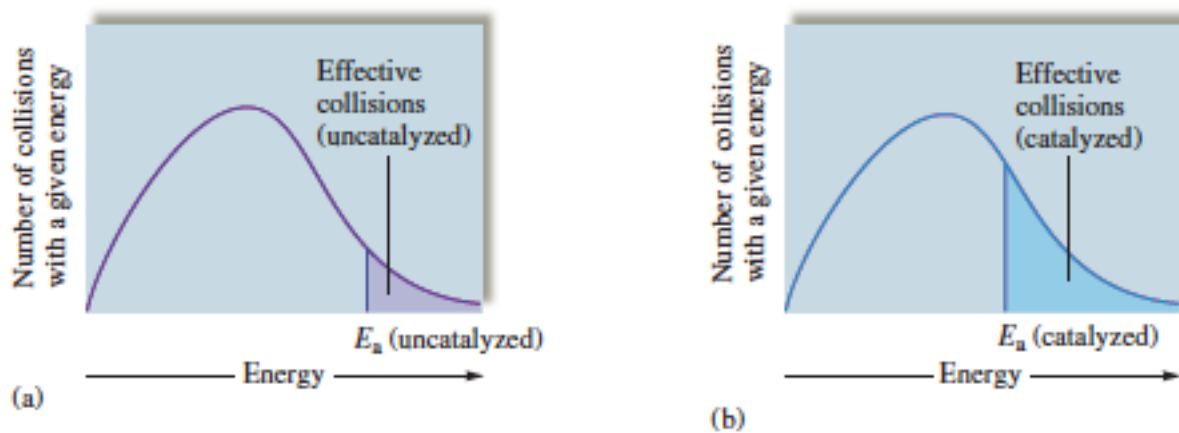
When a catalyst adds an intermediate, the activation energies for both steps must be lower than the activation energy for the un-catalyzed reaction.



Comparison of Pathways for the Decomposition of H_2O_2

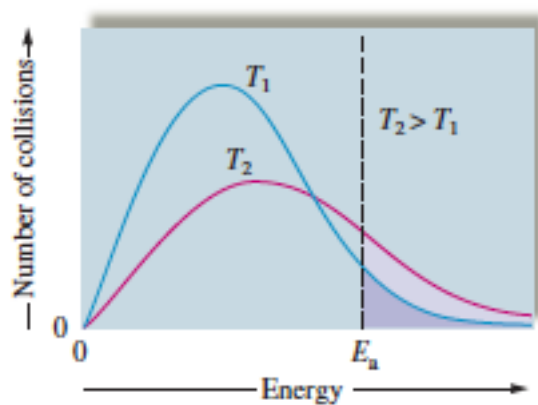


Catalyst can operate by increasing the number of effective collisions.



The higher the temperature, the more energy available to the molecules and the more frequently the molecules collide. Thus rate should increase with an increase in temperature.

However, not all collision lead to products (only small fraction of collision lead to products)



Heterogeneous Catalysis

A heterogeneous catalyst exist in a different phase that the reactants. Often we encounter a situation involving a solid catalyst in contact with gaseous reactants and gaseous products or with reactant in a liquid.

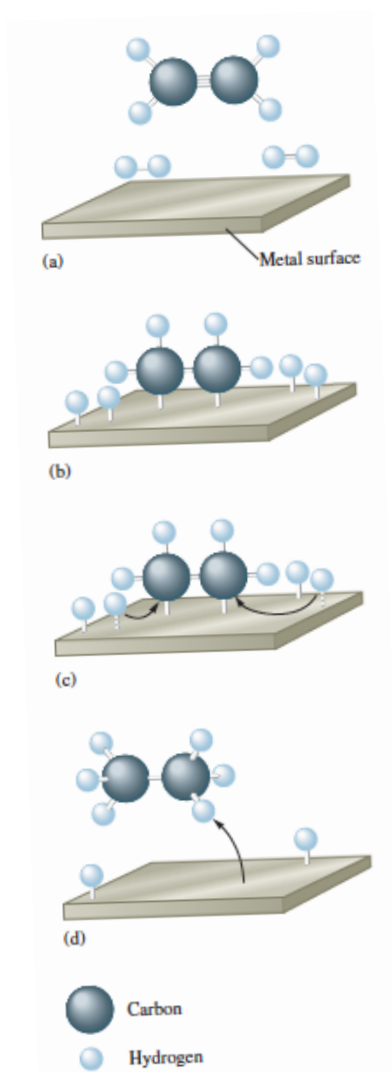
How do they do their job?

The first step is adsorption (the binding of reactant molecules of the catalyst surface). Adsorption occurs due to the high reactivity of atoms or ions on the surface of the solid. Molecules are adsorbed onto active site on the catalyst surface. Less energy is required to break the bond. The activation energy for the reaction is lowered. Thus the rate is increased.

Metal catalyst (Ni, Pt or Pd)

H-H bond breaks and the H atoms migrate about the metal surface.

When H atoms collides with an ethylene molecules on the surface the C-C bond breaks and C-H bond forms.



Enzymes

Enzymes are biological catalyst. Most **enzymes are large protein molecules**.

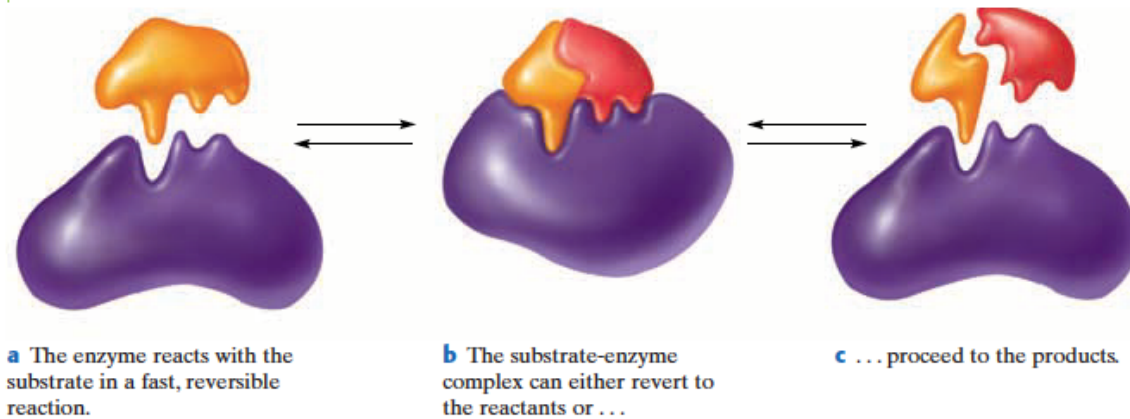
The enzyme catalyzes the reaction at its **active site**.

The substance that undergo reaction at the active site on enzymes are called **substrates**.

A simple view of enzyme specificity is the lock-and key model.

Enzymes are extremely efficient catalysts.

The number of individual catalytic events occurring at an active site per unit time is called the turnover number (typically 10³-10⁷ per second).



If a molecule binds so tightly to an enzyme that substrate molecules cannot displace it, then the **active site is blocked** and the **catalyst is inhibited**. Such molecules are called **enzyme inhibitors**. Inhibitors can be reversible or irreversible.

Example is shown below with the enzyme succinate dehydrogenase. Succinate is a substrate (a) . Malonate is an inhibitor (b).

