

Chemical Kinetics

Chemical Reactions

Motion/Speed of reaction

What is the relation between speed and spontaneity?

Speed

Spontaneity

Speed **→** **Rate of the reaction**

Spontaneity **→** **Feasibility of the reaction**

The area of Chemistry concerned with reaction rates and the sequence of steps by which reaction occur is called **CHEMICAL KINETICS**

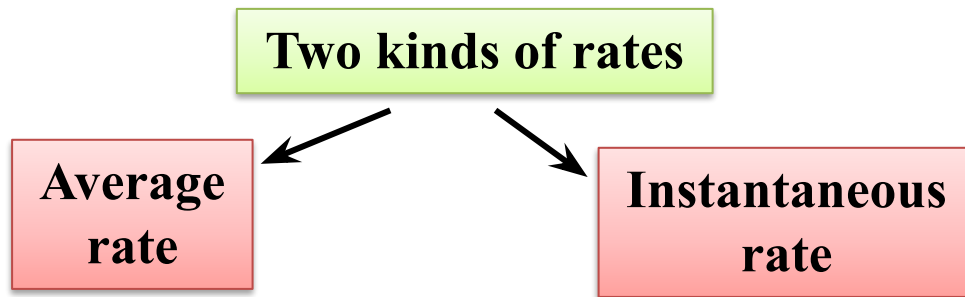
Rate of reaction

Rate of a Reaction

$$\text{Rate of a reaction} = \frac{\text{Change in concentration of reactant or product}}{\text{Time taken}} = \frac{\text{Final conc.} - \text{initial conc.}}{\text{Time taken}} = \frac{\Delta C}{\Delta t}$$

$$\text{Units of rate} = \text{mol L}^{-1} \text{ s}^{-1}$$

How many types of Rate of reaction are there ?



Average rate


An overall rate measured over period of time interval.

$$r_{\text{average}} = \frac{\text{Change of concentration of one of the reactant or products}}{\text{Time}}$$

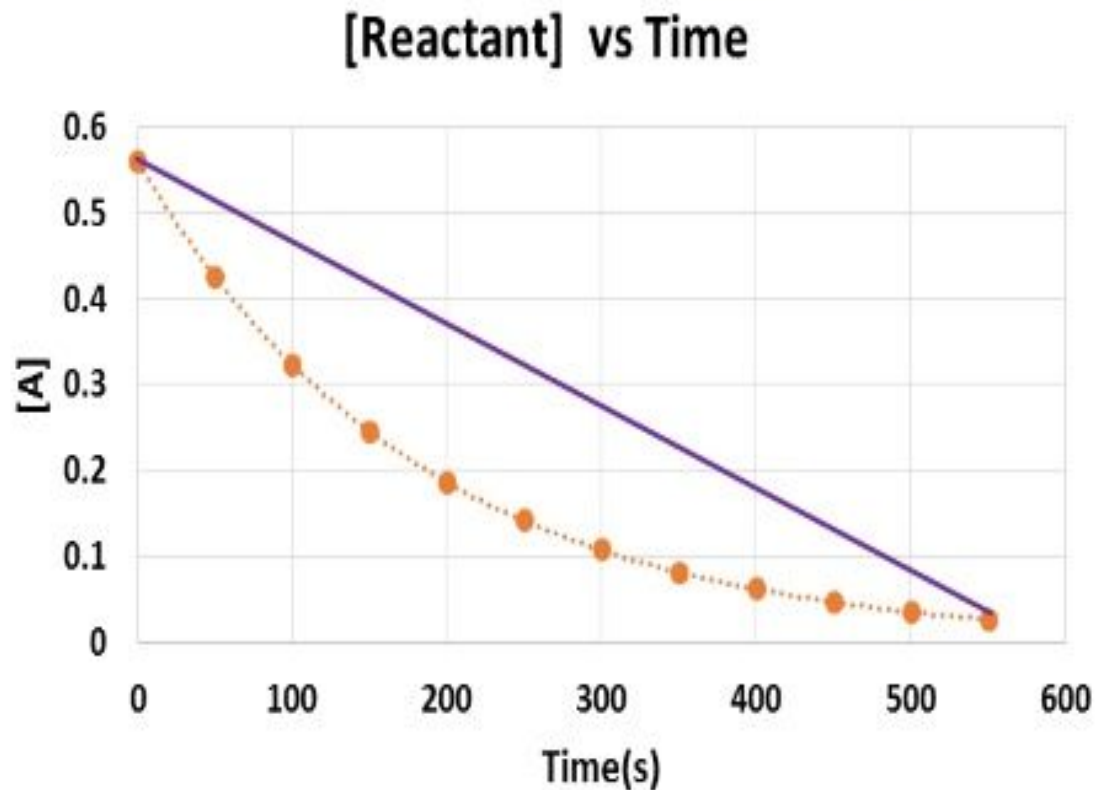
Average Rate

For the reaction $A + B \longrightarrow C$

We can calculate the average rate between any two times during the reaction.

(-) indicates disappearance of A  $-\frac{\Delta[A]}{\Delta t} = \frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1}$

Average Rate Over the Course of the Reaction

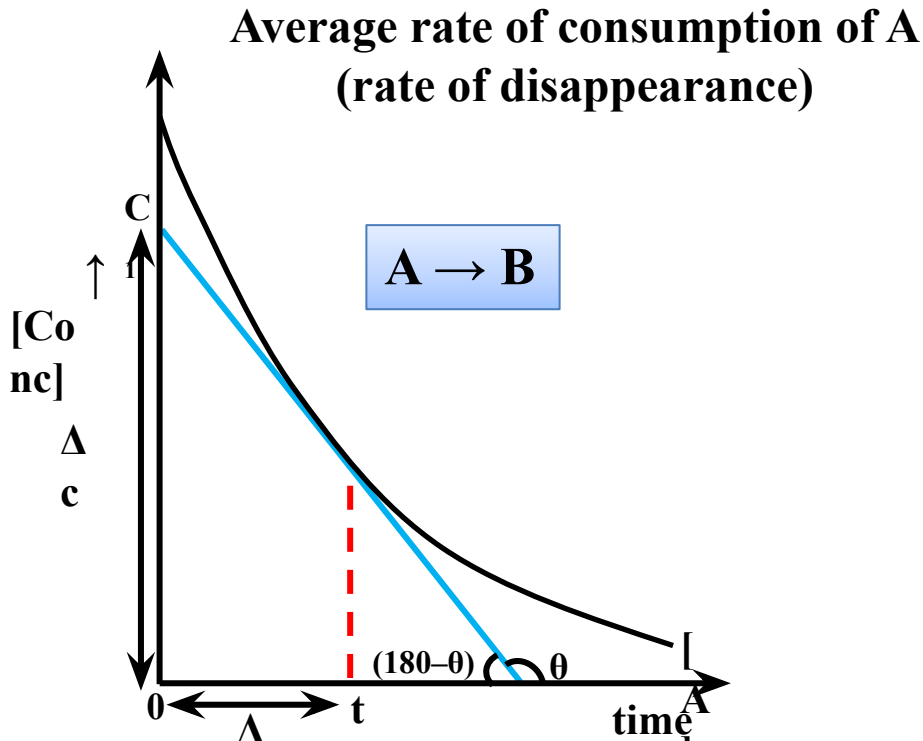


Instantaneous Rate of Reaction

What is instantons rate and Overall Rate of a reaction ?

Instantaneous Rate

Rate measured at any point during the reaction.



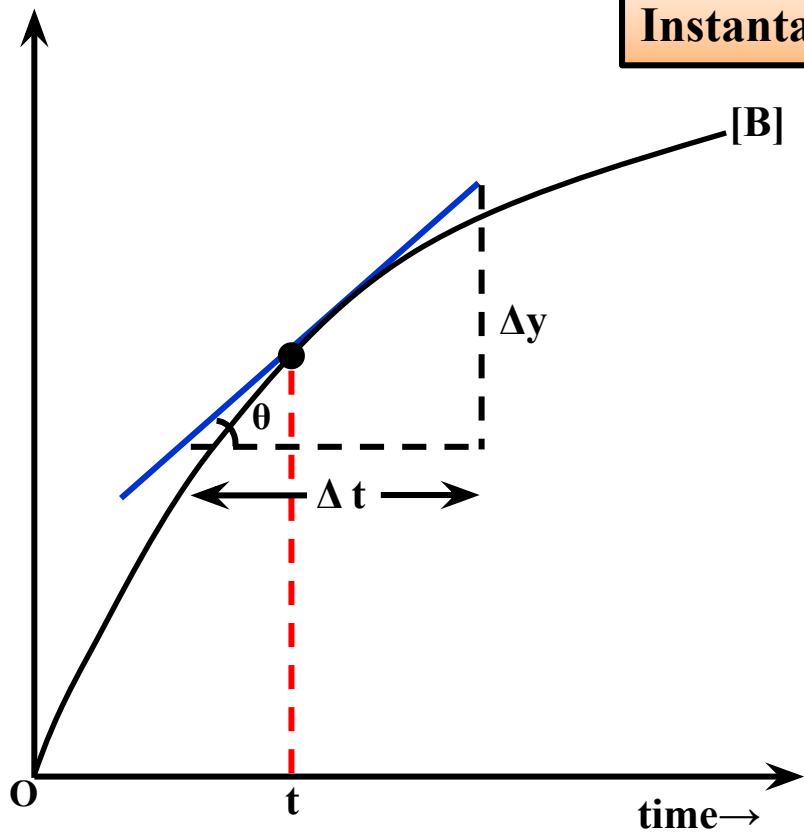
$$= \frac{\text{Intercept along ordinate}}{\text{Intercept along abscissa}}$$

$$= \tan\theta = \left(\frac{-\Delta c}{\Delta t} \right)$$

$$= \lim_{\Delta t \rightarrow 0} \frac{-\Delta C}{\Delta t} = \frac{-dc}{dt}$$

–ve sign implies the decreases in concentration of reactant

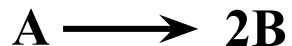
Instantaneous Rate



$$\text{Instantaneous rate} = \frac{\Delta y}{\Delta t} = \tan \theta$$

$$= \lim_{\Delta t \rightarrow 0} \frac{\Delta C}{\Delta t} = \frac{dc}{dt}$$

Overall rate equation



At $t = 0$
(Initial Conc.)

a	$-$
-----	-----

$t = t$
(Final Conc.)

$a - x$	$2x$
---------	------

Rate of disappearance of A

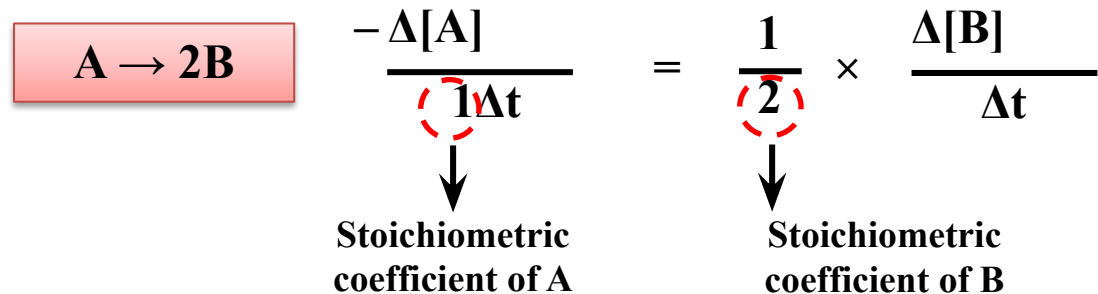
$$\begin{aligned}
 &= \frac{-\Delta[A]}{\Delta t} \\
 &= \frac{-[(a - x) - a]}{\Delta t} \\
 &= \frac{x}{t}
 \end{aligned}$$

Rate of appearance of B

$$\begin{aligned}
 &= \frac{\Delta B}{\Delta t} \\
 &= \frac{2x}{t}
 \end{aligned}$$

$$\text{Rate of appearance of B} = 2 \text{ Rate of disappearance of A}$$

$$\text{Rate of disappearance of A} = \frac{\text{Rate of appearance of B}}{2}$$



**Instantaneous rate and Overall Rate of a reaction in
term of differential rate equation**

Overall Rate of the reaction

In general,



$$\begin{aligned}\text{Overall rate} &= \frac{1}{(-\mathbf{a})} \frac{\Delta[\mathbf{A}]}{\Delta t} = \frac{1}{(-\mathbf{b})} \frac{\Delta[\mathbf{B}]}{\Delta t} \\ &= \frac{1}{\mathbf{c}} \frac{\Delta[\mathbf{C}]}{\Delta t} = \frac{1}{\mathbf{d}} \frac{\Delta[\mathbf{D}]}{\Delta t}\end{aligned}$$

Just divide all the rates with the respective stoichiometric coefficients to get the overall rate of the reaction

Keeping in mind that with reactants we put a negative sign and with products we put a positive sign

Instantaneous Rate

Similarly we can define instantaneous rate for which $\lim_{\Delta t \rightarrow 0}$

Overall instantaneous rate

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

Factors affecting rate of a reaction

Factors affecting reaction rates

Nature of reactants

- Some substances are more reactive than others

Concentration

- Increasing the concentration of reactants, increases the rate of reactions
- The more particles present, the more often they collide

Surface area

- The smaller the size of particle, the greater the surface area.
- Increasing the surface area speeds up the rate of reaction by increasing the collision rate.

Temperature

- Increasing the temperature, increases the rate of reaction
- The higher the temperature, the higher the kinetic energy of particles, the more they collide.

Catalysts and inhibitors

- Catalyst: substance that increases the rate of reaction
- Inhibitor: substance that slows down or inhibits reaction rates.

Explain Rate Law and Order of the reaction.

The Rate Law

The **rate law** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.



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

m, n : orders (may be positive – ve, zero or fractional)

Reaction is **x th order** in A

Reaction is **y th order** in B

Reaction is **$(x + y)$ th order overall**

Sum of powers of concentration terms involved in rate law expression is called order of reaction.

What are Characteristics of rate constant ?

CHARACTERISTICS OF RATE CONSTANT

- 1. Rate Constant is the measure of the rate of the reaction. Greater the value of k , faster is the reaction and vice-versa.**
- 2. The value of rate constant is independent of the concentration of reactant.**
- 3. The value of rate constant of a particular reaction changes with change in Temperature.**
- 4. Units of rate constant depends on the order of reaction.**
- 5. The value of k depends on the nature of reactant. Different reactions have different values of k .**

Units of the Rate Constant k for Several Overall Reaction Orders

Overall Reaction Order

Units of k (t in seconds)

0

mol/L*s (or $\text{mol L}^{-1} \text{s}^{-1}$)

1

$1/\text{s}$ (or s^{-1})

2

L/mol*s (or $\text{L mol}^{-1} \text{s}^{-1}$)

3

$\text{L}^2 / \text{mol}^2 * \text{s}$ (or $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$)

General formula:

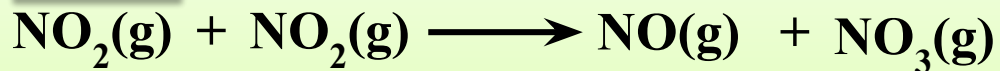
$$\text{Unit of } k = \frac{(\text{L/mol})^{\text{order}-1}}{\text{Unit of time}}$$

Molecularity of Reactions

MOLECULARITY

It represents the number of molecules, colliding with each other in an elementary step.

Step 1



Step 2



Molecularity is not defined for a complex or overall reaction.

Q. What is the molecularity of step 1 ?

Answer : 2

Q. What is the molecularity of step 2?

Answer : 2

**Differentiate between molecularity
and order.**

Molecularity	Order
1. Theoretical term	1. Experimentally determined
2. Whole number	2. Positive, Negative, Zero, Fraction

Reactions with the different molecularities have different names.

Molecularity	Name of reaction
1	Unimolecular
2	Bimolecular
3	Termolecular
4	Quartermolecular

What is integrated rate law for zero order reaction ?

Zero order Reaction ($n = 0$)

This is called integrated rate law for zero order reaction

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

$$\Rightarrow \int_{[A]_0}^{[A]_t} d[A] = -k \int_0^t dt$$
$$\left| [A] \right|_{[A]_0}^{[A]_t} = -k \left| t \right|_0^t$$

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

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

Half life $t_{1/2}$

Time when half of the reactant is consumed

So at $t_{1/2}$, $[A]_t = \frac{[A]_0}{2}$



Integrated rate law for zero order reaction becomes,

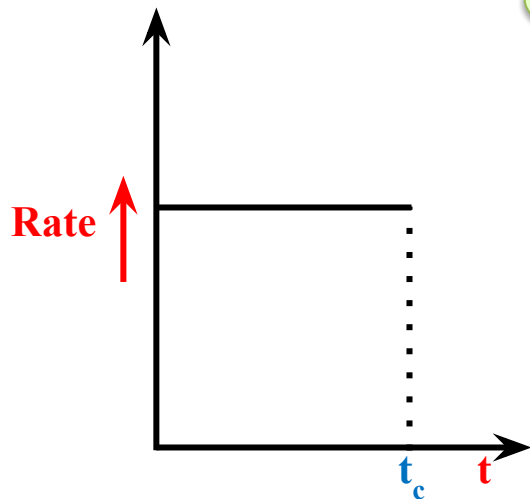
$$\frac{[A]_0}{2} = [A]_0 - k t_{1/2} \Rightarrow$$

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

Graphs of zero order reaction

Graph of Rate v/s Time

Rate of reaction remains constant for 0 order reactions



Graph of $[A]$ v/s t

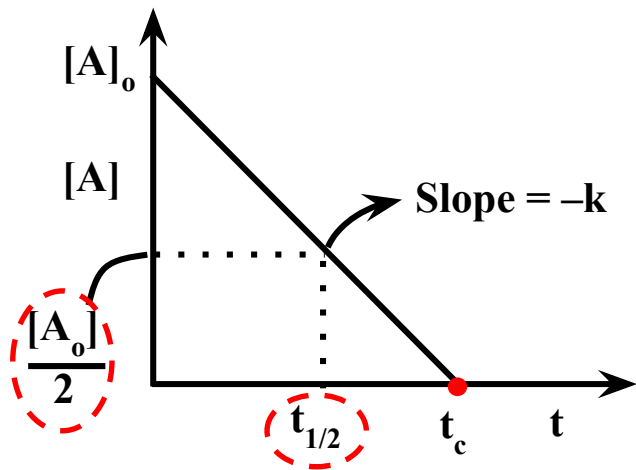


Diagram illustrating the linear relationship between concentration $[A]$ and time t for a first-order reaction, shown within a thought bubble.

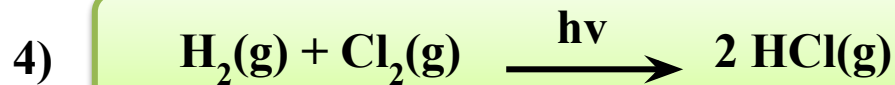
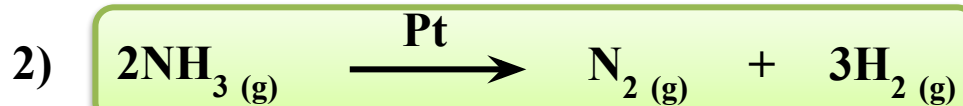
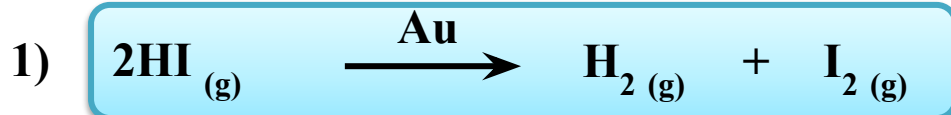
The equation is:

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

The components are identified as follows:

- $y - \text{axis}$ points to $[A]$
- $x - \text{axis}$ points to t
- $[A]_0$ is the **Intercept**
- $-k$ is the **Slope**

Examples of Zero Order Law :



Both gases are at
high pressure

INTEGRATED RATE LAW FOR FIRST ORDER REACTION & GRAPHS

First order Reactions

Differential rate will be

$$\frac{-d[A]}{dt} = k[A]^1$$

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

Integrating between the limits

$$\int_{[A]_0}^{[A]_t} \frac{-d[A]}{[A]} = -k \int_0^t dt$$

$$\left[\ln [A] \right]_{[A_0]}^{[A_t]} = -k dt$$

This is called **integrated rate law** for first order reaction

$$\ln [A_t] - \ln [A_0] = -kt$$

Logarithmic form

$$\therefore \int \frac{dx}{x} = \ln x$$

$$\ln [A_t] = \ln [A_0] - kt$$

$$k = \frac{1}{t} \ln \frac{[A_0]}{[A_t]}$$

$$\Rightarrow \ln \frac{[A_t]}{[A_0]} = -kt$$

$$-\ln \frac{[A_t]}{[A_0]} = kt$$

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

$$\left[\begin{array}{l} \therefore -\ln x = \\ \ln \end{array} \frac{l}{x} \right]$$

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

Logarithmic form

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

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

Exponential form

Half life $t_{1/2}$

Half life of first order reaction is independent of initial concentration

$$\text{At } t = t_{1/2}, [A]_t = \frac{[A_0]}{2}$$

$$\text{Rate law becomes } \Rightarrow \ln \frac{[A_0]}{2} = \ln [A_0] - k t_{1/2}$$

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

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

Time of completion = ∞

In terms of amount consumed

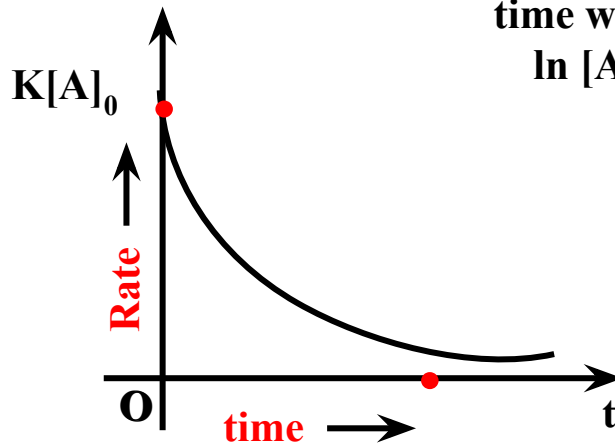
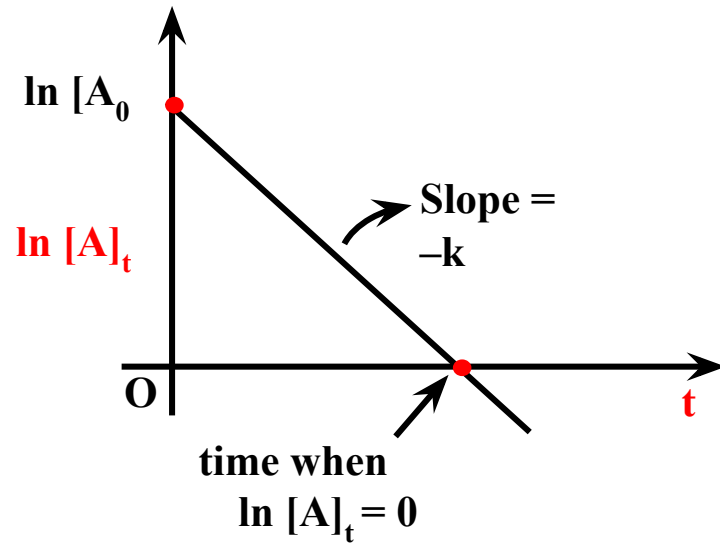
$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$



Graph for first order reaction

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

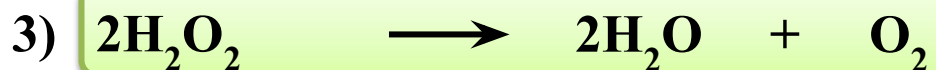
$$\text{Rate} = k[A] = k[A]_0 e^{-kt}$$

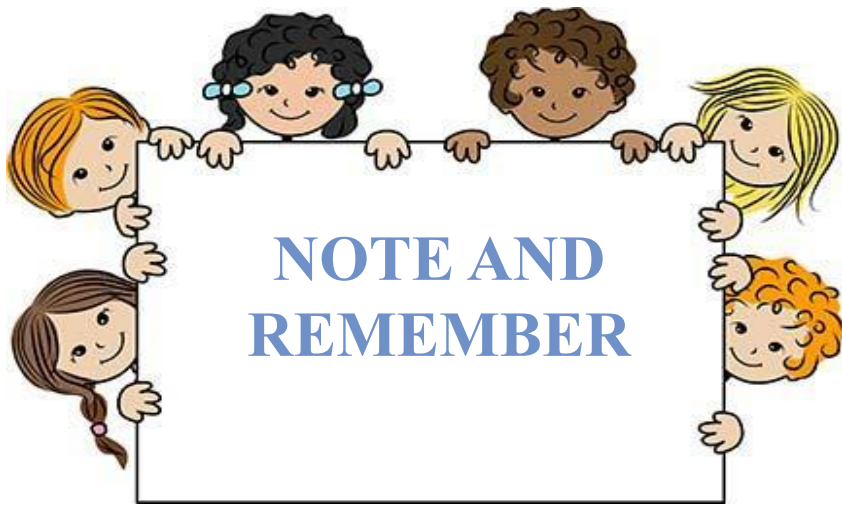


EXAMPLES OF FIRST ORDER REACTION

Examples of first order reaction :

1) All the **radioactive** decays are **first order reactions**





$$t_{3/4} \text{ or } t_{75\%} = 2 t_{1/2}$$

$$t_{87.5\%} = 3 t_{1/2}$$

$$t_{99.9\%} = 10 t_{1/2}$$

Explain practical analysis of first order reaction.

Practical method of analysis of first order reaction.

A \longrightarrow Products,

Integrated rate law is

$$k = \frac{2.303}{t} \log \left(\frac{[A_0]}{[A_t]} \right) = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

Explain practical analysis of first order reaction.

Case I

When **gases are produced**

Explain practical analysis of first order reaction.

Case I When **gases** are produced



$$t = 0 \quad a$$

$$t = t \quad a - x \qquad x \qquad x$$

$$t = \infty \quad 0 \qquad a \qquad a$$

Time

Total pressure

0

P_0

t

P_t

∞

P_∞

$$PV = nRT$$

$P \propto n$ considering
V, R, T to be constant

The pressure after
time t will be more
than initial
pressure (t=0)

Explain practical analysis of first order reaction.

$$\therefore P_t \propto x \quad \dots(\text{i})$$

$$P_\infty \propto a \quad \dots(\text{ii})$$

$$P_\infty - P_t \propto (a - x) \quad \dots(\text{iii})$$

The proportionality constant inequation (ii) and (iii) will be same, so we will get eq. no.(iv) as the constant will cancel out.

$$\Rightarrow \frac{P_\infty}{P_\infty - P_t} = \frac{a}{a - x} \quad \dots(\text{iv})$$

Hence, the integrated rate law becomes

Chemical Kinetics

Case I When **gases** are produced

$A(s) \longrightarrow B(s) + C(g)$

$t = 0$	a			
$t = t$	$a - x$	x	x	
$t = \infty$	0	a	a	

Time	Total pressure
0	P_0
t	P_t
∞	P_∞

$$k = \frac{2.303}{t} \log \left(\frac{P_\infty}{P_\infty - P_t} \right)$$

Example



0	a	0	0
t	$a - x$	x	x
∞	0	a	a

So,

$$\begin{array}{rcl}
 P_t & \propto & x \\
 P_\infty & \propto & 2a \\
 P_\infty - P_t & \propto & 2(a - x)
 \end{array}$$

$$\Rightarrow \frac{P_\infty}{P_\infty - P_t} = \frac{a}{a - x}$$

\therefore integrated rate law becomes

$$k = \frac{2.303}{t} \log \left(\frac{P_\infty}{P_\infty - P_t} \right)$$

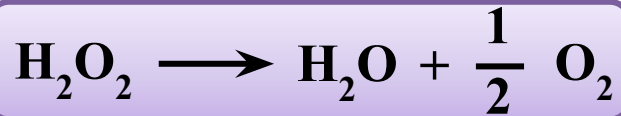
Explain practical analysis of first order reaction.

Case II When one of the components can be determined by titration.

Explain practical analysis of first order reaction.

Case II When one of the components can be determined by titration.

Example Redox Titration



0 : a

t : $a - x$ x $\frac{x}{2}$

Amount of H_2O_2 left,
is determined by
titrating with KMnO_4 .

Given data

Time	Volume of KMnO_4
0	V_0
⋮	⋮
t	V_t

Explain practical analysis of first order reaction.

Here,

$$V_0 \propto a \quad \dots (i)$$

$$V_t \propto a - x \quad \dots (ii)$$

$$(ii) \div (i)$$

$$\Rightarrow \frac{V_0}{V_t} = \frac{a}{a - x}$$

Because the constant in both of the equations is same therefore it will get canceled on dividing both the equations

$$\therefore k = \frac{2.303}{t} \log \left(\frac{V_0}{V_t} \right)$$

What is Rate determining step ?

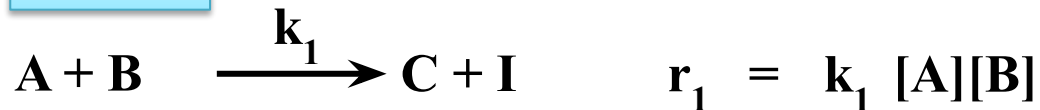
**A complex reaction is a reaction
which comprises of two or
more
elementary reactions**

**Rate of a complex reaction is determined by the rate of slowest step
i.e. **R**ate **D**etermining **S**tep (**RDS**).**

Example



Step 1



Step 2



If it is given that step 1 is R.D.S then overall **rate = $k_1 [A][B]$**

**Overall molecularity = 2 = Molecularity of R.D.S
(limited applicability)**

**In general, molecularity
is not defined for a
complex reaction.**

**But some time molecularity of the
complex reaction is taken equal to
the molecularity of the R.D.S**

Overall order = 2

What is Pseudo first order reactions ?

Pseudo – Unimolecular Reactions / Pseudo first order reactions

When a reactant is made much more concentrated than the other, it is **made to have no effect** on the rate of that particular expt i.e. **appears** to be zero order.

Rate = $k[\mathbf{A}]^1[\mathbf{B}]^1$ reaction is 2nd order

For expt where $[\mathbf{B}] \gg [\mathbf{A}]$,

$[\mathbf{B}] = \text{constant}$

Rate = $k'[\mathbf{A}]^1$ reaction appears to be 1st order
pseudo ('fake') 1st order

Pseudo – Unimolecular Reactions / Pseudo first order reactions

Example



If it is given that the reactions is elementary

$$r = k [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

If H_2O is taken in excess (i.e. H_2O is solvent)

then concentration of H_2O is constant

$$r = (k[\text{H}_2\text{O}]) [\text{CH}_3\text{COOC}_2\text{H}_5]$$

$$= k' [\text{CH}_3\text{COOC}_2\text{H}_5]$$

\therefore Order of the reaction = 1

If it is elementary, \Rightarrow Molecularity = 1

**Other example of
Pseudo-Unimolecular reaction is
inversion of cane sugar.**

Collision theory

Collision Theory

For any reaction to occur -

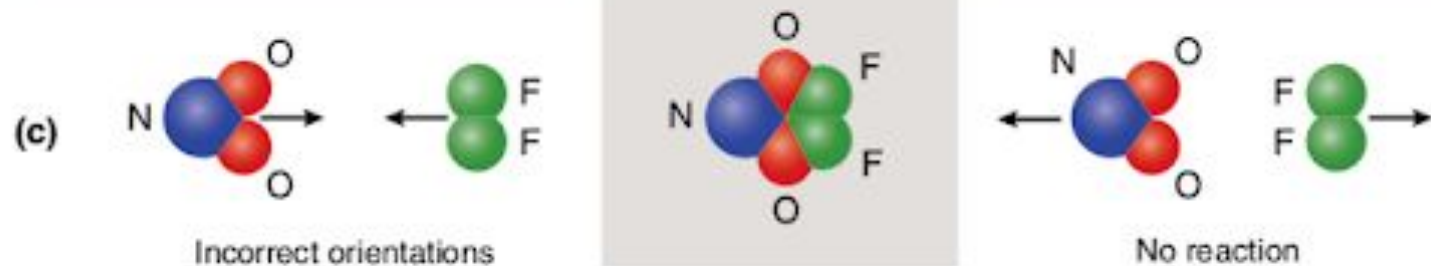
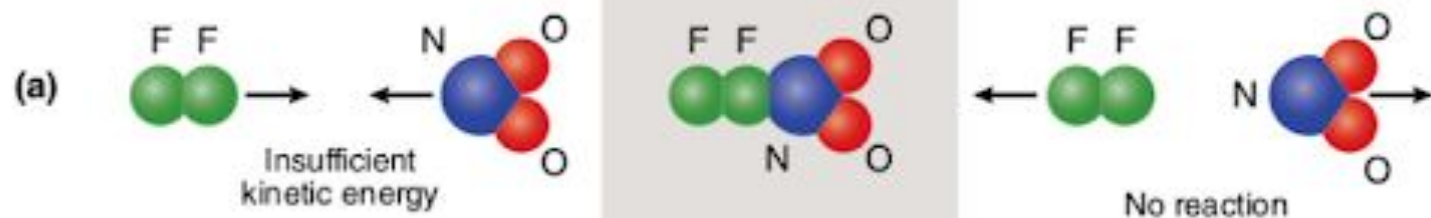
(a) Molecules must collide with each other.

once molecules collide they may react together or they may not -

(b) Molecules must have sufficient energy, and

(c) Molecules must have correct geometry.

Activated Complex



Explain collision frequency and energy factor



∴ Rate law will be, $r = k[A][B]$

We are going to
derive this equation

Collision frequency :

Collision frequency is the no. of collisions taking place
Per second per unit volume at a given temperature

No. of collisions will be proportional to the concentration
of colliding species

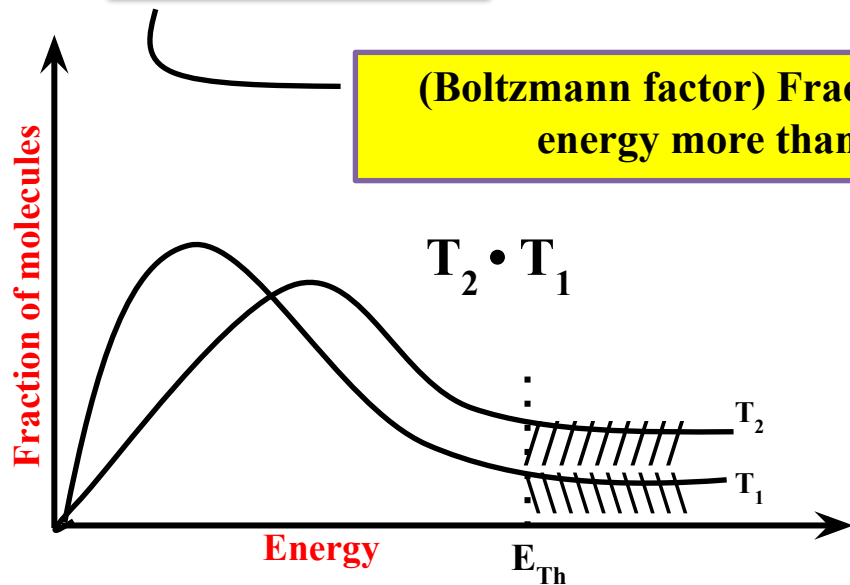
$$\text{Collision frequency} \propto [A][B]$$

$$\text{Collision frequency} = Z [A][B] \quad (Z = \text{Collision freq. constant})$$

Energy factor : Only the molecules having energy more than the **threshold** energy result in successful collisions.

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

(Boltzmann factor) Fraction of molecules having energy more than threshold energy.



(Maxwell boltzmann distribution)

Arrhenius equation

Probability factor : It is the probability that a collision is properly aligned.

$$0 \cdot P \cdot 1$$

Now,

$$\text{Reaction Rate} = \text{Collision frequency} \times \text{Energy factor} \times \text{Probability factor}$$

$$= Z[A][B] \times f \times p$$

$$= (Zpf)[A][B] = k[A][B]$$

$$\Rightarrow k = Zpf = Zpe^{-E_a/RT}$$

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

Arrhenius
equation

$A = Zp \rightarrow$ Arrhenius constant
(Pre-exponent factor).

Derive Arrhenius equation.

Taking logarithm of Arrhenius equation

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

$$\log k = \log A - \frac{E_a}{2.303RT}$$

**Logarithmic form
of Arrhenius equation.**

**Now, let us write Arrhenius Equations for
two different temperatures :**

$$\log k_2 = \log A - \frac{E_a}{2.303 RT_2} \dots (1)$$

$$\log k_1 = \log A - \frac{E_a}{2.303 RT_1} \dots (2)$$

Derive Arrhenius equation.

(1) – (2)

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

**Activation energy
is always a positive
term.**

If $T_2 > T_1$, then $\frac{1}{T_2} < \frac{1}{T_1}$

$\left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ will be positive and hence, $k_2 > k_1$

with rise in temperature, rate constant increases.

**What is temperature
coefficient ?**

Temperature coefficient

$$\text{Temperature coefficient} = \frac{K_T + 10}{K}$$

For most reactions, temperature coefficient lies between **2** and **3**, mostly it is **2**.

Ratio of rate constants at two temperature separated by 10^0C is called temperature coefficient

Activation Energy

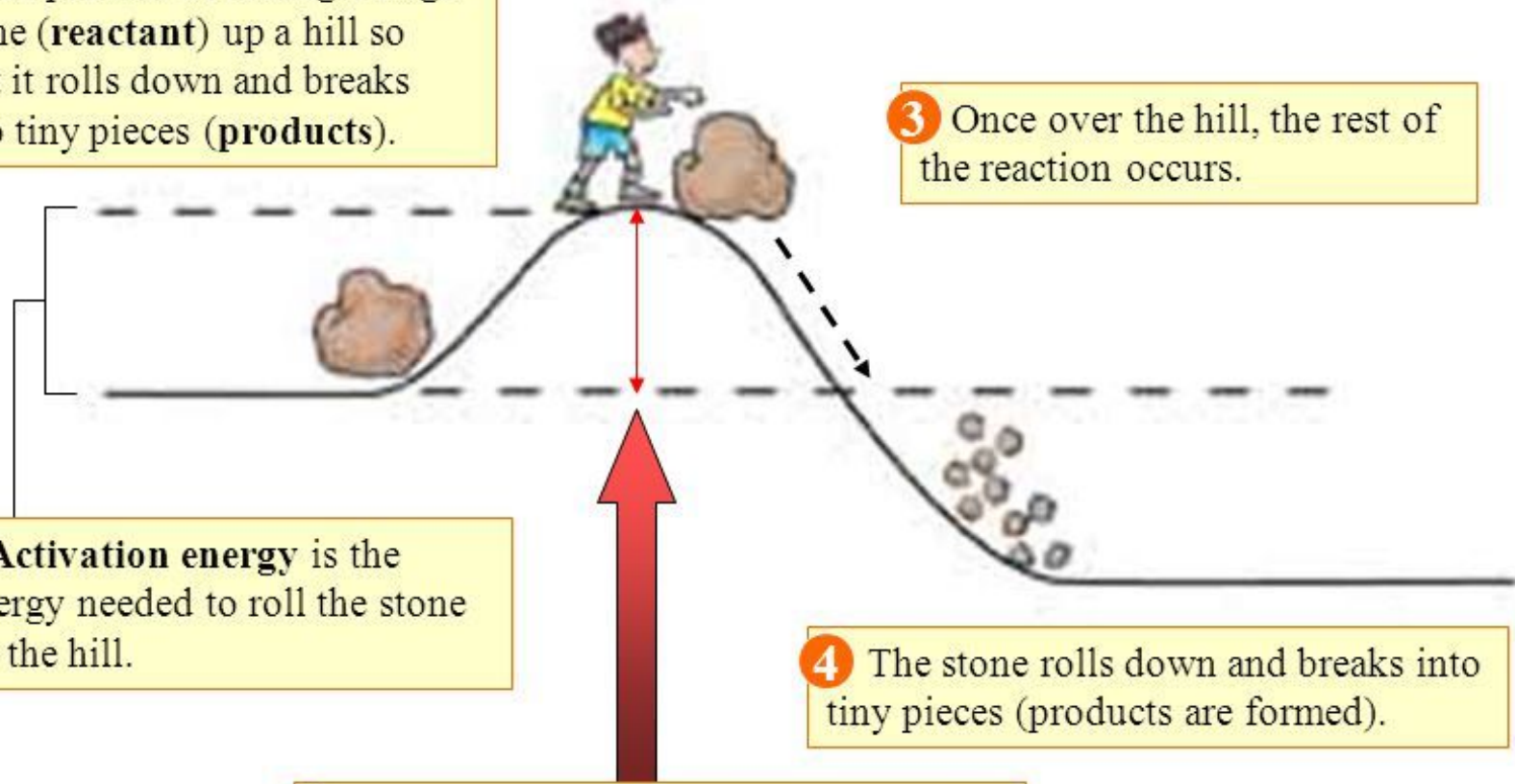
1 Imagine a chemical reaction as the process of rolling a huge stone (**reactant**) up a hill so that it rolls down and breaks into tiny pieces (**products**).

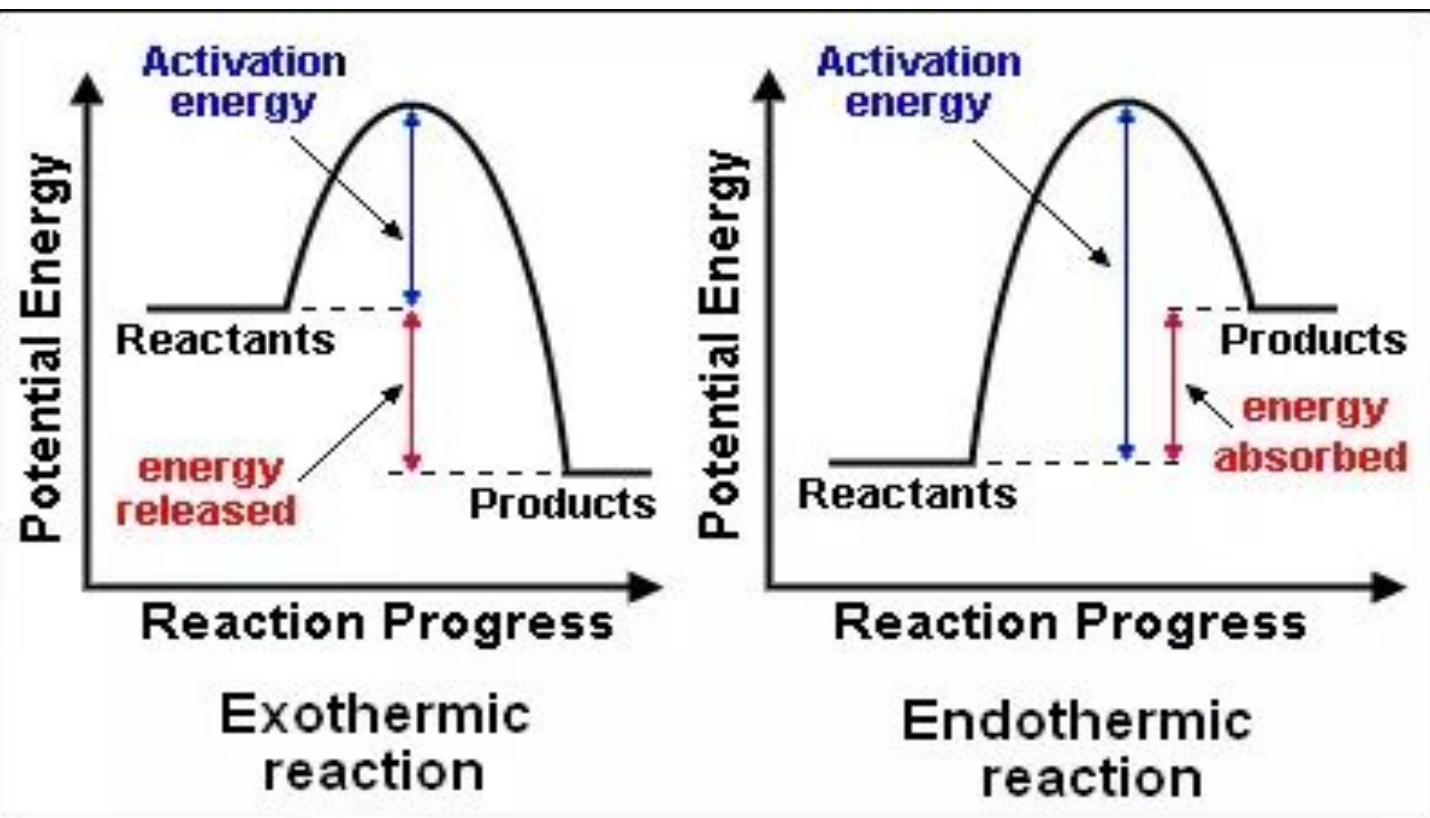
2 **Activation energy** is the energy needed to roll the stone up the hill.

3 Once over the hill, the rest of the reaction occurs.

4 The stone rolls down and breaks into tiny pieces (products are formed).

5 The energy needed to start a chemical reaction is called activation energy.





Effect of temperature on activation energy

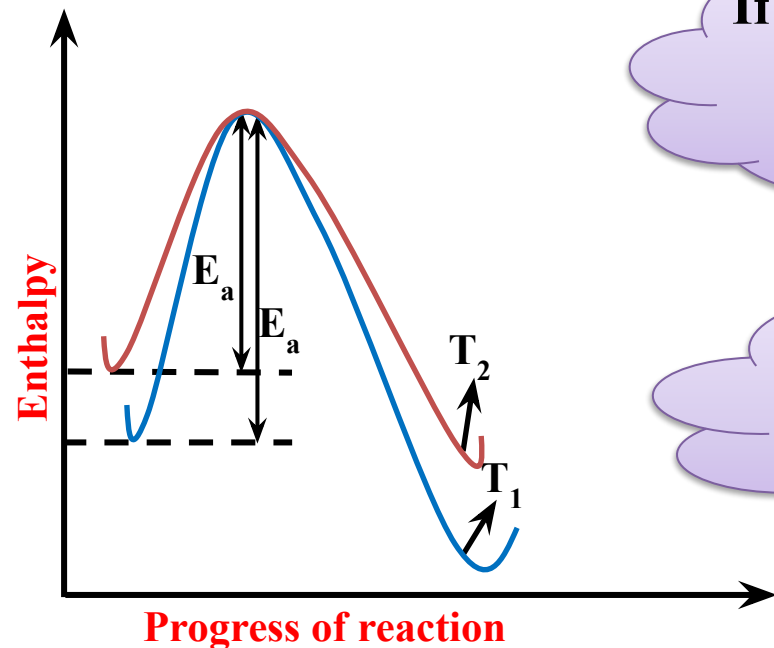
Effect of temperature on activation energy

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

In Arrhenius equation, we considered that E_a is constant during change from T_1 to T_2 , but this is true only for a small change of temperature.

If the change in temperature is large then we will get the following graph.

Effect of temperature on activation energy

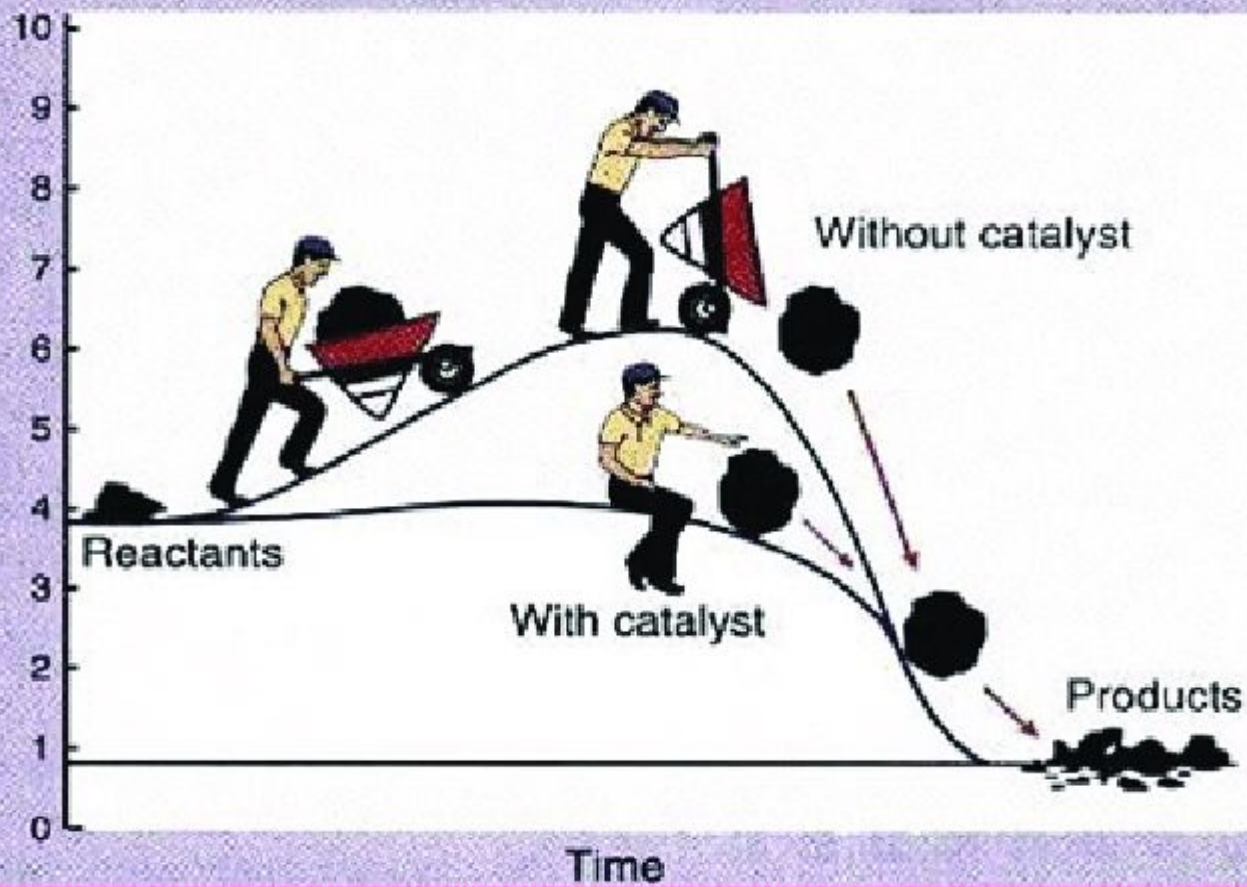


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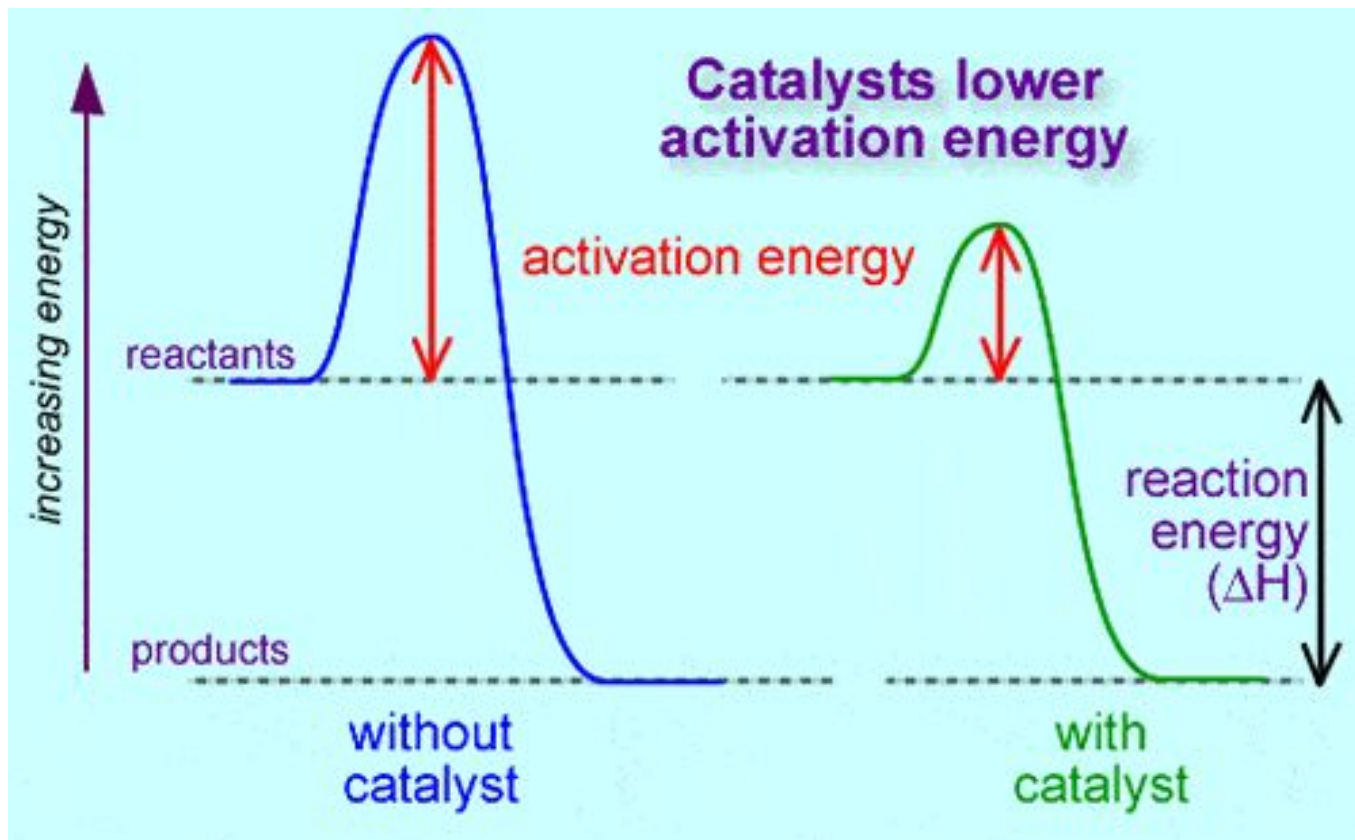
Increasing the T , increases the energy level of reactants thereby lowering the activation energy barrier.

Catalyst and its effect on reaction

Relative Amount of Energy in Molecules



A catalyst speeds up a reaction by providing alternate path for the reaction to occur and the E_a of this path is lower than the actual path.



Some catalysts can change the fundamental mechanism of the reaction, it can change a one transition state pathway to a two transition state pathway.

Catalyst may also form intermediates which have lower energy and form Products through a different path.

