

CHEMICAL KINETICS

These notes
have been verified
by CBSE Science
Toppers &
reputated faulties

COMPLETE NCERT
- No syllabus removed

We have integrated
Previous Year Qs
in the notes

APNI
KAKSHA



#JAO AB PHODO!

Raman
Dhattarwal

Target 100

HOW TO STUDY THE NOTES?

Apni Kaksha

- Coloured and double sided print
- Revise the notes at least 3-4 time
- Write to revise | 10% rule
- Keep track of previous year qs
- See the marking scheme



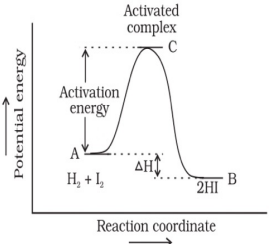
Flow Chart Of Complete Chapter (NCERT)

Chemical Kinetics

Rate of Reaction

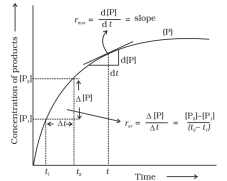
Average Rate

Instantaneous Rate

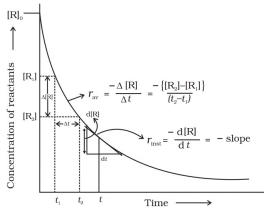


Introduction

Need of Kinetics



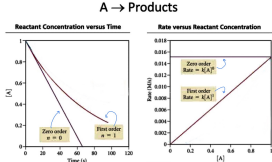
Factors affecting Rate



Integrated Rate Equation

Order and molecularity of a reaction

Zero order Reaction

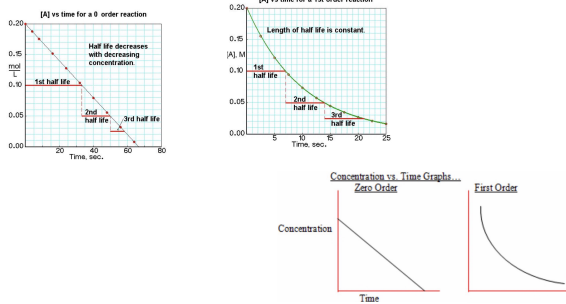


First order Reaction

Pseudo first order Reaction

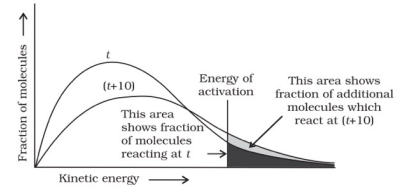
Effect of catalyst

Half life of a reaction

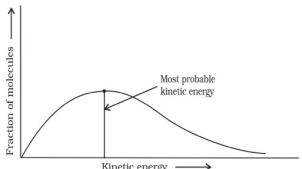


Temperature Dependence of rate of a reaction

Arrhenius Equation



Collision Theory



Chemical Kinetics

→ For a chemical reaction $R \rightarrow P$: Three questions are important.

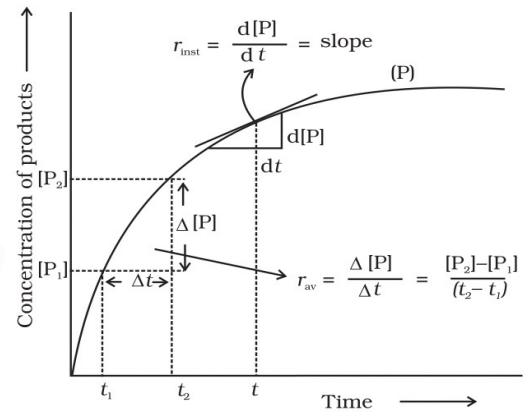
- (i) Reaction will happen or not? : Thermodynamics : Reaction is feasible only if $\Delta G < 0$.
- (ii) To which extent reaction will happen? : Chemical Equilibrium
- (iii) What is the speed of chemical reaction? : Chemical Kinetics : Concept of rate of a reaction.

Rate of reaction :- [Velocity of reaction] (2M) [CBSE 2010/2015 / Delhi 2010]

The rate of change of concentration of any species taking part in a chemical reaction with time is known as rate of reaction.

→ For a reaction $R \rightarrow P$ rate = $\frac{\text{Change in Concentration}}{\text{time}} = \frac{\Delta C}{\Delta t}$

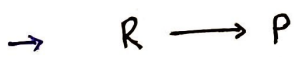
→ Unit : $\frac{\text{mol/L}}{\text{s}}$ or $\frac{\text{atm}}{\text{s}}$ → for gaseous reactant or product.



Types of rate :- [CBSE 2010C] (2M)

(i) Average Rate :- $R_{av} = \frac{\text{Total change in conc}^n}{\text{Total time taken}}$

$$\text{Rate} = -\frac{\Delta[\text{Reactant}]}{\Delta t} = \frac{\Delta[\text{Product}]}{\Delta t} = \frac{c_2 - c_1}{t_2 - t_1} = \frac{\Delta C}{\Delta t}$$



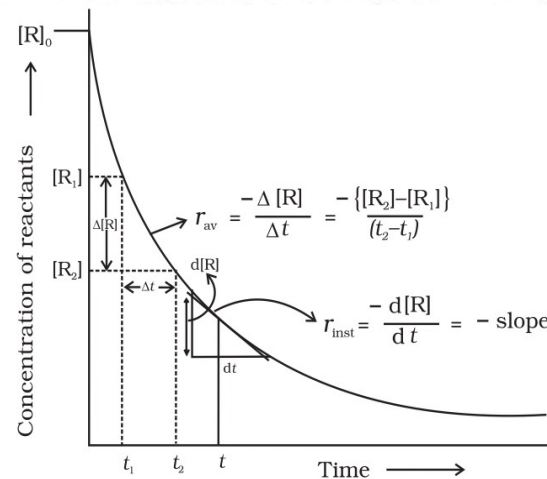
at time t_1 : c_1 [Concentration of product after time t_1]

at time t_2 : c_2

(ii) Instantaneous Rate :- Rate at a given time

$$R_{inst} = \lim_{\Delta t \rightarrow 0} R_{av} = \lim_{\Delta t \rightarrow 0} \frac{\Delta C}{\Delta t} = \frac{dC}{dt}$$

= Slope of concentration and time graph.



#Rate of appearance and rate of disappearance :-

Let us consider a reaction $R \rightarrow P$

At time t_1 : R_1 P_1

t_2 : R_2 P_2

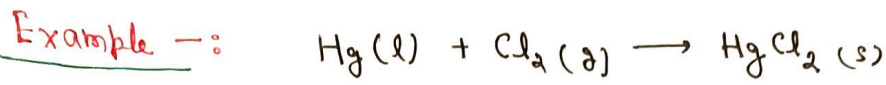
$$\Delta R = R_2 - R_1$$

$$\Delta P = P_2 - P_1$$

$$\Delta t = t_2 - t_1$$

→ Rate of disappearance of R = $\frac{\text{Decrease in } [R]}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t}$

→ Rate of appearance of P = $\frac{\text{Increase in } [P]}{\text{Time taken}} = \frac{\Delta[P]}{\Delta t}$



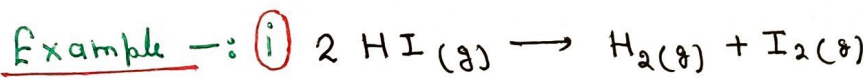
→ Rate of reaction = Rate of disappearance of Hg / Cl_2 = Rate of appearance of HgCl_2

$$= -\frac{\Delta[\text{Hg}]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = \frac{\Delta[\text{HgCl}_2]}{\Delta t}$$

Note :- If stoichiometric coefficients of reactants or products are not equal to one, then rate of disappearance of any of the reactants or rate of appearance of products is divided by their respective stoichiometric coefficients.



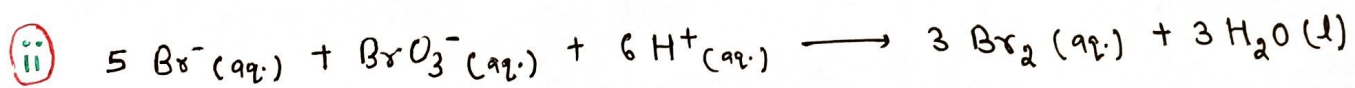
$$\text{Rate of reaction} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$



→ Rate of disappearance of HI = $2 \times$ Rate of appearance of H_2 / I_2

→ Rate of reaction = Rate of appearance of $\text{H}_2 / \text{I}_2 = \frac{1}{2}$ Rate of disappearance of HI.

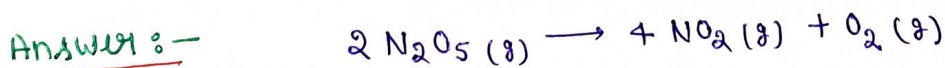
$$= \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$



$$\text{Rate of reaction} = -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$$

Question :- For the reaction $2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$, the rate of formation of $\text{NO}_2(g)$ is $2.8 \times 10^{-3} \text{ M s}^{-1}$. Calculate the rate of disappearance of $\text{N}_2\text{O}_5(g)$!

[CBSE 2018] (2M)



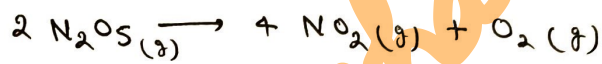
$$\text{Rate of Reaction} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t}$$

$$\rightarrow \text{Rate of disappearance of } N_2O_5 = -\frac{\Delta[N_2O_5]}{\Delta t} = 2 \times \frac{1}{4} \frac{\Delta[NO_2]}{\Delta t}$$

$$\left[\begin{array}{l} \text{Given that rate of formation of } NO_2 = 2.8 \times 10^{-3} \text{ MS}^{-1} \\ = \frac{\Delta[NO_2]}{\Delta t} \end{array} \right] = \frac{1}{2} \times 2.8 \times 10^{-3} \text{ MS}^{-1}$$

$$= 1.4 \times 10^{-3} \text{ MS}^{-1}$$

Question -: The decomposition of N_2O_5 in CCl_4 at 318 K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.33 mol L^{-1} and after 184 minutes, it is reduced to 2.08 mol L^{-1} . Calculate the average rate of this reaction and what is the rate of production of NO_2 during this period?



Answer -: Average Rate $= -\frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = -\frac{1}{2} \left[\frac{(2.08 - 2.33) \text{ mol L}^{-1}}{184 \text{ min}} \right]$

$$= 6.79 \times 10^{-4} \text{ mol L}^{-1} \text{ min} = \frac{6.79 \times 10^{-4} \text{ mol L}^{-1}}{60 \text{ s}}$$

$$\rightarrow \text{Rate} = \frac{1}{4} \left[\frac{\Delta[NO_2]}{\Delta t} \right] = 6.79 \times 10^{-4} \frac{\text{mol L}^{-1}}{\text{min}} = 1.13 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\rightarrow \frac{\Delta[NO_2]}{\Delta t} = 4 \times 6.79 \times 10^{-4} = 2.79 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} = \text{Rate of production of } NO_2$$

Factors influencing rate of a reaction -: [Delhi 2010C] [BSE 2015]

(2M)

(1M)

(i) Concentration :- Rate of reaction increases with concentration of reactant.
 \rightarrow Liquid / Aqueous Medium

\rightarrow In case of gases, pressure $\uparrow \Rightarrow$ Rate \uparrow

(ii) Temperature -: Rate of a reaction increases with increase of temperature.

(iii) Nature of reactants -: Different reactant require different amount of energies for breaking of old bonds and for formation of new bonds.

(iv) Catalyst :- It changes the rate of reaction, without being used (consumed) in the reaction.

Rate Law | Rate Equation | Rate Expression :- [Dependence of rate on concⁿ]

\rightarrow Rate law is expression in which reaction rate is given in terms of molar concⁿ of reactants with each term raised to some power.

[CBSE 2011 | Delhi 2011/2012]

(1M)

→ The power raised on concentration terms in rate expression may or may not be same as stoichiometric coefficient of the reacting species in a balanced chemical equation.

→ Consider a general reaction : $aA + bB \longrightarrow cC + dD$

a, b, c, d are stoichiometric coefficients.

Rate equation : $\text{Rate} \propto [A]^x [B]^y$

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

→ Rate Constant

→ Exponent x and y may or may not be equal to stoichiometric coefficient (a and b).

→ The equation which relate, rate of a reaction to concentration of the reactants is called rate equation or rate expression.

Order of a reaction :- The sum of powers of the concentration of the reactants in rate law expression is called order of that chemical reaction.

For a reaction : $aA + bB \longrightarrow cC + dD$

$\text{Rate} = k [A]^x [B]^y$ then order of reaction = $x+y$

IM [CSE 2011/2010 / Delhi 2011C / 2010]

→ Order of a reaction can be determined only by experiment. We can not predict theoretically.

Apni Kaksha

→ Order of a reaction can be 0, 1, 2 and even a fraction.

<u>Reaction</u>	<u>Experimental rate expression</u>	<u>order of reaction</u>
$\text{CHCl}_3 + \text{Cl}_2 \longrightarrow \text{CCl}_4 + \text{HCl}$	$\text{Rate} = k [\text{CHCl}_3]^1 [\text{Cl}_2]^{1/2}$	$1 + \frac{1}{2} = 1.5$
$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ ↓ $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$	$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]^1 [\text{H}_2\text{O}]^0$	$1 + 0 = 1$

Units of rate constant :- From above : $\text{Rate} = k [A]^x [B]^y$

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

; unit of $k = \frac{\text{concn} / \text{time}}{(\text{concn})^x (\text{concn})^y} = \frac{\text{concn}}{\text{time}} \cdot \frac{1}{[\text{concn}]^{x+y}}$

→ Unit of $k = \frac{(\text{mol L}^{-1})}{s} \times \frac{1}{(\text{mol L}^{-1})^n}$ $n = \text{order of reaction} = x + y$

→ For zero order reaction: $n = 0$ then unit of $k = \text{mol L}^{-1} \text{s}^{-1}$

→ For first order reaction: $n = 1$: unit of $k = \text{s}^{-1}$

→ For second order reaction: $n = 2$: unit of $k = \text{mol}^{-1} \text{L s}^{-1}$

Question :- Identify order of following reaction :- (i) $k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{s}^{-1}$

(ii) $3 \times 10^{-4} \text{ s}^{-1}$

Answer :- (i) $\text{L mol}^{-1} \text{s}^{-1}$: unit of second order

So, this represent second order reaction.

[Delhi 2011 C]

2M

(ii) s^{-1} : unit of first order reaction.

Question :- Write the rate equation for reaction $2\text{NO}(g) + \text{O}_2(g) \rightarrow \text{NO}_2(g)$ by using following experimental data table?

Experiment	Initial $[\text{NO}] / \text{mol L}^{-1}$	Initial $[\text{O}_2] / \text{mol L}^{-1}$	Initial rate of formation of $\text{NO}_2 / \text{mol L}^{-1} \text{s}^{-1}$
1.	0.30	0.30	0.096
2.	0.60	0.30	0.384
3.	0.30	0.60	0.192
4.	0.60	0.60	0.768

Solution :- Let us write rate expression

for reaction: $\text{Rate} = k [\text{NO}]^x [\text{O}_2]^y$ — (i)

Put the data of experiment (i) in equation (i) :-

→ $0.096 \text{ mol L}^{-1} \text{s}^{-1} = k [0.30]^x [0.30]^y$ — (ii)

Similarly, experiment (ii) and equation (i) :- $0.384 \text{ mol L}^{-1} \text{s}^{-1} = k [0.60]^x [0.30]^y$ — (iii)

→ Experiment (iii) and equation (i) :- $0.192 \text{ mol L}^{-1} \text{s}^{-1} = k [0.30]^x [0.60]^y$ — (iv)

Divide equation (ii) by (iii) :- $\frac{0.096}{0.384} = \left[\frac{0.30}{0.60} \right]^x \left[\frac{0.30}{0.30} \right]^y$

$\Rightarrow \frac{1}{4} = \frac{1}{2^x}$ then $x = 2$

Divide (iv) by (ii) :- $\frac{0.192}{0.096} = \left[\frac{0.30}{0.30} \right]^x \left[\frac{0.60}{0.30} \right]^y \Rightarrow 2 = 2^y$ then $y = 1$

Put the value of x and y in equation (i) :-

$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]^1$ — (v)

Order of reaction = $2 + 1 = 3$

value of rate constant :- Put the value of rate, $[\text{NO}]$, $[\text{O}_2]$ in equation (v) from any experiment.

Apni Kaksha

Question:- For the reaction $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NOCl}(\text{g})$, the following data were collected. All the measurements were taken at 263K.

Exp. No.	Initial [NO] (M)	Initial [Cl ₂] (M)	Initial rate of disappearance of Cl ₂ (M/min)
1.	0.15	0.15	0.60
2.	0.15	0.30	1.20
3.	0.30	0.15	2.40
4.	0.25	0.25	?

- (i) Write the expression for rate law.
- (ii) Calculate the value of rate constant and specify its unit.
- (iii) What is the initial rate of disappearance of Cl₂ in experiment 4? [Delhi 2012] (3M)

Answer:- Rate law : $\text{Rate} = k[\text{NO}]^x [\text{Cl}_2]^y$

→ Initial rate becomes $(\text{Rate})_0 = k[\text{NO}]^x [\text{Cl}_2]^y$

→ Comparing experiment 1 and 2 : $(\text{Rate})_1 = k[0.15]^x [0.15]^y = 0.60$ — (i)

$(\text{Rate})_2 = k[0.15]^x [0.30]^y = 1.20$ — (ii)

→ Dividing equation (ii) by equation (i) →

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{1.20}{0.60} = \frac{k[0.15]^x [0.30]^y}{k[0.15]^x [0.15]^y} \quad \text{Then, } 2^y = 2^1$$

$y = 1$

→ Comparing experiments 1 and 3 :

$(\text{Rate})_1 = k[0.15]^x [0.15]^y = 0.60$ — (iii)

$(\text{Rate})_3 = k[0.30]^x [0.15]^y = 2.40$ — (iv)

Dividing equation (iv) by equation (iii) :-

$$\frac{(\text{Rate})_3}{(\text{Rate})_1} = \frac{k[0.30]^x [0.15]^y}{k[0.15]^x [0.15]^y} = \frac{2.40}{0.60}$$

$\Rightarrow 2^x = 4$ then $x = 2$

Rate law : $\text{Rate} = k[\text{NO}]^2 [\text{Cl}_2]$

Rate constant $k = \frac{\text{Rate}}{[\text{NO}]^2 [\text{Cl}_2]} = \frac{0.60}{(0.15)^2 (0.15)} = 177.51 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$

Initial rate of disappearance of Cl₂ in experiment 4 is r_4 .

$$r_4 = k[\text{NO}]^2 [\text{Cl}_2] = 177.51 \times (0.25)^2 (0.25)$$

$$r_4 = 2.77 \frac{\text{M}}{\text{min}}$$

Molecularity of a reaction -:

→ The no. of reacting species [atoms, ions or molecules] taking part in a one step reaction [an elementary reaction], which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

[CBSE 2010 | 2011C | 2014] (1M)

Molecularity

- Unimolecular Reaction → When one reacting species is involved.
- Bimolecular Reaction → Reaction via simultaneous collision between two species.

Example -: (i) $\text{NH}_4\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O}$; Unimolecular.

(ii) $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$; Bimolecular.

Apni
Kaksha

Note:- Generally molecularity greater than 3 is not observed, because simultaneous collisions of more than 3 molecules are not possible.

Difference between order and molecularity [CBSE 2014 / 2010 / Delhi 2011C]

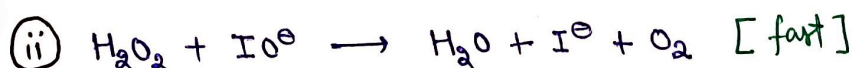
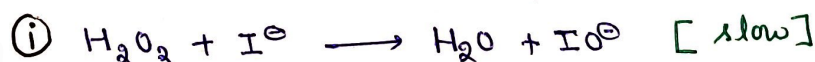
Molecularity

Order

- i) It is defined as the no. of molecules of reactant taking part in a reaction.
- ii) Example -: $\text{NH}_4\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O}$
molecularity = 1
- iii) It is a theoretical value.
- iv) It is always a whole no. It can neither be zero nor fractional.
- v) It is derived from rate determining step in the mechanism of a reaction.
- i) It is defined as the sum of the power of concentration terms that appear in rate law.
- ii) $\text{NH}_4\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O}$
Rate = $k[\text{NH}_4\text{NO}_2]$, order = 1
- iii) It is an experimental value.
- iv) It may be zero, fractional or integer.
- v) It is derived from rate expression.

Note:- Let us consider a reaction $2\text{H}_2\text{O}_2 \xrightarrow[\text{Alkaline Medium}]{\text{I}^-} 2\text{H}_2\text{O} + \text{O}_2$.

Evidences suggest that this reaction takes place in two steps.



[Delhi 2019]

(2M)

→ Slow step [first step] is the rate determining step [RDS].

→ Rate equation for reaction can be written on the basis of RDS.

$$\text{Rate} = - \frac{d[\text{H}_2\text{O}_2]}{dt} = k [\text{H}_2\text{O}_2]^1 [\text{I}^-]^1$$

→ Overall order of reaction = $1 + 1 = 2$

Integrated Rate Equations

Zero Order Reaction :- Let us consider a zero order reaction $R \rightarrow P$

Then rate = $-\frac{d[R]}{dt} = k[R]^0 = k$ Differential rate Equation.

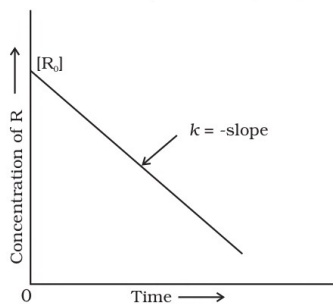
⇒ $d[R] = -k dt$ ⇒ On integrating both side : $\int d[R] = -k \int dt + I$

⇒ $[R] = -kt + I$ — (i) constant of integration.

At $t=0$, the concentration of reactant $R = [R]_0$.

By equation (i) ⇒ $[R]_0 = -k \times 0 + I$ then $I = [R]_0$.

→ Put the value of I in equation (i) —: $[R] = -kt + [R]_0$ Integrated rate Equation.



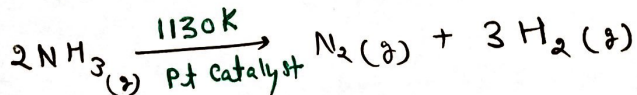
$y = mx + c$

→ Straight line graph between $[R]$ and t

→ slope = $-k$

Example of zero order reaction :- (i) Enzyme catalysed reactions.

(ii) Decomposition of NH_3 on a hot platinum surface at high pressure.

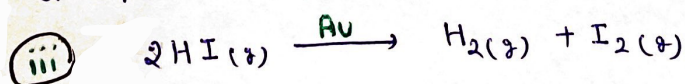


[Delhi 2016]

IM

→ Rate = $k[\text{NH}_3]^0$

Explanation :- At high pressure the metal surface gets saturated with gas molecules. So, a further change in reaction condition is unable to change the amount of ammonia on the surface of the catalyst, making rate of reaction independent of its concentration.



Apni Kaksha :-

Integrated rate equation of first order reactions :-

Consider a first order reaction : $R \rightarrow P$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R] \Rightarrow \frac{d[R]}{[R]} = -k dt$$

on integration $\Rightarrow \int \frac{d[R]}{[R]} = -k \int dt + I$ (i)

→ When $t=0$ then $[R] = [R]_0$

→ Put this value in equation (i) :- $\ln [R]_0 = -k \cdot 0 + I$

$$\ln [R] = -k t + I$$

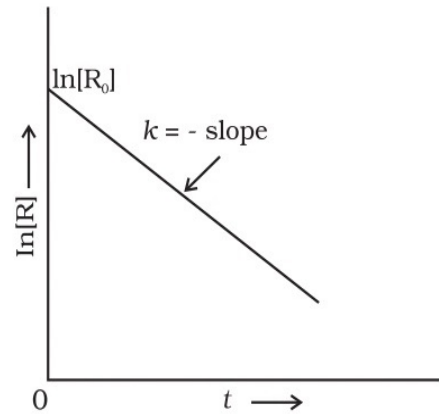
$$I = \ln [R]_0 \text{ --- (ii)}$$

Constant of integration.

→ By equation (i) and (ii) :-

$$\ln [R] = -k \cdot t + \ln [R]_0 \text{ --- (iii)}$$

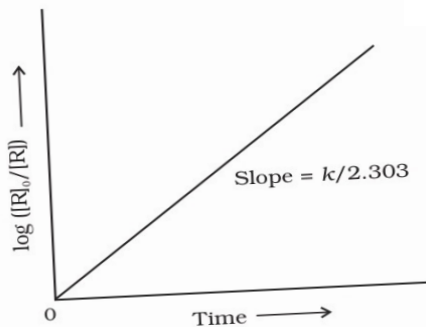
\downarrow \downarrow \downarrow
 y $=$ $m \cdot x$ $+ c$



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

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

\downarrow \downarrow \downarrow
 y $=$ $m \cdot x$



$$\text{Slope} = \frac{k}{2.303}$$

On rearranging equation (iii) : $\ln [R] - \ln [R]_0 = -k t$

$$\rightarrow \ln \frac{[R]}{[R]_0} = -k t$$

$$k = \frac{1}{t} \ln \frac{[R]_0}{[R]}$$

$$\rightarrow \frac{[R]}{[R]_0} = e^{-k t} \text{ then } [R] = [R]_0 e^{-k t}$$

Graph between $[R]$ and time $t \rightarrow$

→ $R \rightarrow P$

At t_1 , $[R]_1$

Then By equation (iii) →

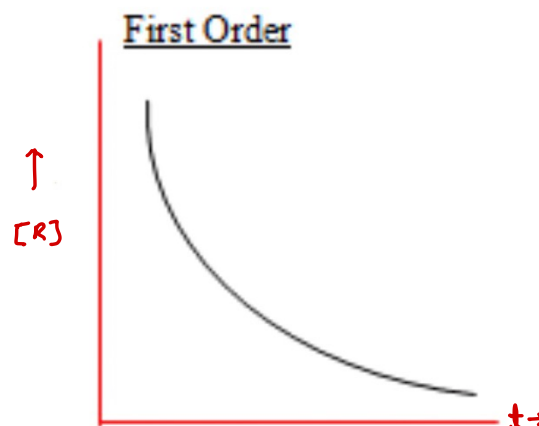
$$\ln [R]_1 = -k t_1 + \ln [R]_0$$

At t_2 , $[R]_2$

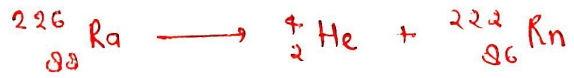
$$\ln [R]_2 = -k t_2 + \ln [R]_0$$

Apni Kaksha :-

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2}$$



Example -: (i) All natural and artificial radioactive decay of unstable nuclei take place by 1st order kinetics.



(ii) Hydrogenation of ethene

$$\hookrightarrow \text{Rate} = k [\text{C}_2\text{H}_4]$$



Question -: The initial concentration of N_2O_5 in the following 1st order reaction $\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ was $1.24 \times 10^{-2} \text{ mol L}^{-1}$ at 318 K. The concentration of N_2O_5 after 60 minutes was $0.20 \times 10^{-2} \text{ mol L}^{-1}$. Calculate the rate constant of the reaction at 318 K?

Answer -: For 1st order reaction: $k = \frac{2.303}{(t_2 - t_1)} \log \frac{[R]_1}{[R]_2}$

$$\rightarrow k = \frac{2.303}{(60 \text{ min} - 0 \text{ min})} \log \frac{1.24 \times 10^{-2} \text{ mol L}^{-1}}{0.20 \times 10^{-2} \text{ mol L}^{-1}} = \frac{2.303}{60} \log 6.2 \text{ min}^{-1}$$

$$\rightarrow k = 0.0304 \text{ min}^{-1}$$

First order gas phase reaction :-

Let us consider a 1st order reaction: $\text{A}(\text{g}) \longrightarrow \text{B}(\text{g}) + \text{C}(\text{g})$

P_i : Initial pressure of A.

At $t = 0$: P_i atm 0 0

P_t : Total pressure at time t .

At time t : $(P_i - x)$ x x

P_A, P_B, P_C : Partial pressure of A, B, C respectively.

x : Decrease in pressure after time t .

Total pressure at time t

$$P_t = P_A + P_B + P_C$$

$$P_t = (P_i - x) + x + x$$

$$\text{then } x = P_t - P_i$$

Partial pressure of A at time t

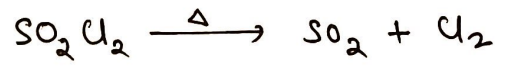
$$P_A = P_i - x = P_i - (P_t - P_i)$$

$$P_A = 2P_i - P_t$$

$$\rightarrow \text{Rate constant } k = \frac{2.303}{t} \log \left(\frac{P_i}{P_A} \right)$$

$$k = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

Question :- Experimental data for the first order thermal decomposition of SO_2Cl_2 at constant volume.



Exp.	Time	Total pressure
1.	0 s	$P_i = 0.4$
2.	100 s	$P_f = 0.7$

[CBSE 2014 | Delhi 2014] 3M

Answer :- $k = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_f}$

$$= \frac{2.303}{100 \text{ s}} \log \frac{0.4}{2 \times 0.4 - 0.7} = \frac{2.303}{100} (2 \log 2) = 1.387 \times 10^{-2} \text{ s}^{-1}$$

Half life of a reaction :- "The time in which the concentration of a reactant is reduced to one half of its initial concentration." [Delhi 2015c] 1M

→ for reaction $R \rightarrow P$
 At $t=0$ $[R]_0$
 At $t=t_{1/2}$ $\frac{[R]_0}{2}$

→ Half life for zero order reaction

↳ Rate constant $k = \frac{[R]_0 - [R]}{t}$

At $t = t_{1/2}$ (Half life) $[R] = \frac{[R]_0}{2}$

↳ $k = \frac{[R]_0 - \frac{[R]_0}{2}}{t_{1/2}}$

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

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

→ Half life of zero order reaction depends on initial concentration of reactant.

a.) $t_{1/2} \propto [R]_0$

b.) $t_{1/2} \propto \frac{1}{k}$

→ Half life $[t_{1/2}]$ for 1st order reaction

↳ Rate constant $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

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

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

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

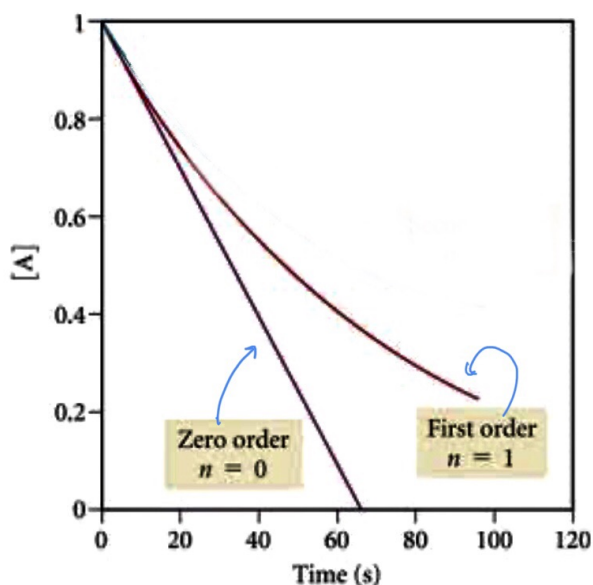
$t_{1/2} = \frac{0.693}{k}$

→ Half life ($t_{1/2}$) is independent of initial concentration. [Delhi 2017] 1M

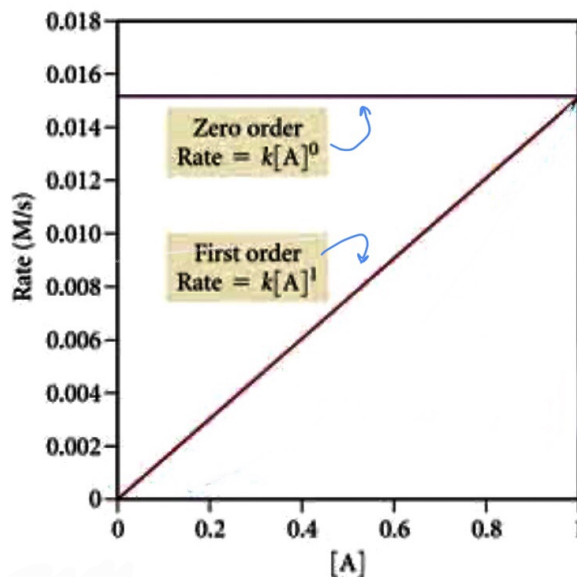
Apni Kaksha :-

A → Products

Reactant Concentration versus Time



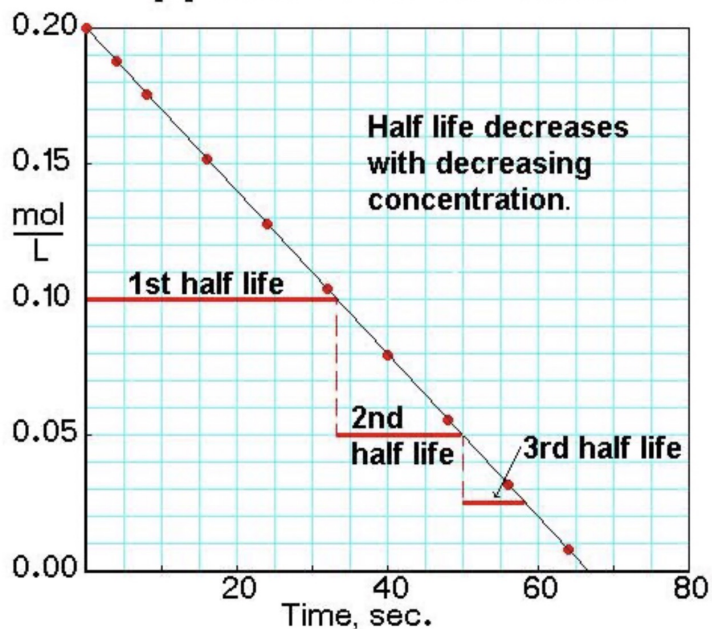
Rate versus Reactant Concentration



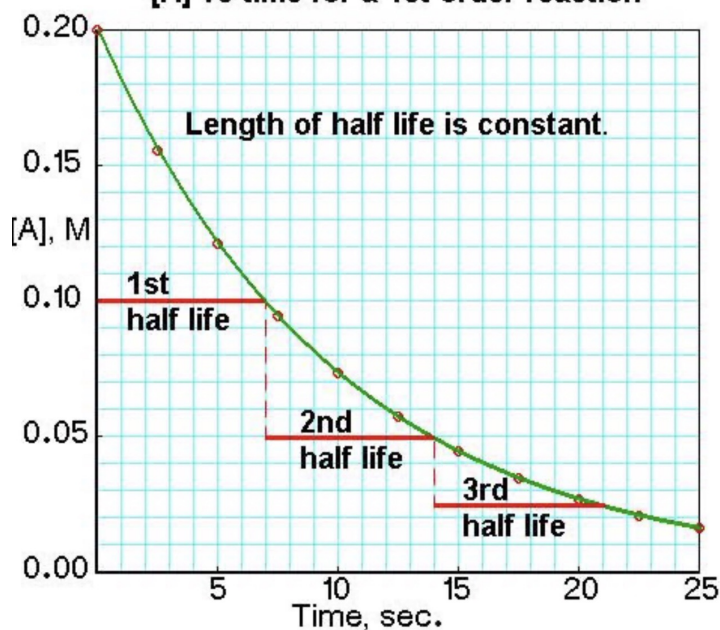
Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	R → P	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	[R] vs t	$[R]_0/2k$	conc time ⁻¹ or mol L ⁻¹ s ⁻¹
1	R → P	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln\{[R]_0/[R]\}$	ln[R] vs t	$\ln 2/k$	time ⁻¹ or s ⁻¹

Apni Kaksha 😊

[A] vs time for a 0 order reaction



[A] vs time for a 1st order reaction



Question :- A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14} \text{ s}^{-1}$. Find the half life of the reaction.

Answer :- For first order, Half life $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}}$

$t_{1/2} = 1.26 \times 10^{14} \text{ s}$ [CBSE 2013]

(1M)

Question :- A first order reaction takes place in 30 min for 50% completion. Calculate the time required for 90% completion of this reaction. Given $\log 2 = 0.3010$

[CBSE 2015 / Delhi 2015]

Answer :- 50% completion time = $t_{1/2} = 30 \text{ min}$

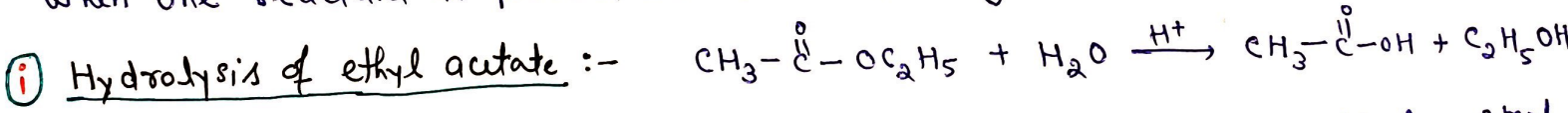
3M

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30 \text{ min}} = 0.023 \text{ min}^{-1}$

→ For the same reaction, time required for 90% completion :-
 $k = 0.023 \text{ min}^{-1}$; $[R]_0 = 100$ $[R] = 100 - 90 = 10$

→ $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} = \frac{2.303}{0.023 \text{ min}^{-1}} \log \frac{100}{10} = 100.13 \text{ min.}$

Pseudo first order reaction :- A chemical reaction between two substances when one reactant is present in excess quantity. [CBSE 2011] (2M)

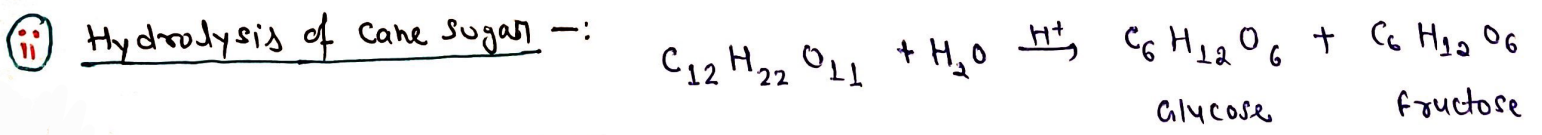


If, At time $t=0$: 0.01 mol 10 mol 0 mol 0 mol
 and, at time t : 0 mol 9.99 mol 0.01 0.01

→ $[\text{H}_2\text{O}]_{t=0} \approx [\text{H}_2\text{O}]_t$ means that concentration of H_2O does not change. So it can not change the rate. $[\text{H}_2\text{O}] = \text{constant}$

→ Rate of reaction = $k' [\text{H}_2\text{O}] [\text{CH}_3\text{COOC}_2\text{H}_5]$ $k' [\text{H}_2\text{O}] = \text{constant} = k$

Rate of reaction = $k [\text{CH}_3\text{COOC}_2\text{H}_5]$ → It indicates 1st order kinetics.



Rate = $k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$

Apni Kaksha :-

Question :- For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained.

(i) If concentration of water remains constant then show that it follows pseudo first order reaction.

Time (second)	0	10	20
$[CH_3COOCH_3] [mol L^{-1}]$	0.10	0.05	0.025

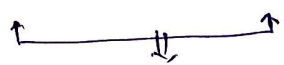
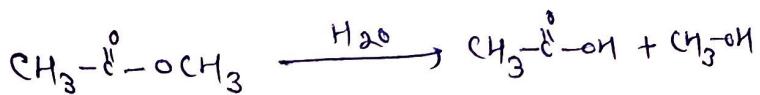
(ii) Calculate average rate of reaction between time interval 10 to 20 second.

[CBSE 2015]

(5M)

Answer - : (i) $[H_2O] = \text{constant}$ (During reaction)

So, rate = $k [\text{methyl acetate}]$



First order, then $k = \frac{2.303}{t} \log \frac{[CH_3COOCH_3]_0}{[CH_3COOCH_3]}$

At time $t_1 = 10$ second $\Rightarrow k_1 = \frac{2.303}{10} \log \frac{0.10}{0.05} = 6.93 \times 10^{-2} s^{-1}$

At time $t_2 = 20$ second $\Rightarrow k_2 = \frac{2.303}{20} \log \frac{0.10}{0.025} = 6.93 \times 10^{-2} s^{-1}$

Rate constant for the reaction has a constant value under any given time interval. Hence the given reaction follows pseudo first order kinetics.

(ii) Average rate = $\frac{-\Delta [CH_3COOCH_3]}{\Delta t} = \frac{-[0.025 - 0.05]}{20 - 10} = 0.0025 \text{ mol L}^{-1} s^{-1}$

Important Previous Year Questions

Apni Kaksha ::

(1) For a first order reaction $H_2O_2 (aq) \rightarrow H_2O (l) + O_2 (g)$, rate constant $k = 1.06 \times 10^{-3} \text{ min}^{-1}$. (2M) [Delhi 2014C]

(a) How long will it take for 15% of a sample of H_2O_2 to decompose?

Answer - : Let us consider $[H_2O_2]_0 = 100 \text{ mol/L}$, then $[H_2O_2]_t = \frac{100}{1.15}$

$$k = \frac{2.303}{t} \log \frac{[H_2O_2]_0}{[H_2O_2]_t} \Rightarrow t = \frac{2.303}{1.06 \times 10^{-3}} \log \frac{100}{95} = 153.3 \text{ min}$$

(b) → How long time it will take for 95% of the sample to decompose?

→ Now: $[H_2O_2]_0 = 100 \text{ mol/L}$ $[H_2O_2]_t = 100 - 95 = 15 \text{ mol/L}$

$$t = \frac{2.303}{k} \log \frac{[H_2O_2]_0}{[H_2O_2]_t} = \frac{2.303}{1.06 \times 10^{-3}} \log 6.667 = \underline{1790.05 \text{ min}}$$

[2.] The rate constant for a zero order reaction is $0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$. How long will it take for the initial concentration to fall from 0.10 M to 0.075 M ?

Answer -: For zero order reaction → $k = \frac{[R]_0 - [R]}{t}$ [Delhi 2010] (2M)

$$[R]_0 = 0.10 \text{ M}$$

$$[R] = 0.075 \text{ M}$$

$$k = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Time } t = \frac{[R]_0 - [R]}{k} = \frac{0.10 - 0.075}{0.0030}$$

$$t = \underline{8.33 \text{ second}}$$

[3.] For a reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$

(i) Show that it follows first order reaction?

(ii) Calculate the half life?

Time (s)	0	300	600
$[N_2O_5] \left(\frac{\text{mol}}{\text{L}}\right)$	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

[Delhi 2017]

Answer -: (i) For first order reaction $k = \frac{2.303}{t} \log \frac{[N_2O_5]_0}{[N_2O_5]}$ (3M)

(a) → At $t = 300 \text{ second}$, $[N_2O_5]_0 = 1.6 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ and $[N_2O_5] = 0.8 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$

$$k = \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} = 2.31 \times 10^{-3} \text{ s}^{-1}$$

(b) → At $t = 600$, $[N_2O_5] = 0.4 \times 10^{-2}$

$$k = \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} = 2.31 \times 10^{-3} \text{ s}^{-1}$$

→ Rate constant remains same in both condition (a & b). So we can say above reaction is first order.

Apni Kaksha ::

(ii) $k = 2.31 \times 10^{-3} \text{ s}^{-1}$ then $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.31 \times 10^{-3}} = 300 \text{ s}$.

[4] → First order reaction $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ at 40°C , data is given below — (3M) [Delhi 2011]

(i) Calculate the rate constant (with its unit).

$[\text{N}_2\text{O}_5] (\text{mol/L})$	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

At time $t = 20 \text{ min}$, $[\text{N}_2\text{O}_5] = 0.289 \frac{\text{mol}}{\text{L}}$

$[\text{N}_2\text{O}_5]_0 = 0.4 \frac{\text{mol}}{\text{L}}$

$k = \frac{2.303}{20} \log \frac{0.4}{0.289} = \frac{2.303}{20} \log 1.384$

$k = 0.01625 \text{ min}^{-1} = 1.62 \times 10^{-2} \text{ min}^{-1}$

(ii) → What will be concentration of N_2O_5 after 100 min?

$k = \frac{2.303}{100} \log \frac{0.4}{[\text{N}_2\text{O}_5]} = 1.62 \times 10^{-2}$ then $\log \frac{0.4}{[\text{N}_2\text{O}_5]} = \frac{1.62}{2.303} = 0.705$

→ $\frac{0.4}{[\text{N}_2\text{O}_5]} = \text{antilog } 0.705 = 5.07$ then $[\text{N}_2\text{O}_5] = \frac{0.4}{5.07} = 0.078 \frac{\text{mol}}{\text{L}}$

(iii) → Initial rate of reaction?

Initial rate = $k [\text{N}_2\text{O}_5] = 0.4 \times 1.62 \times 10^{-2} = 6.4 \times 10^{-3} \frac{\text{mol}}{\text{L min}}$

[5] :- For a reaction $\text{A} + \text{B} \rightarrow \text{P}$ the rate is given by $\text{Rate} = k[\text{A}][\text{B}]^2$ [CBSE 2015 / Delhi 2015]

(a) → How is the rate affected if $[\text{B}]$ is doubled? (2M)

Rate of reaction = $k [\text{A}] [2\text{B}]^2 = 4 [\text{A}] [\text{B}]^2 = 4 \times \text{original rate}$

(b) → What is overall order of reaction if A is present in large excess?

→ If A is present in large excess, then the reaction will be independent of the concentration of A. $\text{Rate} = \underbrace{k [\text{A}]}_{\text{constant}} [\text{B}]^2 = k' [\text{B}]^2$

Then order of reaction = 2

Temperature dependence of the rate

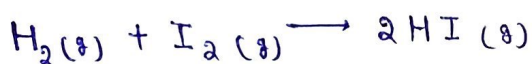
→ The rate of the reaction is dependent on temperature. This is expressed in terms of temperature coefficient. Rate of reaction increases with temperature.

Temperature Coefficient :- It is the ratio of rate constant at temperature 300K [$290 + 10$] to the rate constant at temperature 290K .

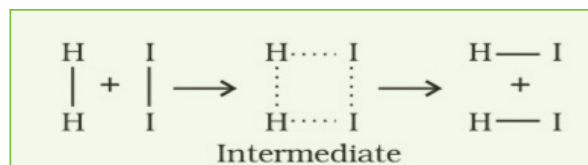
→ It is observed that for a chemical reaction with rise in temperature by 10° , the rate constant is nearly doubled. [CBSE 2014C / Delhi 2010C] (2M)

Arrhenius Theory :-

Arrhenius theory states that products are formed through intermediates or activated complex.



→ When a molecule of H_2 and a molecule of I_2 collide to form an unstable intermediate. Unstable intermediate [activated complex] exist for a very short time and then breaks up to form 2 molecules of HI . [Delhi 2013C] (2M)



Formation of HI through the intermediate

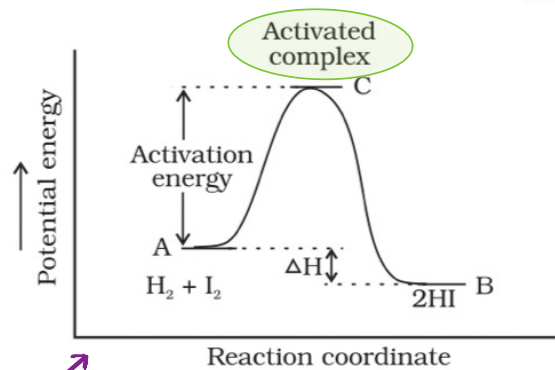


Diagram showing plot of potential energy vs reaction coordinate.

Activation Energy [E_a] :- Minimum energy required to convert a reactant into activated complex is known as activation energy.

E_a = Energy difference between activated complex and reactant molecules.

(1M) [CBSE 2010 / 2011 / 2012]

Arrhenius Equation :- The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation.

$$K = A \cdot e^{\frac{-E_a}{RT}}$$

A :- Frequency factor

E_a :- Activation Energy

T :- Temperature

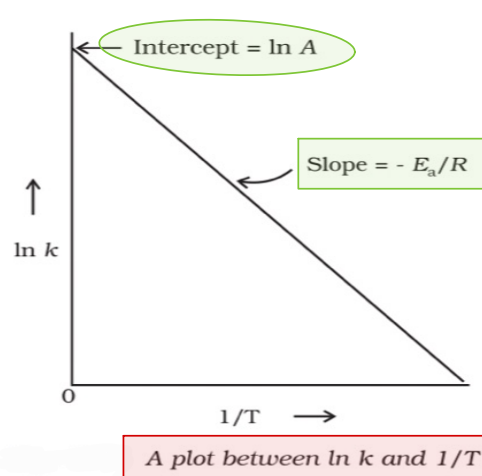
R :- Gas Constant

→ Taking log of both side of Arrhenius Equation :-

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

Graph : $\log k$ vs $\frac{1}{T}$ gives slope = $-\frac{E_a}{2.303 R}$

Intercept = $\log A$



If k_1 is the rate constant at temperature T_1

$$\log k_1 = \log A - \frac{E_a}{2.303 RT_1}$$

→ At $T_2 \Rightarrow$ rate constant k_2

$$\log k_2 = \log A - \frac{E_a}{2.303 RT_2}$$

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

Question :- The rate of most reactions become double when their temperature is raised from 298 K to 308 K. Calculate their activation energy.

[Given, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$]

[Delhi 2011] (2M)

Answer - : $T_1 = 298 \text{ K}$, $T_2 = 308 \text{ K}$, $\frac{k_2}{k_1} = 2$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right] \Rightarrow \log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{308 - 298}{298 \times 308} \right]$$

$$E_a = 52903.05 \text{ J mol}^{-1}$$

Question :- The rate constant for the first order decomposition of H_2O_2 is given by the following equation $\log k = 14.2 - \frac{1 \times 10^4}{T} \text{ K}$.

Calculate E_a for this reaction and rate constant

k , if its half life period be 200 min. [Given $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]

Answer - : $\log k = 14.2 - \frac{1 \times 10^4}{T} \text{ K}$ — (i)

[Delhi 2016] (3M)

Arrhenius Equation : $\log k = \log A - \frac{E_a}{2.303 RT}$ — (ii)

On comparing equation (i) / (ii) : $\frac{E_a}{2.303 R} = 1 \times 10^4 \text{ K}$

$$\Rightarrow E_a = 2.303 \times 8.314 \times 10^4 = 191.4 \text{ KJ mol}^{-1}$$

Calculation of rate constant k :-

Given $t_{1/2} = 200 \text{ min} = 200 \times 60 \text{ s}$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{200 \times 60 \text{ s}} = 5.77 \times 10^{-5} \text{ s}^{-1}$$

Question :- For a decomposition reaction, the values of k at two different temperatures are given below :-

$k_1 = 2.15 \times 10^{-8} \text{ L} / (\text{mol} \cdot \text{s})$ at 650 K

$k_2 = 2.39 \times 10^{-7} \text{ L} / (\text{mol} \cdot \text{s})$ at 700 K

Calculate the value of E_a for the reaction.

[Given $\log 11.11 = 1.046$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]

[CBSE 2014C] 3M

Answer :-

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

$$\rightarrow \log \frac{2.39 \times 10^{-7}}{2.15 \times 10^{-8}} = \frac{E_a}{2.303 \times 8.314} \left[\frac{700 - 650}{700 \times 650} \right]$$

$$\rightarrow \log 11.11 = 1.046 = \frac{E_a}{2.303 \times 8.314} \left[\frac{50}{4.55 \times 10^5} \right]$$

$$E_a = 182.25 \text{ kJ/mol}$$

Question :- The decomposition of A into products has a value of k as $4.5 \times 10^3 \text{ s}^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1} . At what temperature would k be $1.5 \times 10^4 \text{ s}^{-1}$?

Answer :- $T_1 = 10 + 273 = 283 \text{ K}$, $k_1 = 4.5 \times 10^3 \text{ s}^{-1}$, $E_a = 60 \text{ kJ mol}^{-1}$

At $T_2 = ? \Rightarrow k_2 = 1.5 \times 10^4 \text{ s}^{-1}$

$$\rightarrow \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right] \Rightarrow \log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60}{2.303 \times 8.314} \left[\frac{T_2 - 283}{283 T_2} \right]$$

$$\Rightarrow 0.523 = 3133.63 \left[\frac{T_2 - 283}{283 T_2} \right]$$

$$\Rightarrow 0.953 T_2 = 283 \quad \underline{T_2 = 297 \text{ K}}$$

Maxwell Boltzmann Distribution Curve :-

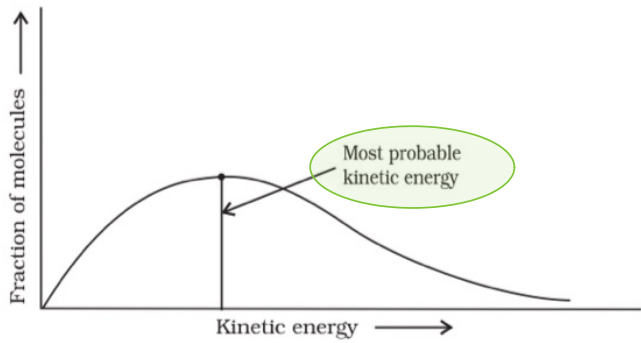
According to Maxwell and Boltzmann, the distribution of kinetic energy may be described by plotting the fraction of molecules with a given kinetic energy.

Apni Kaksha

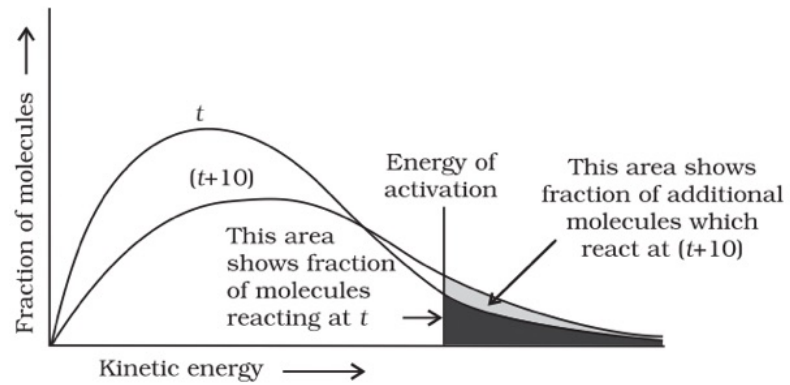
→ The peak of the curve corresponds to the most probable kinetic energy.

The most probable kinetic energy is the kinetic energy of maximum fraction of molecules.

→ When the temperature is raised, the maximum of the curve moves to the higher energy value and curve broadens out and proportion of molecules with higher energy increases.



Distribution curve showing energies among gaseous molecules



Distribution curve showing temperature dependence of rate of a reaction

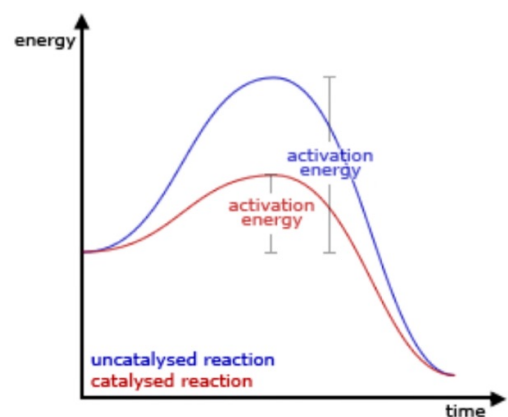
→ Increasing the temperature of the substance increases the fraction of molecules, which collide with energy greater than E_a .

Effect of Catalyst -:

→ The rate of a chemical reaction changes by the presence of catalyst. It alters the rate by providing alternative path of lower / greater activation energy to the reactants.

→ The catalyst [which increases rate of a reaction] reduces the activation energy.

→ A catalyst does not change the enthalpy $[\Delta H]$, Gibbs energy of reaction $[\Delta G]$ and equilibrium constant $[K]$ of a reaction.



1M

[Delhi 2017]

Apni Kaksha 😊

Collision Theory :- This theory is based on kinetic theory of gases.

According to this theory - the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other perfectly.

Collision Frequency :- The no. of collisions per second per unit volume of reaction mixture is known as collision frequency.

→ For a bimolecular elementary reaction $A + B \rightarrow \text{Products}$

$$\text{rate of this reaction} = Z_{AB} e^{-E_a/RT}$$

Z_{AB} : collision frequency of reactants A and B.

$e^{-E_a/RT}$: Represents the fraction of molecules with energies equal to or greater than E_a .

→ The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

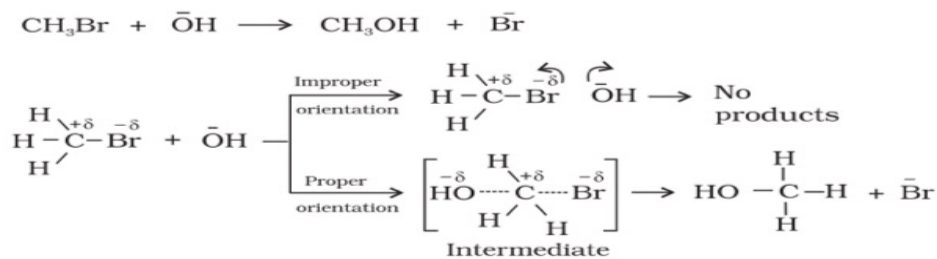


Diagram showing molecules having proper and improper orientation

→ To account for effective collisions, another factor P , called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented.

$$\text{Rate} = P Z_{AB} e^{-E_a/RT}$$

→ In collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

