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Military Institute of Science and Technology

Fundamentals of Chemistry

CHEM 101

Chemical Kinetics

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Chemical Kinetics

The word "kinetics" comes from the Greek word "kinētikos," which means "related to motion."

To understand & predict the behavior of a chemical system one must consider both Thermodynamics & Kinetics

↳ Relationships between heat, energy, and work.

Chemical kinetics is the branch of chemistry that studies the rates and mechanisms of chemical reactions. It involves the study of how fast chemical reactions occur and how different variables such as temperature, pressure, concentration, and catalysts affect the rate of reaction.

REACTION RATE

The rate of a reaction tells at what speed the reaction occurs.

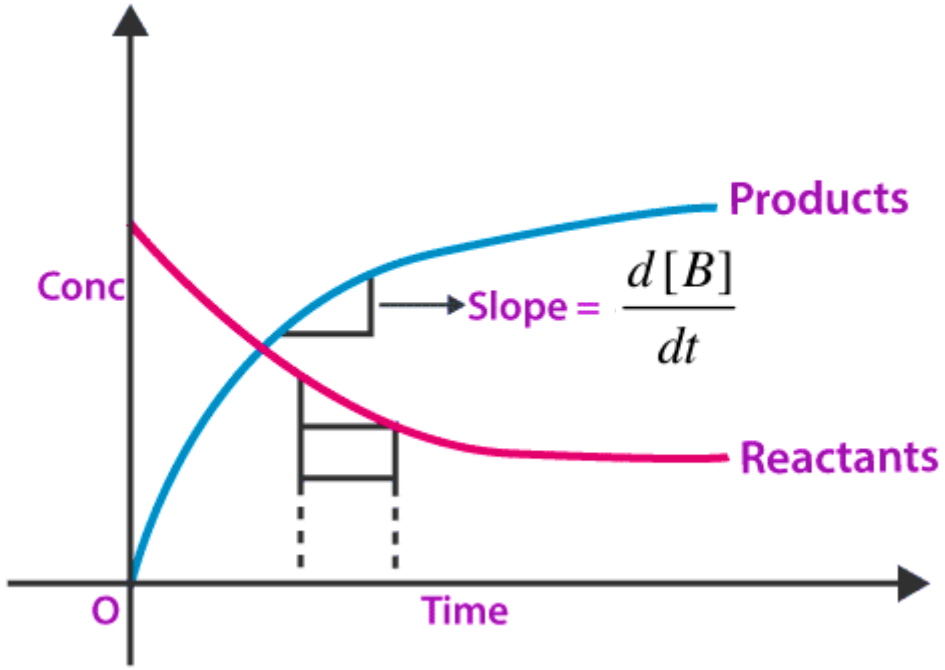
"The rate of reactions is defined as the change in concentration of any of reactant or products per unit time."

$$A \longrightarrow B$$

$$\text{rate of reaction} = \text{rate of disappearance of } A$$
$$= \text{rate of appearance of } B$$

$$\text{rate} = -\frac{d[A]}{dt}$$

$$= +\frac{d[B]}{dt}$$



REACTION RATE

For different stoichiometry,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The rate of **Consumption** The rate of **Production**

The rate at which the H_2 gets consumed is three times the rate of consumption of N_2 and the rate of production of ammonia is twice the consumption of N_2

$$\text{Reaction rate} = -\frac{d\,[N_2]}{dt} = -\frac{1}{3}\frac{d\,[H_2]}{dt} = \frac{1}{2}\frac{d\,[NH_3]}{dt}$$



Reaction Rate: The time derivative of concentration (reactant or product) divided by the appropriate stoichiometric co-efficient

The Rate Law

The rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.

Thus for a substance A undergoing reaction,

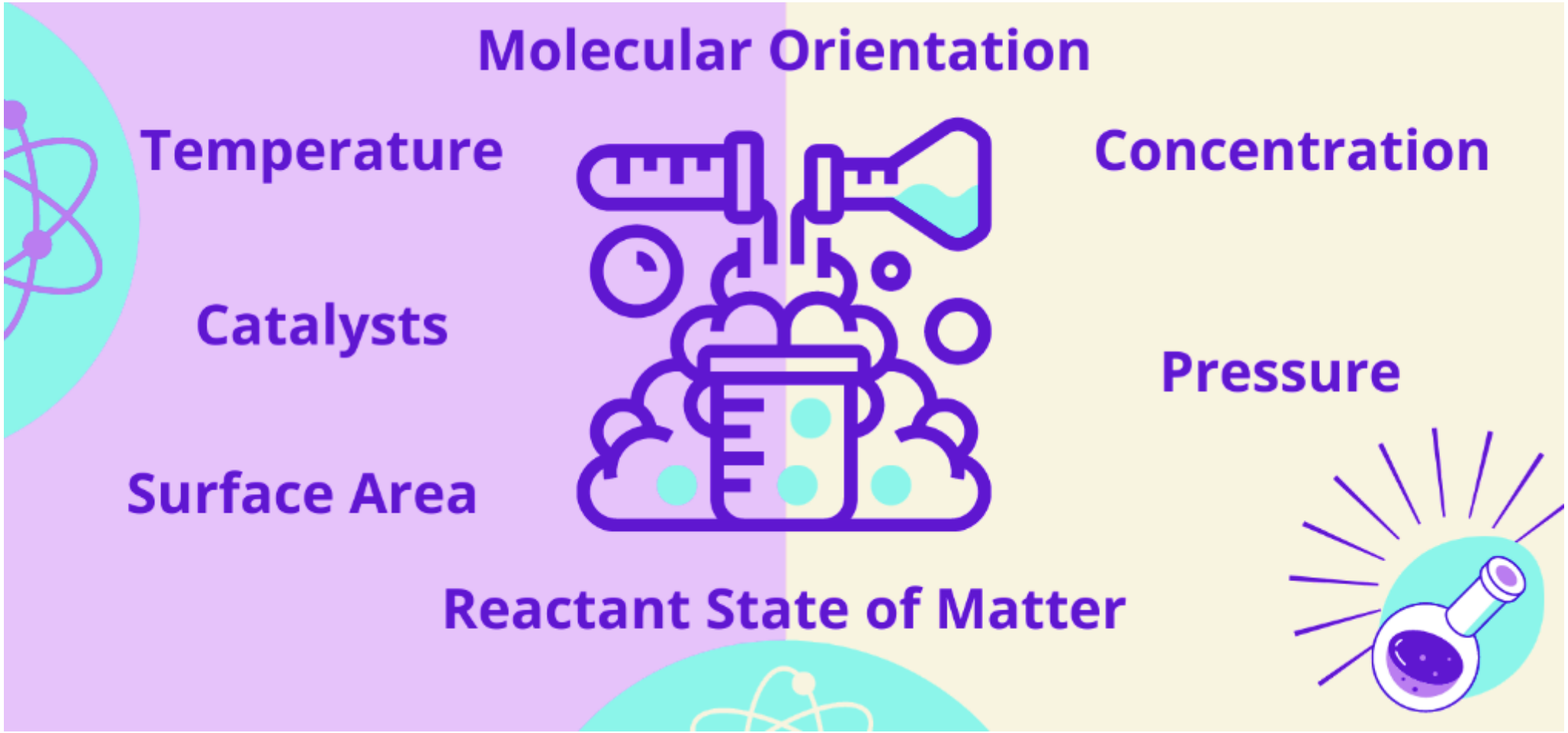
$$\text{rate} \propto [\text{A}]^n$$

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

$2N_2O_5 \longrightarrow 4NO_2 + O_2$	$\text{rate} = k\,[N_2O_5]$
$H_2 + I_2 \longrightarrow 2HI$	$\text{rate} = k\,[H_2]\,[I_2]$
$2NO_2 \longrightarrow 2NO + O_2$	$\text{rate} = k\,[NO_2]^2$
$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$	$\text{rate} = k\,[H_2]\,[NO]^2$

An expression which shows how the reaction rate is related to conc. is called the rate law or rate equation.

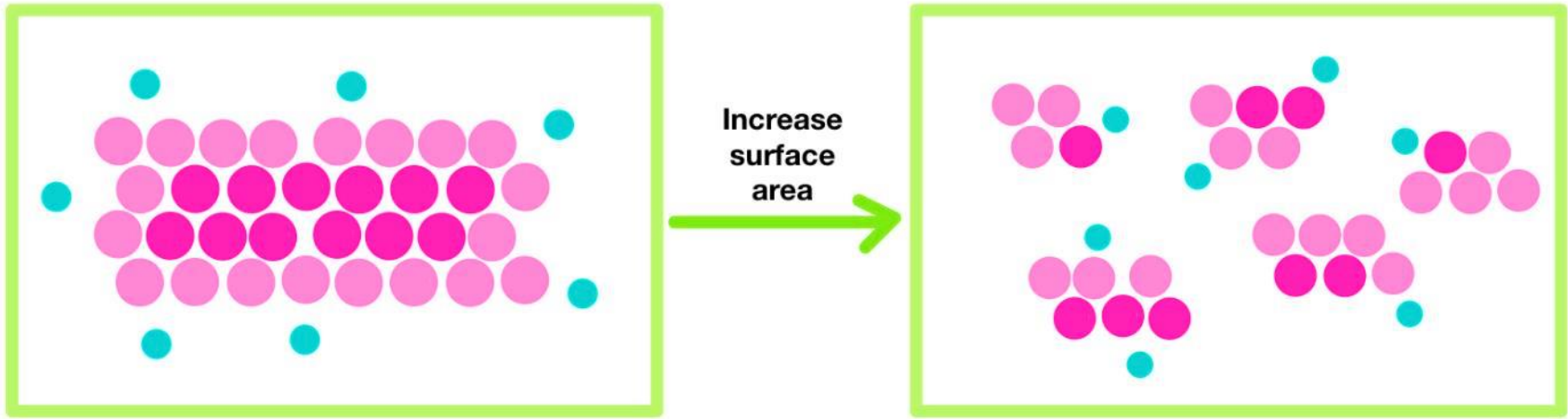
Factors affecting rate of a Reaction



Factors affecting rate of a Reaction

Surface Area of Reactants

- **Surface area increases, area of contact between reactants increases - rate of encounter between reactants increases - Rate increases**
- **Surface area of a solid can be increased by Sub-division i.e. dividing the bigger particles in smaller**



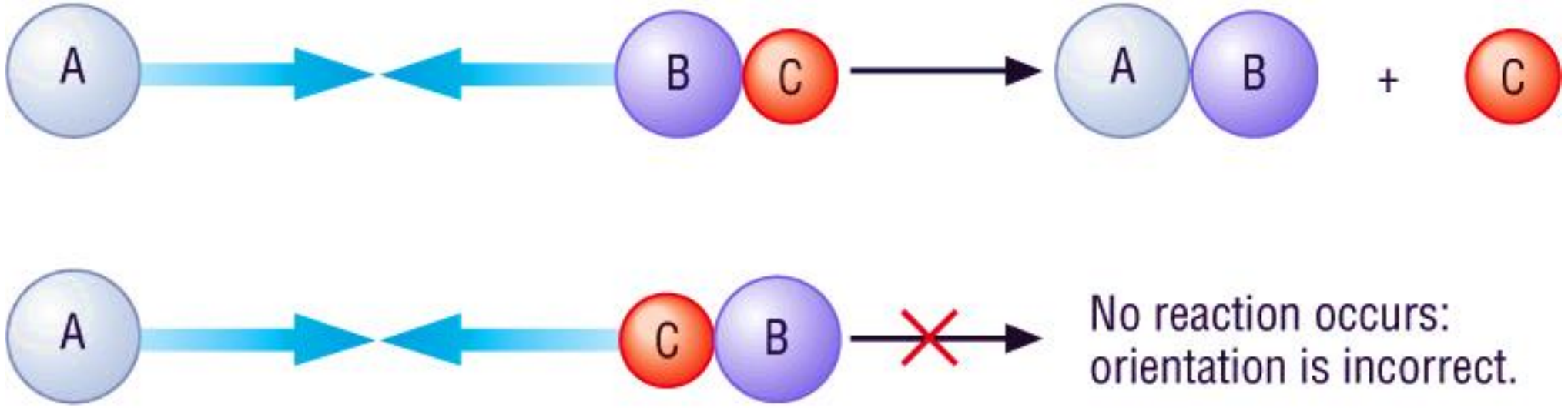
The surface area of the pink compound is too small, causing the blue molecules to not be able to easily interact with the entire molecule (the dark pink parks of the molecule can't even be reached!)

Now this molecule has a higher surface area, making it easy for the blue molecules to interact while the entire molecule (easy interactions between molecules = faster reaction rate!)

Factors affecting rate of a Reaction

Orientation:

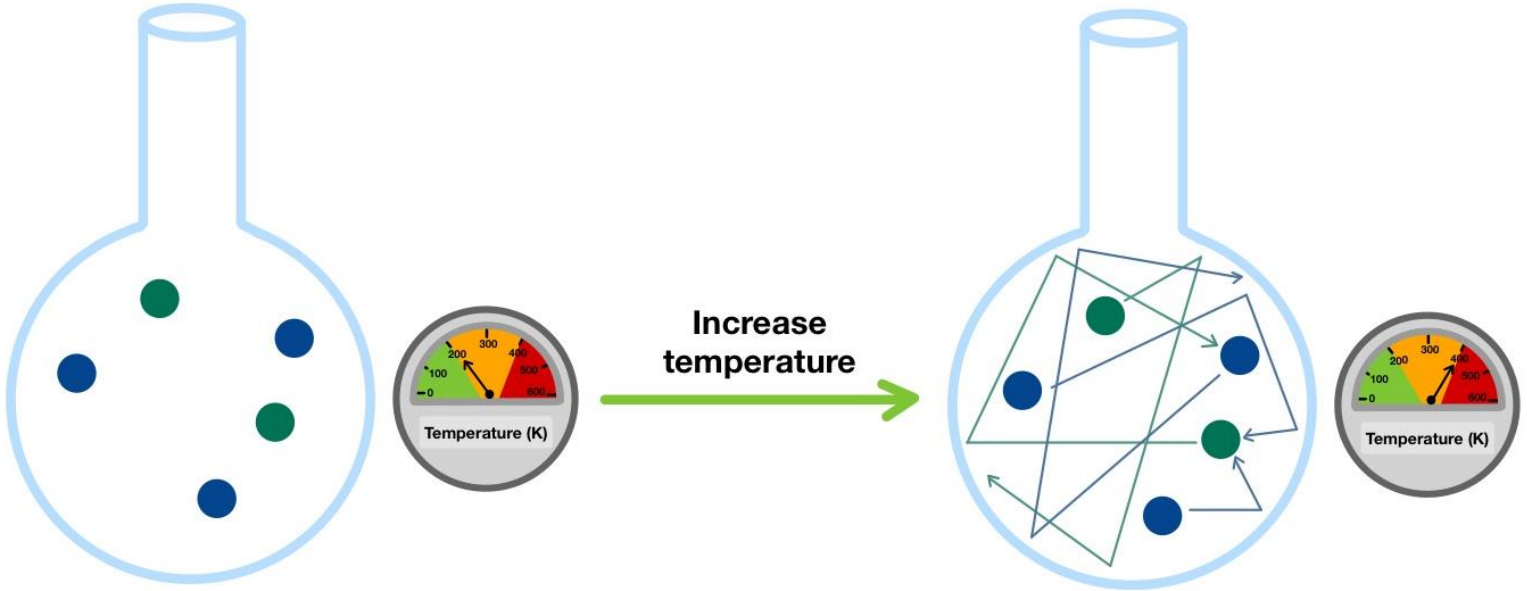
The molecules must collide in correct orientation in order for the products to be made:



Factors affecting rate of a Reaction

Temperature

- **As temperature increases avg K.E increases**
- **As avg. K.E increases, the particles move faster & Collision energy & Collision frequency increases & hence Rate increases**

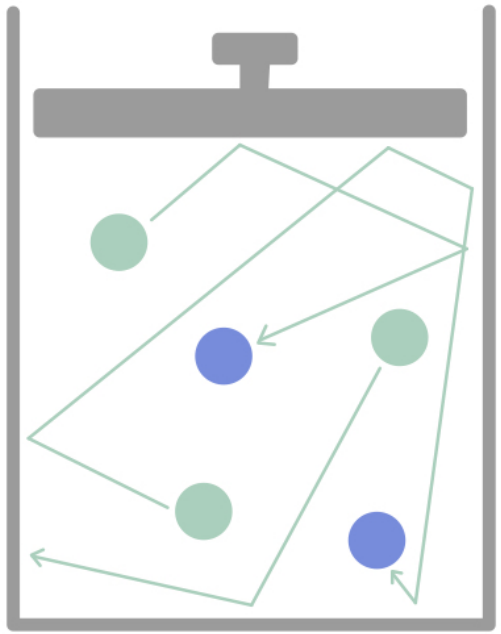


The molecules in this reaction are moving very slowly, which makes it hard for collisions to occur. This is causing the reaction to proceed at a very slow rate

Increasing the temperature causes the kinetic energy of the molecules to increase thus causing the molecules to move faster which causing collisions to occur more frequently. More collisions means the reaction rate increases

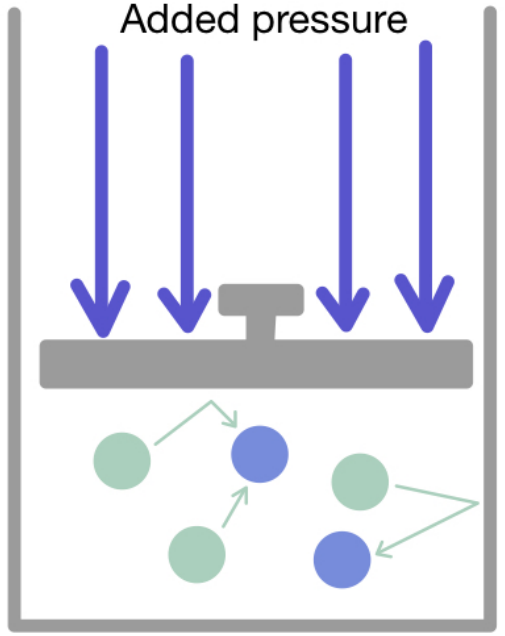
Factors affecting rate of a Reaction

Pressure



The molecules in this reaction need to move and bounce multiple times before making collisions, this means that there are not a lot of collisions happening which makes the reaction rate slow

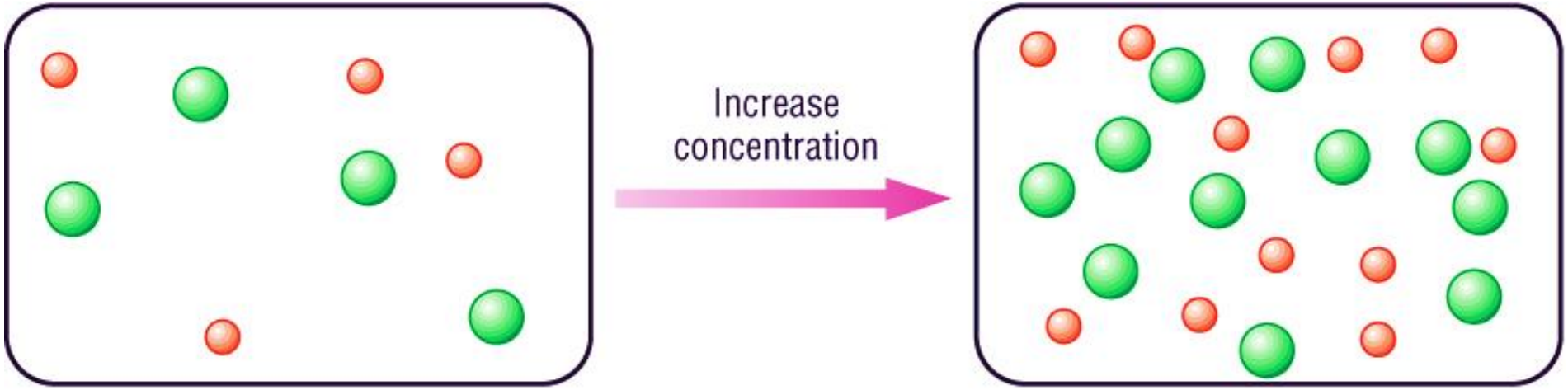
Increase pressure



By increasing the pressure, the molecules are able to have collisions a lot easier than before, thus causing the number of collisions to increase which causes the reaction rate to increase

Factors affecting rate of a Reaction

Concentration



Here we have a few molecules.
There are few collisions.
The rate of reaction is low.

Here we have many molecules.
There are more collisions.
The rate of reaction is greater.

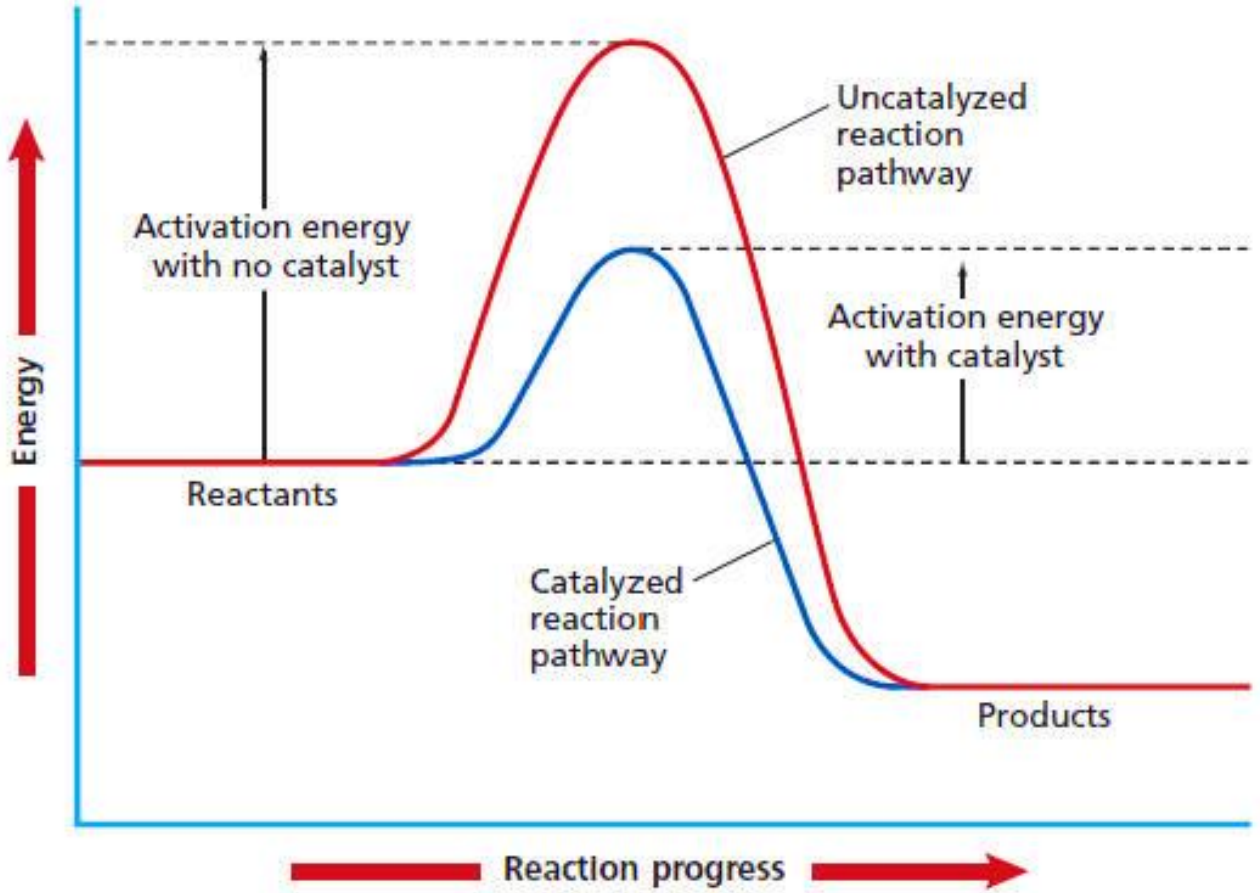
Nature of Reactants

- **Rate of "Homogeneous Reactions" is higher than the "Heterogeneous Reactions"**
- **Rate depends on the physical state of reactants , e.g. liquid/gaseous/solid**
- **Rate depends on the number of collisions or encounters between the reacting species**

Factors affecting rate of a Reaction

Catalyst

- A substance that increases the reaction rate without undergoing a chemical change itself
- Provides an alternate reaction mechanism faster than mechanism in absence of catalyst
- Lowers the activation energy for a chemical reaction



ORDER OF A REACTION

The order of a reaction is the sum of the powers of concentrations in the rate law.

Let us consider the example of a reaction which has the rate law

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

The order of such a reaction is $(m + n)$.

$\text{rate} = k\,[N_2O_5]$	1
$\text{rate} = k\,[H_2]\,[I_2]$	$1 + 1 = 2$
$\text{rate} = k\,[NO_2]^2$	2
$\text{rate} = k\,[[H_2]\,[NO]^2$	$1 + 2 = 3$
$\text{rate} = k\,[CHCl_3]\,[Cl_2]^{1/2}$	$1 + \frac{1}{2} = 1\frac{1}{2}$

Order of a reaction is an experimental Quantity

Molecularity of a Reaction

Chemical reactions may be classed into two types :

(*a*) Elementary reactions

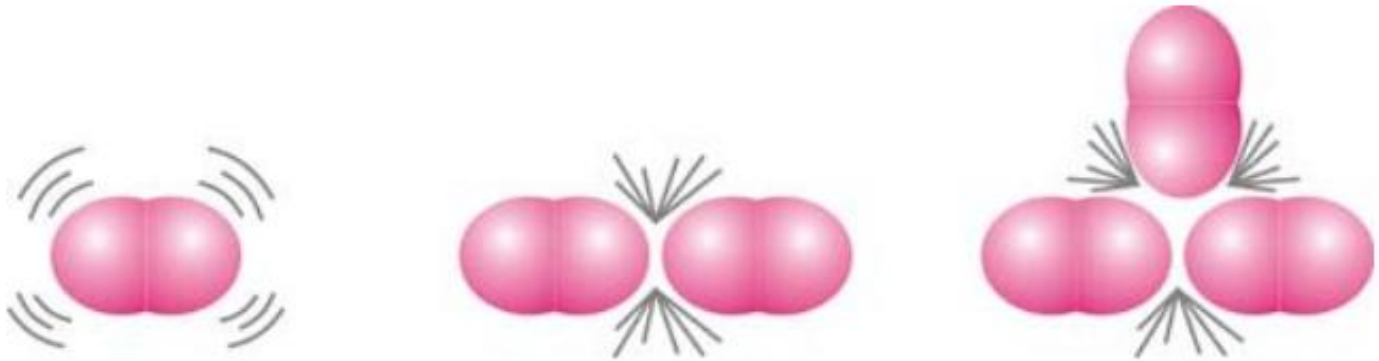
(*b*) Complex reactions

An **elementary reaction** is a simple reaction which occurs in a single step.

A **complex reaction** is that which occurs in two or more steps.

Molecularity of an Elementary Reaction

The molecularity of an elementary reaction is defined as : **the number of reactant molecules involved in a reaction.**



Unimolecular Bimolecular Termolecular

Molecularity of a Reaction

(*a*) **Unimolecular reactions :** (molecularity = 1)

$$A \longrightarrow \text{product}$$

Examples are : (*i*) $Br_2 \longrightarrow 2Br$

(*b*) **Bimolecular reactions :** (molecularity = 2)

$$A + B \longrightarrow \text{products}$$
$$A + A \longrightarrow \text{products}$$

Examples are :

(*i*) $\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \longrightarrow \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$

(*ii*) $2HI \longrightarrow H_2 + I_2$

(*c*) **Termolecular reactions** : (molecularity = 3)

$$A + B + C \longrightarrow \text{products}$$

Examples are :

$$2NO + O_2 \longrightarrow 2NO_2$$
$$2NO + Cl_2 \longrightarrow 2NOCl$$

Molecularity of a Reaction

Molecularity of a Complex Reaction

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an elementary reaction. The stepwise sequence of elementary reactions that convert reactions to products is called the **mechanism of the reaction.** In any mechanism, some of the steps will be fast, others will be slow. A reaction can proceed no faster than its slowest step. Thus the slowest step is the **rate-determining step** of the reaction.

The decomposition of N_2O_5,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is an example of a complex reaction. It occurs by the following steps :

Step 1	$2N_2O_5 \longrightarrow$	$2NO_2 + 2NO_3$	(*slow*)
Step 2	$NO_2 + NO_3 \longrightarrow$	$NO + NO_2 + O_2$	(*slow*)
Step 3	$NO + NO_3 \longrightarrow$	$2NO_2$	(*fast*)
Overall reaction	$2N_2O_5 \longrightarrow$	$4NO_2 + O_2$	

It is meaningless to give the molecularity of the overall reaction because it is made of several elementary reactions, each, perhaps with a different molecularity. At best could be thought of as : **the number of molecules or atoms taking part in the rate-determining step.**

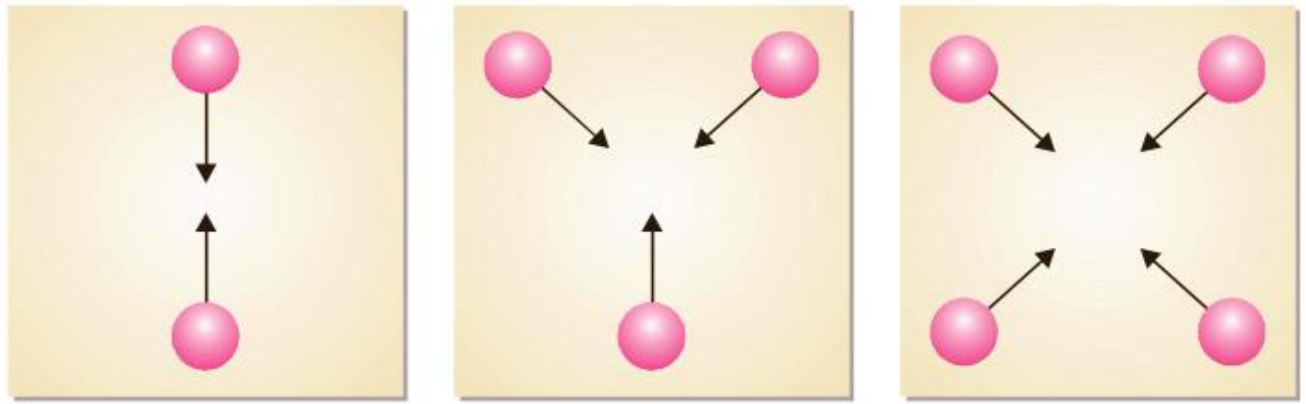
Molecularity of a Reaction

Why High Molecularity Reactions are Rare ?

Most of the reactions involve one, two or at the most three molecules. The reactions involving four or more molecules are very rare.

According to **kinetic molecular theory**, the rate of a chemical reaction is proportional to the number of **collisions** taking place between the reacting molecules. The chances of simultaneous collision of reacting molecules will go on decreasing with increase in number of molecules.

The reactions involving many molecules proceed through a series of steps, each involving two or three or less number of molecules. Such a reaction is called a complex reaction and the slowest step determines the overall rate of the reactions.



Order vs. Molecularity

Differences Between Order and Molecularity

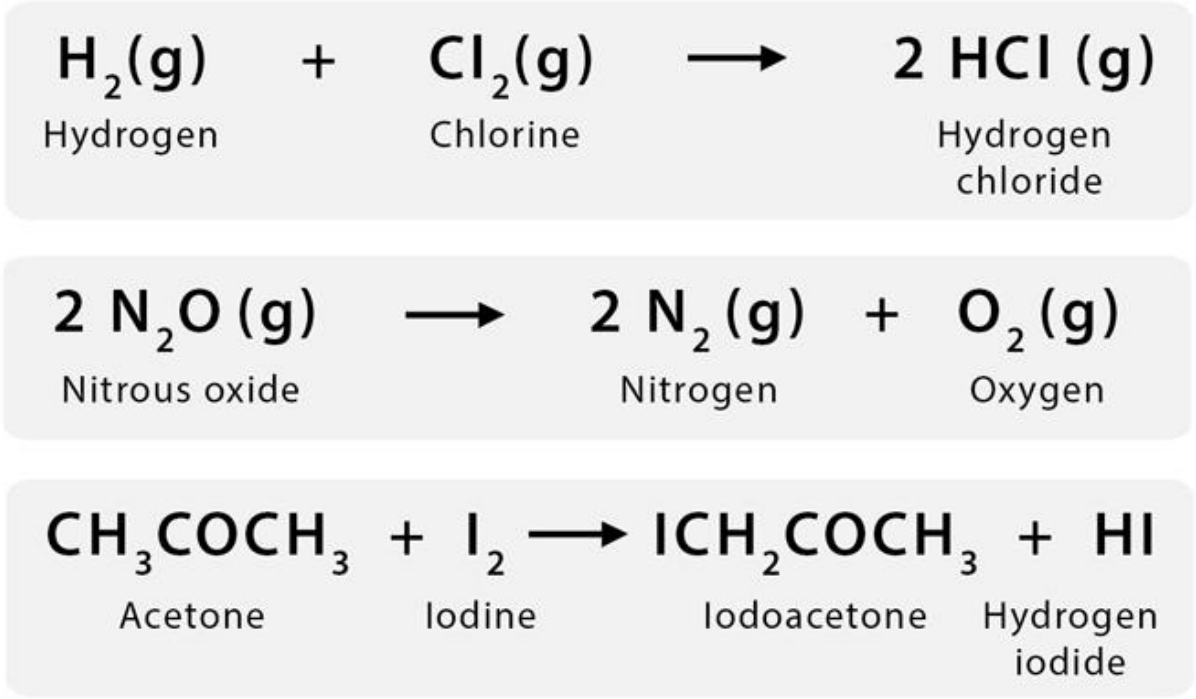
Order of a Reaction	Molecularity of a Reaction
1. It is the **sum of powers** of the concentration terms in the rate law expression.	1. It is number of **reacting species** undergoing simultaneous collision in the elementary or simple reaction.
2. It is an **experimentally** determined value.	2. It is a **theoretical** concept.
3. It can have **fractional** value.	3. It is always a **whole number.**
4. It can assume **zero value.**	4. It **can not have zero value.**
5. Order of a reaction **can change** with the conditions such as pressure, temperature, concentration.	5. Molecularity is **invariant** for a chemical equation.

ORDER OF A REACTION

ZERO ORDER REACTION

A zero order reaction is one whose rate is independent of concentration.

That means the rate does not vary with the increase or decrease in the concentration of the reactants. Therefore, the rate of these reactions is always equal to the rate constant



Reactions wherein a catalyst is required are generally zero order reactions.

ORDER OF A REACTION

ZERO ORDER REACTIONS

In a zero order reaction, rate is independent of the concentration of the reactions. Let us consider a zero-order reaction of the type

	A	⟶	Products
Initial conc.	a		0
Final conc.	$a - x$		x

$$\text{Rate of reaction} = \frac{-d[A]}{dt} = k_0[A]^\circ$$

or
$$\frac{dx}{dt} = \frac{-d\ (a - x)}{dt} = k_0(a - x)^\circ = k_0$$

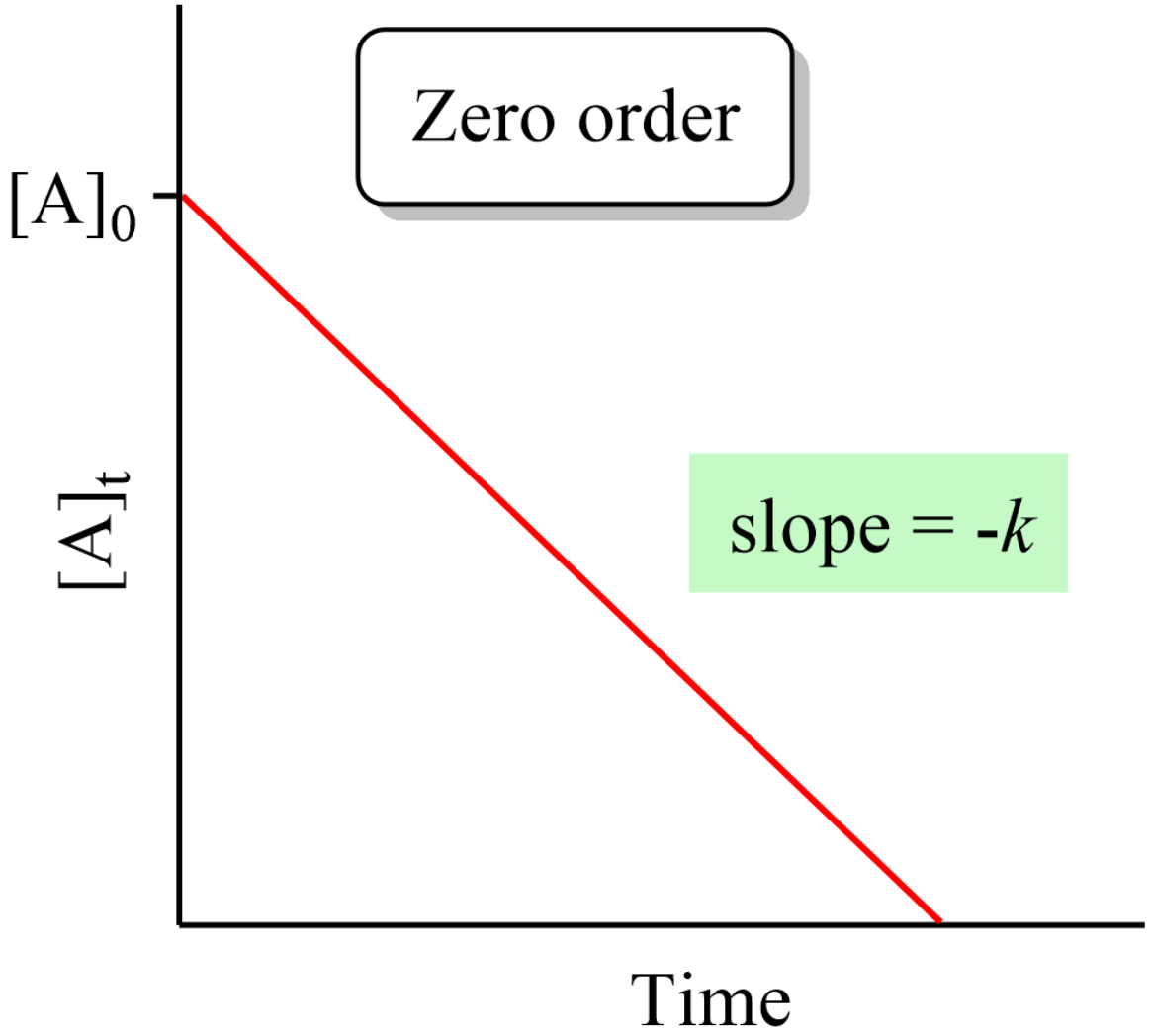
On integrating we get

$$k_0 = \frac{x}{t} \quad \text{or} \quad x = k_0 t$$

where k_0 is the rate constant of a zero-order reaction, the unit of which is concentration per unit time. In zero order reaction, the **rate constant is equal to the rate of reaction at all concentrations.**

ORDER OF A REACTION

Graphs of Zero Order Reaction



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

$$y = mx + b$$

ORDER OF A REACTION

FIRST ORDER REACTIONS

Let us consider a first order reaction

	A	⟶	Products
Initial conc.	a		0
Final conc.	$a - x$		x

$$\frac{dx}{dt} = k\,(a - x)$$

or
$$\frac{dx}{a - x} = k\,dt \qquad \ldots(1)$$

Integration of the expression (1) gives

$$\int \frac{dx}{a - x} = \int k\,dt$$

or
$$-\ln (a - x) = kt + \mathrm{I} \qquad \ldots(2)$$

where I is the constant of integration. The constant k may be evaluated by putting $t = 0$ and $x = 0$.

Thus,

$$\mathrm{I} = -\ln a$$

ORDER OF A REACTION

Substituting for I in equation (2)

$$\ln \frac{a}{a-x} = kt \qquad \ldots(3)$$

or $$k = \frac{1}{t} \ln \frac{a}{a-x}$$

Changing into common logarithms

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \qquad \ldots(4)$$

The value of k can be found by substituting the values of a and $(a-x)$ determined experimentally at time interval t during the course of the reaction.

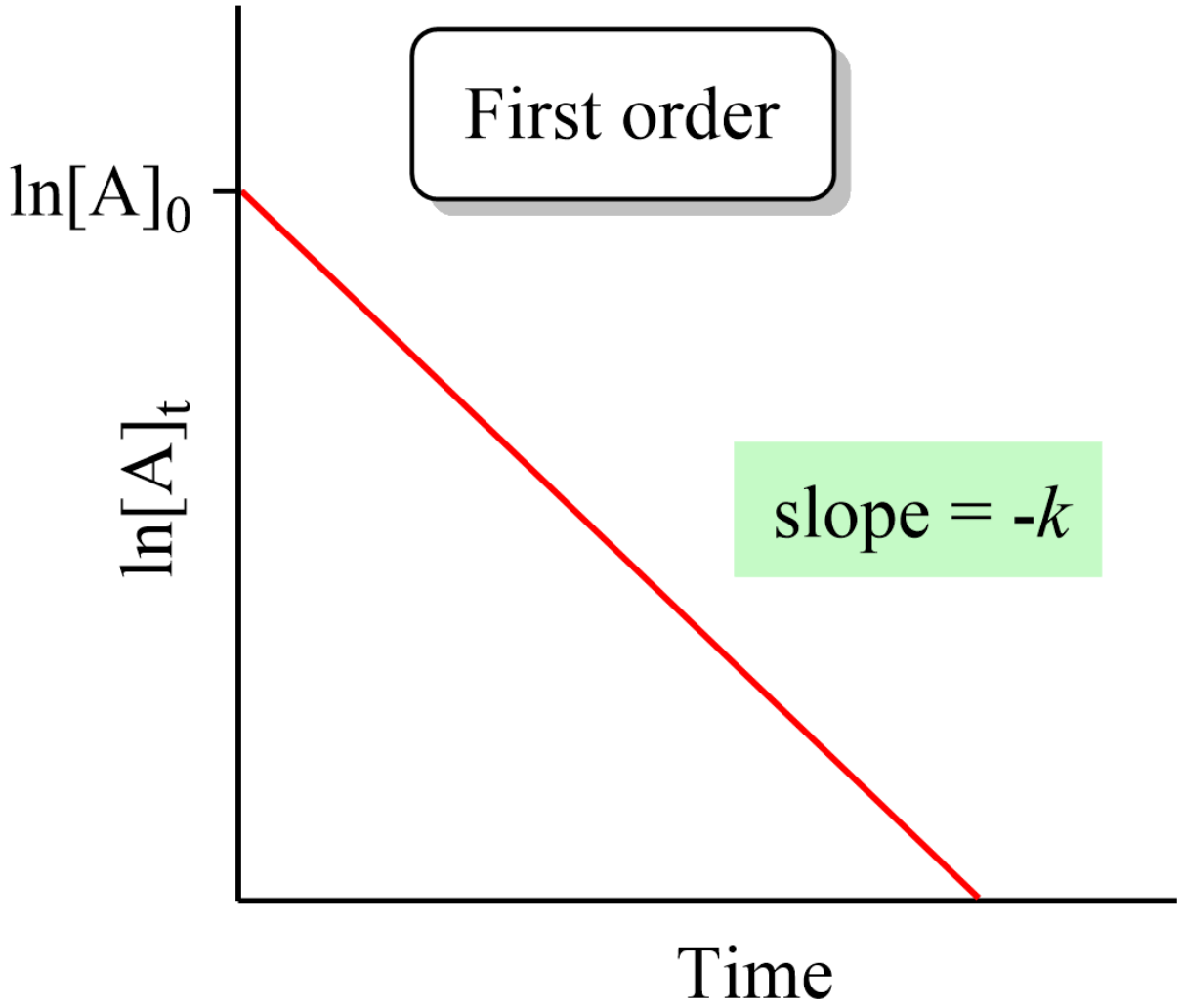
Sometimes the integrated rate law in the following form is also used :

$$k = \frac{2.303}{t_2 - t_1} \log \frac{(a - x_1)}{(a - x_2)}$$

where x_1 and x_2 are the amounts decomposed at time intervals t_1 and t_2 respectively from the start.

ORDER OF A REACTION

Graphs of First Order Reaction



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

$$y = mx + b$$

ORDER OF A REACTION

SECOND ORDER REACTIONS

Let us take a second order reaction of the type

$$2A \longrightarrow \text{products}$$

Initial conc.	a	0
Final conc.	$a - x$	x

$$\frac{dx}{dt} = k(a - x)^2 \qquad ...(1)$$

where k is the rate constant, Rearranging equation (1), we have

$$\frac{dx}{(a - x)^2} = k\,dt \qquad ...(2)$$

On integration, it gives

$$\frac{1}{a - x} = kt + I \qquad ...(3)$$

where I is is integration constant. I can be evaluated by putting $x = 0$ and $t = 0$. Thus,

$$I = \frac{1}{a} \qquad ...(4)$$

ORDER OF A REACTION

Substituting for I in equation (3)

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$kt = \frac{1}{a-x} - \frac{1}{a}$$

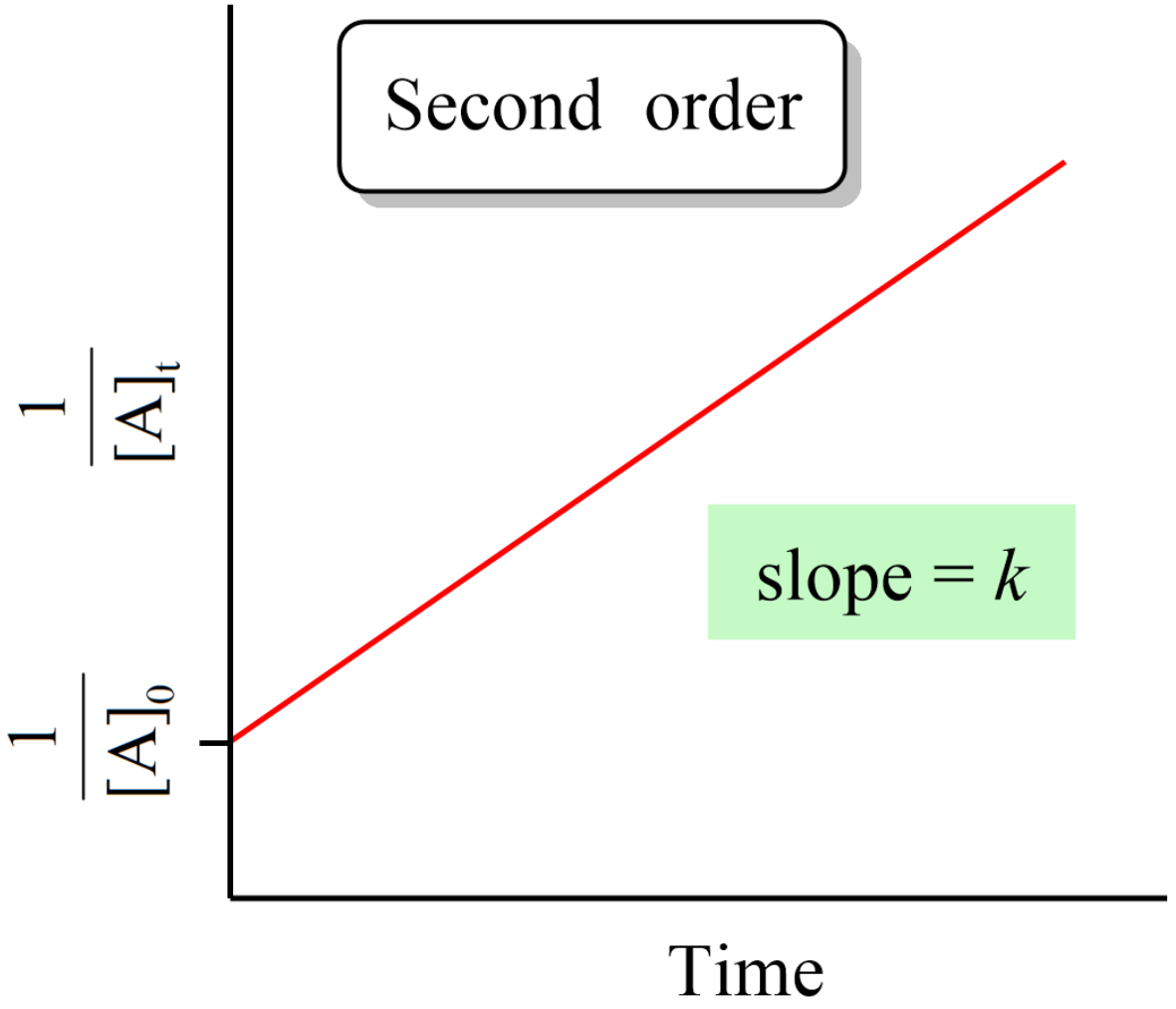
Thus

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

This is the integrated rate equation for a second order reaction.

ORDER OF A REACTION

Graphs of Second Order Reaction



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

ORDER OF A REACTION

SOLVED PROBLEM. Hydrolysis of ethyl acetate by NaOH using equal concentration of the reactants, was studied by titrating 25ml of the reaction mixture at different time intervals against standard acid. From the data given below, establish that this is a second order reaction.

t (mts)	0	5	15	25
ml acid used	16.00	10.24	6.13	4.32

SOLUTION

The second order integrated rate equation is

$$k = \frac{1}{at} \cdot \frac{x}{a(a - x)} \qquad \ldots(1)$$

The volume of acid used at any time is a measure of concentration of the unreacted substances at that time.

Therefore,

a, initial concentration = 16.00

after 5 mts $(a - x)$ = 10.24 and x = 5.76

after 15 mts $(a - x)$ = 6.13 and x = 9.85

after 25 mts $(a - x)$ = 4.32 and x = 11.68

ORDER OF A REACTION

Substituting values in the rate equation (1), we have

$$k = \frac{1}{16 \times 5} \cdot \frac{5.76}{10.24} = 0.0070$$

$$k = \frac{1}{16 \times 15} \cdot \frac{9.85}{6.13} = 0.0067$$

$$k = \frac{1}{16 \times 25} \cdot \frac{11.68}{4.32} = 0.00675$$

The values of k being fairly constant, this reaction is of the second order.

ORDER OF A REACTION

PSEUDO–ORDER REACTIONS

A reaction in which one of the reactants is present in a large excess shows an order different from the actual order. The experimental order which is not the actual one is referred to as the pseudo order.

(1) **Hydrolysis of an ester.** For example, ethyl acetate upon hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.

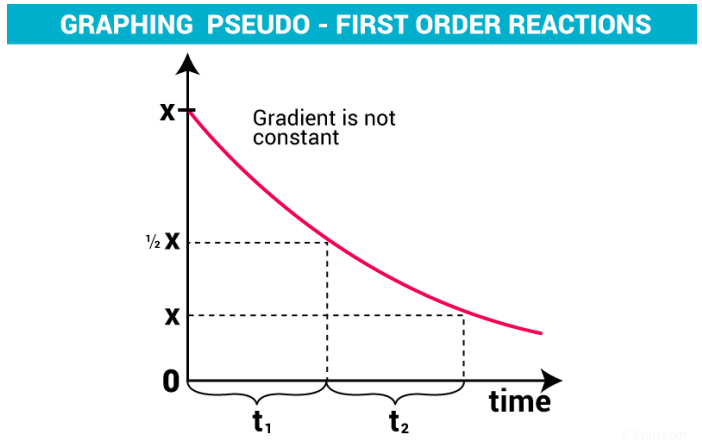
$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

ethyl acetate (excess) acetic acid ethyl alcohol

Here a large excess of water is used and the rate law can be written as

$$\text{rate} = k[CH_3COOH][H_2O]$$
$$= k'[CH_3COOH]$$

The reaction is actually second-order but in practice it is found to be first-order. Thus it is a pseudo-first order reaction.



Determining the ORDER OF A REACTION

(1) Using integrated rate equations

The reaction under study is performed by taking different initial concentrations of the reactant (a) and noting the concentration ($a - x$) after regular time intervals (t). The experimental values of a, ($a - x$) and t are then substituted into the integrated rate equations for the first, second and third order reactions. **The rate equation which yields a constant value of k corresponds to the correct order of the reaction.** This method of ascertaining the order of a reaction is essentially a method of hit-and-trial but was the first to be employed. It is still used extensively to find the order of simple reactions.

Zero-order	$[A]_t = -kt + [A]_0$
First-order	$\ln[A]_t = -kt + \ln[A]_0$
Second-order	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

Determining the ORDER OF A REACTION

(2) Graphical method

For reactions of the type A → products, we can determine the reaction order by seeing whether a graph of the data fits one of the integrated rate equations.

In case of First order

We have already derived the integrated rate equation for first order as

$$\ln \frac{a}{a - x} = k\,t$$

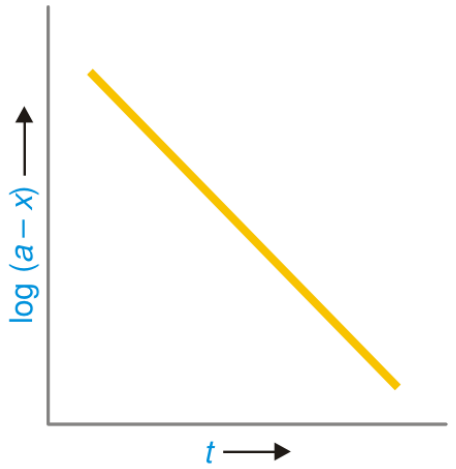
Simplifying, it becomes

$$\underset{\uparrow}{\ln (a - x)} = \underset{\uparrow}{-\,kt} + \underset{\uparrow}{\ln a}$$

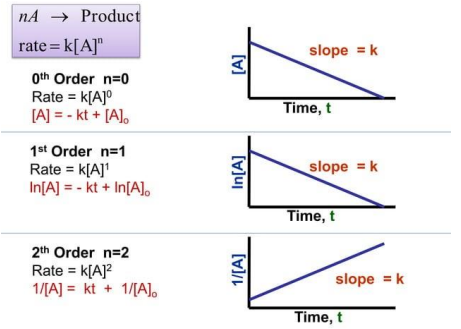
$$y = mx + b$$

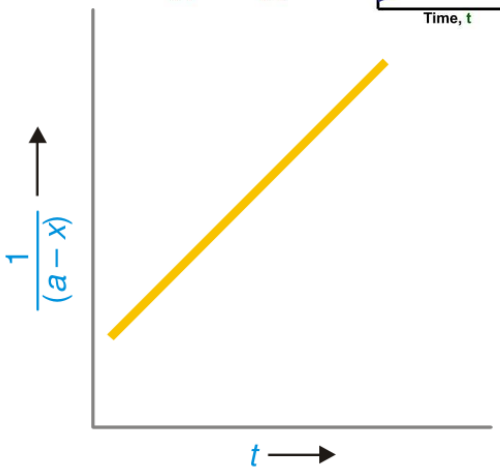
Thus the two variables in the first order rate equation are :

$$\ln \frac{a}{a - x} \text{ and } t$$



■ **Figure 20.7**
Plot of log($a - x$) against t for a first order reaction.





■ **Figure 20.8**
Plot of 1/($a - x$) against t for a second order reaction.

Hence, if $\ln \frac{a}{a - x}$ is plotted against t and straight line results (Fig. 20.7), the corresponding reaction is of the first order. However, if a curve is obtained, the reaction is not first order.

Determining the ORDER OF A REACTION

(3) Using half-life period

Two separate experiments are performed by taking different initial concentrations of a reactant. The progress of the reaction in each case is recorded by analysis. When the initial concentration is reduced to one-half, the time is noted. Let the initial concentrations in the two experiments be $[A_1]$ and $[A_2]$, while times for completion of half change are t_1 and t_2 respectively.

Calculation of order of reaction. We know that half-life period for a first order reaction is independent of the initial concentration, [A]. We also know :

$$\text{half-life} \propto \frac{1}{[A]} \quad \text{for 2nd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^2} \quad \text{for 3rd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^{n-1}} \quad \text{for } n\text{th order reaction}$$

Determining the ORDER OF A REACTION

Substituting values of initial concentrations and half-life periods from the two experiments, we have

$$t_1 \propto \frac{1}{[A_1]^{n-1}} \qquad t_2 \propto \frac{1}{[A_2]^{n-1}}$$

and

$$\frac{t_2}{t_1} = \left[\frac{A_1}{A_2}\right]^{n-1}$$

$$(n-1)\log\left[\frac{A_2}{A_1}\right] = \log\left[\frac{t_1}{t_2}\right]$$

Solving for n, the order of reaction

$$n = 1 + \frac{\log [t_1 / t_2]}{\log [A_2 / A_1]}$$

Determining the ORDER OF A REACTION

(4) The Differential method

This method was suggested by van't Hoff and, therefore, it is also called **van't Hoff's differential method.** According to it, the rate of a reaction of the *n*th order is proportional to the *n*th power of concentration.

$$-\frac{dC}{dt} = k\,C^n$$

where C = concentration at any instant. In two experiments performed with different initial concentrations, we can write

$$-\frac{dC_1}{dt} = k\,C_1^n \qquad \ldots(1)$$

$$-\frac{dC_2}{dt} = k\,C_2^n \qquad \ldots(2)$$

Determining the ORDER OF A REACTION

Taking logs of the expression (1) and (2)

$$\log\left(-\frac{dC_1}{dt}\right) = \log k + n \log C_1 \qquad \ldots(3)$$

$$\log\left(-\frac{dC_2}{dt}\right) = \log k + n \log C_2 \qquad \ldots(4)$$

On substracting (4) from (3), we get

$$n = \frac{\log\left(-\frac{dC_1}{dt}\right) - \left(-\frac{dC_2}{dt}\right)}{\log C_1 - \log C_2} \qquad \ldots(5)$$

To find n, $\left(-\frac{dC}{dt}\right)$ in the two experiments is determined by plotting concentrations against time (t). The slope, $\left(-\frac{dC}{dt}\right)$ at a given time interval is measured by drawing tangents. Using the values of slopes $\left(-\frac{dC_1}{dt}\right)$ and $\left(-\frac{dC_2}{dt}\right)$ in the equation (5), n can be calculated.

Determining the ORDER OF A REACTION

(5) Ostwald's Isolation method

This method is employed in determining the order of complicated reactions by 'isolating' one of the reactants so far as its influence on the rate of reaction is concerned. Suppose the reaction under consideration is :

$$A + B + C \longrightarrow \text{products}$$

The order of the reaction with respect to A, B and C is determined. For the determination of the order of reaction with respect to A, B and C are taken in a large excess so that their concentrations are not affected during the reaction. The order of the reaction is then determined by using any of the methods described earlier. Likewise, the order of the reaction with respect to B and C is determined. If n_A, n_B and n_C are the orders of the reaction with respect to A, B and C respectively, the order of the reaction n is given by the expression.

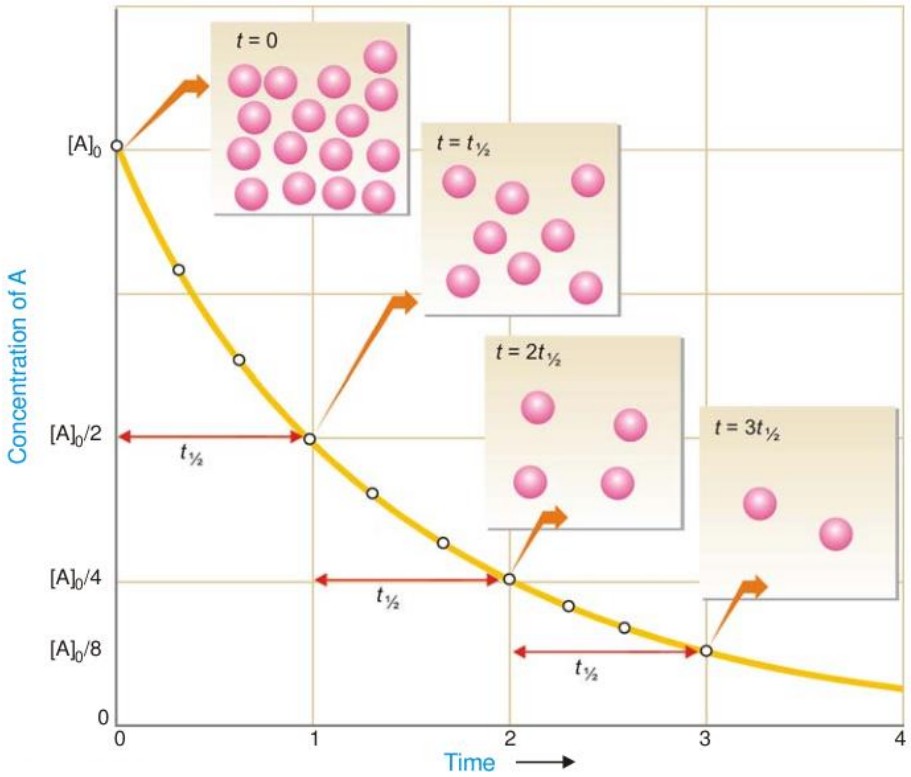
$$n = n_A + n_B + n_C$$

Half Life of a Reaction

HALF–LIFE OF A REACTION

The time required for the concentration of a reactant to decrease to half its initial value.

In other words, half-life is the time required for one-half of the reaction to be completed. It is represented by the symbol $t_{1/2}$ or $t_{0.5}$.



Calculation of Half-life of a First order Reaction

The integrated rate equation (4) for a first order reaction can be stated as :

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

where $[A]_0$ is initial concentration and $[A]$ is concentration at any time t. Half-life, $t_{1/2}$, is time when initial concentration reduces to $\frac{1}{2}$ *i.e.*,

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

Substituting values in the integrated rate equation, we have

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A]_0}{1/2[A]_0} = \frac{2.303}{t_{1/2}} \log 2$$

or

$$t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.3010$$

or

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

"Independent of the initial concentration"

Half Life of a Reaction

Half-Life of a Zero Order Reaction

$$A \longrightarrow \text{Products}$$

For zero order reaction, $-\frac{d\,[A]_0}{dt} = k\,[A\text{-}x]^0$

From the integral form, we have the following equation,

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

For half-life, $t = t_{1/2}$ and $[A] = \frac{[A]_0}{2}$

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

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

"depends on initial concentration"

Half Life of a Reaction

Half-life for a Second order Reaction

For the simple second order reaction 2A → Products, the integrated rate equation is

$$k\,t = \frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0}$$

where $[\mathrm{A}]_0$ is the initial concentration and [A] is the concentration when time t has elapsed.

When one-half life has elapsed.

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

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

or

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

Solving for $t_{1/2}$ we find that

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

"depends on initial concentration"

Half Life of a Reaction

Zero-Order	First-Order	Second-Order
$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Larger $[A]_0$	*constant*	Larger $[A]_0$
Larger $t_{1/2}$	$t_{1/2}$ does not depend on $[A]_0$	Smaller $t_{1/2}$
$[A]_0$ ↑ ↑ $t_{1/2}$	$[A]_0$ ✗ $t_{1/2}$	$[A]_0$ ↑ ↓ $t_{1/2}$

Units of Rate Constant

Units of Zero order Rate constant

For a zero order reaction, the rate constant k is given by the expression

$$k = \frac{d[A]}{dt} = \frac{\text{mol}}{\text{litre}} \times \frac{1}{\text{time}}$$

Thus the units of k are

$$\textbf{mol l}^{-1}\ \textbf{time}^{-1}$$

Time may be given in seconds, minutes, days or years.

Units of First order Rate constant

The rate constant of a first order reaction is given by

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

Thus the rate constant for the first order reaction is independent of the concentration. It has the unit

$$\textbf{time}^{-1}$$

Units of Rate Constant

Units of Second order Rate constant

The rate constant for a second order reaction is expressed as

$$k = \frac{1}{t} \times \frac{x}{[A]_0\,([A]_0 - x)}$$

or

$$= \frac{\text{concentration}}{\text{concentration} \times \text{concentration}} \times \frac{1}{\text{time}}$$

$$= \frac{1}{\text{concentration}} \times \frac{1}{\text{time}}$$

$$= \frac{1}{\text{mole/litre}} \times \frac{1}{\text{time}}$$

$$= \text{mol}^{-1}\,\text{l}\,\text{time}^{-1}$$

Thus the units for k for a second order reactions are

mol^{-1} l time^{-1}

Reaction	Order	Units of rate constant
Zero order reaction	0	$\text{mol L}^{-1}\,\text{s}^{-1}$
First order reaction	1	s^{-1}
Second order reaction	2	$\text{mol}^{-1}\,\text{L}\,\text{s}^{-1}$

Unit of rate constant k for different reaction orders

Half Life of a Reaction

For the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$

the rate is directly proportional to $[N_2O_5]$. At 45°C, 90% of the N_2O_5 reacts in 3600 seconds. Find the value of the rate constant k.

SOLUTION

Since rate is $\propto [N_2O_5]$ it is first order reaction. The integrated rate equation is

$$k = \frac{2.303}{t} \log \frac{[N_2O_5]_0}{[N_2O_5]}$$

When 90% of N_2O_5 has reacted, the initial concentration is reduced to $\frac{1}{10}$ That is,

$$[N_2O_5] = \frac{1}{10}[N_2O_5]_0$$

Substituting values in the rate equation,

$$k = \frac{2.303}{3600} \log \frac{[N_2O_5]_0}{\frac{1}{10}[N_2O_5]_0}$$

$$= \frac{2.303}{3600} \log 10 = \frac{2.303}{3600} \times 1$$

Thus $$k = \frac{2.303}{3600} = \mathbf{6.40 \times 10^{-4}\ s^{-1}}$$

Half Life of a Reaction

Calculation of time required for 100% completion

We know that for first order reaction

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

If reaction is 100% complete in, say, t_1 time, we have, $[A] = 0$. Thus,

$$t_1 = \frac{2.303}{0.00558} \log \frac{[A]_0}{0} = \infty$$

Numericals



For a certain first order reaction, $t_{0.5}$ is 100 sec. How long will it take for the reaction to be completed 75% ?



A second order reaction is 25% completed in 600 sec. How much time will be required for the reaction to go to 75% completion.



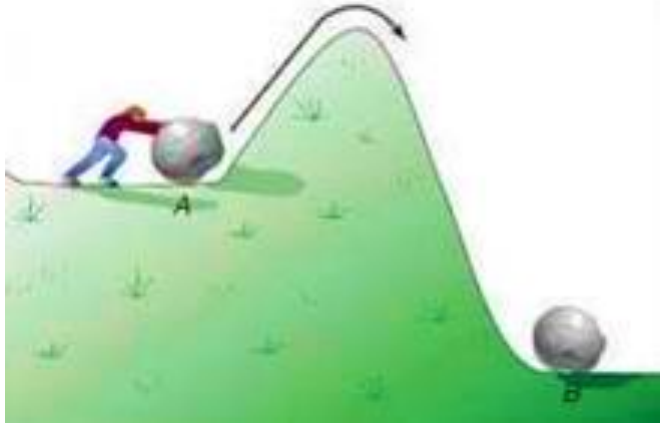
50% of a first order reaction is completed in 50 minutes. Calculate the time required to complete 90% of the reaction.

Theories of Reaction Rates

Collision Theory



Absolute Reaction rate Theory (Transition State Theory)



Collision Theory

According to this theory, **a chemical reaction takes place only by collisions between the reacting molecules.** But not all collisions are effective. Only a small fraction of the collisions produce a reaction. The two main conditions for a collision between the reacting molecules to be productive are :

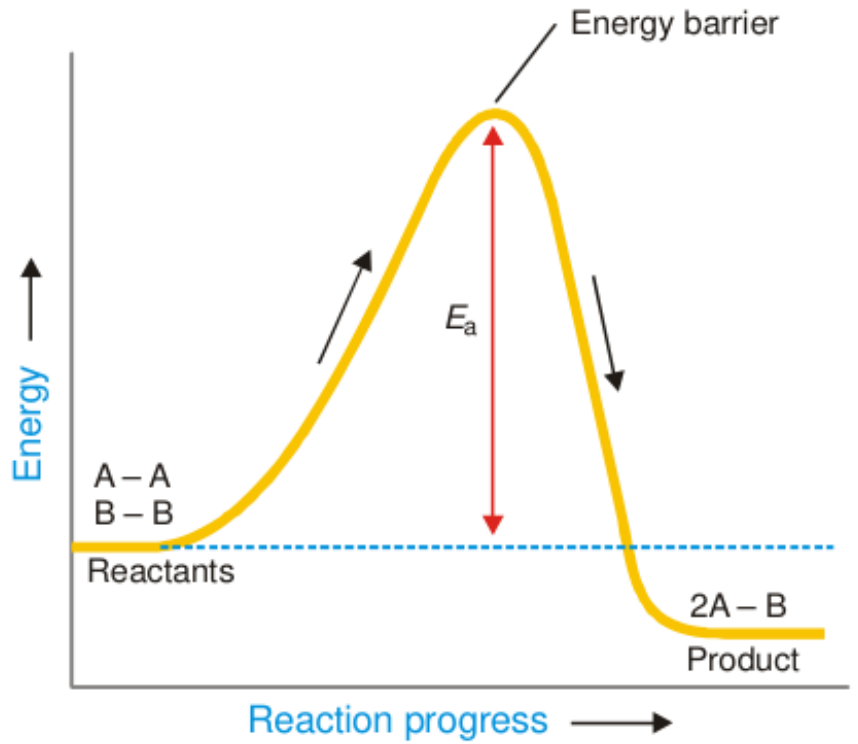
(1) The colliding molecules must posses sufficient kinetic energy to cause a reaction.

(2) The reacting molecules must collide with proper orientation.

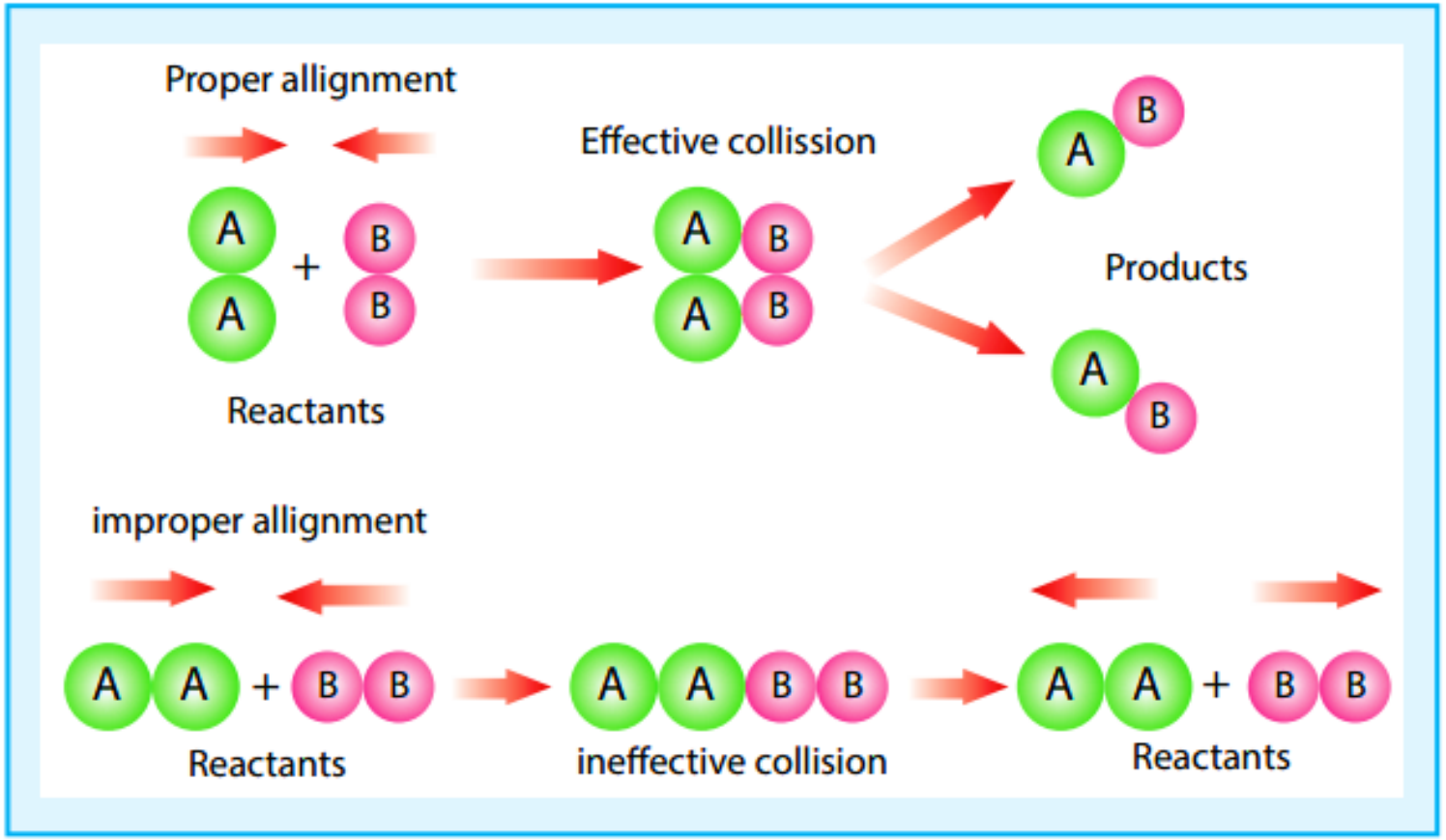
$$A - A + B - B \longrightarrow 2A - B$$

Activation energy, E_a, that is the minimum energy necessary to cause a reaction between the colliding molecules.

- **Only the molecules that collide with a kinetic energy greater than E_a, are able to get over the barrier and react.**



Collision Theory



Orientation of reactants - schematic representation

Proper Orientation

The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming of bonds

Collision Theory

EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by 10°C doubles the reaction rate. Thus the ratio of rate constants of a reaction at two different temperatures differing by 10 degree is known as **Temperature Coefficient.**

$$\textit{i.e.,}\ \text{Temperature Coefficient} = \frac{k_{35^\circ}}{k_{25^\circ}} = \frac{k_{308}}{k_{298}}$$

$$= 2 \text{ to } 3$$

It has been found that **generally an increase of temperature increases the rate of reaction.** As a rule, an increase of temperature by 10°C doubles the reaction rate.

Collision Theory

Temperature Dependence of Reaction Rate and Arrhenius Equation

- We know that the kinetic energy of a gas is directly proportional to its temperature. Thus as the temperature of a system is increased, more and more molecules will acquire necessary energy greater that E_a to cause productive collisions. This increases the rate of the reaction.

In 1889, Arrhenius suggested as simple relationship between the rate constant, k, for a reaction and the temperature of the system.

$$k = A\, e^{-E_a/RT} \qquad \ldots(1)$$

Taking natural logs of each side of the Arrhenius equation, it can be put in a more useful form :

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad \ldots(2)$$

$$\log k = \frac{-E_a}{2.303\,RT} + \log A \qquad \ldots(3)$$

If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively, we can derive

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right] \qquad \ldots(4)$$

Collision Theory

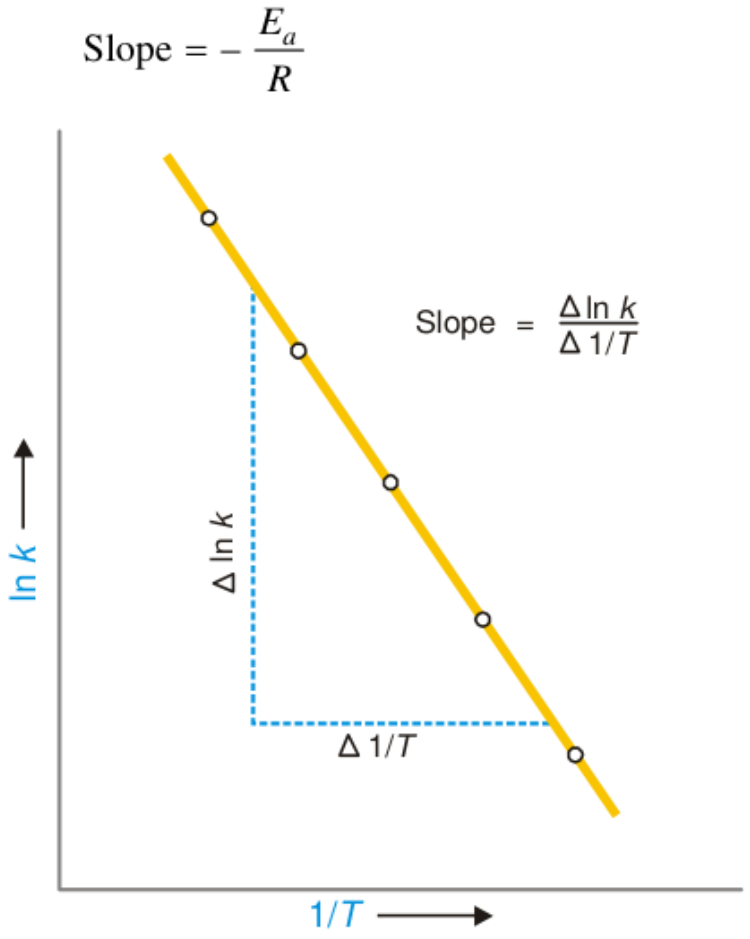
Calculation of E_a Using Arrhenius Equation

In slightly rearranged form Arrhenius equation (2) can be written as

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$y = mx + b$$

Thus if we plot the natural logarithm of k against 1/T, we get a straight line. From the slope of the line, we can calculate the value of E_a



Collision Theory

Limitations of the Collision Theory

(1) **The theory applies to simple gaseous reactions only.** It is also valid for solutions in which the reacting species exist as simple molecules.

(2) The values of rate constant calculated from the collision theory expression (Arrhenius equation) are in agreement with the experimental values only for simple bimolecular reactions. **For reactions involving complex molecules, the experimental rate constants are quite different from the calculated values.**

(3) There is no method for determining the steric effect (p) for a reaction whose rate constant has not been determined experimentally.

(4) In the collision theory it is supposed that only the kinetic energy of the colliding molecules contributes to the energy required for surmounting the energy barrier. There is no reason why the rotational and vibrational energies of molecules should be ignored.

(5) **The collision theory is silent on the cleavage and formation of bonds involved in the reaction.**

Transition State Theory

The **transition state** or **activated complex theory** was developed by Henry Erying (1935). This theory is also called the **absolute rate theory** because with its help it is possible to get the absolute value of the rate constant. The transition state theory assume that simply a collision between the reactant molecules does not really causes a reaction. During the collision, **the reactant molecules form a transition state or activated complex which decomposes to give the products.**

Thus,

$$\underbrace{A + B{-}C}_{\text{Reactants}} \longrightarrow \underset{\substack{\text{Activated}\\ \text{complex}}}{ABC^{\ddagger}} \longrightarrow \underbrace{A{-}B + C}_{\text{Products}}$$

The double dagger superscript ($\ddagger$) is used to identify the activated complex.

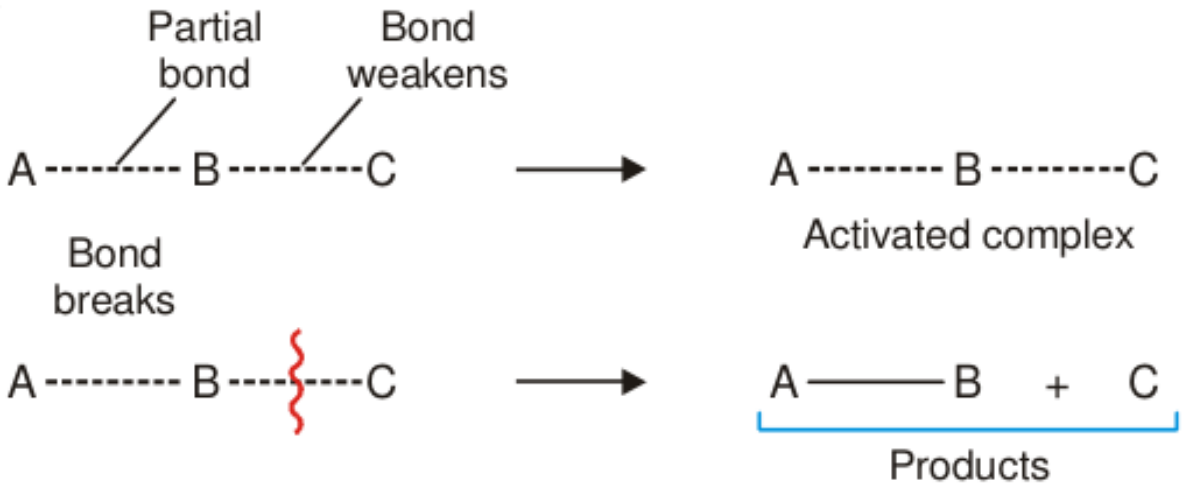
Transition State Theory

The transition state theory may be summarised as follows :

(1) In a collision, the fast approaching reactant molecules (A and BC) slow down due to gradual repulsion between their electron clouds. In the process **the kinetic energy of the two molecules is converted into potential energy.**

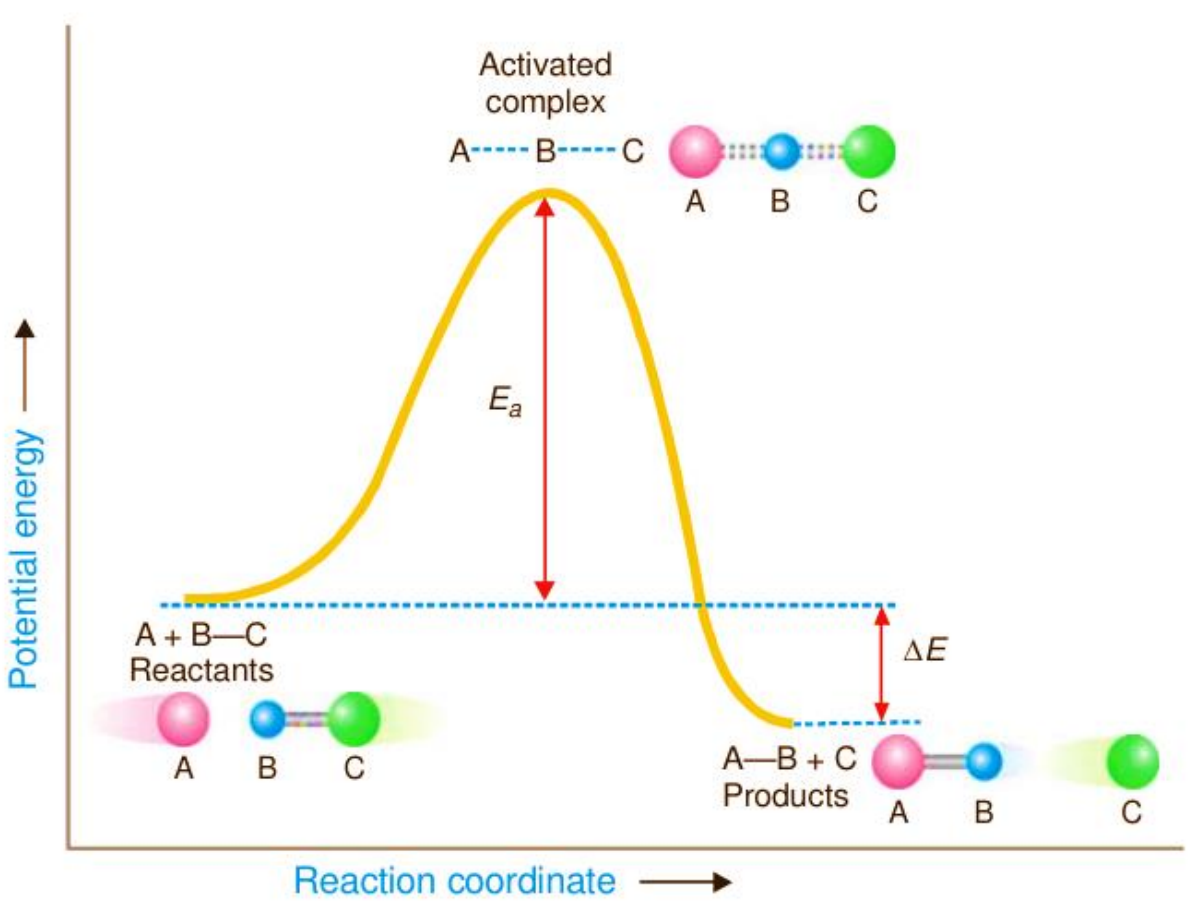
(2) As the molecules come close, **the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.**

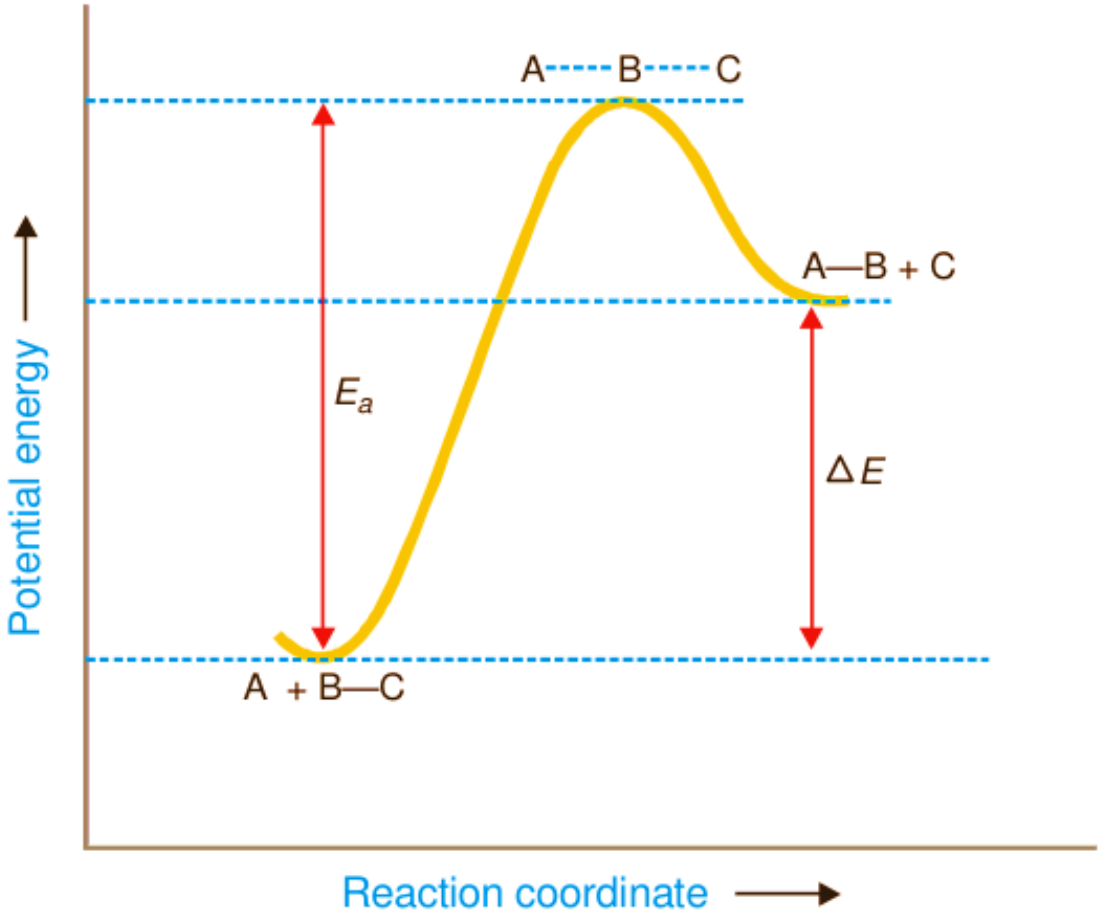
(3) A partial bond is formed between the atoms A and B with corresponding weakening of B – C bond. This leads to formation of an **activated complex** or **transition state.** The activated complex is momentary and decomposes to give the products (A–B + C)



Transition State Theory

Potential energy diagram for an exothermic and endothermic reaction



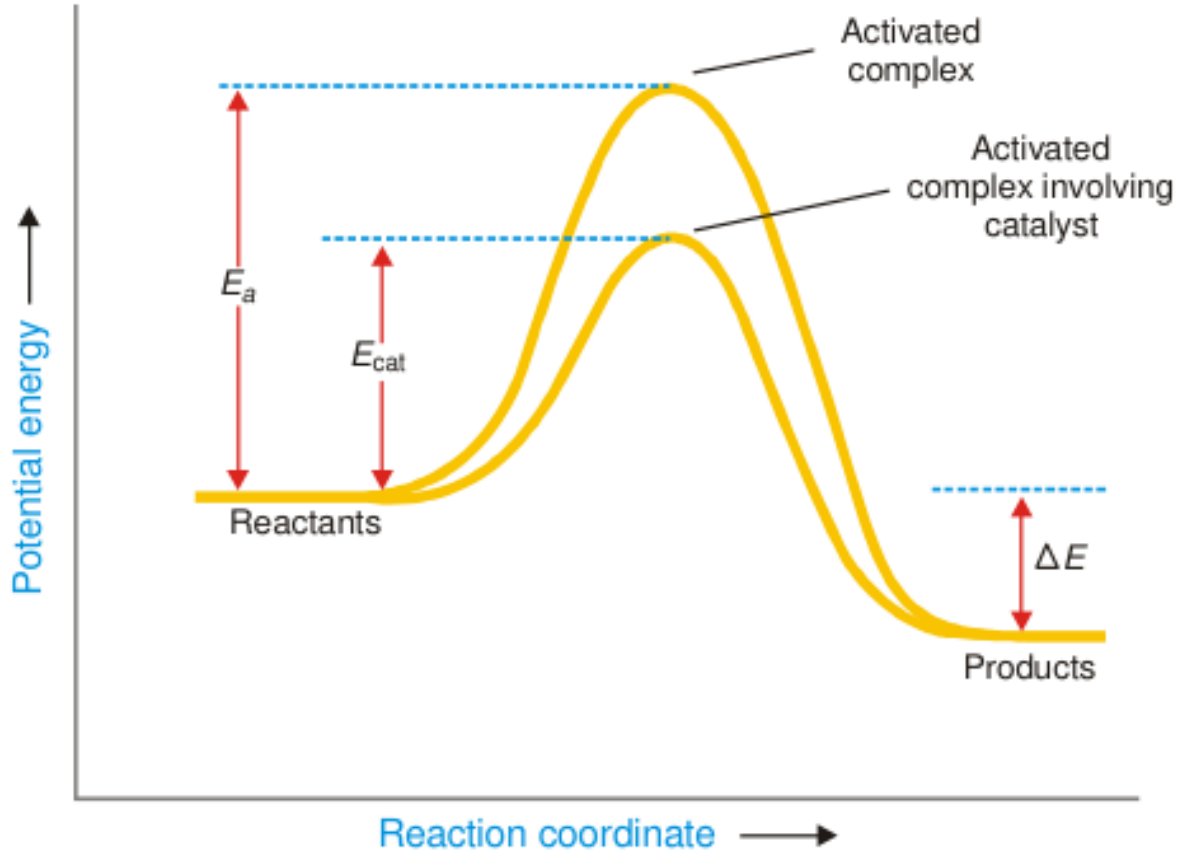


Which product is more stable ?

Transition State Theory

Activation Energy and Catalysis

We know that for each reaction a certain energy barrier must be surmounted.



- **The catalyst functions by providing another pathway with lower activation energy, E_{cat}**

A much large number of collisions becomes effective at a given temperature. Since the rate of reaction is proportional to effective collisions, the presence of a catalyst makes the reaction go faster, other conditions remaining the same.

REMINDER

Although a catalyst lowers the activation energy, the energy difference, ΔE, between products and reactants remains the same.