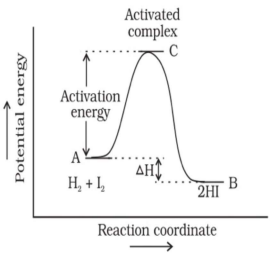
Flow Chart Of Complete Chapter (NCERT)

Chemical Kinetics

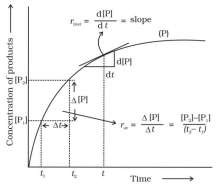
Rate of Reaction



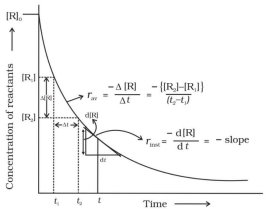
- Average Rate
- Instantaneous Rate

Introduction

Need of Kinetics

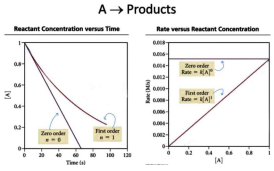


Factors affecting Rate



Integrated Rate Equation

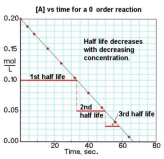
- Zero order Reaction

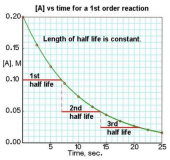


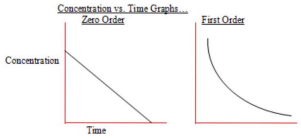
- First order Reaction
- Pseudo first order Reacti

Order and molecularity of a reaction

Half life of a Reaction





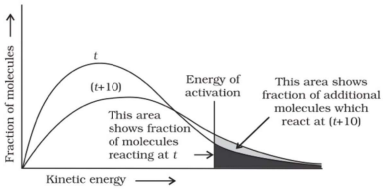


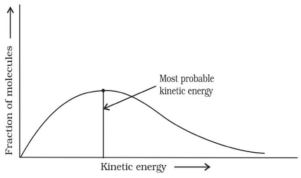
Effect of catalyst

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.

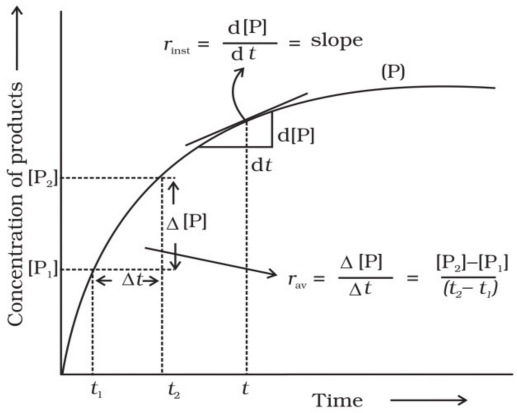
Rate of reaction –: [Velocity of reaction]

(1M) [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 $R \longrightarrow P$ rate $= \dfrac{\text{Change in concentration}}{\text{time}} = \dfrac{\Delta C}{\Delta t}$

→ Unit : $\dfrac{(mol/L)}{s}$ or $\dfrac{(atm)}{s}$ → For gaseous reactant or product.



Types of rate –:

[CBSE 2010C] (2M)

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

$$\text{Rate} = -\frac{\Delta[\text{Reactant}]}{\Delta t} = \frac{\Delta[\text{Product}]}{\Delta t} = \frac{C_2 - C_1}{t_2 - t_1} = \frac{\Delta C}{\Delta t}$$

→ $R \longrightarrow P$

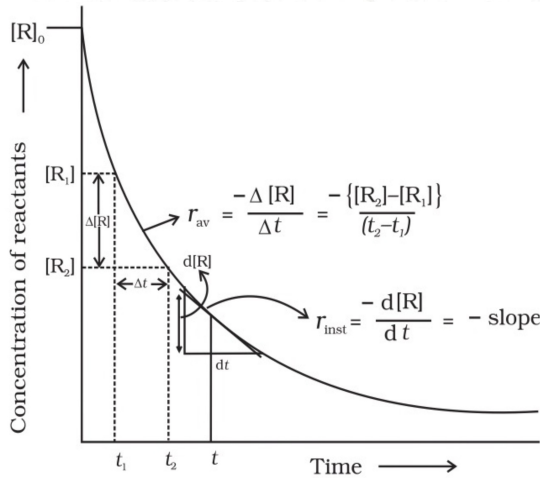
at time t_1 : C_1 [Concentration of product after time t_1]

at time t_2 : C_2

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

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

= Slope of concentration and time graph.



#Rate of appearance and rate of disappearance :–

Let us consider a reaction $R \longrightarrow P$

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

Example :- $Hg(l) + Cl_2(g) \longrightarrow HgCl_2(s)$

→ Rate of reaction = Rate of disappearance of $Hg \mid Cl_2$ = Rate of appearance of $HgCl_2$

$$= -\frac{\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = \frac{\Delta[HgCl_2]}{\Delta t}$$

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.

→ $aA + bB \longrightarrow cC + dD$

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

Example :- (i) $2HI(g) \longrightarrow H_2(g) + I_2(g)$

→ Rate of disappearance of HI = 2 × Rate of appearance of $H_2 \mid I_2$

→ Rate of reaction = Rate of appearance of $H_2 \mid I_2$ = $\frac{1}{2}$ Rate of disappearance of HI.

$$= \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

(ii) $5Br^-(aq.) + BrO_3^-(aq.) + 6H^+(aq.) \longrightarrow 3Br_2(aq.) + 3H_2O(l)$

$$\text{Rate of reaction} = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t}$$

Question :- For the reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$, the rate of formation of $NO_2(g)$ is $2.8 \times 10^{-3}\ M\,s^{-1}$. Calculate the rate of disappearance of $N_2O_5(g)$? [CBSE 2018] (2M)

Answer :- $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

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

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

[Given that rate of formation of $NO_2 = 2.8 \times 10^{-3}$ MS^{-1} $= \frac{\Delta[NO_2]}{\Delta t}$]

$= \frac{1}{2} \times 2.8 \times 10^{-3} MS^{-1}$

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

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?

$$2 N_2O_{5(g)} \longrightarrow 4 NO_{2(g)} + O_{2(g)}$$

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

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

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

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

Factors influencing rate of a reaction -: [Delhi 2010C] (2M) [CBSE 2015] (1M)

(i) **Concentration :-** Rate of reaction increases with concentration of reactant.
↳ Liquid | Aqueous Medium

→ In case of gases, pressure ↑ ⇒ Rate ↑

(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 Conc^n]

→ Rate law is expression in which reaction rate is given in terms of molar Conc^n 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 : $\text{Rate} \propto [A]^x [B]^y$

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

K → 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 $= x+y$

(1M) [CBSE 2011/2010/Delhi 2011C/2010]

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

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

Reaction	Experimental rate expression	order of reaction
→ $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$	$\text{Rate} = K [CHCl_3]^1 [Cl_2]^{1/2}$	$1 + \frac{1}{2} = 1.5$
→ $CH_3-\overset{O}{\overset{\|\|}{C}}-OC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$	$\text{Rate} = K [CH_3COOC_2H_5]^1 [H_2O]^0$	$1 + 0 = 1$

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

Then $K = \dfrac{\text{Rate}}{[A]^x [B]^y}$; unit of $K = \dfrac{\text{Conc}^n / \text{time}}{(\text{Conc}^n)^x (\text{Conc}^n)^y} = \dfrac{\text{Conc}^n}{\text{time}} \cdot \dfrac{1}{[\text{Conc}^n]^{x+y}}$

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

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

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

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

Question :- Identify order of following reaction -: (i) $k = 2.3 \times 10^{-5}\ L\ mol^{-1}\ s^{-1}$ (ii) $3 \times 10^{-4}\ s^{-1}$

Answer -: (i) $L\ mol^{-1}\ s^{-1}$: 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 $2NO_{(g)} + O_{2(g)} \rightarrow NO_{2(g)}$ by using following experimental data table?

Experiment	Initial [NO]/ mol L^{-1}	Initial $[O_2]$/ mol L^{-1}	Initial rate of formation of NO_2/ mol $L^{-1}s^{-1}$
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 : Rate $= k[NO]^x [O_2]^y$ — (i)

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

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

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

→ Experiment (iii) and equation (i) -: $0.192\ mol\ L^{-1}\ s^{-1} = k[0.30]^x [0.60]^y$ — (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) :- $\boxed{Rate = k[NO]^2 [O_2]^1}$ — (v)

Order of reaction = $2+1 = 3$

Value of rate constant -: Put the value of rate, $[NO]$, $[O_2]$ in equation (v) from any experiment.

Question:- For the reaction $2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}$, 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 Cl_2 in experiment 4? [Delhi 2012] (3M)

Answer -: Rate law : $\text{Rate} = K[NO]^x [Cl_2]^y$

→ Initial rate becomes $(\text{Rate})_0 = k[NO]^x [Cl_2]^y$

→ 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) →

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{1.20}{0.60} = \frac{K[0.15]^x [0.30]^y}{K[0.15]^x [0.15]^y}$$

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 : $\text{Rate} = K[NO]^2 [Cl_2]$

Rate constant $K = \dfrac{\text{Rate}}{[NO]^2 [Cl_2]} = \dfrac{0.60}{(0.15)^2 (0.15)} = 177.51 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$

Initial rate of disappearance of Cl_2 in experiment 4 is r_4.

$r_4 = K[NO]^2 [Cl_2] = 177.51 \times (0.25)^2 (0.25)$

$r_4 = 2.77 \dfrac{M}{min}$

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.

Molecularity → Bimolecular Reaction → Reaction via simultaneous collision between two species.

Example :- (i) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$: Unimolecular.

(ii) $2HI \longrightarrow H_2 + I_2$: Bimolecular.

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.	i) It is defined as the sum of the power of concentration terms that appear in rate law.
ii) Example :- $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$ molecularity = 1	ii) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$ Rate = $k[NH_4NO_2]$, order = 1
iii) It is a theoretical value.	iii) It is an experimental value.
iv) It is always a whole no. It can neither be zero nor fractional.	iv) It may be zero, fractional or integer
v) It is derived from rate determining step in the mechanism of a reaction.	v) It is derived from rate expression

Note :- Let us consider a reaction $2H_2O_2 \xrightarrow[\text{Alkaline Medium}]{I^-} 2H_2O + O_2$.

Evidences suggest that this reaction takes place in two step. [Delhi 2019] (2M)

(i) $H_2O_2 + I^\ominus \longrightarrow H_2O + IO^\ominus$ [slow]

(ii) $H_2O_2 + IO^\ominus \longrightarrow H_2O + I^\ominus + O_2$ [fast]

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

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

$$\text{Rate} = -\frac{d[H_2O_2]}{dt} = k\,[H_2O_2]^1[I^-]^1$$

→ 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.

$\Rightarrow d[R] = -k\,dt \Longrightarrow$ on integrating both side : $\int d[R] = -k\int dt + I$

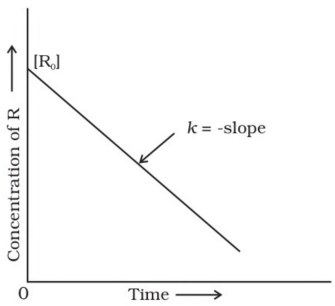
$\Rightarrow [R] = -kt + I$ — (i) constant of integration.

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

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

→ Put the value of I in equation (i) —: $\boxed{[R] = -kt + [R]_0}$ 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.

$$2NH_{3(g)} \xrightarrow[\text{Pt catalyst}]{1130K} N_{2(g)} + 3H_{2(g)}$$

[Delhi 2016] 1M

→ Rate $= k[NH_3]^0$

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.

(iii) $2HI_{(g)} \xrightarrow{Au} H_{2(g)} + I_{2(g)}$

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) —: $\ln[R]_0 = -k \times 0 + I$

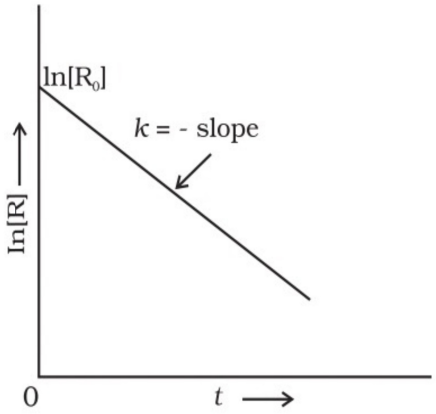
$$I = \ln[R]_0 \quad \text{— (ii)}$$

$\ln[R] = -kt + I$

Constant of integration.

→ By equation (i) and (ii) —:

$$\underbrace{\ln[R]}_{y} = \underbrace{-k}_{m} \cdot \underbrace{t}_{x} + \underbrace{\ln[R]_0}_{c} \quad \text{— (iii)}$$

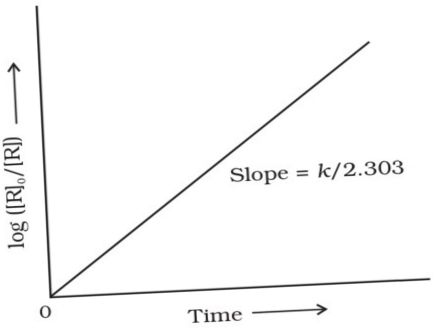


→ $2.303 \log \frac{[R]_0}{[R]} = kt$

→ $\underbrace{\log \frac{[R]_0}{[R]}}_{y} = \underbrace{\frac{k}{2.303}}_{m} \cdot \underbrace{t}_{x}$

$y = m \cdot x$

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



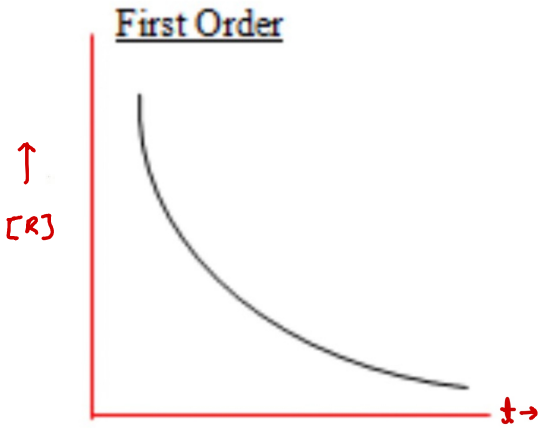
On rearranging equation (iii) : $\ln[R] - \ln[R]_0 = -kt$

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

→ $\ln \frac{[R]}{[R_0]} = -kt$

→ $\frac{[R]}{[R]_0} = e^{-kt}$ then $\boxed{[R] = [R]_0 e^{-kt}}$

Graph between $[R]$ and time t →



→ $R \rightarrow P$

At t_1, $[R]_1$

At t_2, $[R]_2$

Then By equation (iii) →

$$\ln[R]_1 = -kt_1 + \ln[R]_0$$

$$\ln[R]_2 = -kt_2 + \ln[R]_0$$

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

Example –: (i) All natural and artificial radioactive decay of unstable nuclei take place by 1st order kinetics. $^{226}_{88}Ra \longrightarrow ^{4}_{2}He + ^{222}_{86}Rn$

Rate = k [Ra]

(ii) Hydrogenation of ethene

$C_2H_4(g) + H_2(g) \xrightarrow{Pt} C_2H_6(g)$: Rate = k [C_2H_4]

Question –: The initial concentration of N_2O_5 in the following 1st order reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318K ?

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

At $t = 0$:	P_i atm	0	0
At time t :	$(P_i - x)$	x	x

P_i : Initial pressure of A.

P_t : Total pressure at time t.

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

$P_t = P_A + P_B + P_C$

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

then $x = P_t - P_i$

$\rightarrow$ Rate Constant $K = \frac{2.303}{t} \log \left(\frac{P_i}{P_A}\right)$

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

\# Partial pressure of A at time t

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

$$\boxed{P_A = 2P_i - P_t}$$

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

$$SO_2Cl_2 \xrightarrow{\Delta} SO_2 + Cl_2$$

[CBSE 2014 | Delhi 2014] (3M)

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

Answer :-

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

$$= \frac{2.303}{100\ s} \log \frac{0.4}{2\times0.4 - 0.7} = \frac{2.303}{100}(2 \log 2) = 1.307 \times 10^{-2}\ s$$

Half life of a reaction :- "The time in which the concentration of a reactant is reduced to one half of its initial concentration." [Delhi 2015 C] (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) $[R] = \frac{[R]_0}{2}$

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

$K = \frac{[R]_0}{2\, t_{1/2}}$ $\boxed{t_{1/2} = \frac{[R]_0}{2K}}$

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

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

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

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

$K = \frac{0.693}{t_{1/2}}$ $\boxed{t_{1/2} = \frac{0.693}{K}}$

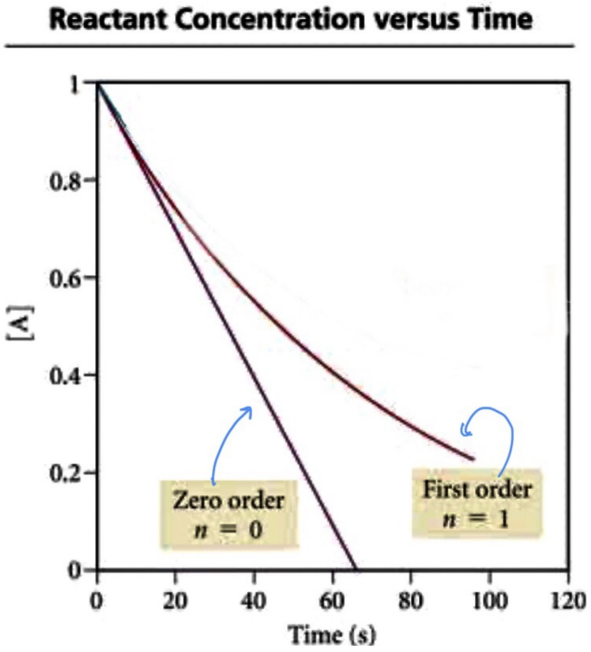
→ Half life of zero order reaction depends on initial concentration of reactant.

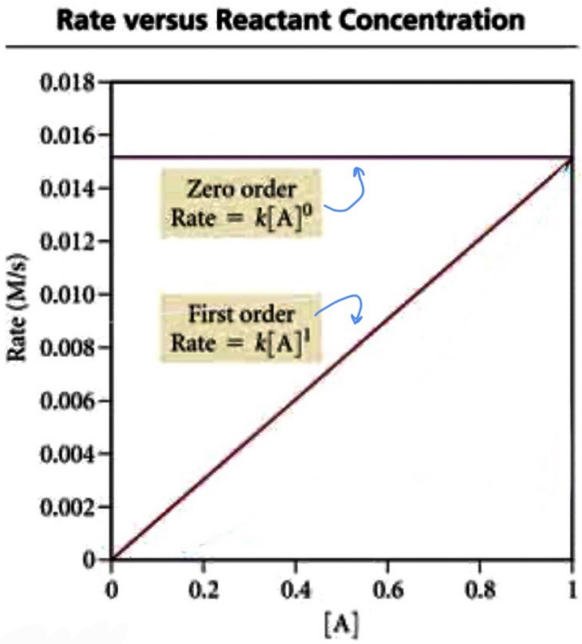
a.) $t_{1/2} \propto [R]_0$

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

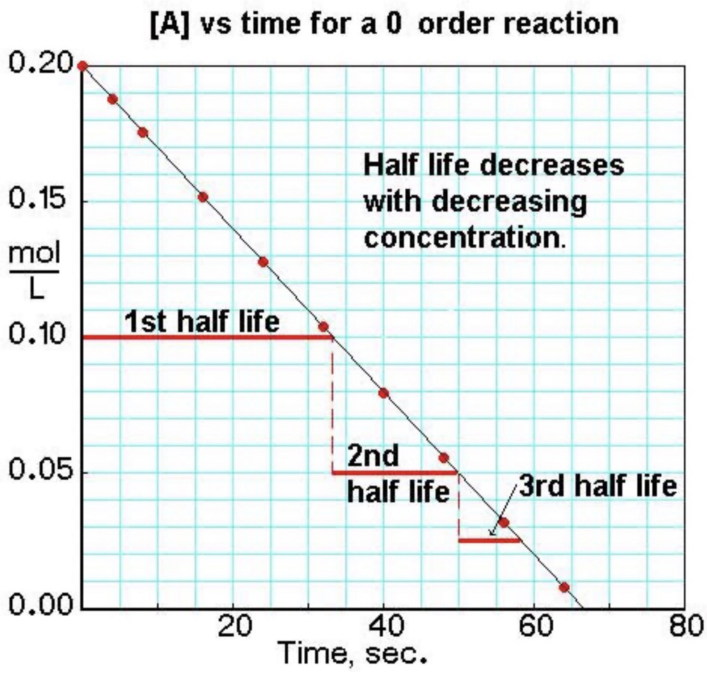
→ Half life ($t_{1/2}$) is independent of initial concentration. [Delhi 2017] (1M)

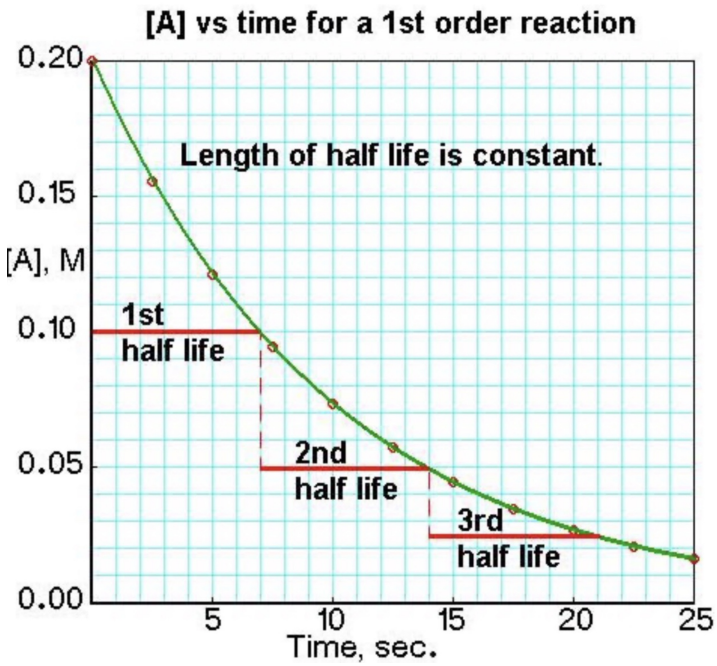
A → Products





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	$d[R]/dt = -k[R]$	$[R] = [R]_0e^{-kt}$ or $kt = \ln\{[R]_0/[R]\}$	ln[R] vs t	ln 2/k	time^{-1} or s^{-1}





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

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

$t_{1/2} = 1.26 \times 10^{14} s$ [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] 3M

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

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

→ 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)

(i) **Hydrolysis of ethyl acetate :-** $CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_2O \xrightarrow{H^+} CH_3-\overset{O}{\overset{\|}{C}}-OH + C_2H_5OH$

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

→ $[H_2O]_{t=0} \simeq [H_2O]_t$ means that concentration of H_2O does not change. So it can not change the rate. $[H_2O] = \text{Constant}$

→ Rate of reaction $= k'[H_2O][CH_3COOC_2H_5]$ $k'[H_2O] = \text{Constant} = k$

$\boxed{\text{Rate of reaction} = k[CH_3COOC_2H_5]}$ → It indicates 1st order kinetics.

(ii) **Hydrolysis of cane sugar :-** $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

Glucose Fructose

$\boxed{\text{Rate} = k[C_{12}H_{22}O_{11}]}$

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

Time (second)	0	10	20
$[CH_3-\overset{O}{\overset{\|}{C}}-OCH_3]$ [mol L^{-1}]	0.10	0.05	0.025

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

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

[CBSE 2015] (5M)

Answer -: (i) $[H_2O]$ = Constant (During reaction)

So, rate = k [Methyl acetate]

$$CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 \xrightarrow{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-OH$$

First order, then $k = \frac{2.303}{t} \log \frac{[CH_3-\overset{O}{\overset{\|}{C}}-OCH_3]_0}{[CH_3-\overset{O}{\overset{\|}{C}}-OCH_3]}$

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 $= -\frac{\Delta[CH_3-\overset{O}{\overset{\|}{C}}-OCH_3]}{\Delta t} = \frac{-[0.025 - 0.05]}{20-10} = 0.002$ mol $L^{-1} s^{-1}$

Important Previous Year Questions

(1) For a first order reaction $H_2O_2(aq) \longrightarrow H_2O(l) + O_2(g)$, rate constant $k = 1.06 \times 10^{-3}$ 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 mol/L, then $[H_2O_2]_t = \frac{100 - 15}{85}$ mol/L

$k = \frac{2.303}{t} \log \frac{[H_2O_2]_0}{[H_2O_2]} \Rightarrow t = \frac{2.303}{1.06 \times 10^{-3}} \log \frac{100}{85} = 153.3$ min.

(b) → How long time it will take for 85% of the sample to decompose?

→ Now; $[H_2O_2]_0 = 100$ mol/L $\quad [H_2O_2]_t = 100 - 85 = 15$ 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 mol $L^{-1} s^{-1}$. How long will it take for the initial concentration to fall from 0.10 M to 0.075 M?

[Delhi 2010]

(2M)

Answer –: For zero order reaction → $K = \frac{[R]_0 - [R]}{t}$

$[R]_0 = 0.10$ M

$[R] = 0.075$ M

$K = 0.0030$ mol $L^{-1} s^{-1}$

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

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

[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
$[N_2O_5]$ (mol/L s)	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

[Delhi 2017]

(3M)

Answer –: (i) For first order reaction $K = \frac{2.303}{t} \log \frac{[N_2O_5]_0}{[N_2O_5]}$

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

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

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

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

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

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

[4] → First order reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ at 40°c, data is given below — (3M) [Delhi 2011]

$[N_2O_5]$ (mol/L)	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

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

At time $t = 20$ min, $[N_2O_5] = 0.289\ \frac{mol}{L}$

& $[N_2O_5]_0 = 0.4\ \frac{mol}{L}$

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

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

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

$$K = \frac{2.303}{100} \log \frac{0.4}{[N_2O_5]} = 1.62 \times 10^{-2} \quad \text{then} \quad \log \frac{0.4}{[N_2O_5]} = \frac{1.62}{2.303} = 0.70$$

$$\rightarrow \frac{0.4}{[N_2O_5]} = \text{antilog } 0.705 = 5.07 \quad \text{then} \quad [N_2O_5] = \frac{0.4}{5.07} = 0.078\ \frac{mol}{L}$$

(iii) → Initial rate of reaction?

$$\text{Initial rate} = K[N_2O_5] = 0.4 \times 1.62 \times 10^{-2} = 6.4 \times 10^{-3}\ \frac{mol}{L\,min}$$

[5.] :- For a reaction $A + B \longrightarrow P$ the rate is given by $\boxed{\text{Rate} = K[A][B]^2}$ [CBSE 2015 | Delhi 2015] (2M)

(a) → How is the rate affected if [B] is doubled?

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

(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. $\text{Rate} = \underbrace{K[A]}_{\text{constant}}[B]^2 = K'[B]^2$

Then $\boxed{\text{order of reaction} = 2}$

Temperature dependence of the rate

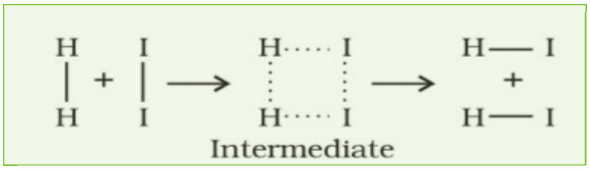
→ The rate of the reaction is dependent on temperature. This is expressed in terms of temperature coefficient. Rate of reaction increases with temperature

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

→ 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 state that products are formed through intermidiates or activated complex.



Formation of HI through the intermediate

$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$

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

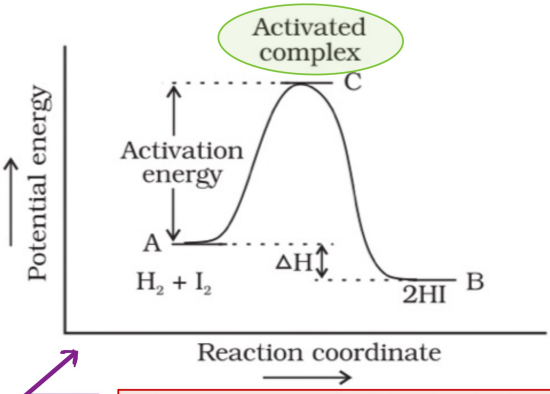


Diagram showing plot of potential energy vs reaction coordinate.

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

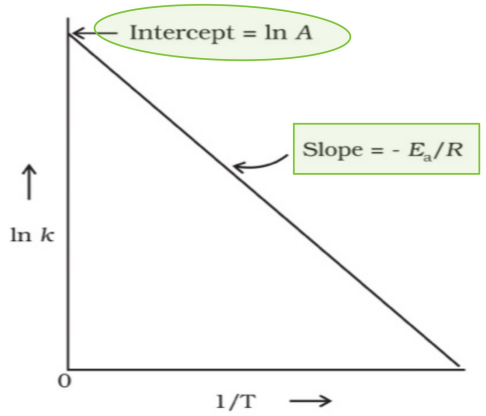
E_a –: Activation Energy

T –: Temperature

R –: Gas Constant

→ Taking log of both side of Arrhenius Equation :-

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



A plot between ln k and 1/T

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 $\quad \log K_1 = \log A - \frac{E_a}{2.303\,RT_1}$

→ At T_2 ⇒ rate constant K_2 $\quad \log K_2 = \log A - \frac{E_a}{2.303\,RT_2}$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 \cdot T_2}\right]$$

Question :- The rate of most reactions become double when their temperature is raised from 298 K to 308 K. Calculate their activation energy.
[Given, $R = 8.314\ J\ mol^{-1}\ K^{-1}$] [Delhi 2011C] (2M)

Answer :- $T_1 = 298\ K$, $T_2 = 308\ K$, $\frac{K_2}{K_1} = 2$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 \cdot T_2}\right] \Rightarrow \log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{308 - 298}{298 \times 308}\right]$$

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

Question :- The rate constant for the first order decomposition of H_2O_2 is given by the following equation $\log K = 14.2 - \frac{1 \times 10^4}{T}\ K$.
Calculate E_a for this reaction and rate constant K, if its half life period be 200 min. [Given $R = 8.314\ J\ K^{-1}\ mol^{-1}$]
[Delhi 2016] (3M)

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

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

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

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

Calculation of rate constant K :-

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

Question :- For a decomposition reaction, the values of K at two different temperatures are given below -: $K_1 = 2.15 \times 10^{-8} \text{ L/(mol.s)}$ at 650K

$K_2 = 2.39 \times 10^{-7} \text{ L/(mol.s)}$ at 700K

Calculate the value of Ea for the reaction.

[CBSE 2014C] (3M)

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

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 $T_2 = ?$ $\Rightarrow K_2 = 1.5 \times 10^4 \text{ s}^{-1}$

$$\rightarrow \log \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right] \Rightarrow \log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60}{2.303 \times 8.314} \left[\frac{T_2 - 283}{283 T_2} \right]$$

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

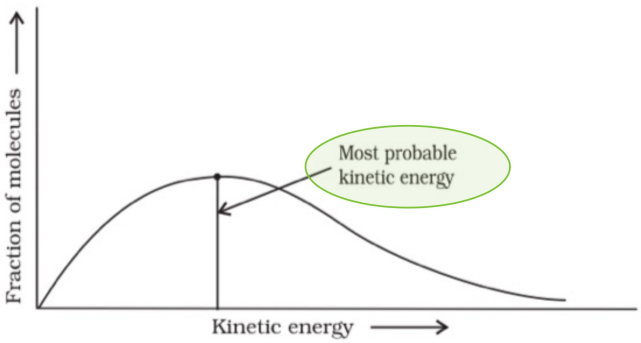
$$\Rightarrow 0.953 T_2 = 283 \quad \underline{T_2 = 297 \text{ K}}.$$

Maxwell Boltzmann Distribution Curve :-

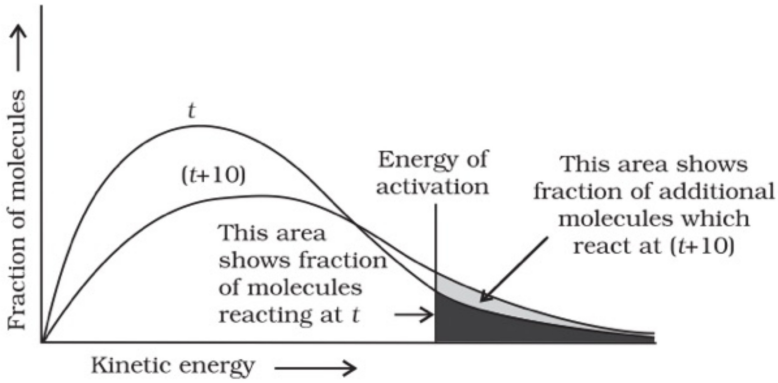
According to Maxwell and Boltzmann, the distribution of Kinetic Energy may be described by plotting the fraction of molecules with a given Kinetic energy.

→ 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



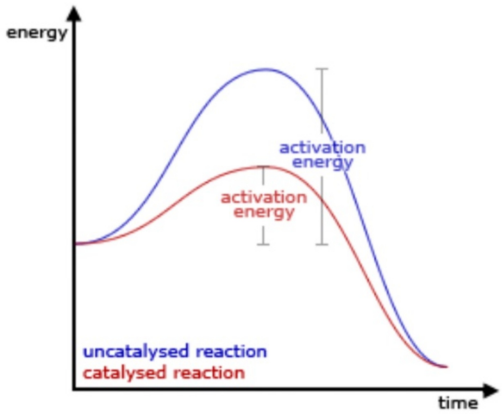
Distribution curve showing temperature dependence of rate of a reaction

→ 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 [ΔH], Gibbs energy of reaction [ΔG] and equillibrium constant [K] of a reaction.

(1M) [Delhi 2017]

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 biomolecular elementary reaction $A + B \longrightarrow$ Products

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

$\boxed{Z_{AB}}$: Collision frequency of reactants A and B.

$\boxed{e^{-E_a/RT}}$: 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.

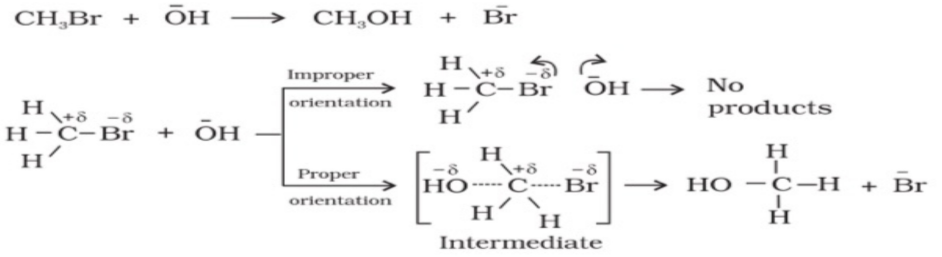


Diagram showing molecules having proper and improper orientation

→ 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.

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

→ 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.