02 Chemical Kinetics

Introduction :

Chemical Kinetics is the branch of physical chemistry which deals with the study of rate of reactions, the mechanism by which the reactions proceed and factors affecting rate of reaction. On the basis of rate, chemical reaction are broadly divided into three categories :-

(a) Very fast or Instantaneous reactions :

(b) Very slow reactions :

(c) Moderate or slow reactions :

(a) Very fast or Instantaneous reactions :

Generally these reactions involve ionic species and known as ionic reactions. These reactions take about 10^{-14} or 10^{-16} seconds for completion. So, it is almost impossible to determine the rate of these reactions.

Example

$HCl + NaOH \rightarrow NaCl + H_2O$

(b) Very slow reactions :

These reactions proceed very slowly, may take days or months to show any measurable change at room temperature.

Example

1. Rusting of iron.
2. Reaction between H_2 and O_2 to form H_2O at ordinary temperature in absence of catalyst.

(c) Moderate or slow reactions :

This type of reactions proceed with a measurable rates at normal temperature and we can measure the rate of these reactions easily. Mostly these reactions are molecular in nature.

Example

1. Decomposition of H_2O_2

   $2H_2O_2 \rightarrow 2H_2O + O_2$
2. Decomposition of N_2O_5

   $2N_2O_5 \rightarrow 4NO_2 + O_2$

Rate of disappearance of reactant/appearance of product :

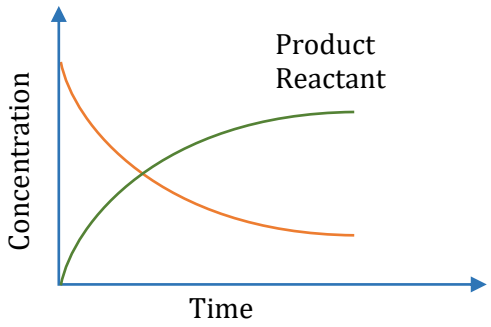
It is defined as the change in concentration or pressure (for gaseous substances) of reactant or product per unit time. It is always a positive quantity.

$$\text{Rate of reactant / product} = \frac{\text{Change in concentration of reactant or product}}{\text{Time taken in change}}$$

(Unit of Rate = M time^{-1}) $\qquad$ $\text{Rate} = \pm\frac{\Delta C}{\Delta t}$

Where ΔC = change in concentration in a small interval Δt

[+] sign is used when we refer for product concentration or appearance of product.
[–] sign is used when we refer for reactant concentration or disappearance of reactant.



Rate of reaction is defined as the change in concentration or pressure of reactant or product per unit time per unit stoichiometric coefficient of reactant and product. It is always a positive quantity.

$$\text{Rate of reactant / product} = \frac{\text{Change in concentration of reactant or product}}{\text{stoichiometric coefficeint} \times \text{time taken}}$$

(Unit of Rate = M time^{-1})

Example

	2A	→	3B
t = 0 Conc.	a		
t = t	a – 2x		3x

Rate of disappearance of A $= -\frac{\Delta A}{\Delta t} = \frac{2x}{t}$

Rate of appearance of B $= +\frac{\Delta B}{\Delta t} = \frac{3x}{t}$

Rate of reaction w.r.t. A $= \frac{1}{2}\left(-\frac{\Delta A}{\Delta t}\right) = \frac{x}{t}$

Rate of reaction w.r.t B $= \frac{1}{3}\left(\frac{\Delta B}{\Delta t}\right) = \frac{x}{t}$

Relation between rate of different species of reaction :

- In general, for the reaction, $aA + bB \longrightarrow cC + dD$
  the rate is given by
- Rate of reaction $= -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$
- For the reaction in terms : $N_2 + 3H_2 \rightarrow 2NH_3$
- Rate of reaction $= -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

Types of rate of chemical reaction :

1. Average rate of reaction

The rate of reaction over a certain measurable period of time during the course of reaction is called average rate of reaction. It is denoted by....

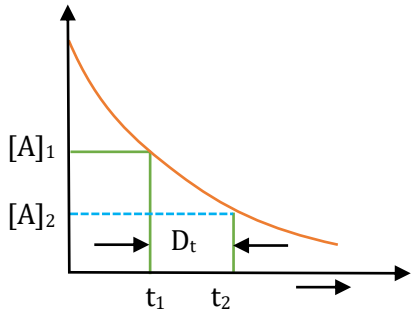
For a reaction $A \longrightarrow B$

$$r_{avg.} = -\frac{[A]_2 - [A]_1}{t_2 - t_1} = -\frac{\Delta A}{\Delta t} = \frac{\Delta B}{\Delta t}$$

Where

$[A]_1$ = Concentration of reactant A at time t_1,

$[A]_2$ = Concentration of reactant A at time t_2.



2. Instantaneous rate of reaction

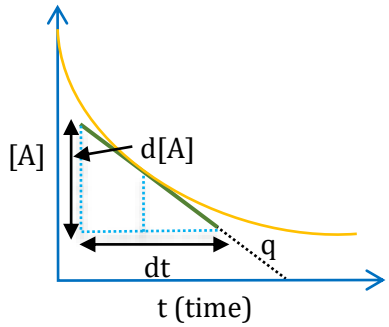
The rate of reaction at any particular instant during the course of reaction is called instantaneous rate of reaction.

For a reaction A $\longrightarrow$ B

Mathematically Instantaneous rate = $\lim_{\Delta t \to 0}$ (Average rate)

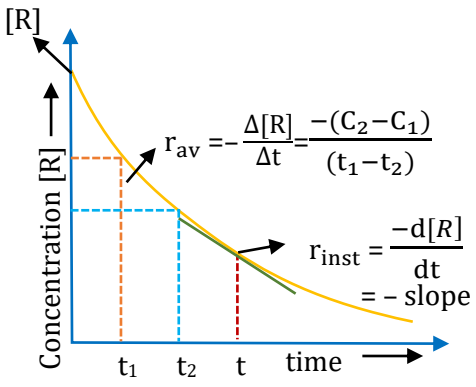
$$r_{inst} = \lim_{\Delta t \to 0}\left(-\frac{\Delta[A]}{\Delta t}\right) = +\lim_{\Delta t \to 0}\left(\frac{\Delta[B]}{\Delta t}\right) \text{ or } r_{inst} = (-)\frac{d[A]}{dt} = (+)\frac{d[B]}{dt}$$

Hence, Slope of the tangent at time t in plot of concentration with time gives instantaneous rate of reaction.



Initial rate

Instantaneous rate at 't = 0' is called initial rate [Slope of tangent at t = 0].



Important facts about rate of reaction :

1. ROR or any rate in kinetics is always positive.
2. ROR depend on stoichiometric coefficients but ROD or ROA doesn't depend on stoichiometric coefficients.
3. For gas phase reaction, rate of reaction is also expressed in atm/sec, provided temperature is constant.
   For gaseous reactions

   $r = \pm\frac{\Delta P}{\Delta t}$ (unit of rate = pressure time−1)

   $PV = nRT \rightarrow P = \frac{n}{V}RT$

   $P = CRT$; $C = \frac{P}{RT}$

   $r = \frac{1}{RT} \times \left[\pm\frac{\Delta P}{\Delta t}\right]$ (unit of rate = M time−1)

Factors affecting rate of chemical reaction :

1. Concentration :

For most of the reactions, rate depends on concentration of reactants. So, rate of reaction decreases with passage of time, since concentration of reactants decreases.

Rate of reaction $\propto$ concentration of reactant (Except for zero order)

2. Temperature :

Generally, rate of reaction increases on increasing temperature.

On increasing temperature rate of reaction increases whether the reaction is exothermic or endothermic. when temperature increases KE of molecules increases, number of activated molecules increases, No. of effective collisions increases thus rate of reaction increases.

3. Effect of nature of reactants and products :

(a) Physical state of reactants :

Increasing order of rate of reaction – Solid < liquid < gas

(Intermolecular attractive force decreases which provides more freedom for collisions)

(b) Physical size of reactants :

In heterogeneous reactions, as we decrease the particle size, rate of reaction increases since surface area increases.

Rate of reaction $\propto \frac{1}{\text{physical size}} \propto$ surface area

(c) Chemical nature of reactants :

If more bonds are to be broken, rate of reaction will be slow.

Similarly, if bond strength in reactants is more, rate of reaction will be slow.

4. Catalyst :

Presence of catalyst or positive catalyst lowers down the activation energy hence increases the rate of reaction. Presence of inhibitor or negative catalyst increases activation energy hence decreases the rate of reaction.

5. Effect of pH of solution :

$[Fe(CN)_6]^{4\ominus}$ $[Fe(CN)_6]^{3\ominus}$

This reaction take place with appreciable rate in acidic medium but does not take place in basic medium.

6. Dielectric constant :

More is the dielectric constant of the medium greater will be the rate of ionic reactions.

7. Effect of radiations / light :

Radiations are useful for photochemical reactions.

8. Effect of pressure :

Pressure is important factor for gaseous reactions.

Effect of pressure on Rate of reaction is negligible when reactants are solid or liquid. But if reactants are in gaseous state then rate of reaction increases on increasing pressure because number of effective collisions increases.

9. Effect of electrical & magnetic field

Electric and magnetic fields are rate determining factors if a reaction involves polar species.

Illustration 1:

For reaction $2A \longrightarrow 3B + 4C$, number of moles of B increased by 6×10^{-3} mole in 10 sec in a 10 L container. Find out rate of appearance of B and C and rate of disappearance of A and rate of reaction.

Solution:

$$-\frac{1}{2}\frac{d[A]}{dt} = \frac{1}{3}\frac{d[B]}{dt} = \frac{1}{4}\frac{d[C]}{dt}$$

$$\frac{d[B]}{dt} = 6 \times 10^{-5}\ M/sec$$

$ROA(B) = 6 \times 10^{-5}$ M/sec

$ROA(C) = 8 \times 10^{-5}$ M/sec

$ROD(A) = \times 10^{-5}$ M/sec

$ROR = 2 \times 10^{-5}$ M/sec

Illustration 2:

For the reaction $aA + bB \longrightarrow cC$, if $\frac{-d[A]}{dt} = 2 \times \frac{-d[B]}{dt} = 1.5 \times \frac{d[C]}{dt}$; then calculate a : b : c ?

Solution:

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

6 : 3 : 4

Illustration 3:

If the reaction $2NO_2 \longrightarrow 2NO + O_2$, the rate of formation of NO is 6 g min^{-1}, calculate rate of disappearance of NO_2 ?

Solution:

$$\frac{d[NO]}{dt} = \frac{6}{30} \Rightarrow \frac{1}{5}\ \frac{mol}{min}$$

9.2g/min

Illustration 4:

For reaction $2A + 3B \longrightarrow 4C$

If rate of disappearance of B is 9×10^{-3} M/min, then calculate rate of appearance of C and rate of chemical reaction.

Solution:

$$-\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{4}\frac{d[C]}{dt}$$

$$\frac{d[C]}{dt} = 12 \times 10^{-3}\,M/min$$

Rate law :

- The experimental expression of rate of reaction in terms of concentration of reactants is known as rate law.
- In this expression the rate of a reaction is proportional to the product of molar concentration of reactants with each term raised to the power or exponent that has to be found experimentally.
- In a chemical reaction :- $aA + bB \longrightarrow$ Product
  the rate law is :- Rate $\propto [A]^x[B]^y$
- The values of exponents x and y are found experimentally which may or may not be same as stoichiometric coefficients.
- Rate = $k[A]^x[B]^y$. This is the differential rate equation or rate expression.
- Where k is a proportionality constant known as rate constant or specific reaction rate.
- Rate of reaction at unit concentration of reactants is called as rate constant or specific reaction rate.
- Rate constant does not depend on concentration of reactant but it depends only on temperature and catalyst.
- Rate $\propto$ (conc.)^{order}
- Rate = k (conc.)^{order}
- This is the differential rate equation or rate expression.
  Where k = Rate constant = specific reaction rate
  Unit of K = (conc)$^{1-\,order}$ time^{-1}

Order of reaction :

- The sum of powers of concentration terms present in rate law expression is known as order of reaction.
- For the reaction $aA + bB \rightarrow$ Product
- Rate law is Rate = $k[A]^x[B]^y$
- where x may or may not be equal to a and similarly where y may or may not be equal to b .
- Here x = order of reaction with respect to A
  y = order of reaction with respect to B
  x + y = n (overall order of reaction)
- Order of reaction may be zero, positive, fractional or negative with respect to a particular reactant.
- Order of reaction is an experimental quantity.
- It shows dependency of ROR on concentration of reactant.

Units of rate constant :

A $\longrightarrow$ Product

Rate = $k[A]^n$

$$k = \frac{r}{[A]^n} = \frac{\text{unitofrate}}{[\text{unitofconcentration}]^n} = \frac{\frac{\text{mol}}{\text{L}} \times \text{time}^{-1}}{\left[\frac{\text{mol}}{\text{L}}\right]^n}$$

- Unit of $k = \left[\frac{\text{mol}}{\text{L}}\right]^{1-n} \times \text{time}^{-1}$
- For gaseous reaction unit of k may be = $(\text{atm})^{1-n} \times \text{time}^{-1}$

(i) If n = 0 (zero order reaction)

$k = (\text{mol L}^{-1})^{1-0}\ \text{time}^{-1} = \text{mol L}^{-1}\ \text{time}^{-1}$

(ii) If n = 1 (first order reaction)

$k = (\text{mol L}^{-1})^{1-1}\ \text{time}^{-1} = \text{time}^{-1}$

(iii) If n = 2 (second order reaction)

$k = (\text{mol L}^{-1})^{1-2}\ \text{time}^{-1} = \text{mol}^{-1}\ \text{L time}^{-1}$

Illustration 5:

For the given reaction $2NH_3 \longrightarrow N_2 + 3H_2$, if $\frac{-d[NH_3]}{dt} = k_1[NH_3]$, $\frac{d[N_2]}{dt} = k_2[NH_3]$, $\frac{d[H_2]}{dt} = k_3[NH_3]$. Then find relation between k_1, k_2 & k_3.

Solution:

$3k_1 = 6k_2 = 2k_3$

Illustration 6:

Rate law of a gaseous reaction :- $A_{(g)} + 2B_{(g)} \longrightarrow C_{(g)}$ is $r = k[A][B]^2$, Find the effect on rate of reaction, if :-

(1) Concentration of both A & B are tripled

(2) Pressure of only B is halved

(3) Volume of container is reduced to $1/4^{th}$ of the initial volume

Solution:

(1) r' =27r

(2) $r' = \frac{r}{4}$ (concentration is reduced to half)

(3) r' =64r (concentration is increase by 4 times)

Mechanism of reaction :

Elementary reactions :

Those reactions which completes in single step are elementary reactions. Such reactions involve no intermediate products.

For an elementary reaction, the orders in the rate law equal the coefficients of the reactants.

If $aA + bB \longrightarrow$ Products; is an elementary reaction then, rate law will be Rate = $k[A]^a[B]^b$

Order of reaction = a+b provided the reaction is elementary reaction.

Their order can never be zero / negative / fractional because stoichiometric coefficient can never be zero / negative / fraction.

If $2A + B \longrightarrow C$; is an elementary reaction

then rate law will be –

Rate = $k[A]^2[B]^1$

Where x = 2, y = 1

Complex reaction :

Those reactions which complete in multistep. For these reactions a mechanism is proposed.

For complex reactions the overall rate of reaction is controlled by the slowest step which is called as rate determining step (R.D.S.).

In rate law expression rate of reaction depends on concentration of reactants of slowest step which must be free from intermediate.

If R.D.S. contains intermediate, its value is solved using K_{eq} of fast step (assumed as reversible).

In certain complex reaction product is also considered in order calculation.

Molecularity of reaction :

- The number of molecules that react in an elementary step is the molecularity of the elementary reaction.
- Molecularity is defined only for the elementary reactions and not for complex reactions.
- No elementary reactions involving more than three molecules are known, because of very low probability of simultaneous collision of more than three molecules.
- Molecularity is a whole number. It cannot have fractional value.

Example

1. $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$
   (Molecularity = 1, unimolecular reaction)
2. $2HI \xrightarrow{\Delta} H_2 + I_2$
   (Molecularity = 2, bimolecular reaction)
3. $2NO + O_2 \xrightarrow{\Delta} 2NO_2$
   (Molecularity = 3, trimolecular reaction)

Comparison between order and molecularity

S. No.	Molecularity of reaction	Order of reaction
1.	It is defined as number of molecules of reactant taking part in a chemical reaction. $NH_4NO_2 \rightarrow N_2 + 2H_2O$ Molecularity =1	It is defined as sum of power of concentration terms that appear in rate law. $NH_4NO_2 \rightarrow N_2 + 2H_2O$ Rate= k[NH_4NO_2], order =1
2.	It is always a whole number. Cannot be zero or fractional.	It may be zero, fractional or integer.
3.	It is derived from stoichiometric coefficient of elementary reaction.	It is derived from rate expression.
4.	It is theoretical value.	It is experimental value.
5.	Reaction with molecularity >3 are rare.	Reaction with order > 4 are rare.
6.	Independent of pressure and temperature	It may depend on pressure and temperature.

Integrated Rate Law :

For a single reactant reaction where the chemical equation has the form

$A \longrightarrow$ products

and the rate law is assumed to be of the form

Rate = $-d[A]/dt = k[A]^m$

Where m is the order of the reaction with respect to substance A. Three important cases can be treated : m = 0, m = 1, and m = 2. These are called zeroth order, first order, and second order respectively.

Zero order reaction :

Reactions in which rate of reaction remains independent of concentration of the reactant are said to be zero order reactions.

For zero order reaction, rate of reaction is equal to rate constant (r= k).

Zero order reactions are relatively uncommon but they occur under special conditions.

Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions.

Example

(a) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

(b) $2NH_3(g) \xrightarrow{Pt\Delta} N_2(g) + 3H_2(g)$ at high pressure.

(c) Adsorption of gases on metal surface :- At high P, complete surface gets covered by gas & rate becomes independent of P & concentration hence order is 0.

- For a single reactant reaction where the chemical equation has the form $A \rightarrow B$ and the rate law is assumed to be of the form Rate = $-d[A]/dt = k[A]^0$
- Let A_0 be the initial conc of reactant and A_t be concentration of reactant at time t.
  $-\int_{C_0}^{Ct} d[A] = \int_0^t kdt$
- Integrating [A] from C_0 to C_t and time from 0 to t.
- We get $kt = C_t - C_0$ or $C_t = C_0 - kt$

  Unit of K is same as that of Rate = mol lit^{-1} sec^{-1}.

  Time for completion = $\frac{C_0}{k}$, when $C_t = 0$

  $t_{1/2}$ (half-life period) (Half-life period is time taken for half of the reactant to react.)

  At $t_{1/2}$, $C_t = \frac{C_0}{2}$,

  So, $kt_{1/2} = \frac{C_0}{2} \Rightarrow t_{1/2} = \frac{C_0}{2k}$

Graph's related to zero order :

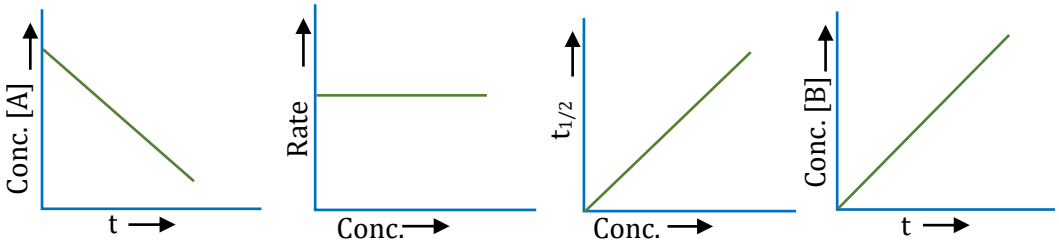


Illustration 7:

For this A ⟶ B, zero order reaction, initial concentration of A is 0.01 M and concentration of A after 10 seconds is equal to 0.008 M, then find out $t_{50\%}$ and $t_{100\%}$.

Solution:

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

$0.008 = 0.01 - k \times 10$

$K = 0.0002$

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

$t_{50\%} = 25$ sec

$t_{100\%} = 50$ sec

Illustration 8:

If time for 75% completion is 5 min. in zero order reaction then $t_{50\%}$?

Solution:

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

$k = 15$

$50 = 100 - 15 \times t$

$t = \frac{50}{15}$ min

Illustration 9:

For a reaction concentration of reactant is 0.5 M after 25 s. Then, find out initial concentration of reactant if $k = 2 \times 10^{-2}$ mol L^{-1} s^{-1}.

Solution:

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

$0.5 = [A]_0 - 2 \times 10^{-2} \times 25$

$[A]_0 = 1$ M

First order reaction :

Reactions in which the rate of reaction is directly proportional to concentration of reactant.

Example

(a) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

(b) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

(c) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^{\oplus}} CH_3COOH + C_2H_5OH$

(d) All radioactive decay

Let us consider a first order reaction

$A \rightarrow B$ (rate const. = k = sec^{-1})

Let C_0 be the initial conc of reactant and C_t be concentration of reactant at time t. B_t is product concentration at time t as shown below.

t = 0	$C_0(a)$	0
t = t	$C_t(a-x)$	$B_t(x)$

$ROR = k[A]^1$ $\int_{[C]_0}^{[C]_t} \frac{d[A]}{[A]} = \int_{t=0}^{t=t} -kdt$ $\ln\left(\frac{C_t}{C_0}\right) = -kt$

$kt = \ell n\frac{C_0}{C_t} = \ln\frac{a}{a-x}$ $\quad k = \frac{1}{t}\ \ln\frac{C_0}{C_t}$

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

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

$t = \frac{1}{k}\ell n\frac{C_0}{C_t}$

$C_t = C_0e^{-kt}$

$(a-x) = ae^{-kt}$

$x = a\left(1-e^{-kt}\right)$

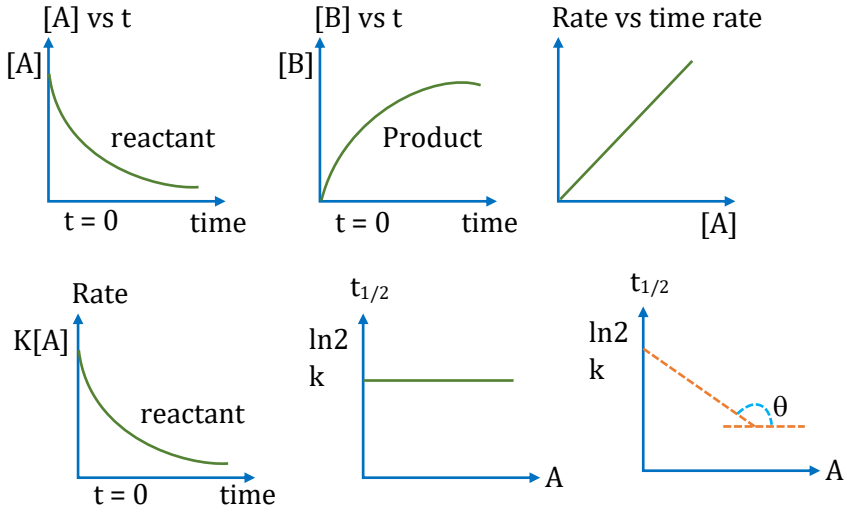
$B_t = C_0\left(1-e^{-kt}\right)$

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

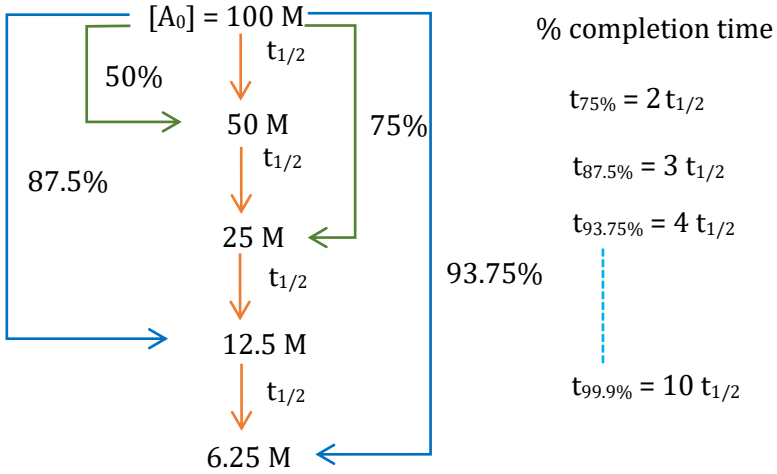
$T_{Completion} = \infty$

$C_t = C_0e^{-kt}$

Graphs related to 1st orders :



Short Conclusion for 1st Order Reaction :



Special Case 1 :

If initial concertation of reactant is not given but concertation at time $t = t_1$ and time $t = t_2$ are given as C_1 and C_2 respectively. Then rate constant of first order reaction

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

$t = t_1 \quad C_1$

$t = t_2 \quad C_2$

$$k = \frac{1}{t_2 - t_1} \ln \frac{C_1}{C_2}$$

Special Case 2 :

In first order reaction in equal time equal percentage of reactant will decomposed

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

$t = 0 \quad a$

$t = t_{x\%} \quad a - \frac{ax}{100}$

$$\left(k = \frac{1}{t_{x\%}} \ln \frac{100}{100 - x}\right)$$

Illustration 10:

Calculate $\frac{t_{0.75}}{t_{0.50}}$ for a first order reaction :

Solution:

$$k = \frac{2.303}{t_{3/4}} \log \frac{C_0}{\frac{1}{4}C_0} = \frac{2.303}{t_{1/2}} \log \frac{C_0}{\frac{C_0}{2}} \Rightarrow \frac{t_{3/4}}{t_{1/2}} = \frac{\log 4}{\log 2} = \frac{2 \log 2}{\log 2} = 2$$

Illustration 11:

90% of a first order reaction was completed in 10 hours. When will 99.9% of the reaction complete ?

Solution:

$$K = \frac{2.303}{t} \log \frac{a}{a - x}$$

$a = 100$, $x = 90$, $t = 10$

So $K = \frac{2.303}{10} \log \frac{100}{10}$

$K = 2.303 \times 10^{-1}$ hour^{-1}

Now for 99.9% completion -

$a = 100$ and $x = 99.9$

$$t = \frac{2.303}{K} \log \frac{100}{0.1} = \frac{2.303}{2.303 \times 10^{-1}} \times 3 = 30 \text{ hours}$$

Illustration 12:

A first order reaction is 90% complete after 40 min. Calculate the half life of reaction.

Solution:

$a = 100, \ x = 90$

$$K = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$K = \frac{2.303}{40} \log \frac{100}{10}$$

$$= \frac{2.303}{40} = 5.757 \times 10^{-2} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{K_1} = \frac{0.693}{5.757 \times 10^{-2}} = 12.03 \text{ min.}$$

Second order reactions :

Case-I :

$$A \longrightarrow B \qquad (2^{nd} \text{ order})$$

$t = 0 \quad a = C_0 \qquad k\left(\frac{\text{litre}}{\text{molex sec}}\right)$

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

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

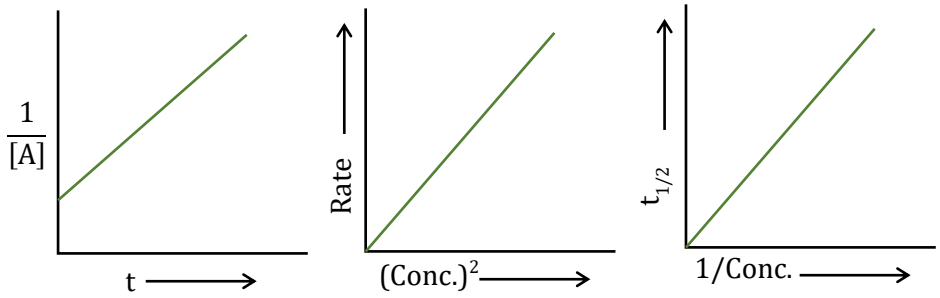
$$\int_{C_0}^{C_t} \frac{d[A]}{[A]^2} = \int_{t=0}^{t} -kdt$$

$$\frac{1}{C_t} - \frac{1}{C_0} = kt$$

$$t = \frac{1}{k}\left[\frac{1}{C_t} - \frac{1}{C_0}\right] \quad t = \frac{1}{k}\left[\frac{1}{a-x} - \frac{1}{a}\right]$$

Graphs related to 2nd order reaction

$$t_{1/2} \Rightarrow \frac{1}{kC_0}$$



Case-II :

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

a b 0

a – x b – x

Rate law

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

$$\int_0^x \frac{dx}{(a-x)(b-x)} = \int_0^t kdt$$

$$\boxed{k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}} \quad \text{(no need to remember)}$$

where $a \neq b$

Illustration 13:

For a second order reaction in which both the reactants have equal initial concentration, the time taken for 60% completion of reaction is 3000 second. What will be the time taken for 20% of the reaction?

Solution:

$$k_2 = \frac{1}{t}\frac{x}{a(a-x)}$$

Let a = 1,

$$k_2 = \frac{1}{t}\frac{x}{(1-x)}$$

$$= \frac{1}{3000}\left(\frac{0.6}{1-0.6}\right)$$

$$= \frac{1}{3000}\times\frac{0.6}{0.4} = \frac{1}{2000}$$

So time for the 20% completion :

$$t = \frac{1}{k_2}\frac{x}{a(a-x)}$$

$$= 2000\times\frac{0.20}{0.80} = 500 \text{ sec.}$$

Pseudo first order reaction :

A second order (or of higher order) reactions can be converted into a first order reaction if the other reactant is taken in large excess. Such first order reactions are known as pseudo first order reactions.

For,	A	+	B	⟶	Products
t=0	a		b		
t=t	a–x		b–x		

Rate = $K [A]^1 [B]^1$

If [B] = constant ⇒ [b – x] ≈ constant

Rate = $k' [A]^1$

when $k' = K[B]^1$

Case 1 :

If concentration of B is much greater than A, then [B] = Constant ⇒ [b – x] ≈ Constant.

Case 2 :

If B is a catalyst, then [B] = Constant ⇒ [b – x] ≈ Constant.

Case 3 :

If B is a solvent, then [B] = Constant ⇒ [b – x] ≈ Constant

∴ For A + B ⟶ Products [Rate] = $k [A]^1 [B]^1$

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

Now if 'B' is taken in large excess b > > a.

$$\therefore\ k = \frac{2.303}{-bt}\log\frac{(a-x)}{a} \Rightarrow k = \frac{2.303}{bt}\log\frac{a}{a-x}$$

$$\Rightarrow\ k' = \frac{2.303}{t}\log\frac{a}{a-x} \Rightarrow k' = (k\times b)$$

k′ is pseudo first order rate constant.

k′ will have units of first order.

k will have units of second order.

n^{th} order reaction :

Let us consider a n^{th} order reaction.

$A \longrightarrow B$ (rate constant = k)

Let concentration of A at time

t = 0 be C_0 & at t = t be C_t

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

$$\int_{C_0}^{C_t} \frac{d[A]}{[A]^n} = \int_{t=0}^{t=t} -kdt$$

Integrating :

$$\frac{1}{(-n+1)}\left[C_t^{-n+1} - C_0^{-n+1}\right] = -kt$$

$$t = \frac{1}{k(n-1)}\left[\frac{1}{C_t^{(n-1)}} - \frac{1}{C_0^{(n-1)}}\right]$$

$$\frac{1}{C_t^{(n-1)}} = \frac{1}{C_0^{(n-1)}} + k(n-1)t$$

it is general formula for nth order (except n = 1)

Calculation of $t_{1/2}$:

at $t = t_{1/2}$ $Ct = \frac{C_0}{2}$

$$t_{1/2} = \frac{1}{k(n-1)}\left[\frac{2^{n-1}}{C_0^{n-1}} - \frac{1}{C_0^{n-1}}\right]$$

$$t_{1/2} = \frac{1}{k(n-1)}\frac{\left(2^{n-1}-1\right)}{C_0^{n-1}} (n \neq 1)$$

$$t_{1/2} \propto \frac{1}{C_0^{(n-1)}} (n \neq 1)$$

Methods to determine order of reaction :

By comparison of different initial rates of a reaction by varying the concentration of one of the reactants while others are kept constant.

then for two different initial concentrations of A we have

$$r_{0_1} = k[C_0]_1^a \quad r_{0_2} = k[C_0]_2^a \quad \Rightarrow \quad \frac{r_{0_1}}{r_{0_2}} = \left(\frac{[C_0]_1}{[C_0]_2}\right)^a$$

Illustration 14:

Consider the following data for the reaction :

$A + B \longrightarrow$ Products

S.N.	Initial concentration	Initial concentration	Initial rate (mol s^{-1})
1.	0.10 M	1.0 M	2.1×10^{-3}
2.	0.20 M	1.0 M	8.4×10^{-3}
3.	0.20 M	2.0 M	8.4×10^{-3}

Determine the order of reaction with respect to A and with respect B and the overall order of reaction.

Solution:

Order w.r.t. to A = 2

Order w.r.t. to B = 0

Overall order = 2

Integrated rate law method :

It is method of hit and trial. By checking if the kinetic data (experimental data) best fits into particular integrated rate law, we determine the order. It can also be done graphically.

Illustration 15:

The rate of decomposition of N_2O_5 in CCl_4 solution has been studied at 318 K and the following results have been obtained :

t/min	0	135	342	683	1693
c/M	2.08	1.91	1.67	1.35	0.57

Find the order of the reaction and calculate its rate constant. What is the half-life period?

Solution:

First order reaction with $k = 6.31 \times 10^{-4}$ min^{-1}.

$t_{1/2} = 1.094 \times 10^3$ min^{-1}

Illustration 16:

The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different time and the results are given below

t (sec)	0	100	200	300
Pr. (Pascal)	4×10^3	3.5×10^3	3×10^3	2.5×10^3

Determine the order of reaction and its rate constant.

Solution:

Zero order,

K= 5Pa/sec

Method of half lives :

The half lives of each order is unique so by comparing half lives we can determine order for n^{th} order reaction

$$t_{1/2} \propto \frac{1}{[C_0]^{n-1}}$$

$$\frac{(t_{1/2})_1}{(t'_{1/2})_2} = \frac{[C'_0]_2{}^{n-1}}{[C_0]_1{}^{n-1}}$$

Ostwald's isolation method :

This method is useful for reactions which involve a large number of reactants. In this method, the concentration of all the reactants are taken in large excess except that of one, so if

Rate = $k [A]^a [B]^b [C]^c = k_0 [A]^a$

Then value of 'a' can be calculated by previous methods and similarly 'b' and 'c' can also be calculated.

Application of first order reaction :

Case 1 : First order gaseous reaction :

Progress of gaseous reactions can be monitored by measuring total pressure at a fixed volume & temperature. This method can be applied for those reactions also in which a gas is produced because of decomposition of a solid or liquid. We can get an idea about the concentration of reacting species at a particular time by measuring pressure.

The pressure data can be given in terms of
(i) Partial pressure of the reactant
(ii) Total pressure of the reaction system
(iii) Pressure at only some points of time.

Illustration 17:

In the given reaction,

$A(g) \longrightarrow n(B)(g)$,

Initially only A is present. If P_0 is the initial pressure, P_t is pressure at time t find the expression of k in terms of P_0, P_t & n.

Solution:

$$\begin{array}{lll} & \mathbf{A(g)} & \longrightarrow \quad \mathbf{nB(g)} \\ & P_0 & \\ & P_A = (P_0 - x) & nx \end{array}$$

$\therefore$ P_t (Total pressure at time 't') $= P_0 - x + nx = P_0 + (n-1)x$

$\therefore$ $x = \dfrac{P_t - P_0}{n-1}$

$\therefore$ $P_A = P_0 - \dfrac{P_t - P_0}{n-1} = \dfrac{P_0 n - P_t}{n-1}$

$\therefore$ $a \propto p_0$ & $(a-x) \propto P_A = \dfrac{nP_0 - P_t}{n-1}$

$\therefore$ $k = \dfrac{2.303}{t} \log \dfrac{P_0(n-1)}{(nP_0 - P_t)}$

Final total pressure after infinite time $= P_f = nP_0$

Do not remember the formula but derive it for each question.

Case 2 : Volume measurement :

1. **By measuring the volume of product formed we can monitor the progress of reactions.**

Illustration 18:

In the given reaction,

$NH_4NO_2(s) \xrightarrow{\Delta} 2H_2O(l) + N_2(g)$

Initially only $NH_4NO_2(s)$ is present.

If V_t is the volume of N_2 collected at time 't' and V_∞ if the volume of collected at the end of the reaction find expression of k in terms of t, V_∞ and V_t

Solution:

Let, V_t be the volume of N_2 collected at time 't'

V_∞ = be the volume of N_2 collected at the end of the reaction.

$a \propto V_\infty$ and $x \propto V_t$

$(a-x) \propto V_\infty - V_t$

$\therefore$ $k = \dfrac{2.303}{t} \log \dfrac{V_\infty}{V_\infty - V_t}$

2. **By titration method :**
   By measuring the volume of titrating agent we can monitor amount of reactant remaining or amount of product formed at any time. It is the titer value. Here the milliequivalent or millimoles are calculated using valence factors.

Illustration 19:

From the following data show that the decomposition of hydrogen peroxide in aqueous solution is a first - order reaction. What is the value of the rate constant?

Time in minutes	0	10	20	30	40
Volume V in mL	25.0	20.0	15.7	12.5	9.6

Where V is the volume in mL of standard $KMnO_4$ solution required to react with a definite volume of hydrogen peroxide solution.

Solution:

The equation for a first order reaction is,

$$2H_2O_2\,(l) \xrightarrow{\Delta} 2H_2O(l) + O_2\,(g)$$

the volume of $KMnO_4$ used, evidently corresponds to the undecomposed hydrogen peroxide. Hence the volume of $KMnO_4$ used, at zero time corresponds to the initial concentration a and the volume used after time t, corresponds to (a – x) at that time. Inserting these values in the above equation, we get

When t = 10 min. $k_1 = \frac{2.303}{10} \log \frac{25}{20.0} = 0.022318\ min^{-1} = 0.000372\ s^{-1}$

When t = 20 min. $k_1 = \frac{2.303}{20} \log \frac{25}{15.7} = 0.023265\ min^{-1} = 0.000387\ s^{-1}$

When t = 30 min. $k_1 = \frac{2.303}{30} \log \frac{25}{12.5} = 0.02311\ min^{-1} = 0.000385\ s^{-1}$

When t = 40 min. $k_1 = \frac{2.303}{40} \log \frac{25}{9.6} = 0.023932\ min^{-1} = 0.0003983\ s^{-1}$

The constancy of k, shows that the decomposition of H_2O_2 in aqueous solution is a **first order** reaction. The average value of the rate constant is $0.0003879\ s^{-1}$.

Illustration 20:

Study of acid hydrolysis of an ester.

$$CH_3COOCH_3 + \underset{(excess)}{H_2O} \xrightarrow[(HCl)]{H^{\oplus}} CH_3COOH + CH_3OH$$

The progress of this reaction is monitored or determined by titrating the fixed volume of reaction mixture at different time intervals against a standard solution of NaOH using phenolphthalein as indicator. Find out rate constant of the reaction in terms of volume of NaOH consumed at t = 0, V_0, at t = ∞, V_∞ & at time t, V_t .

Solution:

Let, V_0 = Volume of NaOH used at t = 0 [this is exclusively for HCl.]

V_t = Volume of NaOH used at 't'

V_∞ = Volume of NaOH used at t = ∞

$a \propto (V_\infty - V_0)$

$(a - x) \propto (V_\infty - V_t)$

$x \propto (V_t - V_0)$

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Case : 3 Optical rotation measurement :

It is used for optically active sample. It is applicable if there is at least one optically active species involved in chemical reaction.

- The optically active species may be present in reactant or product.

It is found that $(r_\infty - r_0) \propto a$ (a = concentration, x = amount consumed)

$(r_\infty - r_t) \propto (a - x)$

Where are r_0, r_t, r_∞ are angle of optical rotation at time t = 0, t = t and t = ∞.

$$k = \frac{1}{t} \ln \frac{r_\infty - r_0}{r_\infty - r_t}$$

$$k = \frac{2.303}{t} \log \frac{r_\infty - r_0}{r_\infty - r_t}$$

Illustration 21:

Study of hydrolysis of sucrose, progress of this reaction is monitored with the help of polarimeter because a solution of sucrose is dextrorotatory and on hydrolysis, the mixture of glucose and fructose obtained becomes levorotatory. That's why this reaction is also known as inversion of cane sugar.

$$\underset{\text{excess}}{C_{12}H_{22}O_{11} + H_2O} \xrightarrow{H^\oplus} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Let the readings in the polarimeter be

t = 0, q_0; t = 't', q_t and at t = ∞, q_∞

Then calculate rate constant 'k' in terms of these readings.

Solution:

$$k = \frac{1}{t} \ln \frac{\theta_\infty - \theta_0}{\theta_\infty - \theta_t}$$

Case : 4 First order growth reaction :

For bacteria multiplication or virus growth use following concept.

Consider a growth reaction,

Time	Population (or colony)
0	a
t	(a + x)

$$\frac{dx}{dt} = k(a + x) \text{ or } \frac{dx}{(a+x)} = kdt$$

On integration

$\ln(a + x) = kt + C$ at $t = 0 ; x = 0 \Rightarrow C = \ln a$

$$kt = -\ln \frac{a}{(a+x)} \quad ; \quad k = -\frac{1}{t} \ln \left(\frac{a}{(a+x)}\right)$$

$$k = \frac{1}{t} \ln \left(\frac{a+x}{a}\right) \quad k = \frac{2.303}{t} \log_{10} \left(\frac{a+x}{a}\right)$$

Generation time :

At t = generation time, x = a $\quad \therefore \quad t = \frac{0.693}{k}$

First order reversible reactions :

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

t = 0	a	0
t = t	a –x	x
t = $t_{eq.}$	a – $x_{eq.}$	$x_{eq.}$

$x_{eq.}$ = eq. conc. of product

(i) $\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0$ (∵ At equilibrium, conc. will not change)

(ii) $\frac{d[A]}{dt} = -k_f[A] + k_b[B] \Rightarrow \frac{d[B]}{dt} = -k_b[B] + k_f[A]$

$\frac{d(a-x)}{dt} = -k_f(a-x) + k_b x$

$-\frac{dx}{dt} = -k_f a + (k_f + k_b)x$

At equilibrium, $\frac{dx}{dt} = 0 = k_f a - (k_f + k_b)x_{eq}$

$k_f a = (k_f + k_b)x_{eq}$

$-\frac{dx}{dt} = -(k_f + k_b)x_{eq} + (k_f + k_b)x$

$\frac{dx}{dt} = (k_f + k_b)(x_{eq} - x)$

$\int_0^x \frac{dx}{(x_{eq}-x)} = (k_f + k_b)\int_0^t dt$

$k_f + k_b = \frac{1}{t} \ln\left(\frac{x_{eq.}}{x_{eq.}-x}\right)$

Effect of temperature on rate of reaction :

In early days the effect of temperature on reaction rate was expressed in terms of temperature coefficient (m) which was defined as the ratio of rate of reaction at two different temperature differing by 10°C (usually these temperatures were taken as 25°C and 35°C.

$\frac{R_{T+10}}{R_T} = \frac{K_{T+10}}{K_T} = 2$ or 3 (for most of the reactions)

Note :

Rate of reaction increases on increasing temperature. (Generally, T.C >1)

But the method of temperature coefficient was not exact to explain the effect of temperature on reaction rate. For that a new theory was evolved.

Illustration 22:

For a reaction T.C. =2, calculate $\frac{k_{40°c}}{k_{25°c}}$ for this reaction. Assuming T.C remains constant.

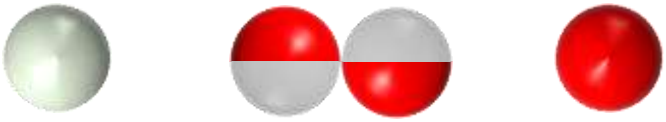
Solution:

$\frac{k_2}{k_1} = (T.C.)^{\frac{\Delta t}{10}} = (2)^{\frac{15}{10}} = (2)^{\frac{3}{2}} = \sqrt{8}$

Collision theory of reaction rate :

Ineffective collision

Effective collision



It was developed by Max Traits and William Lewis. It gives insight in to the energetics and mechanistic aspects of reactions.

It is based upon kinetic theory of gases.

According the this theory :

(i) A chemical reaction takes place due to the collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).

(ii) Every collision does not bring a chemical change. The collision that actually produce the products are effective collision. For a collision to be effective the following two barriers are to be cleared.

Energy barrier : The minimum amount of absolute energy which the colliding molecules must possess as to make the chemical reaction to occur is known as threshold energy.

Reactant molecules having energy equal or greater than the threshold are called active molecules and those having energy less than the threshold are called passive molecules.

At a given temperature there exists a dynamic equilibrium between active and passive molecules. The process of transformation from passive to active molecules being endothermic, increase of temperature increases the number of active molecules and hence the reaction.

Passive molecules $\rightleftharpoons$ Active molecules, ΔH = +ve

"The minimum amount of excess energy required by reactant molecules to participate in a reaction is called activation energy (E_a)".

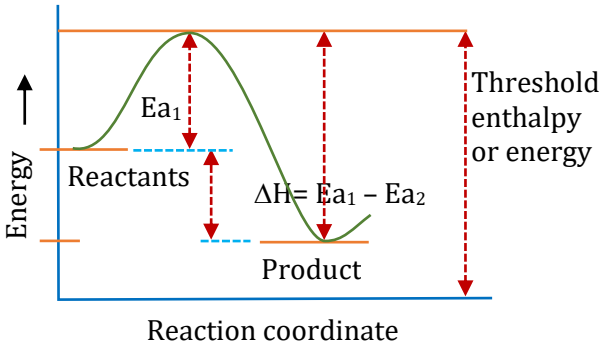
Concept of energy of activation (E_a) :

The average extra amount of energy which the reactant molecules (having energy less than the threshold) must acquire so that their mutual collision may lead to the breaking of bond(s) and hence the energy is known as energy of activation of the reaction. It is denoted by the symbol E_a. Thus,

E_a = Threshold energy – Actual average energy of reactants

E_a is expressed in kcal $mole^{-1}$ or kJ $mole^{-1}$.

The essence of Collision Theory of reaction rate is that there exists an energy barrier in the reaction path between reactant(s) and product(s) and for reaction to occur, the reactant molecules must climb over the top of the barrier which they do by collision. The existence of energy barrier and concept of E_a can be understood from the following diagram.

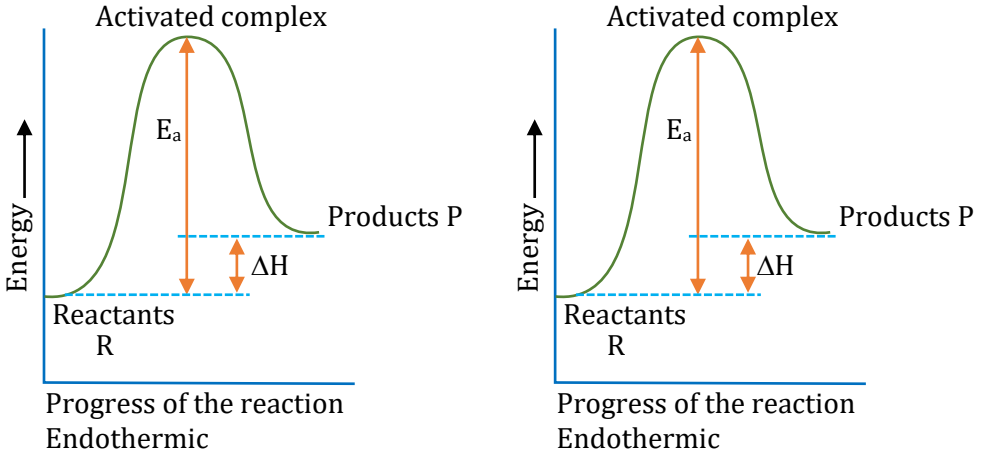


ΔH = Enthalpy change during the reaction ($R \rightarrow P$)

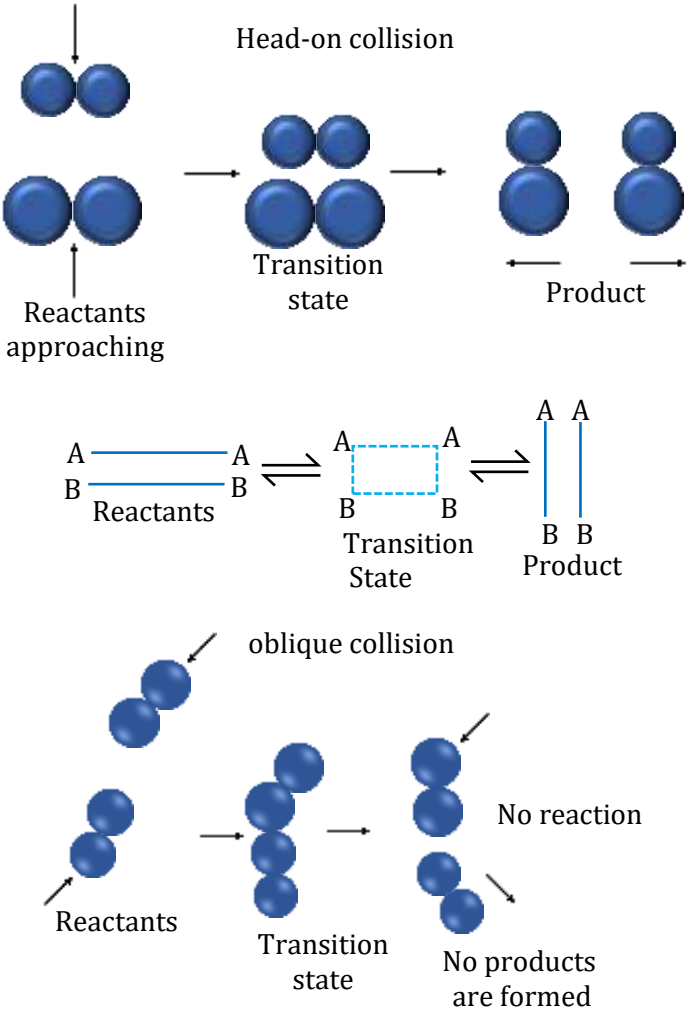
Ea_1 = Energy of activation of the forward reaction

Ea_2 = Energy of activation of the backward reaction

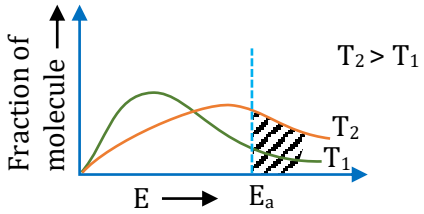
From the figure above, it can be concluded that the minimum activation energy of any exothermic reaction will be zero while minimum activation energy for any endothermic reaction will be equal to ΔH.
Greater the height of energy barrier, greater will be the energy of activation and more slower will be the reaction at a given temperature.



Orientation barrier : Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper direction to make collision effective.
Following diagrams can explain importance of suitable direction for collision. Consider reaction :
$A_2 + B_2 \rightarrow 2AB$



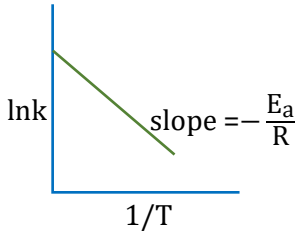
Rate of any chemical reaction = Collision frequency × fraction of the total number of effective collision.
= Collision frequency × fraction of the total number of collision in which K.E. of the colliding molecules equals to E_a or exceeds over it × fraction of collision in proper orientation.
From Maxwellian distribution, it is found that fraction of molecules having excess energy greater than threshold energy lead to the formation of product.



$e^{-E_a/RT}$ Represents fraction of molecules having K.E. greater than or equal to E_a.
Rate $\propto e^{-E_a/RT}$
Dependence of rate on temperature is due to dependence of k on temperature.
$k \propto e^{-E_a/RT}$
$k = Ae^{-E_a/RT}$ [Arrhenius equation]
'A' is pre-exponential factor or frequency factor representing collisions taking place with proper orientation. A and E_a are assumed to be independent of temperature.

$\ell nk = \ell n A - \frac{E_a}{RT}$

As $T \to \infty$, $K \to A$
At temperature T_1, Rate constant = k_1
At temperature T_2, Rate constant = k_2



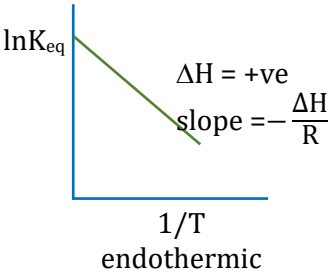
$$\ell nk_1 = \ell nA - \frac{E_a}{RT_1} \;\&\; \ell nk_2 = \ell nA - \frac{E_a}{RT_2} \Rightarrow \ell n\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Reversible reactions :

$k_f = A_f e^{-E_{af}/RT}$
$k_b = A_b e^{-E_{ab}/RT}$

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f e^{-E_{af}/RT}}{A_b e^{-E_{ab}/RT}} = \left(\frac{A_f}{A_b}\right) e^{-(E_{af}-E_{ab})/RT}$$

$$\ell nK_{eq} - \frac{\Delta H}{RT} + \ell n\left(\frac{A_f}{A_b}\right)$$



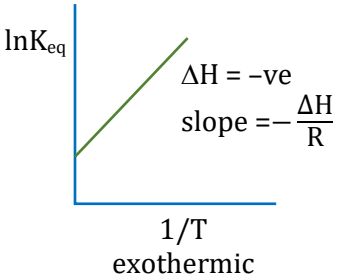


Illustration 23:

For a reaction, temperature coefficient = 2, then calculate the activation energy (in kJ) of the reaction.

Solution:

Given : Temperature coefficient = $\frac{K_2}{K_1} = 2$

$T_1 = 25 + 273 = 298$ k

$T_2 = 35 + 273 = 308$ k

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \left(\frac{10}{298 \times 308}\right)$$

Illustration 24:

For first order gaseous reaction, log k when plotted against $\frac{1}{T}$, it give a straight the with a slope of –8000. Calculate the activation energy of the reaction.

Solution:

For an arrhenius equation $k = Ae^{-Ea/RT}$

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

when curve is plotted between log k and $\frac{1}{T}$. A straight line is obtained and a slope of this curve

$$= -\frac{E_a}{2.303R}$$

Then, $\frac{E_a}{2.303R} = 8000$

or $E_a = 8000 \times 2.303 \times 2 = 36848$ calories

Illustration 25:

The slope of the plot of log k vs $\frac{1}{T}$ for a certain reaction was found to be -5.4×10^3. Calculate the energy of activation of the reaction. If the rate constant of the reaction is 1.155×10^{-2} sec^{-1} at 373 K , what is its frequency factor ?

Solution:

(a) Slope $= \frac{-E_a}{2.303\ R} = -5.4 \times 103$

$E_a = 5.4 \times 10^3 \times 2.303 \times 1.987$

$= 24.624$ cal mol^{-1}

(b) $K = Ae^{-E_a/RT}$; $\log 1.155 \times 10^{-2} = \log A - \frac{24.624}{2.303 \times 1.987 \times 373}$

or $A = 1.764 \times 10^3$ sec^{-1}

Catalyst and Catalysis :

A catalyst is a substance, which increases the rate of a reaction without itself being consumed at the end of the reaction, and the phenomenon is called catalysis.

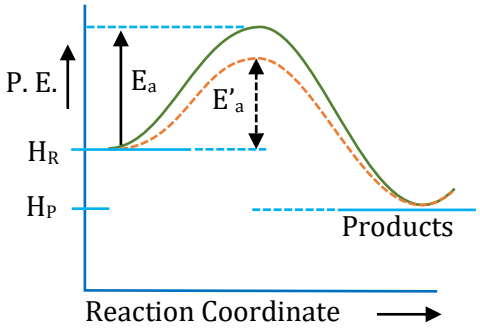
Thermal decomposition of $KClO_3$ is found to be accelerated by the presence of MnO_2. Here MnO_2 acts as a catalyst.

$$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 + [MnO_2]$$

- MnO_2 can be received in the same composition and mass at the end of the reaction.
- The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called inhibitor.
- Analyst are generally foreign substances but sometimes one of the products may act as a catalyst and such catalyst is called "auto catalyst" and the phenomena is called auto catalysis.

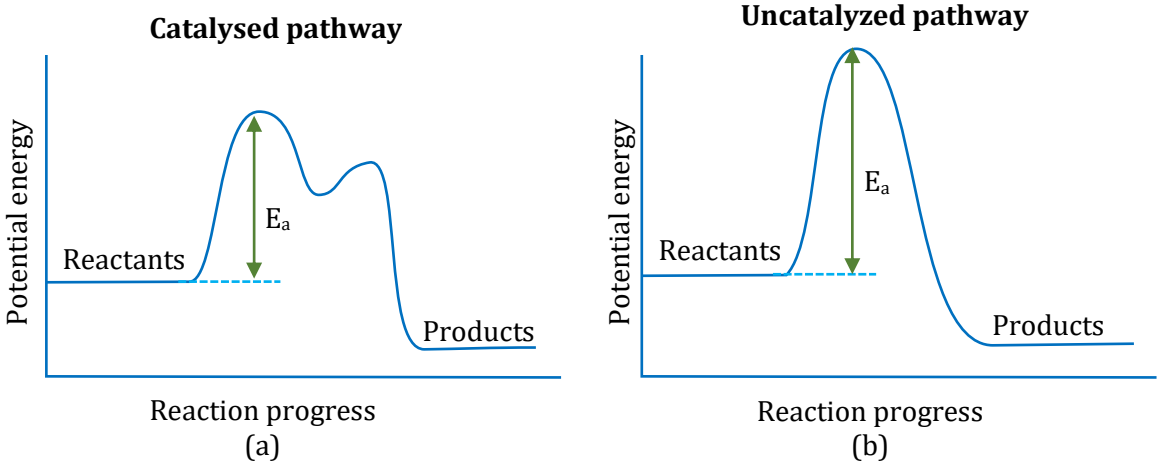
In the permanganate titration of oxalic acid initially there is slow discharge of the color of permanganate solution but afterwards the discharge of the cooler become faster. This is due to the formation of $MnSO_4$ during the reaction which acts as a catalyst for the same reaction. Thus, $MnSO_4$ is an "auto catalyst" for this reaction. This is an example of auto catalyst.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_2 \rightarrow K_2SO_4 + 8H_2O + 10CO_2 + MnSO_4$$



General characteristics of catalyst :

- A catalyst does not initiate the reaction normally. It simply fastens it.
- Only a small amount of catalyst can catalyse the reaction.
- A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant. It simply lowers the time needed to attain equilibrium. This means if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst, the reaction will still go to 75% of completion on the attainment of equilibrium but the time needed for this will be less than 20 minutes.



A catalyst drives the reaction through a low energy path and hence E_a of the catalyst is to lower down the activation energy.

E_a = Energy of activation in absence of catalyst.

E_a' = Overall Energy of activation in presence of catalyst.

$E_a - E_a'$ = Lowering of activation energy by catalyst.

Comparison of rates of reaction in presence and absence of catalyst

If k and k_{cat} be the rate constant of a reaction at a given temperature T, E_a and E'_a are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{cat}}{k} = \frac{Ae^{-E'_a/RT}}{Ae^{-E_a/RT}} = Ae^{(Ea-Ea')/R}$$

Since $E_a - E'_a$ is positive so $k_{cat} > k$. the ratio $\frac{kcat}{k}$ gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature.

The rate of reaction in the presence of catalyst at any temperature T_1 may be made equal to the rate of reaction in absence of catalyst but for this sake we will have to raise the temperature. Let this temperature be T_2.

Then $e^{-E'_a/RT_1} = e^{-E_a/RT_2}$ or $\frac{Ea'}{T_1} = \frac{Ea}{T_2}$.

Calculation of rate law/order :

For complex reactions the overall rate of reaction is controlled by the slowest step which is called as rate determining step (R.D.S.).

In rate law expression rate of reaction depends on concentration of reactants of slowest step which must be free from intermediate.

If R.D.S. contains intermediate, its value is solved using K_{eq} of fast step (assumed as reversible).

Illustration 26:

Find out order of this reaction

$2NO_2 + F_2 \longrightarrow 2NO_2$

Mechanism :-

$NO_2 + F_2 \xrightarrow{K_1} NO_2F + F$ (slow step)

$NO_2 + F \xrightarrow{K_2} NO_2F$ (fast)

Solution:

According to RDS

Rate = $k_1 [NO_2] [F_2]$

Order of reaction = 2

Illustration 27:

Find our order and rate law for the reaction

$P_2 + Q_2 \rightarrow 2PQ$

Mechanism:

(i) $P_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} P + P$ (fast)

(ii) $P + Q_2 \xrightarrow{k_3} PQ + Q$ (slow)

(iii) $P + Q \xrightarrow{k_4} PQ$ (fast)

Solution:

$K_1 [P_2] = K_2[P]^2$

$[P] = \left(\frac{K_1}{K_2}\right)^{1/2} [P_2]^{1/2}$

$R = K_3 [P] [Q_2]$

$r = k_3\left(\frac{k_1}{k_2}\right)^{1/2} [Q_2] [P_2]^{1/2}$

Order = 3/2