CHEMICAL KINETICS

- Kinetics - Concept of activation energy and energy barrier
- Arrhenius equation- effect of catalysts (homo and heterogeneous)
- Enzyme catalysis (lock and key mechanism)

Thermodynamics favors the process (ΔG: -ve)

Kinetics makes this reaction nearly impossible

(Requires a very high pressure and temperature over long time)

Why Chemical Kinetics?

Thermodynamics:

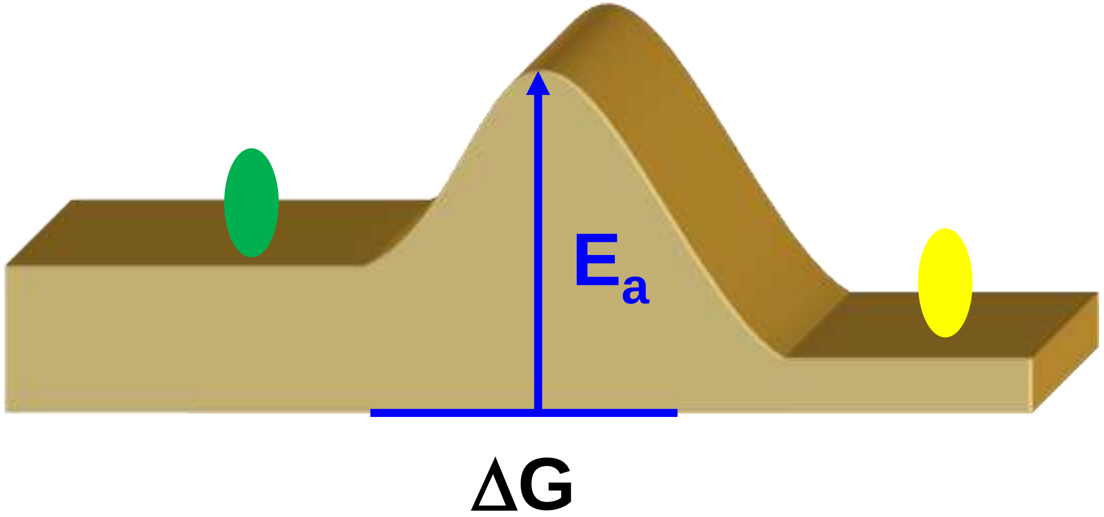
Is the reaction feasible? ($\Delta_r G$ = – ve?)

Which product is stable? (at equilibrium)

Kinetics:

How fast (rate) is the chemical process!

Mechanism of reaction! (any intermediate!)



- The chemistry that deals with the reaction rates is known as **chemical kinetics**.
- It plays an important role in the production of chemicals on an industrial scale and the decay of radioactive isotopes used in medicine.
- Chemical kinetics is also useful in providing information about how reactions occur—the order in which chemical bonds are broken and formed during the course of a reaction.
- Experimental information on the rate of a given reaction provides important evidence that helps us formulate a *reaction mechanism*, which is a step-by-step, molecular-level view of the pathway from reactants to products.

It is to be contrasted with thermodynamics, which deals with the direction in which a process occurs but in itself tells nothing about its rate

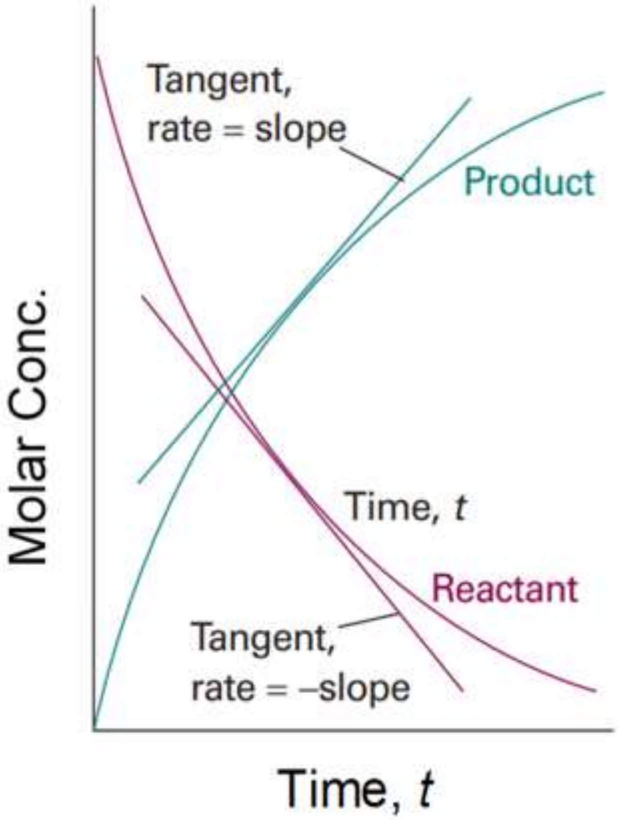
Factors That Affect Reaction Rates:

1. ***Physical state of the reactants-*** *homogeneous*, involving either all gases or all liquids, or as *heterogeneous*, in which reactants are in different phases.
2. ***Reactant concentrations.***
3. ***Reaction temperature.***
4. ***The presence of a catalyst.***

Reaction Rates

On a molecular level, reaction rates depend on the frequency of collisions between molecules. *The greater the frequency of collisions, the higher the reaction rate.*

- ➢ The change in concentration of reactants or products per unit time.
- ➢ Here, the instantaneous rate of disappearance of one of the reactants (A or B) at a given time, t (at constant volume) is −d[R]/dt.
- ➢ Similarly, the rate of formation of one of the products is d[P]/dt. (*Note the change in the sign*)
- ➢ The negative sign indicates that the concentration is decreasing with time.



Concentration and **the rates of reactions**

Consider a general reaction, $\mathbf{A + B \rightarrow C}$

- The rate of this reaction can be expressed either as the rate of disappearance of reactant ‘A’ and ‘B’ or as the rate of appearance of product ‘C’.
- The rate of reaction will be:
- **Average rate of appearance /disappearance of A, B or C = $\frac{\text{change in concentration of A, B or C}}{\text{change in time}}$**

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

Now, consider another general reaction: $\mathbf{aA + bB \rightarrow cC + dD}$

where a, b, c & d are stoichiometric coefficients

The rate of reaction will be:

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

The rates of reactions

Sample Questions:

Write rate expressions for the following reactions:

1. $NO_2\ (g) + CO\ (g) \rightarrow NO\ (g) + CO_2\ (g)$
2. $2HI\ (g) \rightarrow H_2\ (g) + I_2\ (g)$

Solution:

1. $$-\frac{d[NO_2]}{dt} = -\frac{d[CO]}{dt} = \frac{d[NO]}{dt} = \frac{d[CO_2]}{dt}$$

2. $$-\frac{1}{2}\frac{d[HI]}{dt} = \frac{d[H_2]}{dt} = \frac{d[I_2]}{dt}$$

Rate laws and rate constants

- *The rate law is the relationship between the rate and the concentration*, *which are related by a proportionality constant ‘k’, known as* ***rate constant****.*

For the general reaction:

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

the rate law generally has the form

$$\text{rate} = k\,[A]^m[B]^n$$

where exponents ‘***m***’ and ‘***n***’ are **order of reaction in ‘A’ and ‘B’,** respectively and ‘***k***’ is the **rate constant**.

This above equation is called the ***rate law of the reaction***.

Exponents ‘***m*** ‘and ‘***n’*** are typically small whole numbers, whose values are not necessarily equal to the coefficients ‘***a’*** and ‘***b*** ‘from the balanced equation.

Rate laws and rate constants…

Important points about rate laws and rate constant:

- Rate law is a result of experimental observation. You **CANNOT** look at the stoichiometry of the reaction and predict the rate law (*unless the reaction is an elementary reaction*).
- The rate law is not limited to reactants. It can have a product term, For example: **rate =** $\boldsymbol{k\,[A]^m[B]^n[C]^c}$
- The rate constant is **independent of the concentrations** but **depends on the temperature.**
- The units for '*k*' vary. We can determine units for '*k*' by considering units for rate and for concentration.

Order of a reaction

- *It is the **sum of the exponents of the concentrations in the rate law equation***
- *It can be **integers, fractions, negative or positive.***
- *It can be **determined only experimentally***
- *It may **not be equal to the number of molecules of reactants***

Ex. For the reaction: **$A + B \rightarrow C$**

rate = $k\,[A]^m\,[B]^n$

- ***where, 'm'* is the order of reaction with respect to 'A', '*n*' is the order of reaction with respect to B.**
- ***The overall reaction order is the sum of the exponents in the rate law = $m + n$***

❖ **$m = 0$ (Zero order $k\,[A]^0$)**
❖ **$m = 1$ (First order $k\,[A]^1$)**
❖ **$m = 2$ (Second order $k\,[A]^2$)**

Examples:

$H_2 + Cl_2 \rightarrow 2HCl$.	Rate = $k\,[H_2]^0\,[Cl_2]^0$	**(Zero order)**
$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$	Rate = $k\,[SO_2Cl_2]^1$	**(First order)**
$2NO_2 \rightarrow 2\,NO + O_2$	Rate = $k\,[NO_2]^2$	**(Second order)**
$2NO(g) + 2H_2(g) \rightarrow 2N_2\,(g) + 2H_2O\,(g)$	Rate = $k\,[NO]^2\,[H_2]^1$	**(Third order)**
$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$	Rate = $k\,[CH_3COOC_2H_5]^1[H_2O]^0$	**(pseudo-first-order)**

Molecularity of a reaction

- ***It is the number of molecules or ions that participate in the 'rate determining step'***
- ***It is a 'theoretical concept' and it can be determined from 'rate determining step' (slowest step).***
- ***It is always an integer between 1 to 3, as*** *it is not possible to colliding of four or more molecules simultaneously**.***
- ***For elementary reactions (single step reactions):***
  - ***It is the sum of stoichiometry coefficients of the reactants***

    Ex. $H_2 + I_2 \rightarrow 2HI$

    Molecularity = 1 + 1 = 2
- ***For complex reactions:***
  - ***The sum of the number of reactant in the rate determining steps gives the molecularity***

First-Order Reactions

A **first-order reaction** is one whose rate depends on the concentration of a single reactant raised to the first power. If a reaction of the type **A → products** is first order, the rate law is:

$$\textbf{Rate} = -\frac{d[A]}{dt} = k[A]$$

Separate concentration and time terms

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

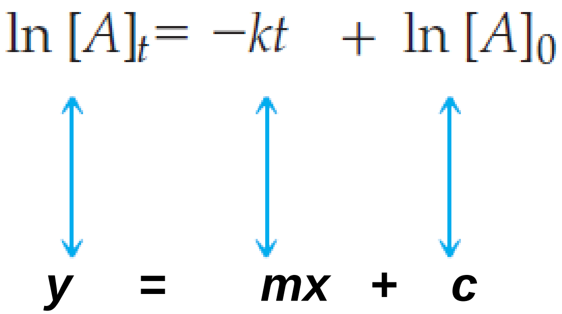
Integrating over the limits $[A]^0$ to $[A]^t$ and 0 to t,

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

$$\int_{[A]0}^{[A]t} \frac{d[A]}{[A]} = -k\int_{0}^{t} dt$$

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

Straight line equation ($y = mx + c$)

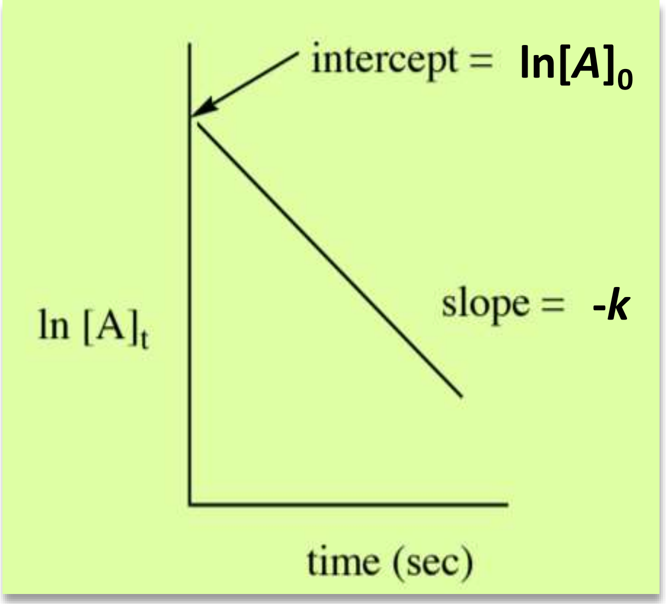


$$\ln [A]_t = -kt + \ln [A]_0$$

$$y = mx + c$$

If we plot ln $[A]_t$ versus time, then we will get a straight line having negative slope ($-k$).

Rate constants can be determined from experiment by plotting data in this manner.



Half-Life of First Order Reaction

The **half-life** of a reaction ($t_{1/2}$)

- It is the time required for the concentration of a reactant to reach half its initial value, **$[A]t_{1/2} = ½ [A]_0$.**
- Half-life is a convenient way to describe how fast a reaction occurs, especially if it is a first-order process.
- A fast reaction has a short half-life.
- We can determine the half-life of a first-order reaction by substitutin

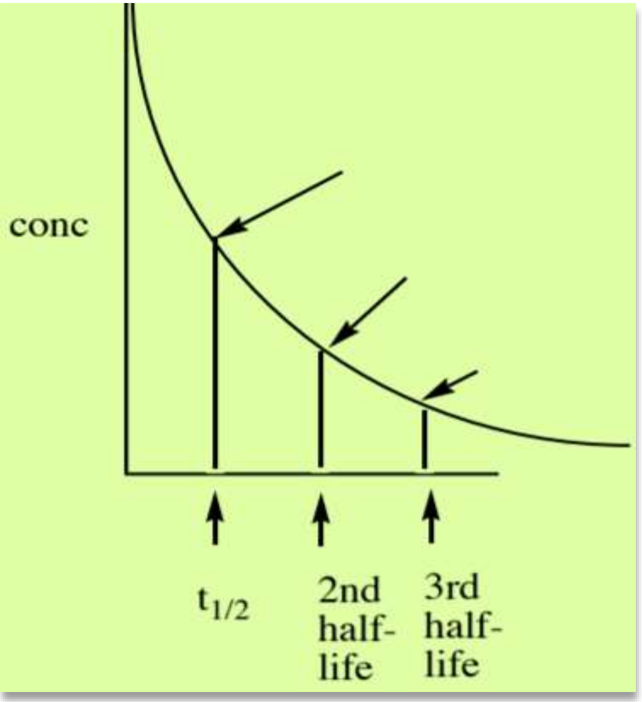
$[A]t_{1/2} = ½ [A]_0$ for **$[A]_t$** and **$t_{1/2}$** for ***t*** in Equation :

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

$$\ln \left[\frac{½ [A]_0}{[A]_0}\right] = -k\,t_{1/2}$$

$$\ln ½ = -k\,t_{1/2}$$

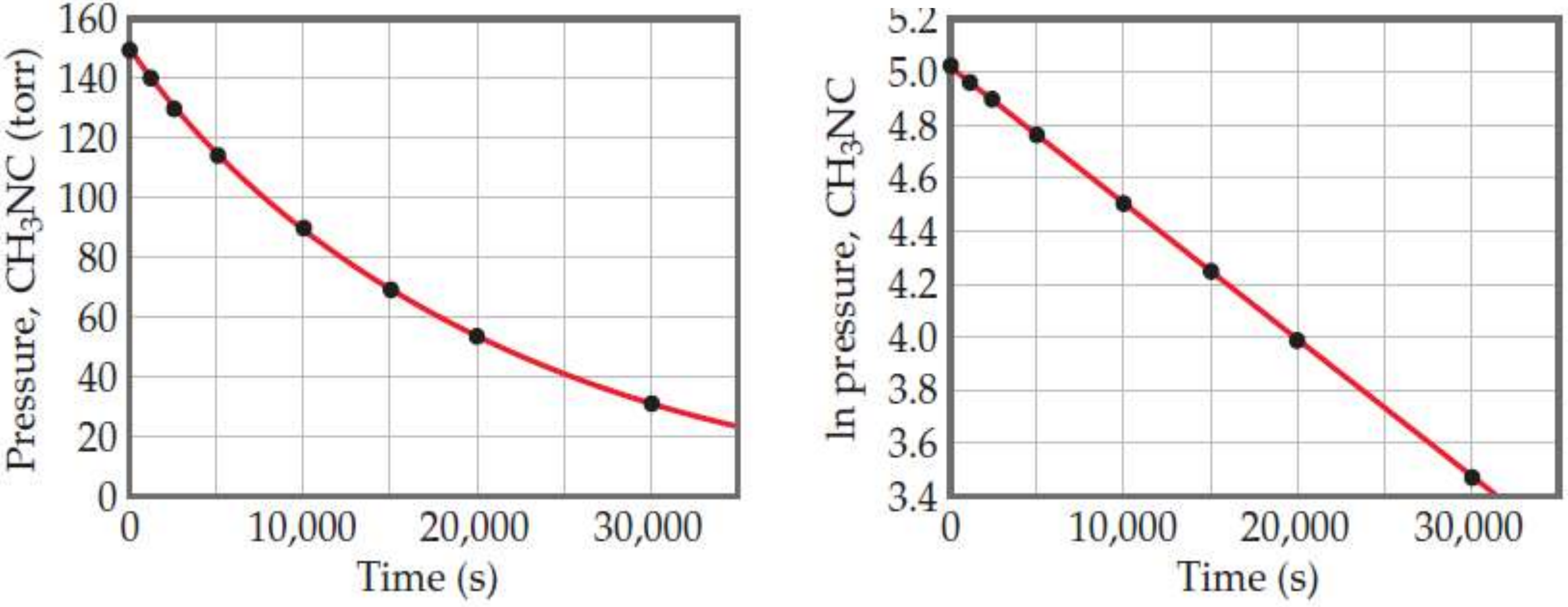
$$\boldsymbol{t_{1/2}} = \frac{-\ln ½}{k} = \frac{\mathbf{0.693}}{\boldsymbol{k}}$$



Ex. The conversion of methyl isonitrile (CH_3NC) to its isomer acetonitrile (CH_3CN) at 199 °C.

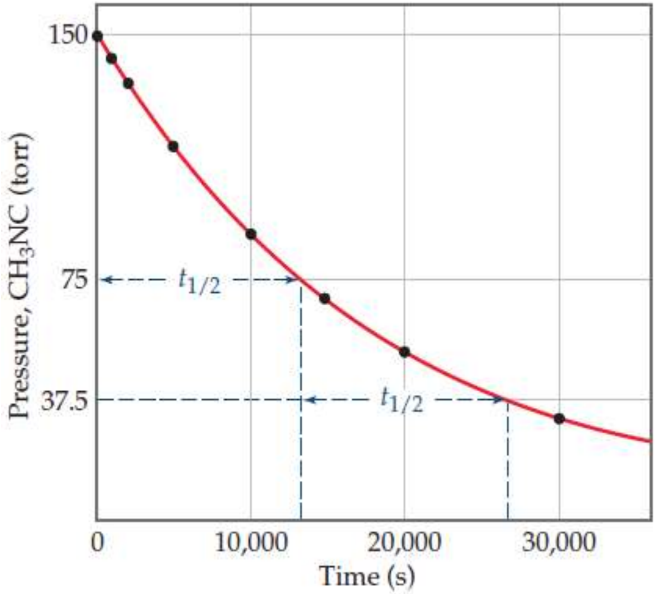
$$\ln[CH_3NC]_t = -kt + \ln[CH_3NC]_0$$

Kinetic data for conversion of methyl isonitrile into acetonitrile.



(a)

(b)



▲ **Figure** Kinetic data for the rearrangement of methyl isonitrile to acetonitrile at 199 °C, showing the half-life of the reaction.

Figure (**a**) shows how the pressure of this gas varies with time.

Figure (**b**) shows that a plot of the natural logarithm of the pressure versus time is a straight line.

The slope of this line is $-5.1 \times 10^{-5}\ s^{-1}$. $\therefore$ **$k = 5.1 \times 10^{-5}\ s^{-1}$**

1. The half-life of a first-order reaction was found to be 10 min at a certain temperature. What is its rate constant?

Solution: $k = 0.693/600\ \text{s} = 0.00115\ \text{s}^{-1}$

2. If 3.0 g of substance '*A*' decomposes for 36 minutes the mass of unreacted '*A*' remaining is found to be 0.375 g. What is the half-life of this reaction if it follows first-order kinetics?

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

Solution:

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

$$\ln \frac{[A]_t}{[A]_0} / t = -k$$

$$k = -\frac{\ln \frac{0.375g}{3g}}{36\,\text{min}}$$

$$\boldsymbol{k = 0.0578\ \text{min}^{-1}}$$

$$t_{1/2} = 0.693 / k$$
$$= 0.693/0.0578$$
$$= 12\ \text{min}$$

3. The decomposition of dimethyl ether, : $(CH_3)_2O$, at 510 °C is a first-order process with a rate constant of $6.8 \times 10^{-4}\ s^{-1}$: $(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$
If the initial pressure of $(CH_3)_2O$ is 135 torr, what is its pressure after 1420 s?

Solution:

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

$k = 6.8 \times 10^{-4}\ s^{-1}$

$[A]_0 = 135$ torr.

T = 1420 sec

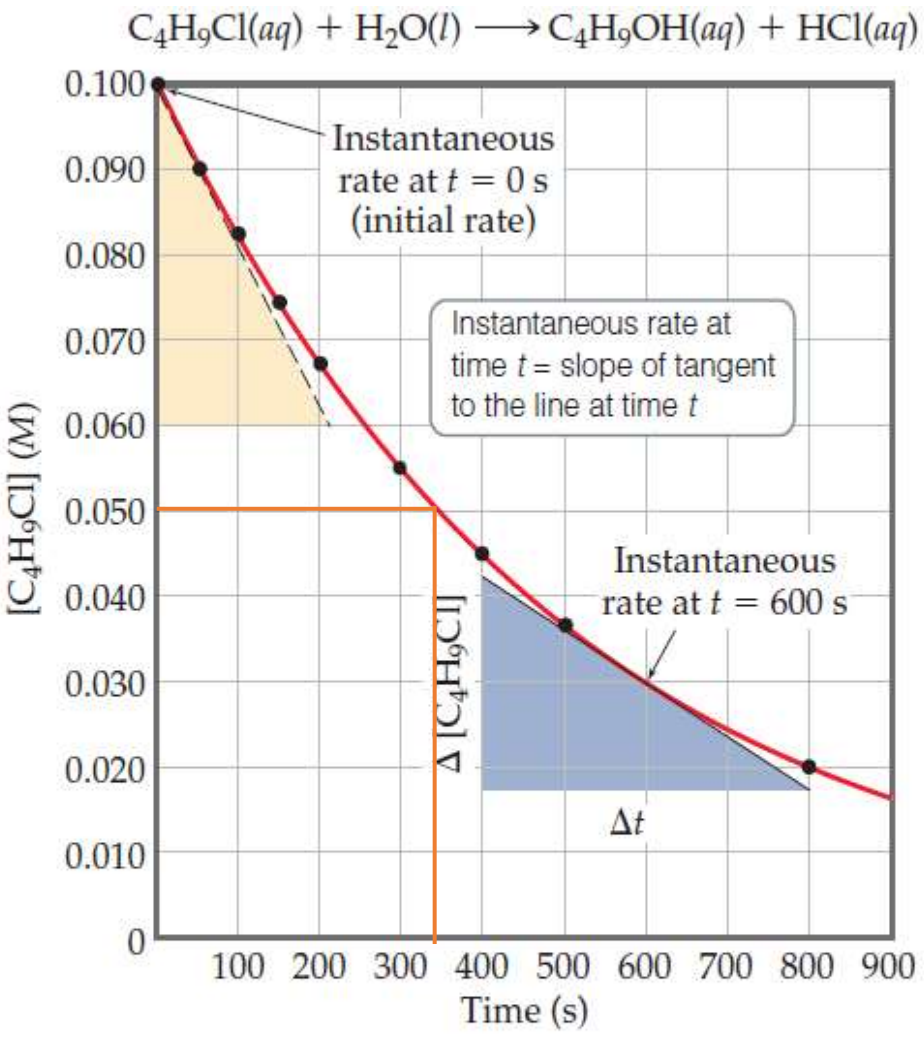
$[A]_t$ = ???

$$\ln [A]_t = \ln [135] - 6.8 \times 10^{-4} (1420) = \mathbf{3.939}$$

To obtain **pressure of $[(CH_3)_2O]_{(t\,=\,1420\ s)}$**, we use the **inverse natural logarithm, or e^x, function on the calculator**:

$$[(CH_3)_2O]_{(t\,=\,1420\ s)} = e^{3.939} = \mathbf{51.367\ torr}.$$

The reaction of C_4H_9Cl with water is a first-order reaction. (**a**) Use Figure 14.3 to estimate the half-life for this reaction. (**b**) Use the half-life from (a) to calculate the rate constant.



▲ Figure 14.3 Concentration of butyl chloride (C_4H_9Cl) as a function of time.

SOLUTION

(**a**) From the graph, we see that the initial value of $[C_4H_9Cl]$ is 0.100 *M*. The half-life for this first-order reaction is the time required for $[C_4H_9Cl]$ to decrease to 0.050 *M*, which we can read off the graph. This point occurs at approximately 340 s.

(**b**) Solving Equation 14.17 for *k*, we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{340\ \text{s}} = 2.0 \times 10^{-3}\ \text{s}^{-1}$$

Second-Order Reactions

A **second-order reaction** is one for which the rate depends either on a reactant concentration raised to the second power or on the concentrations of two reactants each raised to the first power.

Ex: in reactions **A ⟶ products** or **A + B ⟶ products** that are second order with respect to only one reactant, A:

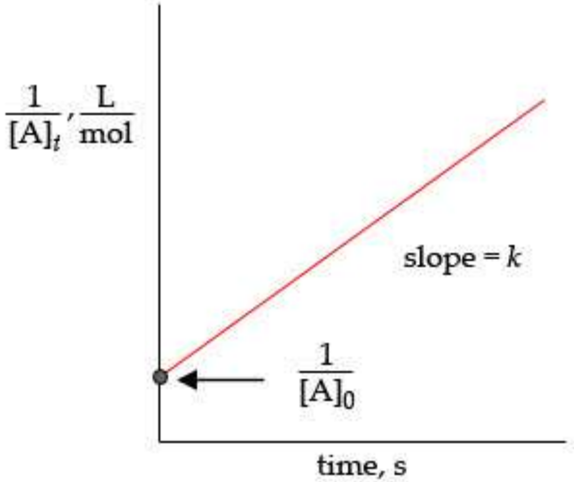
Rate = $$-\frac{d[A]}{dt} = k[A]^2$$

$$\frac{d[A]}{[A]^2} = -kdt$$

With the use of calculus, this differential rate law can be used to derive the integrated rate law for second-order reactions:

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

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



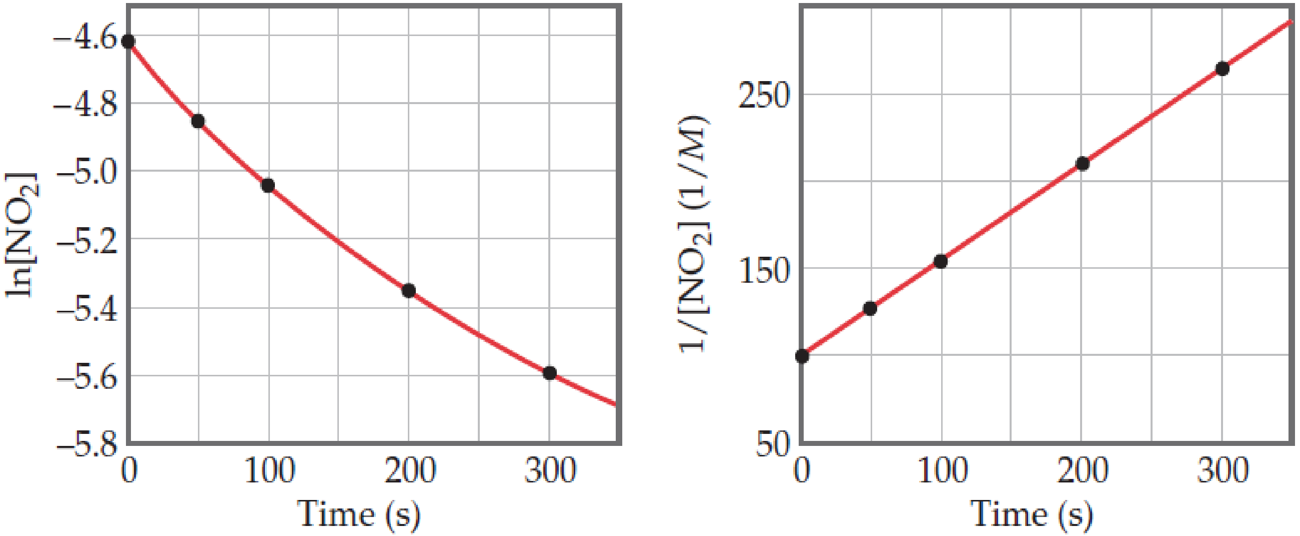
- This equation, has **four variables, *k*, *t*, $[A]_0$, and $[A]_t$,** and any one of these can be calculated knowing the other three.
- This Equation also has the form of a straight line (*y* = *mx* + *c*).
- **If the reaction is second order, a plot of '1/ $[A]_t$' versus '*t*' yields a straight line with slope *k* and *y*-intercept 1/ $[A]_0$.**
- **One way to distinguish between first and second-order rate laws is to graph both ln$[A]_t$ and 1/ $[A]_t$ against *t*.**
- **If the ln$[A]_t$ plot is linear, the reaction is first order;**
- **if the 1/ $[A]_t$ plot is linear, the reaction is second order.**

1. The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300 °C, $NO_2(g) \rightarrow NO(g) + 1/2\, O_2(g)$. Is the reaction first order or second order with respective to NO_2?

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

Solution: Plot **ln $[NO_2]$** and **1/ $[NO_2]$** against time.
If one plot or the other is linear, we will know the reaction is either first or second order.
To graph **ln $[NO_2]$** and **1/ $[NO_2]$** against time, we first make the following calculations from the data given:

Time (s)	$[NO_2]$(M)	ln $[NO_2]$	1/ $[NO_2]$ (1/M)
0.0	0.01000	-4.605	100
50.0	0.00787	-4.845	127
100.0	0.00649	-5.037	154
200.0	0.00481	-5.337	208
300.0	0.00380	-5.573	263



Kinetic data for decomposition of NO_2.

As **Figure** shows, only the plot of **1/ $[NO_2]$ versus time** is **linear.**
Thus, the reaction obeys a second-order rate law: Rate = $k\,[NO_2]^2$.
From the slope of this straight-line graph, we can determine that $k = 0.543\ M^{-1}\ s^{-1}$ for the disappearance of NO_2.

Half-Life of Second-Order Reactions

The half-life of a chemical reaction is the time taken for half of the initial amount of reactant to undergo the reaction.

Therefore, while attempting to calculate the half life of a reaction, the following substitutions must be made:

$$[A]_t = \frac{[A]_0}{2} \text{ and, } t = t_{1/2}$$

Now, substituting these values in the integral form of the rate equation of second order reactions, we get:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \quad \gg \quad \frac{1}{\frac{[A]_0}{2}} - \frac{1}{[A]_0} = k\, t_{1/2}$$

Therefore, the required equation for the half life of second order reactions can be written as follows.

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

This equation for the half life implies that the half life is inversely proportional to the concentration of the reactants.

Zero-Order Reactions

- We have seen that in a first-order reaction the concentration of a reactant ‘A’ decreases nonlinearly, as shown by the red curve in **Figure**.
- As [A] declines, the *rate* at which it disappears declines in proportion
- A **zero-order reaction** is one in which the rate of disappearance of A is *independent* of [A].
- The rate law for a zero-order reaction is

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^0$$

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

The integrated rate law for a zero-order reaction is

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

where $[A]_t$ is the concentration of A at time *t* and $[A]_0$ is the initial concentration.

This is the equation for a straight line with vertical intercept $[A]_0$ and slope -*k*, as shown in the blue curve in Figure.

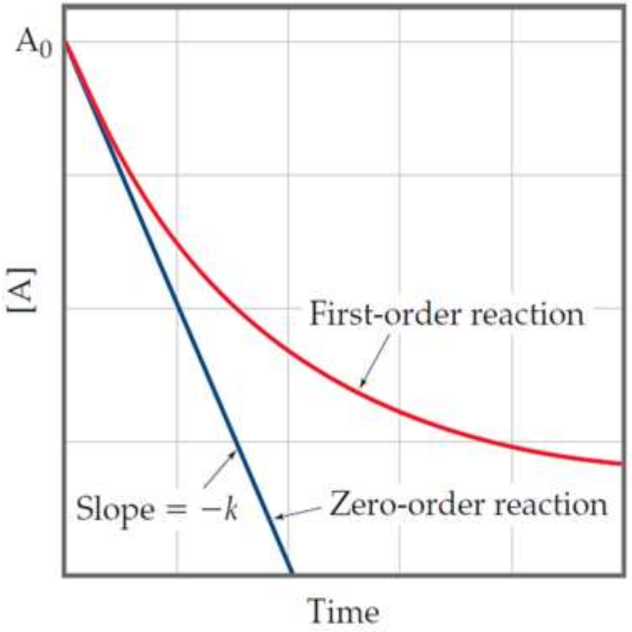


Figure. Comparison of first-order and zero-order reactions for the disappearance of reactant A with time

Ex. The **most common type of zero-order reaction** occurs when a **gas undergoes decomposition on the surface of a solid.**

$$2N_2O \xrightarrow{\text{Pt(hot)}} 2N_2 + O_2$$

Photochemical reaction:

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

Half-Life of a Zero Order Reaction

The timescale in which there is a 50% reduction in the initial population is referred to as half-life. Half-life is denoted by the symbol ‘$t_{1/2}$’.

From the initial form, we have the following equation

$[A]_t = [A_0] - k\,t$

Replacing t with half-life $t_{1/2}$ we get:

$\frac{1}{2}[A_0] = [A_0] - k\,t_{1/2}$

Therefore, $t_{1/2}$ can be written as:

$k\,t_{1/2} = \frac{1}{2}[A_0]$ ≫ $\boldsymbol{t_{1/2} = \frac{1}{2k}[A_0]}$

Pseudo First Order Reaction

A pseudo first-order reaction can be defined as a second-order or bimolecular reaction that is made to behave like a first-order reaction.

- This reaction occurs when one reacting material is present in great excess or is maintained at a constant concentration compared with the other substance.

$$A + B \rightarrow C$$

So, if component B is in large excess and the concentration of B is very high as compared to that of A, the reaction is considered to be a **pseudo-first-order reaction** with respect to A.

If component A is in large excess and the concentration of A is very high as compared to that of B, the reaction is considered to be pseudo-first order with respect to B.

For example:

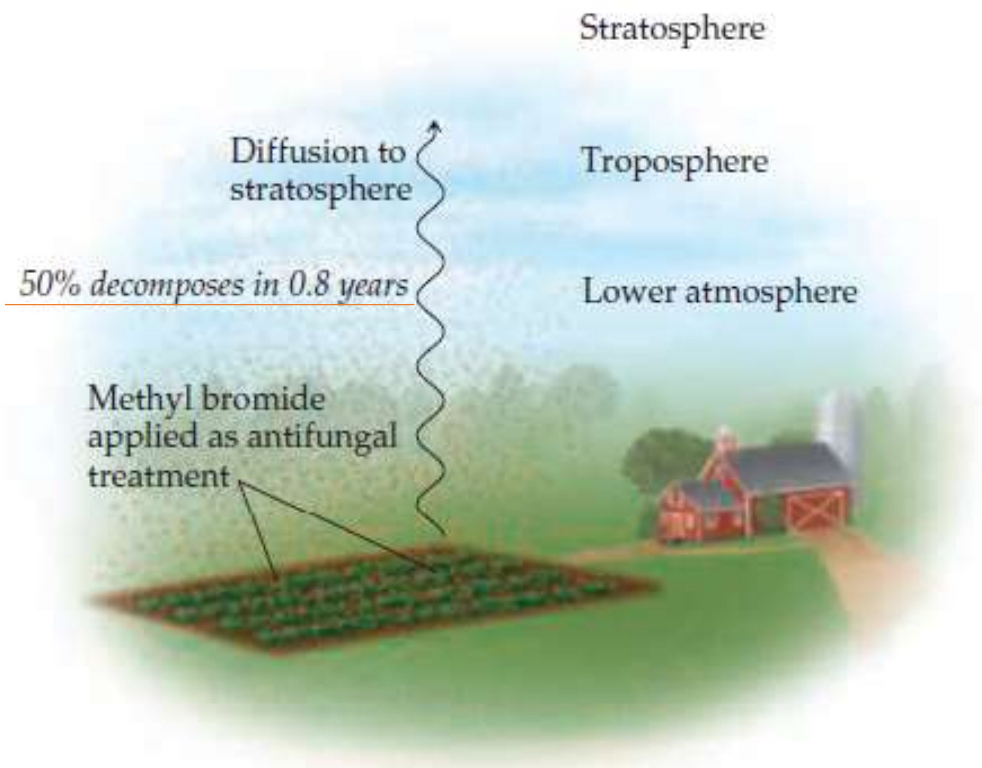
$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k\,[CH_3COOC_2H_5]$$

****The concentration of water is very high and thus does not change much during the course of the reaction.**

CHEMISTRY PUT TO WORK Methyl Bromide in the Atmosphere

The compounds known as chlorofluorocarbons (CFCs) are well-known agents responsible for the destruction of Earth's protective ozone layer. Another simple molecule that has the potential to destroy the stratospheric ozone layer is methyl bromide, CH_3Br (**Figure 14.11**). Because this substance has a wide range of uses, including antifungal treatment of plant seeds, it has been produced in large quantities in the past (about 150 million pounds per year worldwide in 1997, at the height of its production). In the stratosphere, the C—Br bond is broken through absorption of short-wavelength radiation. The resultant Br atoms then catalyze decomposition of O_3.



Distribution and fate of methyl bromide in Earth's atmosphere.

Methyl bromide is removed from the lower atmosphere by a variety of mechanisms, including a slow reaction with ocean water:

$$CH_3Br(g) + H_2O(l) \longrightarrow CH_3OH(aq) + HBr(aq) \qquad [14.18]$$

To determine the potential importance of CH_3Br in destruction of the ozone layer, it is important to know how rapidly the reaction in Equation 14.18 and all other reactions remove CH_3Br from the lower atmosphere before it can diffuse into the stratosphere.

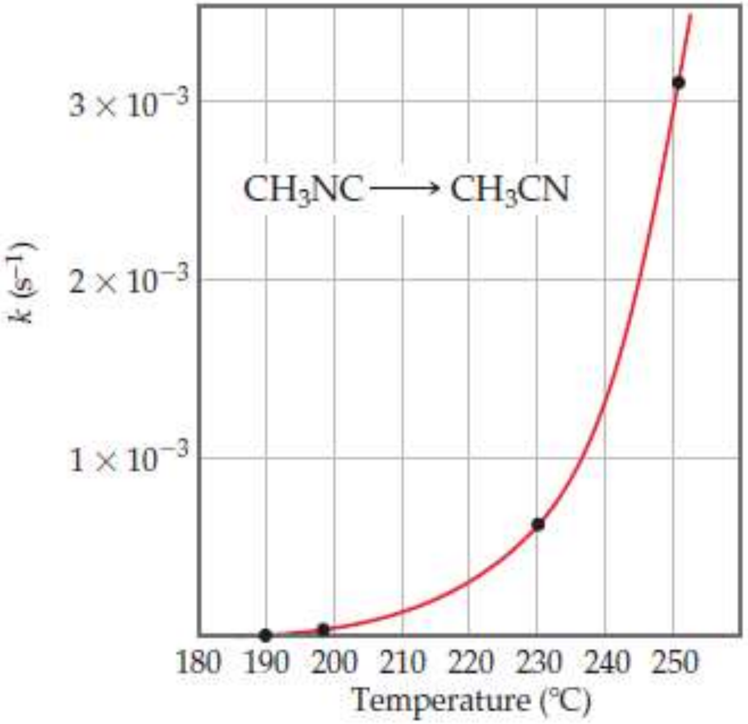
The average lifetime of CH_3Br in Earth's lower atmosphere is difficult to measure because the conditions that exist in the atmosphere are too complex to be simulated in the laboratory. Instead, scientists analyzed nearly 4000 atmospheric samples collected above the Pacific Ocean for the presence of several trace organic substances, including methyl bromide. From these measurements, it was possible to estimate the *atmospheric residence time* for CH_3Br.

The atmospheric residence time is related to the half-life for CH_3Br in the lower atmosphere, assuming CH_3Br decomposes by a first-order process. From the experimental data, the half-life for methyl bromide in the lower atmosphere is estimated to be 0.8 ± 0.1 yr. That is, a collection of CH_3Br molecules present at any given time will, on average, be 50% decomposed after 0.8 yr, 75% decomposed after 1.6 yr, and so on. A half-life of 0.8 yr, while comparatively short, is still sufficiently long so that CH_3Br contributes significantly to the destruction of the ozone layer.

In 1997 an international agreement was reached to phase out use of methyl bromide in developed countries by 2005. Although exemptions for critical agricultural use have been granted, global consumption in 2013 was only 3% of the levels seen in the early 1990s.

Temperature and Rate

- The rates of most chemical reactions increase as the temperature rises.
- The faster rate at higher temperature is due to an increase in the rate constant with increasing temperature.
- For example, $\mathbf{CH_3NC \rightarrow CH_3CN}$
- The rate constant and the rate of the reaction increase rapidly with temperature, approximately doubling for each 10 °C rise.



Temperature dependence of the rate constant for methyl isonitrile conversion to acetonitrile

The Collision Model

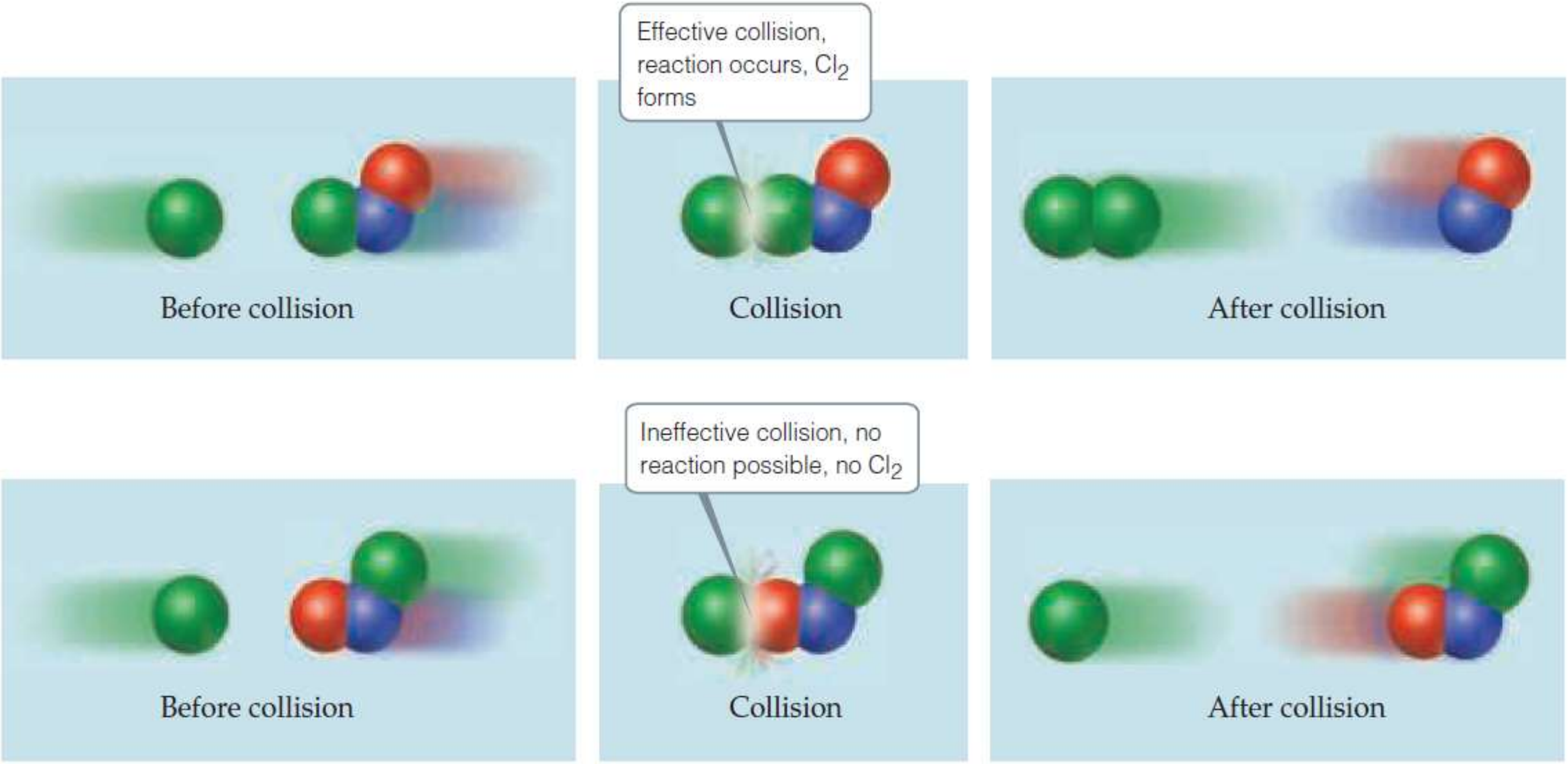
- *The greater the number of collisions per second, the greater the reaction rate.*
- *As reactant concentration increases, therefore, the number of collisions increases, leading to an increase in reaction rate.*
- *According to the kinetic-molecular theory of gases, increasing the temperature increases molecular speeds. As molecules move faster, they collide more forcefully (with more energy) and more frequently, both of which increase the reaction rate.*

The Orientation Factor:

- *In most reactions, collisions between molecules result in a chemical reaction only if the molecules are oriented in a certain way when they collide.*
- *The relative orientations of the molecules during collision determine whether the atoms are suitably positioned to form new bonds.*

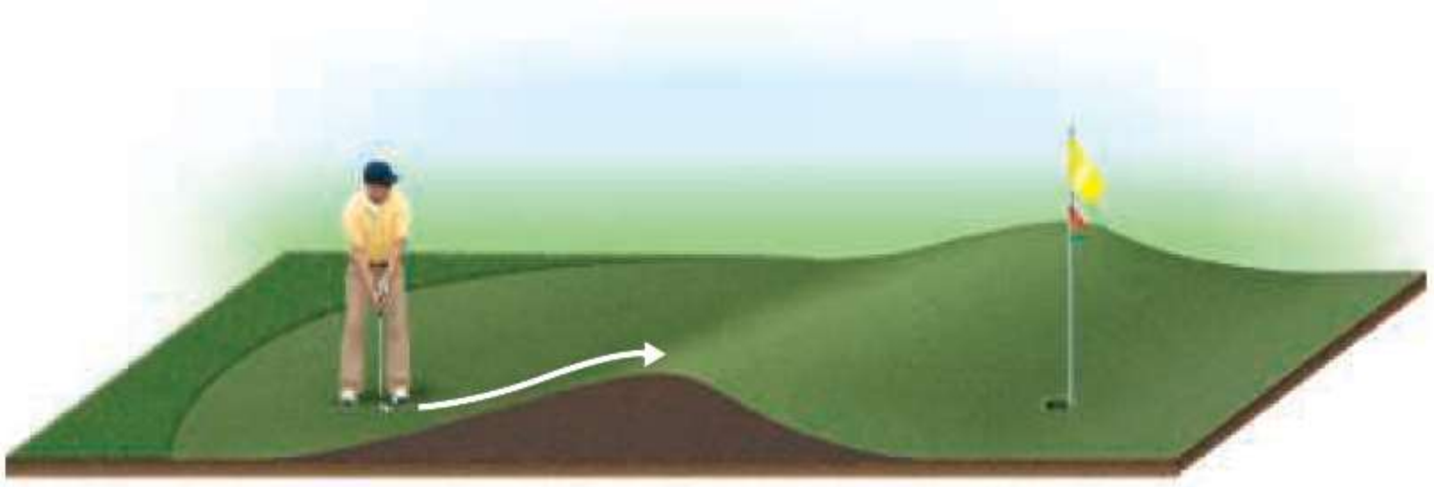
For example, **$Cl + NOCl \rightarrow NO + Cl_2$**

- **Molecular collisions may or may not lead to a chemical reaction between Cl and NOCl.**



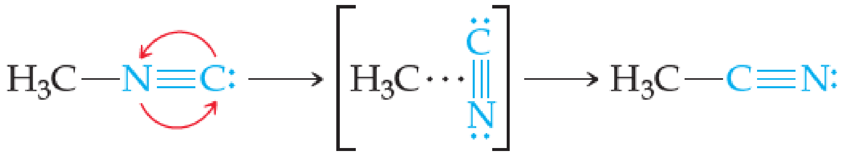
Activation Energy:

- *In 1888 the Swedish chemist Svante Arrhenius suggested that **molecules must possess a certain minimum amount of energy to react.***
- According to the collision model, **this energy comes from the kinetic energies of the colliding molecules.**
- Upon collision, **the kinetic energy of the molecules can be used to stretch, bend, and ultimately break bonds, leading to chemical reactions.**
- ***The minimum energy required to initiate a chemical reaction is called the 'activation energy' (E_a), and its value varies from reaction to reaction.***

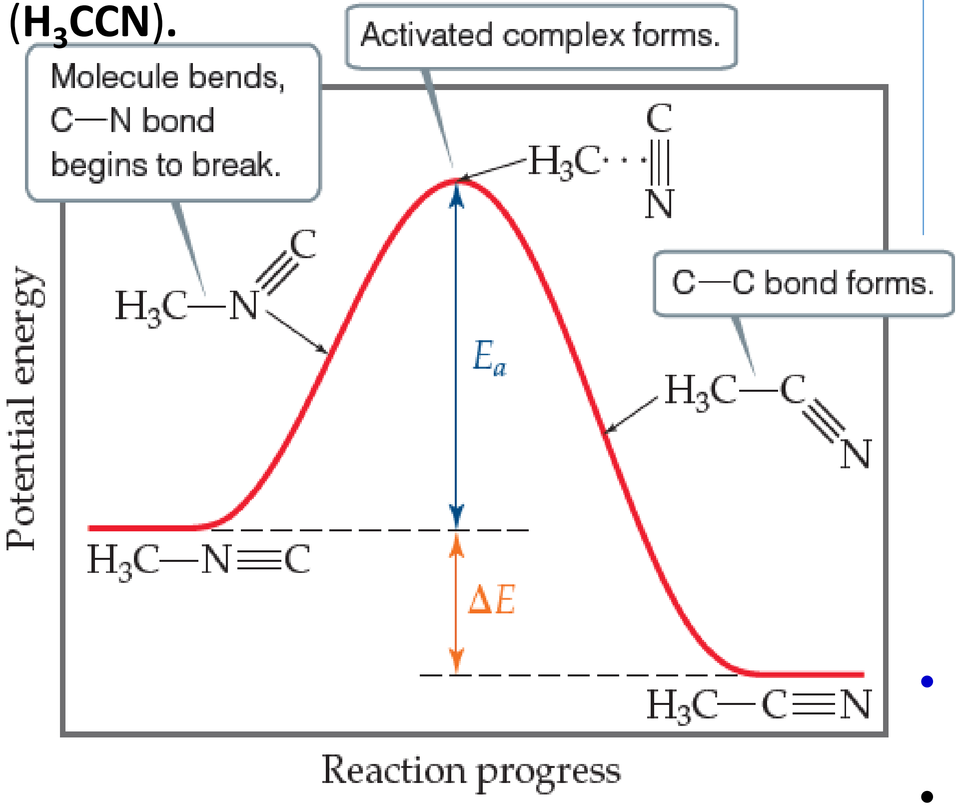


Energy is needed to overcome a barrier between initial and final states

For example,

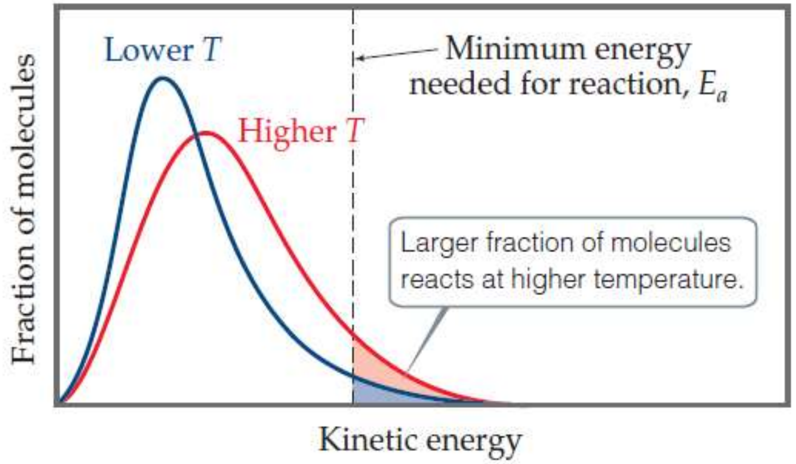


Energy profile for conversion of methyl isonitrile (H_3CNC) to its isomer acetonitrile (H_3CCN).



- The difference between the energy of the starting molecule and the highest energy along the reaction pathway is the **activation energy, E_a**.
- The molecule having the arrangement of atoms shown at the top of the barrier is called either the **activated complex** or the **transition state**.
- *The rate constant depends on the magnitude of E_a*
- *Generally, the* ***lower the value of E_a is, the larger the rate constant and the faster the reaction****.*

The effect of temperature on the distribution of kinetic energies of molecules in a sample.



- Figure shows the distribution of kinetic energies for two temperatures, comparing them with the minimum energy needed for reaction, E_a.
- **At the higher temperature a much greater fraction of the molecules have kinetic energy greater than E_a, which leads to a greater rate of reaction.**

Arrhenius equation

- Arrhenius noted that for most reactions the increase in rate with increasing temperature is nonlinear.
- The Arrhenius equation gives the dependence of the rate constant of a chemical reaction on the absolute temperature as $k = A\, e^{-\frac{E_a}{RT}}$.

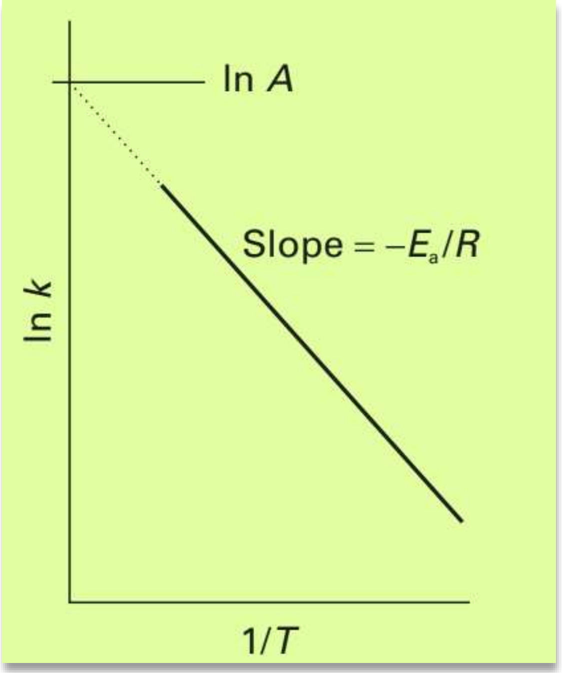
where, k is rate constant, E_a is the activation energy, **A** is the pre-exponential (frequecy) factor is constant, and ***RT*** is the average kinetic energy i.e., R is the gas constant (8.314 J/mol-K), and T is the absolute temperature.

Arrhenius equation (non exponential form)

$$\ln k = \ln e^{-\frac{E_a}{RT}} + \ln A$$

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

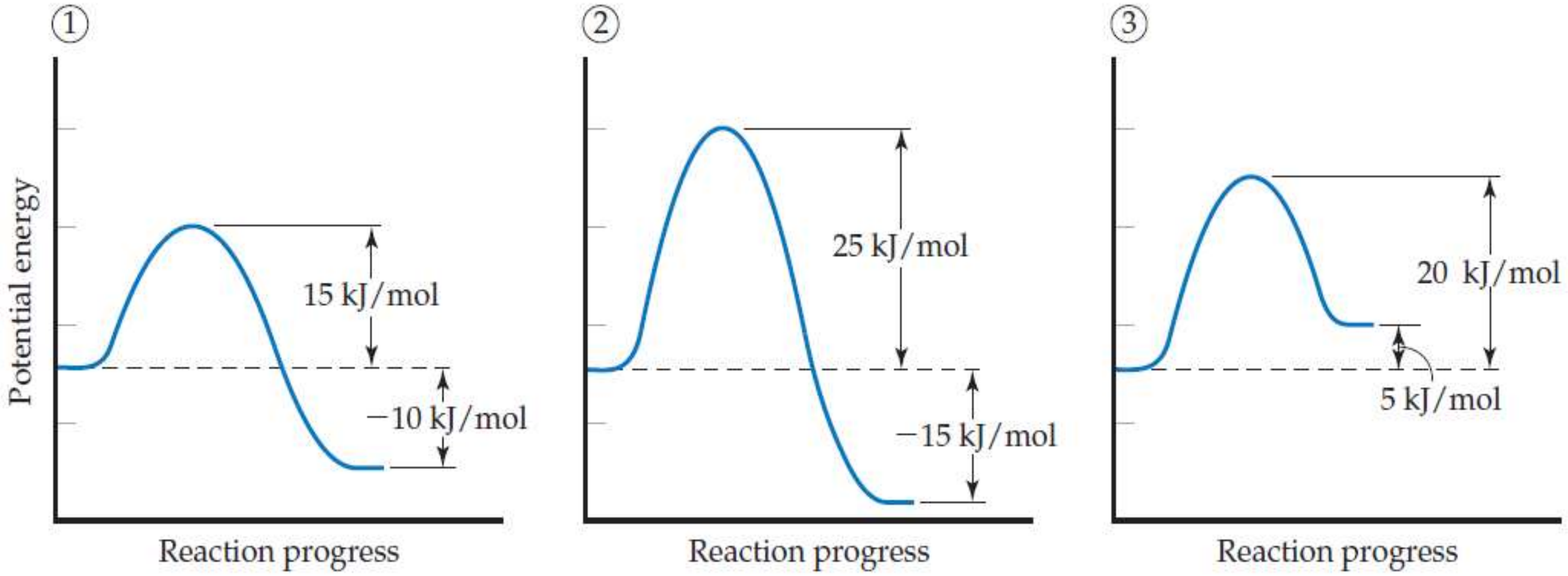
- ❖ A graph of ln*k* versus 1/T is a straight line when the reaction follows the behavior described by the Arrhenius equation.
- ❖ The higher the activation energy, the stronger the temperature dependence of the rate constant (i.e., the steeper the slope).
- ❖ If a reaction has zero activation energy, its rate is independent of temperature.



- value of A from intercept at infinite T (i.e.; 1/T=0)
- value of E_a from the slope.

Consider a series of reactions having these energy profiles:

Rank the forward rate constants from smallest to largest assuming all three reactions have nearly the same value for the frequency factor A.



SOLUTION

- The **lower the activation energy, the larger the rate constant and the faster the reaction**.
- The value of **ΔE does not affect the value of the rate constant.**
- Hence, **the order of the rate constants is 2 < 3 < 1.**

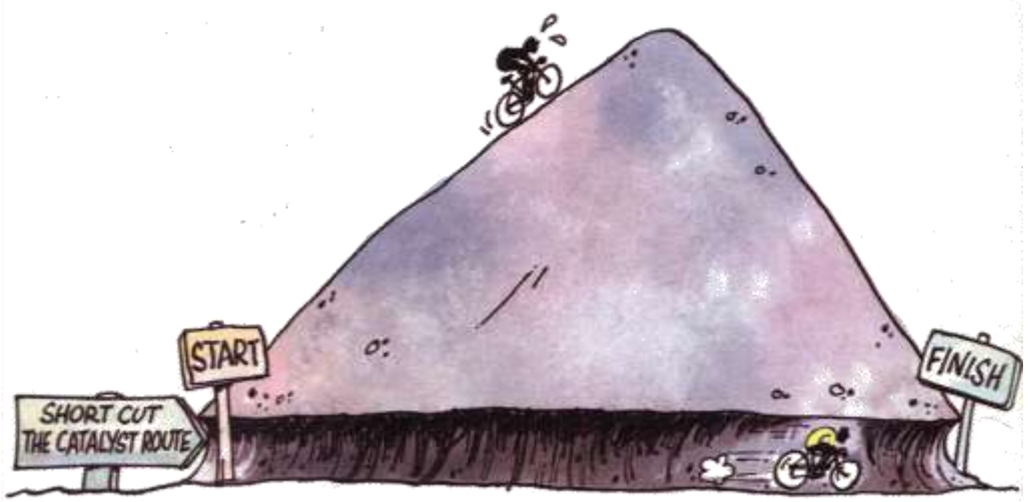
Catalysis

- *A **catalyst** is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself.*
- Most reactions in the body, the atmosphere, and the oceans occur with the help of catalysts.
- Most of the industrial chemical research is devoted to the search for more effective catalysts for reactions of commercial importance.
- **The phenomenon of alteration of the rate of a reaction by a catalyst is known catalysis.**
- The science and technology of catalysis is of great significance as it affects our daily life.
- The catalytic processes contribute greater than 30-40% of global GDP
- Four major sectors of the world economy involve catalytic processes.
  - ✓ Petroleum and Energy Production,
  - ✓ Chemicals and Polymer Production,
  - ✓ Food industry and
  - ✓ Pollution control.

Catalytic reactions

- *Catalysts work by providing alternative mechanism involving a different transition state of lower energy.*

Catalyst provides an alternative pathway



By providing an alternative pathway (or mechanism) with lower activation energy.

- *Thereby, the activation energy* of the catalytic reaction is lowered compared to the uncatalyzed reaction.*

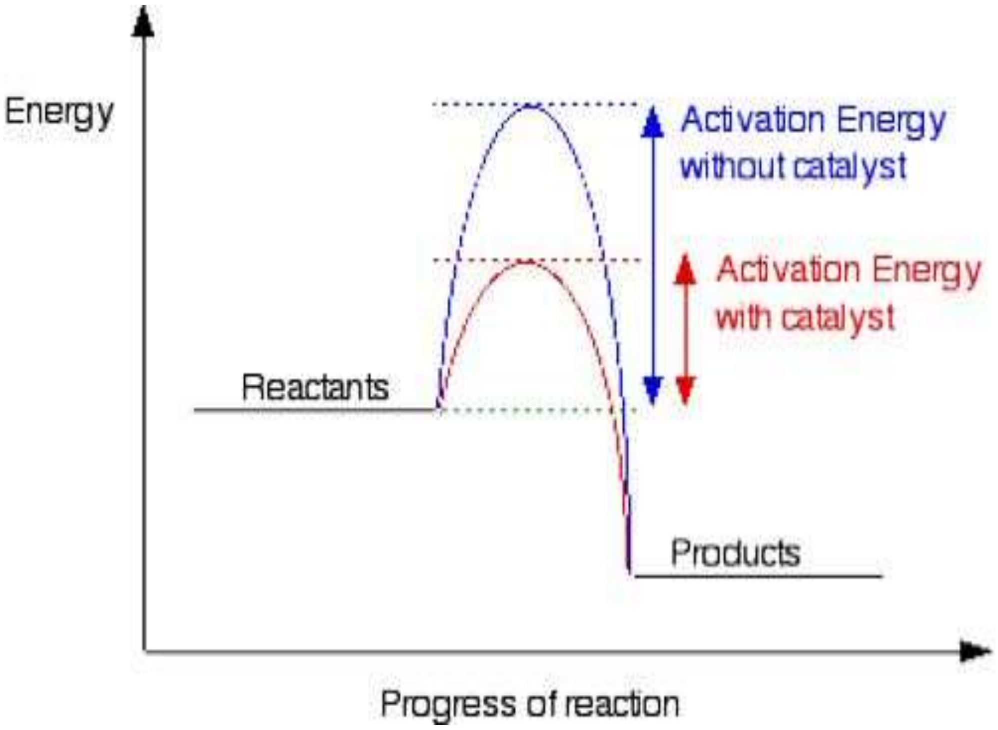
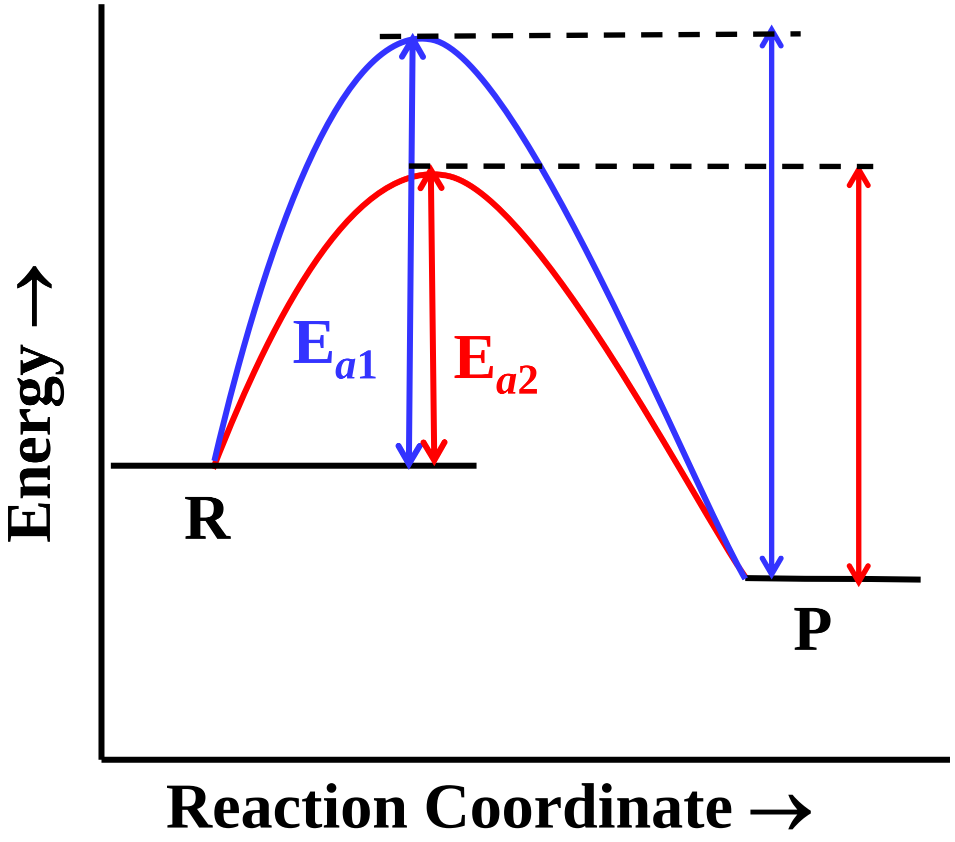


Figure: Schematic diagram to illustrate the effect of catalyst on activation energy of reactions.

Presence of a Catalyst

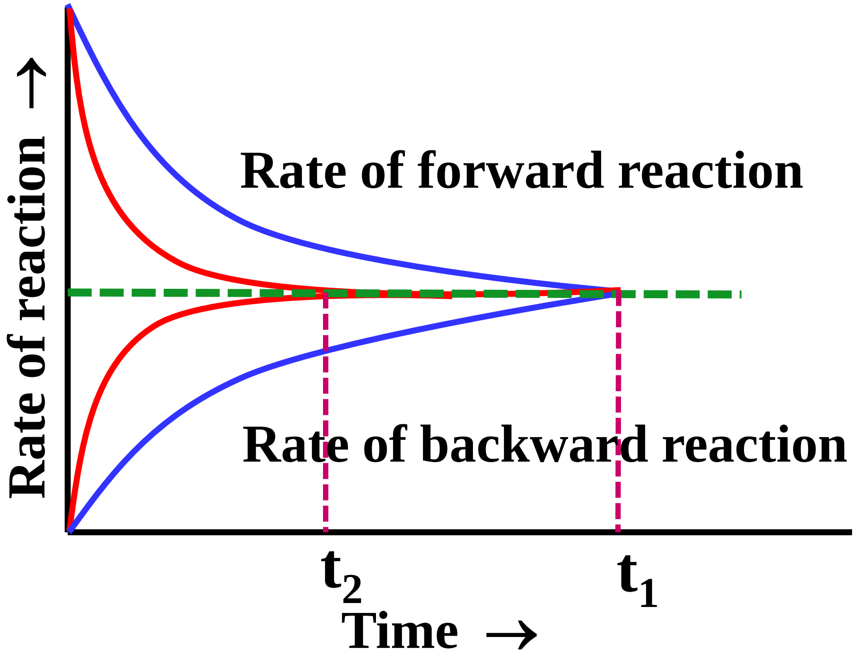
A catalyst is a substance that may increase or decrease the rate of a reaction

- Increase in rate ⇒ +ve catalyst or promoter
- Decrease in rate ⇒ –ve catalyst or inhibitor



A catalyst affects both the forward and backward reaction equally.

- Thus it doesn't change the state of equilibrium, it only accelerates the approach of equilibrium.



Types of catalysis

Following are the main types of catalysis:

1. **Homogeneous catalysis**
2. **Heterogeneous catalysis**
3. **Enzyme catalysis**

1. Homogeneous catalysis

In a reaction, if the catalyst is present in the **same phase** as the reactants, it is called a **homogeneous catalyst and the phenomenon is homogeneous catalysis**. Such catalysis can take place in gaseous reaction or reactions in solution.

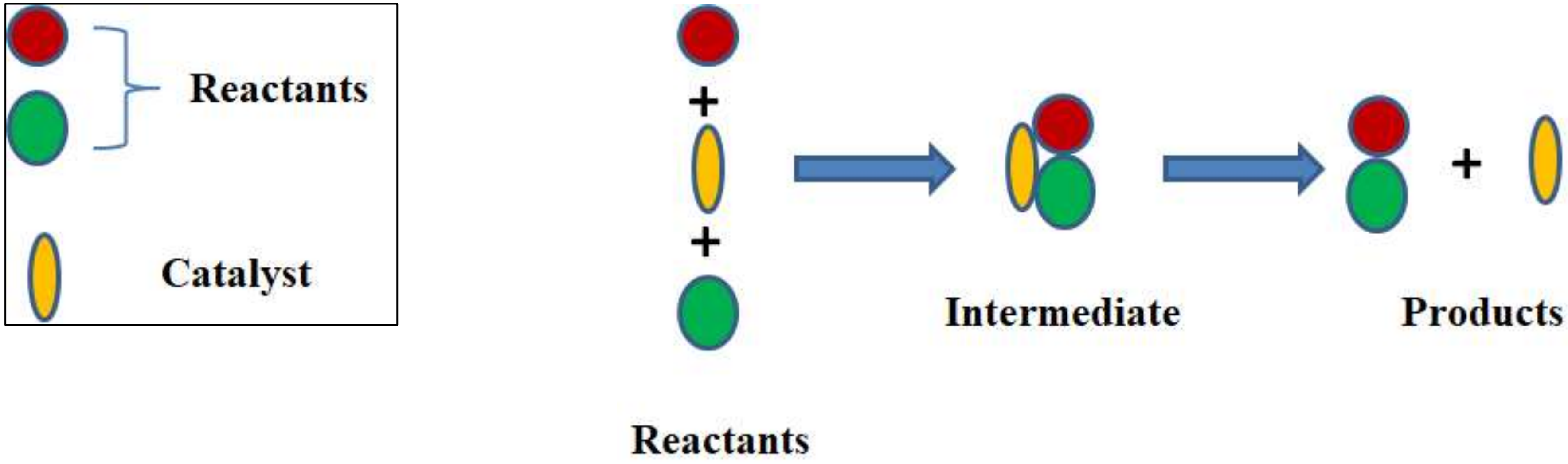


Figure: Schematic diagram to illustrate the homogeneous catalysis.

These chemicals help in attaining the equilibrium more quickly by increasing the rates of both the forward and reverse reactions to an extent.

Examples of homogeneous catalysis in the gas phase

(1) Oxidation of sulphur dioxide, SO_2, by oxygen to sulphur trioxide, SO_3, in presence of **nitric oxide, NO** (in the Chamber Process for sulphuric acid manufacture).

$$\mathbf{2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3\,(g)}$$

here, **NO** acts as a catalyst.

(2) The following reaction in the gas phase is catalyzed by **traces of chlorine gas**, particularly in presence of light.

$$\mathbf{2N_2O\,(g) \rightarrow 2N_2\,(g) + O_2\,(g)}$$

In presence of light chlorine forms chlorine radicals, which react with N_2O forming the intermediate radical ClO.*

The proposed mechanism is:

Step 1: $N_2O\,(g) + Cl^*\,(g) \rightarrow N_2\,(g) + ClO^*(g)$

Step 2: $2ClO^*(g) \rightarrow Cl_2\,(g) + O_2\,(g)$

Examples of homogeneous catalysis in the solution phase

(3) Hydrolysis of ester in the presence of acid and alkali:

$$CH_3COOC_2H_5\ (l) + H_2O\ (l) \rightarrow CH_3COOH\ (aq) + C_2H_5OH\ (aq)$$

(4) Hydrolysis of sucrose (cane sugar) into glucose and fructose in presence of minerals acids acting as catalysts:

$$\underset{\text{(cane sugar)}}{C_{12}H_{22}O_{11}\ (aq)} + H_2O\ (l) \rightarrow \underset{\text{(glucose)}}{C_6H_{12}O_6\ (aq)} + \underset{\text{(fructose)}}{C_6H_{12}O_6\ (aq)}$$

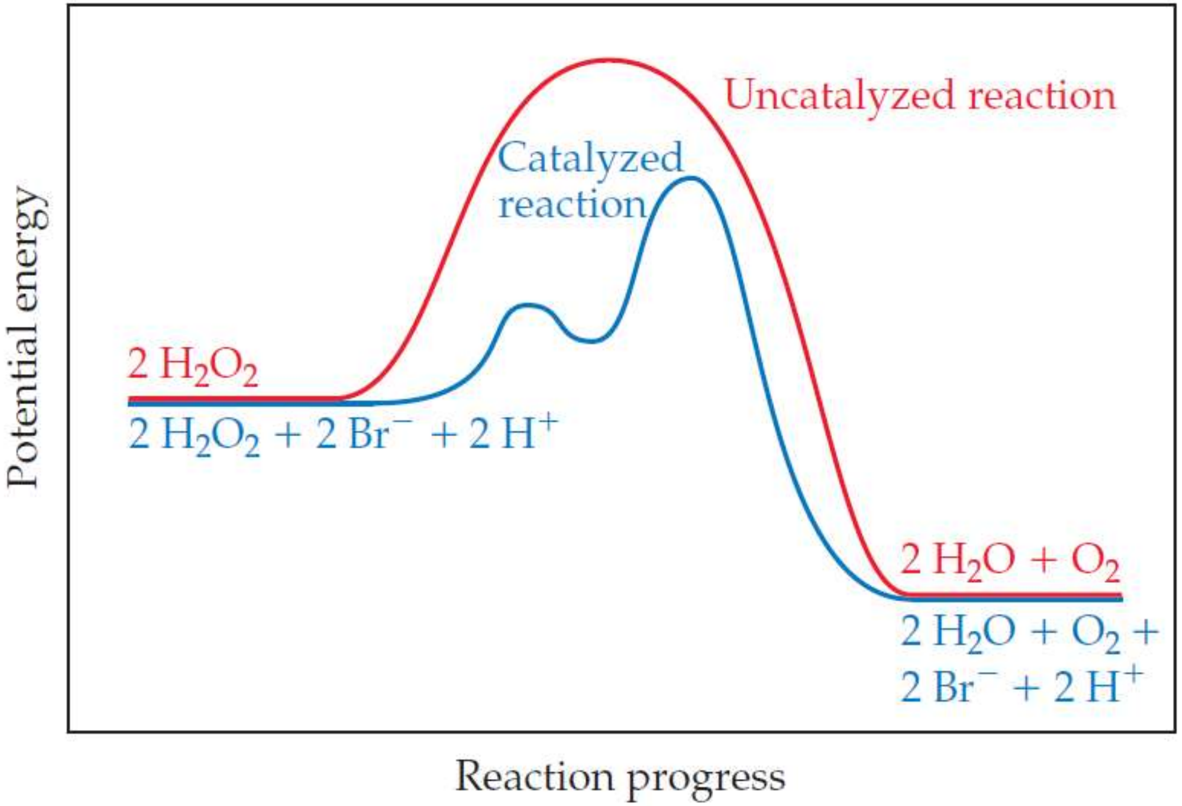
The decomposition of aqueous hydrogen peroxide, $H_2O_2(aq)$, into water and oxygen:

$$2\,H_2O_2(aq) \rightarrow H_2O(l) + O_2\,(g)\uparrow$$

In presence of catalyst:

$$2Br^{-}\,(aq) + H_2O_2(aq) + 2H^{+}\,(aq) \rightarrow Br_2\,(aq) + 2H_2O(l)$$

$$Br_2\,(aq) + H_2O_2(aq) \rightarrow 2Br^{-}\,(aq) + 2H^{+}\,(aq) + O_2\,(g)\uparrow$$



2. Heterogeneous catalysis

If the catalyst is present in a **different phase** than the reactants is called **heterogeneous catalyst** and the **phenomenon is known heterogeneous catalysis.**

- In heterogeneous catalysis the reactions take place at the interface of two phases.
- The catalyst is, often a solid and adsorbs a liquid or a gas. This type of catalysis is of great importance in many industrial processes.

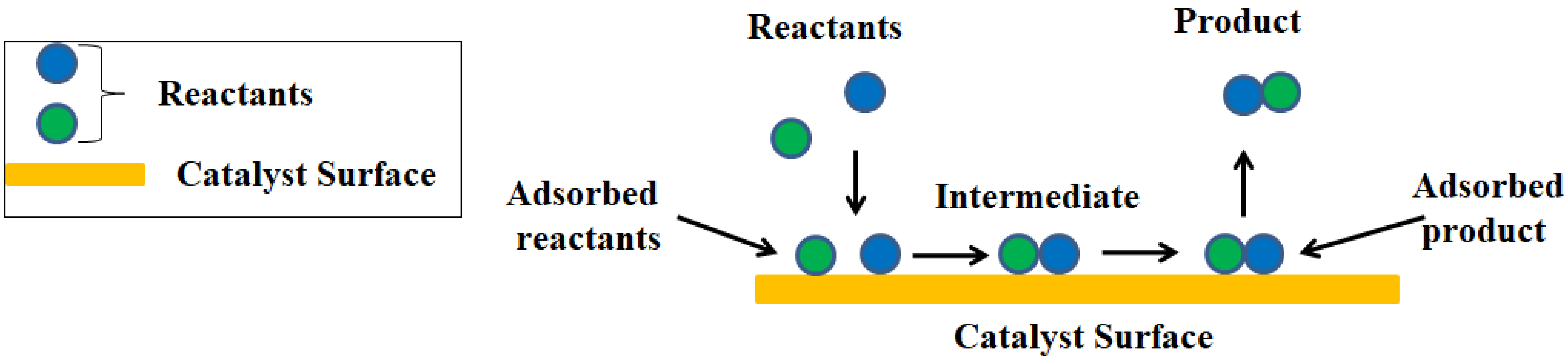


Figure: Schematic diagram to illustrate the heterogeneous catalysis.

Examples of Heterogeneous catalyst

A. Heterogeneous catalysis where a reaction in the gaseous phase is catalysed by a substance in the solid state

Ex. (i) Manufacture of **ammonia by the Haber process**. Iron (Fe) acts as catalyst.

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

(ii) Manufacture of **sulphuric acid by the Contact process**. Vanadium pentoxide (V_2O_5) or platinum are catalysts for the production of SO_3 (g) from SO_2 (g) and O_2 (g).

$$2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3\,(g)$$

(iii) Catalysts used in many reactions in the petroleum and polymer industries.

B. Heterogeneous catalysis where a reaction in the liquid phase is catalysed by a substance in the solid state.

Ex. The decomposition of H_2O_2 (aqueous) by MnO_2 (s).

$$2H_2O_2\,(aq) \rightarrow 2\,H_2O\,(l) + O_2\,(g)$$

C. Heterogeneous catalysis where a reactions in which both the reactant and the catalyst are in the solid phase.

Ex. The decomposition of $KClO_3$ is catalysed by solid MnO_2.

$$2\,KClO_3\,(s) \rightarrow 2KCl\,(s) + 3O_2\,(g)$$

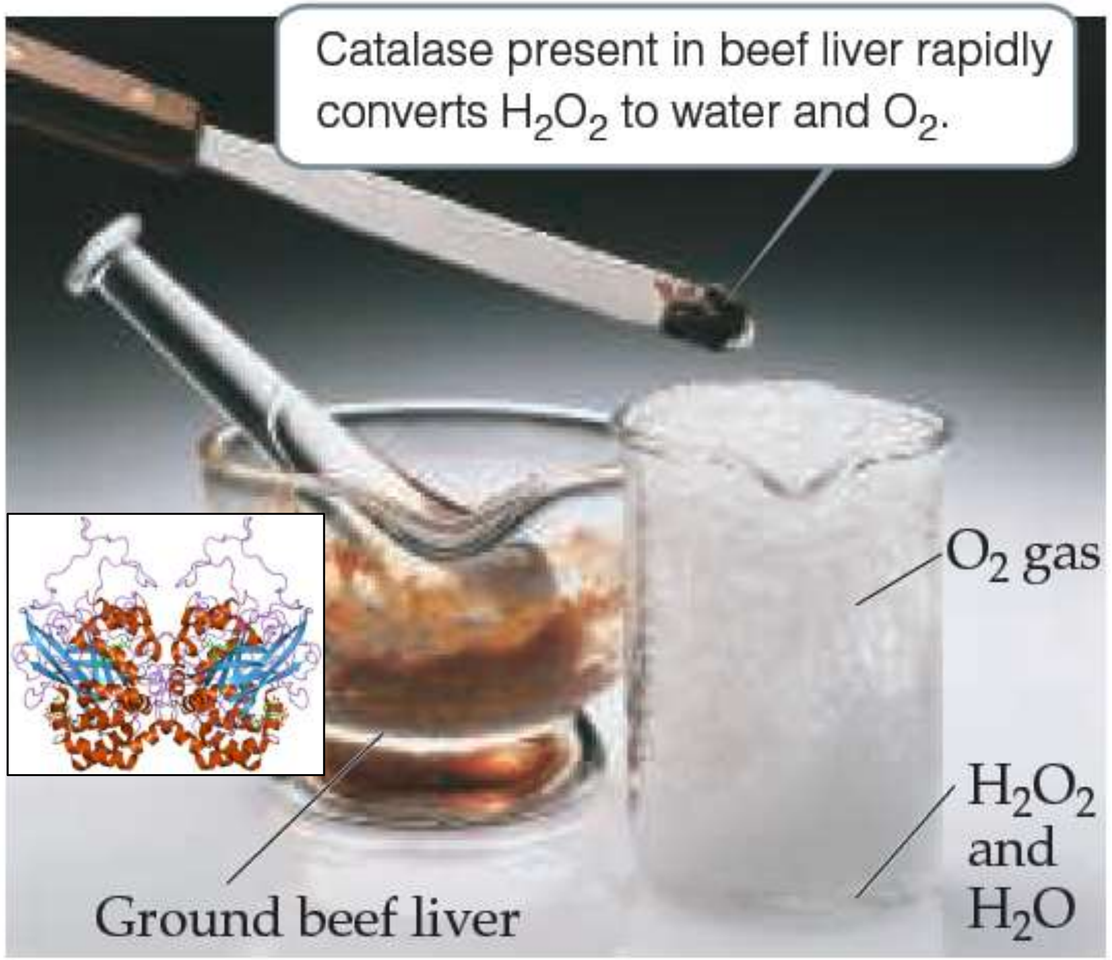
Enzyme catalysis

- *Biological catalysts known as **enzymes** are necessary for many of the chemical reactions occur in an extremely complex system of the human body.*

- Enzymes are **protein-based molecules** that can process certain chemical reactions
- These reactions occur at a **localized site**, called the **active site**, at the rate much faster than a normal chemical reaction.
- **Substrate** is the molecule that fits into the active site of the enzyme and undergoes transformation to a product.
- Example of an enzyme catalysed reaction is catalase that converts hydrogen peroxide to water and oxygen.
- It is an important enzyme protecting the cell from oxidative damage by reactive oxygen species (ROS)

Reaction catalysed by the enzyme, catalase

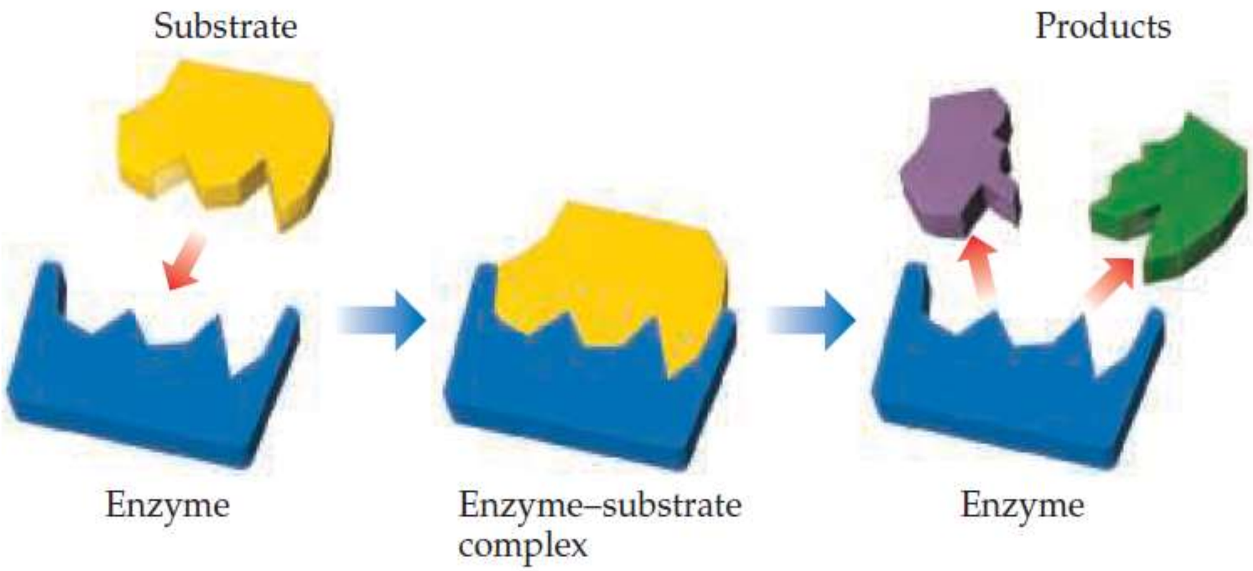
$$H_2O_2 \rightarrow H_2O + O_2$$



Catalase present in beef liver rapidly converts H_2O_2 to water and O_2.

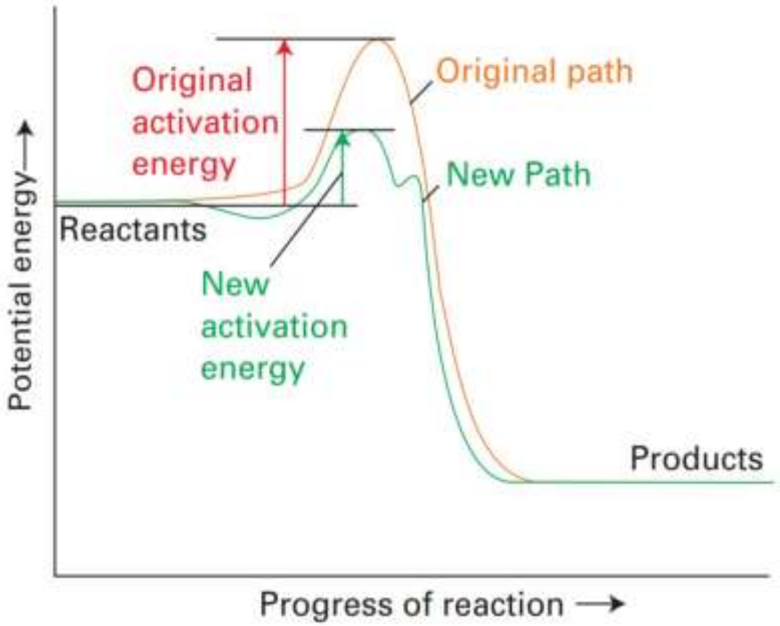
Enzymes speed up reactions.

Mechanism of enzyme-catalyzed reactions



- ❑ Enzyme-catalyzed reactions work in a **lock and key** fashion.
- ❑ The substrate uniquely fits like a key into the active site of the enzyme, forming a **lock-key complex**.
- ❑ The substrate is converted into the product by the enzyme at the active site.
- ❑ The product is then released from the active site.

Enzymes’ effect on the activation energy



- ❑ Enzymes lower the activation energy for reactions. The lower the activation energy, the faster the rate of the reactions.
- ❑ Ex: The enzyme **catalase** reduces the activation energy for the decomposition of hydrogen peroxide to **8** kJ mol^{-1}, corresponding to an acceleration of the reaction by a factor of **10^{15}** at 298 K.
- ❑ A generic equation for the complex formation is as follows:

$$E + S \longleftrightarrow ES \longleftrightarrow P + E$$

Michaelis-Menten equation

$$\mathrm{E + S} \longleftrightarrow \mathrm{ES} \longleftrightarrow \mathrm{P + E}$$

- Michaelis-Menten equation is a commonly used model that assumes that the concentration of the enzyme remains constant.

- The enzyme reacts with the substrate for form an enzyme-substrate complex, which leads to the synthesis of the product and the release of the enzyme

$$\mathrm{E + S} \underset{k_a'}{\overset{k_a}{\longleftrightarrow}} \mathrm{ES} \overset{k_b}{\longleftrightarrow} \mathrm{P + E}$$

- Where, k_a is the rate of formation of ES, k_a' is the rate of dissociation of ES, and k_b is the rate of formation of P from ES.

Michaelis-Menten Mechanism

One of the earliest descriptions of the action of enzymes is the **Michaelis-Menten mechanism**.

The proposed mechanism, with all species in an aqueous environment, is as follows.

Step 1: The bimolecular formation of a combination, ES, of the enzyme E and the substrate S:

$$\mathrm{E + S \rightarrow ES} \qquad \text{Rate of formation of ES} = k_a\,[\mathrm{E}]\,[\mathrm{S}]$$

Step 2: Unimolecular decomposition of the complex:

$$\mathrm{ES \rightarrow E + S} \qquad \text{Rate of decomposition of ES} = k_a{}'\,[\mathrm{ES}]$$

Step 3: The unimolecular formation of products P and the release of the enzyme from its combination with the substrate:

$$\mathrm{ES \rightarrow P + E} \qquad \text{Rate of formation of P} = k_b\,[\mathrm{ES}]$$