"Self belief is the key to success"

7769940815
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RATE OF REACTANT OR PRODUCT

$$A(\text{reactant}) \longrightarrow B(\text{Product})$$

$$\text{Rate of reactant A} = -\frac{\Delta[A]}{\Delta t}$$

☑ [-] Sign explain that as time spend rate of reactant decreases.

$$\text{Rate of product B} = +\frac{\Delta[B]}{\Delta t}$$

☑ [+] Sign explain that as time spend rate of product increases.

Where, ☑ ΔC = change in concentration in a small interval Δt

RATE OF REACTION

$$nA \longrightarrow \text{product}$$

$$\text{Rate of reaction (r)} = \frac{\text{Change in concentration of reactant or product}}{\text{stoichiometric coefficeint} \times \text{time taken}} = -\frac{1}{n}\frac{\Delta[A]}{\Delta t}$$

Stoichiometric coefficient

NOTE

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

GRAPHICAL REPRESENTATION

Let, a chemical reaction

$$A \longrightarrow B$$

For reactant

$$r_{avg} = -\frac{\Delta[A]}{\Delta t} = \frac{-(A_2 - A_1)}{(t_2 - t_1)}$$

$$r_{inst} = \frac{-d[A]}{dt} = \text{-Slope} = \text{-tan}\theta$$

NOTE

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

GRAPHICAL REPRESENTATION

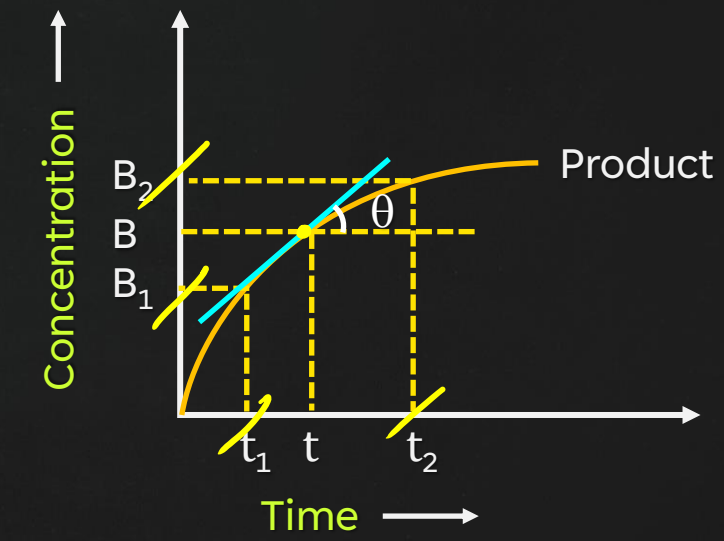
Let, a chemical reaction

$$A \longrightarrow B$$

For product

$$r_{avg} = +\frac{\Delta[B]}{\Delta t} = \frac{(B_2 - B_1)}{(t_2 - t_1)}$$

$$r_{inst} = \frac{d[B]}{dt} = \text{Slope} = \tan\theta$$



NOTE

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

STOICHIOMETRIC RELATION OF RATE

For a general reaction

$$aA + bB \longrightarrow cC + dD$$

$$r_{avg} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

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

r_{inst} / r_{avg} → Rate of reaction

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IMPORTANT POINTS

$-\frac{1}{a}\frac{\Delta[A]}{\Delta t}$ rate of reaction

$-\frac{1}{b}\frac{\Delta[B]}{\Delta t}$ rate of reaction

$-\frac{\Delta[A]}{\Delta t}$ rate of disappearance or consumption of A

$\frac{\Delta[D]}{\Delta t}$ rate of appearance or formation of D

FACTORS AFFECTING RATE OF CHEMICAL REACTION

1. Concentration

2.Temperature

3. Effect of nature of reactants and products

(A) Physical state of reactants

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

(B) Physical size of reactants

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

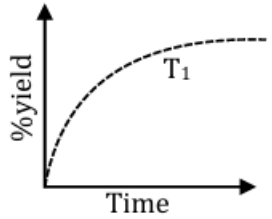
(C) Chemical nature of reactants

Example

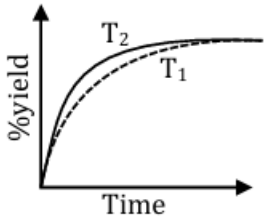
The % yield of ammonia as a function of time in the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H < 0$

at (P, T_1) is given below -



If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by - [JEE-2015]

(A)


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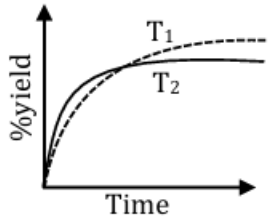

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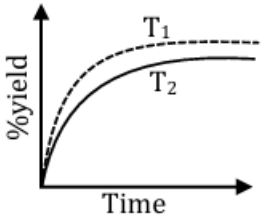
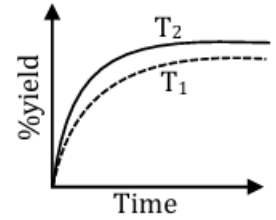


(D)


Solution

Ans. (B)

FACTORS AFFECTING RATE OF CHEMICAL REACTION

4. Catalyst

5. Effect of pressure

RATE LAW

Rate Law is experimentally determined mathematical expression which gives relation between rate of reaction & concentration of reactants

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

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

Where

k = rate constant/velocity constant/specific rate of reaction

$x + y$ = Order or over all order of reaction (n)

x = Order of reaction with respect to A

y = Order of reaction with respect to B

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UNITS OF RATE CONSTANT(k)

Let, a chemical reaction

$A \longrightarrow$ Product

$r = k[A]^n$

$$k = \frac{r}{[A]^n} = \frac{\text{unit of rate}}{[\text{unit of concentration}]^n} = \frac{\left(\frac{\text{mol}}{L}\right) \times (\text{time})^{-1}}{\left(\frac{\text{mol}}{L}\right)^n}$$

$$\text{Unit of } k = \left(\frac{\text{mol}}{L}\right)^{1-n} \times (\text{time})^{-1}$$

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

NOTE For gaseous reaction unit of k may be = $(\text{atm})^{1-n} \times \text{time}^{-1}$

ORDER AND MOLECULARITY OF REACTION

ORDER OF REACTION

The sum of powers of concentration terms present in rate law expression is known as order of reaction.

For a reaction : $aA + bB + cC \longrightarrow$ product.

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

Here,

Order or over all order of reaction(n) = $x + y + z$

Order of reaction with respect to A = x

Order of reaction with respect to B = y

Order of reaction with respect to C = z

MOLECULARITY OF REACTION

- It is defined only for the elementary reactions.
- For elementary reaction, it is defined as minimum no. of molecules, ions or atoms required for a reaction to occur.
- For an elementary reaction, molecularity & order of reaction are equal. It means fractional order or zero order reactions are always complex in nature.
- Probability that more than 3 molecules collide at a point simultaneously is extremely low. Hence molecularity more than 3 has not be observed.

Example

For the elementary reaction M → N, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is

(A) 4 (B) 3 (C) 2 (D) 1 [JEE- 2014]

Solution

$$\text{Rate} = k[m]^n$$

$$\frac{8R}{R} = \frac{k[2m]^n}{k[m]}$$

$$n = 3$$

Ans. (B)

Zero order kinetics

ZERO ORDER REACTION

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

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

$$\int_{[A]_0}^{[A]} d[A] = \int_0^t K dt$$

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

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

NOTE : Unit of k is same as that of Rate = mol lit^{-1} sec^{-1}

ZERO ORDER REACTION

Half Life ($t_{1/2}$) or ($t_{50\%}$) of reaction

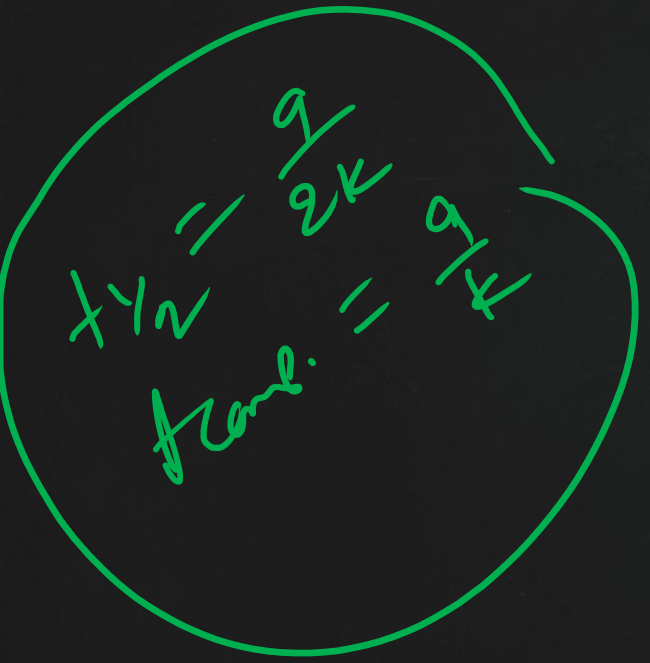
For Zero order reaction

$x = k\,t$ At $t_{1/2}$, $x = \frac{a}{2}$

$$\frac{a}{2} = k\,t_{1/2}$$

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

$t_{1/2} \propto$ initial concentration



ZERO ORDER REACTION

Completion of reaction (t_{comp})

$x = k\,t$ At $t_{comp.}$ $x = a$

$a = k\,t_{comp}$

$$t_{comp} = \frac{a}{k}$$

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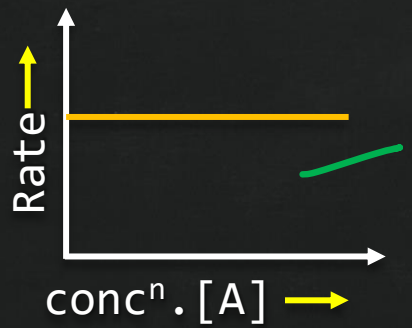
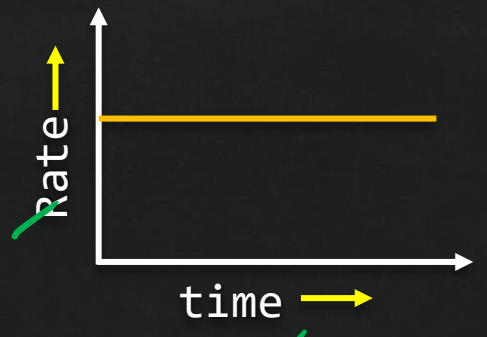
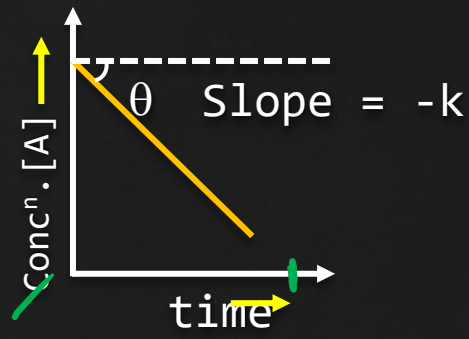
ZERO ORDER REACTION

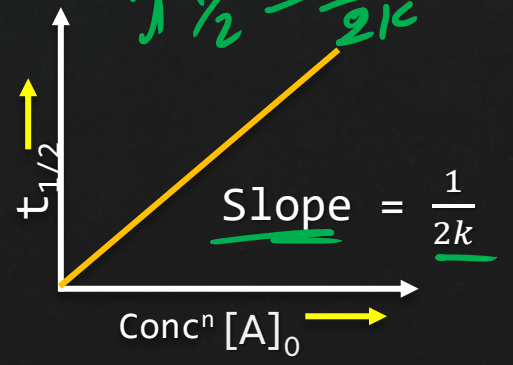
Graph

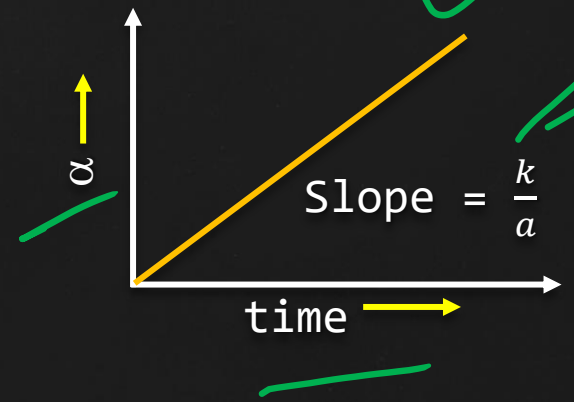






$t_{1/2} = \frac{a}{2k}$





First Order kinetics

x → reacted part of reactant

FIRST ORDER REACTION

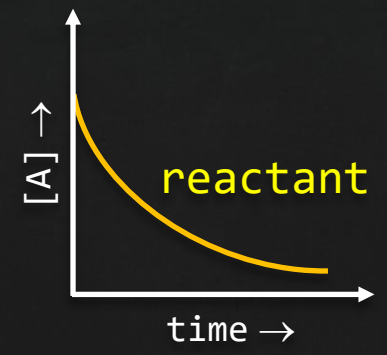
$$\text{rate} = \frac{-d[A]}{dt} = k[A]^1$$

(i) $$ln\frac{[A]_0}{[A]} = kt$$

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

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

Graph

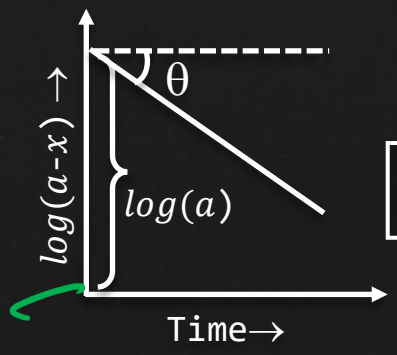


(ii) $$K = \frac{2.303}{t} log\left(\frac{a}{a-x}\right)$$

$$\log(a - x) = \log(a) - \frac{kt}{2.303}$$

[a-x] = [A]

Graph



$$\text{Slope} = \tan\theta = -\frac{k}{2.303}$$

FIRST ORDER REACTION

Half Life ($t_{1/2}$) of reaction

It is the time in which amount of reactant becomes half of initial amount.

For first order reaction

At $t_{1/2}$, $x = \frac{a}{2}$

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

For first order $t_{1/2}$ is independent of concentration of reactant

Completion of reaction (t_{comp})

At $t_{comp.}$ $x = a$

$$k = \frac{1}{t_{comp}} ln\left(\frac{a}{a-a}\right)$$

$$t_{comp} = \infty$$

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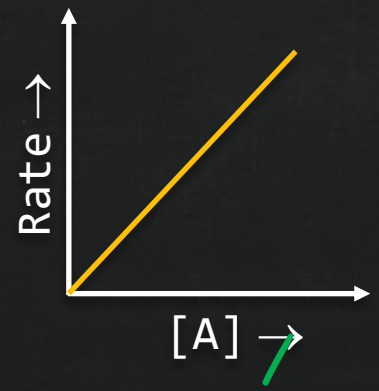
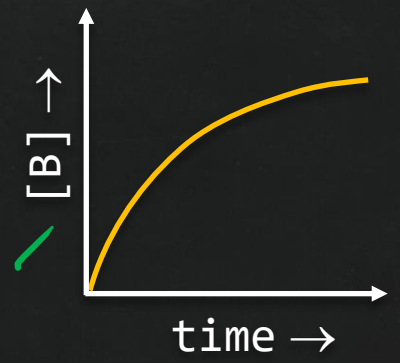
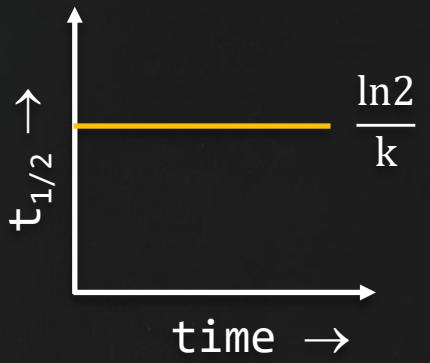
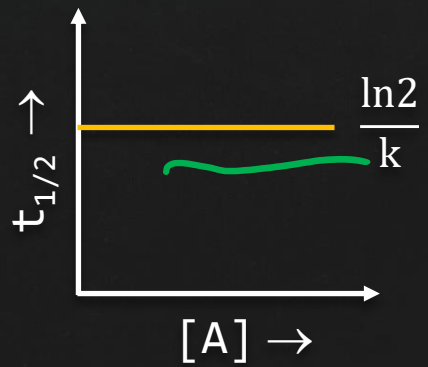
FIRST ORDER REACTION

Graphs related to 1st orders :-









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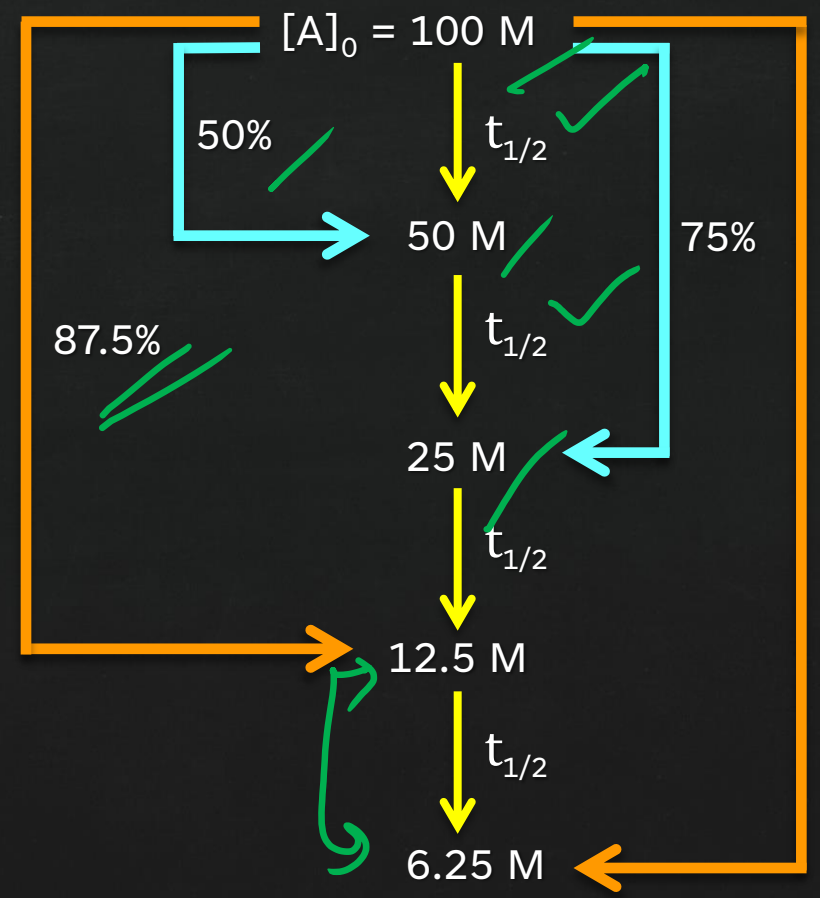
SHORT CONCLUSION FOR 1ST ORDER REACTION



% completion time

$t_{75\%} = 2 \times t_{1/2}$

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

$t_{93.75\%} = 4 \times t_{1/2}$

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

FIRST ORDER REACTION

NOTE

$$n = \frac{total\ time}{t_{1/2}}$$

Where n = Number of half-life

After n half-life

$$\text{Amount of A left unreacted} = \frac{a}{2^n}$$

$$\text{Fraction of A left unreacted} = \frac{1}{2^n}$$

$$\text{Amount of A reacted} = \left(a - \frac{a}{2^n}\right)$$

$$\text{Fraction of A reacted} = \left(1 - \frac{1}{2^n}\right)$$

FIRST ORDER REACTION

Special Case :

If initial concentration of reactant is not given but concentration at time $t = t_1$ and time $t = t_2$ are given as A_1 and A_2 respectively. Then rate constant of first order reaction.

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

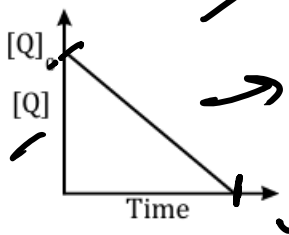
$t = t_1$	A_1
$t = t_2$	A_2

$$k = \frac{1}{t_2 - t_1} \ln \frac{A_1}{A_2}$$

Example

In the reaction :

$P + Q \longrightarrow R + S$



the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is - [JEE-2013]

(A) 2 (B) 3 (C) 0 (D) 1

Solution

Ans. (D)

$$t = \frac{1}{k} \ln\left(\frac{A_0}{A_t}\right)$$

Example

An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{t_{1/10}} \times 10$? (take $\log_{10} 2 = 0.3$)

[JEE- 2012]

Solution

$$\frac{t_{1/8}}{t_{1/10}} \times 10 = \frac{\frac{1}{k} \ln\left(\frac{A_0}{A_0/8}\right)}{\frac{1}{k} \ln\left(\frac{A_0}{A_0/10}\right)} \times 10$$

$$= \frac{\ln(8)}{\ln 10} \times 10 = \frac{3 \times 0.3}{1} \times 10$$

(9)

Ans. (9)

Example

[JEE- 2011]

For the first order reaction.

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

(A) the concentration of the reactant decreases exponentially with time

(B) the half-life of the reaction decreases with increasing temperature.

(C) the half-life of the reaction depends on the initial concentration of the reactant.

(D) the reaction proceeds to 99.6% completion in eight half-life duration.

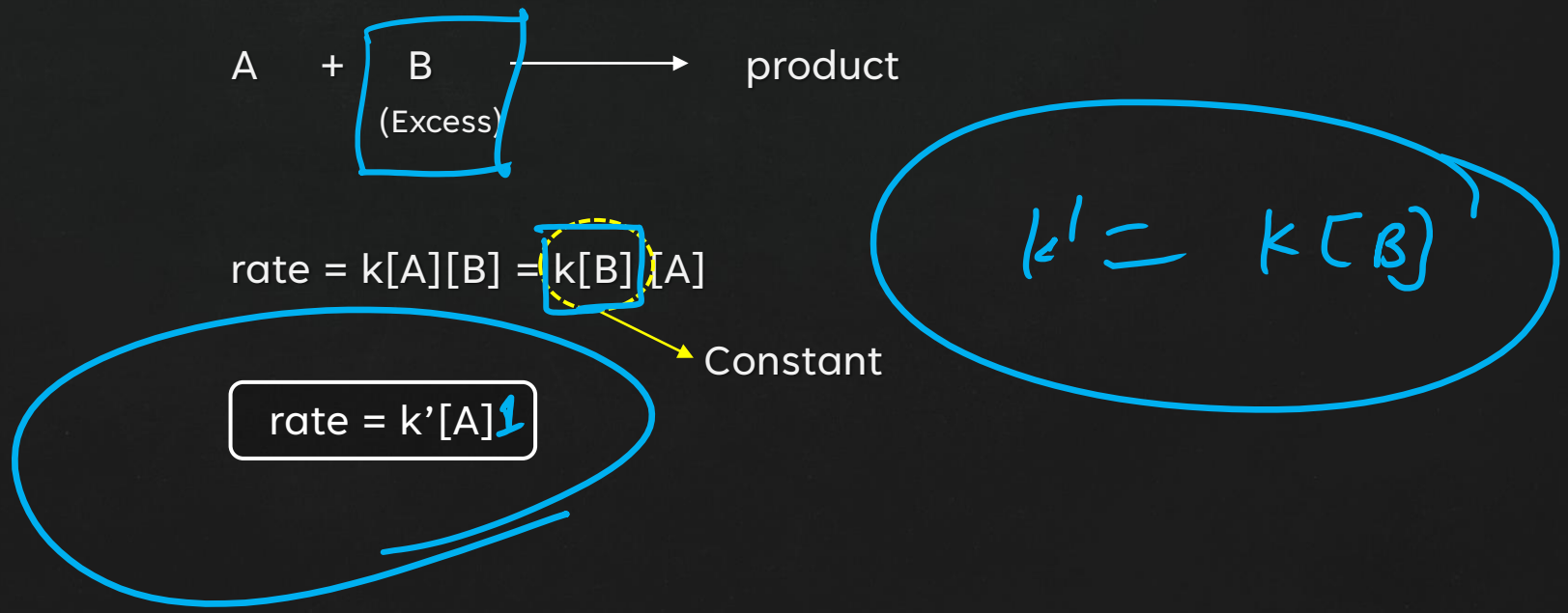
Solution

Ans. (A,B,D)

Pseudo first order reaction

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 excess. Such second order (or of higher order) reactions are known as pseudo first order reactions.



Second Order Reaction

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$\frac{1}{[A]_t} - \frac{1}{[A_0]} = kt$

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

SECOND ORDER REACTIONS

Kinetics of Second order (when concentration of both the reactant are equal) :

For a second-order reaction :

	A	+	B	⟶	Products
t = 0	a		a		0
t = t	a-x		a-x		x

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

$$\frac{-d(a-x)}{dt} = k[A]\,[B]$$

$\frac{dx}{dt} = k[A]\,[B]$, $\frac{dx}{dt} = k(a-x)\,(a-x)$

$$\int_0^x \frac{dx}{(a-x)^2} = \int_0^t k\,dt$$

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

NOTE

Unit of k = mol^{-1} lit sec^{-1}

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order $\begin{cases} 0 \rightarrow & t_{1/2} \propto a \\ 1 \rightarrow & t_{1/2} \propto a^0 \\ 2 \rightarrow & t_{1/2} \propto \frac{1}{a} \end{cases}$

$t_{1/2} = \frac{1}{ka}$

SECOND ORDER REACTIONS

Half Life ($t_{1/2}$) of reaction

It is the time in which amount of reactant becomes half of initial amount.

For Second order reaction

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

At $t_{1/2}$, $x = \frac{a}{2}$

$$\frac{1}{\left(a-\frac{a}{2}\right)} - \frac{1}{a} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{ka}$$

$$t_{1/2} \propto \frac{1}{(initial\ concentration)}$$

Completion of reaction (t_{comp})

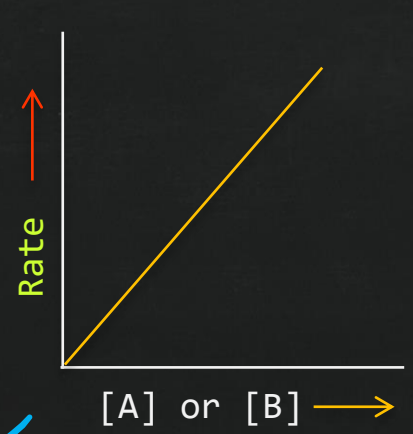
At $t_{comp.}$ $x = a$

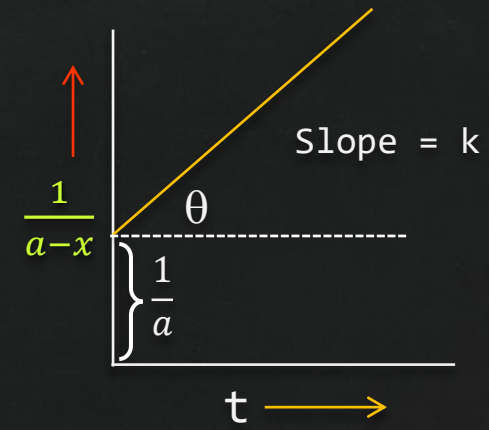
$$\frac{1}{(a-a)} - \frac{1}{a} = kt_{comp.}$$

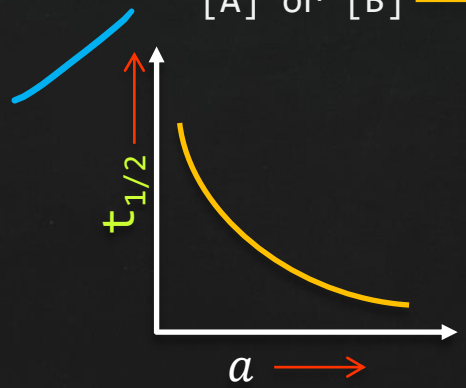
$$t_{comp.} = \infty$$

SECOND ORDER REACTIONS

Graphs







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SECOND ORDER REACTIONS

Kinetics of Second order (when concentration of both the reactant are different) :

For a second-order reaction :

	A	+	B	⟶	Products
t = 0	a		b		0
t = t	a-x		b-x		x

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

$$\frac{-d(a-x)}{dt} = k[A]\,[B]$$

$\frac{dx}{dt} = k[A]\,[B]$, $\frac{dx}{dt} = k(a-x)\,(b-x)$

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

$$k = \frac{1}{t\,(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

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

NOTE : Unit of k = mol^{-1} lit sec^{-1}

n^{th} order kinetics

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N^{TH} ORDER REACTION

Kinetics of nth order reaction

$$A \longrightarrow B$$

t = 0	$a = [A]_0$	0
t = t	$a - x = [A]$	x

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

$$\frac{-d(a-x)}{dt} = k[A]^n$$

$$\frac{dx}{dt} = k[A]^n$$

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

$$\int_0^x \frac{dx}{(a-x)^n} = \int_0^t k\,dt$$

$$\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} = (n-1)\,kt \qquad n \neq 1$$

$$\frac{1}{[A_t]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)\,kt$$

NOTE : Unit of k = $mol^{(1-n)}\ lit^{(n-1)}\ sec^{-1}$

N^{TH} ORDER REACTION

$t_{1/2} \propto \frac{1}{a^{n-1}}$

Half Life ($t_{1/2}$) of reaction

It is the time in which amount of reactant becomes half of initial amount.

For n^{th} order reaction

$$\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} = (n-1)\,kt$$

At $t_{1/2}$, $x = \frac{a}{2}$

$$\frac{1}{\left(a-\frac{a}{2}\right)^{n-1}} - \frac{1}{a^{n-1}} = (n-1)\,kt_{1/2}$$

$$t_{1/2} = \frac{(2^{n-1}-1)}{(n-1)\,K\,a^{n-1}}$$

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

Example

Consider the kinetic data given in the following table for the reaction A + B + C → Product. [JEE- 2019]

Experiment No.	[A] (mol dm^{-3})	[B] (mol dm^{-3})	[C] (mol dm^{-3})	Rate of reaction (mol dm^{-3} s^{-1})
1	0.2	0.1	0.1	6.0×10^{-5}
2	0.2	0.2	0.1	6.0×10^{-5}
3	0.2	0.1	0.2	1.2×10^{-4}
4	0.3	0.1	0.1	9.0×10^{-5}

The rate of the reaction for [A] = 0.15 mol dm^{-3}, [B] = 0.25 mol dm^{-3} and [C] = 0.15 mol dm^{-3} is found to be $Y \times 10^{-5}$ mol dm^{-3} s^{-1}.

The value of Y is –––––.

Solution

Solution

Consider the kinetic data given in the following table for the reaction A + B + C → Product. [JEE- 2019]

Experiment No.	[A] (mol dm^{-3})	[B] (mol dm^{-3})	[C] (mol dm^{-3})	Rate of reaction (mol dm^{-3} s^{-1})
1	0.2	0.1	0.1	6.0×10^{-5}
2	0.2	0.2	0.1	6.0×10^{-5}
3	0.2	0.1	0.2	1.2×10^{-4}
4	0.3	0.1	0.1	9.0×10^{-5}

The rate of the reaction for [A] = 0.15 mol dm^{-3}, [B] = 0.25 mol dm^{-3} and [C] = 0.15 mol dm^{-3} is found to be Y × 10^{-5} mol dm^{-3} s^{-1}. The value of Y is -----.

Ans. (6.75)

ALLEN

Rate constant (k) for 1st order reaction in different parameters

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RATE CONSTANT (κ) IN TERMS OF PRESSURE FOR GASEOUS REACTANTS

	A (g) ⟶	B (g)
t = 0	a = $[A]_0$	0
t = t	(a–x) = [A]	x

$\because p = [conc^n]RT$

Concentration $\propto p$

$\therefore [A]0 \propto p^0$

$[A] \propto p^t$

	A (g) ⟶	B (g)
t = 0	P^0	0
t = t	$P^0 - x = p^t$	x

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

$$k = \frac{2.303}{t}\log\frac{p^0}{p^t}$$

$$k = \frac{2.303}{t}\log\left(\frac{p^0}{p^0 - x}\right)$$

ALLEN

RATE CONSTANT (k) FOR DECOMPOSITION OF (H_2O_2) IN TERMS OF VOLUME OF $KMnO_4$

$$H_2O_2 \text{ (aq.)} \longrightarrow H_2O\ (\ell) + \frac{1}{2}O_2(g)$$

t = 0	$[A]_0$
t = t	$[A]$

Equal volume of H_2O_2 solution was taken out at different time & titrated with known concentration of acidic $KMnO_4$

$$H_2O_2 + MnO_4^- \xrightarrow{H^+} O_2 + Mn^{+2}$$

At eq. point, $N_{H_2O_2} V_{H_2O_2} = N_{MnO_4^-} V_{MnO_4^-}$

$$\frac{N_{H_2O_2} \propto V_{KMnO_4}}{M_{H_2O_2} \propto V_{KMnO_4}}$$

Let;

V_0 = volume of $KMnO_4$ at t=0

V_t = volume of $KMnO_4$ at t=t

$$\left.\begin{matrix}[A]_0 \propto V_0 \\ [A] \propto V_t\end{matrix}\right\} \frac{[A]_0}{[A]} = \frac{V_0}{V_t}$$

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

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

ALLEN

RATE CONSTANT (K) FOR ACID CATALYSED HYDROLYSIS OF ESTER IN TERMS OF VOLUME OF NaOH

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+(\text{catalyst})} CH_3COOH + C_2H_5OH$$

	$CH_3COOC_2H_5$	H_2O	CH_3COOH	C_2H_5OH
t=0	a	Excess	0	0
t=t	$a-x$	-	x	x
t=∞	0	-	a	a

☑ Three experiments are done in which solution is titrated with known concentration of NaOH.

☑ NaOH react with acid present in solution.

V_0 = volume of NaOH at t=0

V_t = volume of NaOH at t=t

V_∞ = volume of NaOH at t=∞

$$V_0 \propto [H^+]_{catalyst}$$

$$V_t \propto \{[H^+]_{catalyst} + x\}$$

$$V_\infty \propto \{[H^+]_{catalyst} + a\}$$

$$\frac{a}{a-x} = \frac{V_\infty - V_0}{V_\infty - V_t}$$

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

RATE CONSTANT (K) IN TERMS OF ANGLE OF ROTATION

Acid catalysed hydrolysis of sugar(sucrose)

$$C_{12}H_{22}O_{11}(\text{sucrose}) + \underset{\text{Excess}}{H_2O} \longrightarrow C_6H_{12}O_6(\text{Glucose}) + C_6H_{12}O_6(\text{Fructose})$$

- ☑ Sucrose & Glucose are dextrorotatory
- ☑ Fructose is laevorotatory.
- ☑ Initially (Sucrose) was present, hence solution was dextrorotatory.
- ☑ When reaction is completed then (Glucose) & (Fructose) are left. In this solution laevorotation of (Fructose) is more than dextrorotation of (Glucose) hence Final solution is laevorotatory. This called inversion of cane sugar.

RATE CONSTANT (K) IN TERMS OF ANGLE OF ROTATION

Acid catalysed hydrolysis of sugar(sucrose)

Polarimeter

- r = angle of rotation
- $r \propto \ell \times$ (concentration)
- For a polarimeter, ℓ = constant
- $r \propto$ (concentration)
- r = k(concentration)
- Here, k = specific rotation in degree/molar

$\theta \rightarrow$ angle of rotation

$t=0 \rightarrow$ sucrose (K_1)

$\theta_0 = K_1 \times a$

$\theta_t = K_1(a-x) + K_2 x - K_3 x$

$= K_1(a-x) + x(K_2 - K_3)$

$\theta_\infty = K_2 \cdot a - K_3 \cdot a = a(K_2 - K_3)$

$\theta_\infty - \theta_0 = K_2 a - K_3 a - K_1 a$

$= a(K_2 - K_3 - K_1)$

$\theta_\infty - \theta_t = a(K_2 - K_3) - K_1(a-x) - x(K_2 - K_3)$

$= (K_2 - K_3)(a-x) - K_1(a-x)$

$\theta_\infty - \theta_t = (a-x)[K_2 - K_3 - K_1]$

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$\frac{\theta_\infty - \theta_0}{\theta_\infty - \theta_t} = \frac{a(k_2 - k_3 - k_1)}{(a-x)(k_2 - k_3 - k_1)}$

$\frac{a}{a-x} \quad \frac{V_\infty - V_0}{V_\infty - V_t} \quad \frac{\theta_\infty - \theta_0}{\theta_\infty - \theta_t} \quad \frac{V_0}{V_t}$

$\frac{\theta_\infty - \theta_0}{\theta_\infty - \theta_t} = \frac{a}{a-x}$

RATE CONSTANT (K) IN TERMS OF ANGLE OF ROTATION

Acid catalysed hydrolysis of sugar(sucrose)

$$C_{12}H_{22}O_{11}(\text{sucrose}) + H_2O \longrightarrow C_6H_{12}O_6(\text{Glucose}) + C_6H_{12}O_6(\text{Fructose})$$

t=0	a	Excess	0	0
t=t	a–x	-	x	x
t=∞	0	-	a	a

Let, k_1, k_2 & k_3 are specific rotation of Sucrose, Glucose & Fructose respectively (in degree/molar)

r_o = angle of rotation at t = o
r_t = angle of rotation at t = t
r_∞ = angle of rotation at t = ∞

$r_o = k_1 a$ ..... eqⁿ (i)

$r_t = k_1(a - x) + k_2 x + k_3 x$ ..... eqⁿ (ii)

$r_\infty = k_2 a + k_3 a \longrightarrow$ eqⁿ (iii)

$$\frac{r_\infty - r_o}{r_\infty - r_t} = \frac{(k_2 + k_3 - k_1)}{(k_2 + k_3 - k_1)} \frac{a}{(a-x)}$$

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

RATE OF REACTION FOR REVERSIBLE REACTION

Let reversible reaction :

$$m_1A + m_2B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} n_1C + n_2D$$

$$rate = r_f - r_b$$

r_f = rate of forward reaction = $k_f[A]^{m_1}[B]^{m_2}$

r_b = rate of backward reaction = $k_b[C]^{n_1}[D]^{n_2}$

$$rate = k_f[A]^{m_1}[B]^{m_2} - k_b[C]^{n_1}[D]^{n_2}$$

$r_{dis,A} = (rate \times m_1)$

$r_{app,D} = (rate \times n_2)$

TEMPERATURE CO-EFFICIENT (η)

Ratio of rate constant at two different temperature differ by 10°C or 10K is called temperature co-efficient.

$$\eta = \frac{k_{t+10}}{k_t} = 2 \text{ or } 3 \quad \text{(for most of the reactions)}$$

$$\frac{k_2}{k_1} = (\eta)^{\frac{\Delta T}{10}}$$

Example

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

$$\frac{k_{40}}{k_{25}} = (2)^{15/10}$$

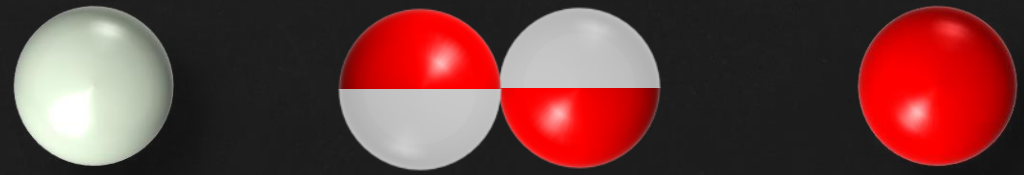
$$= 2^{3/2} = \sqrt{8}$$

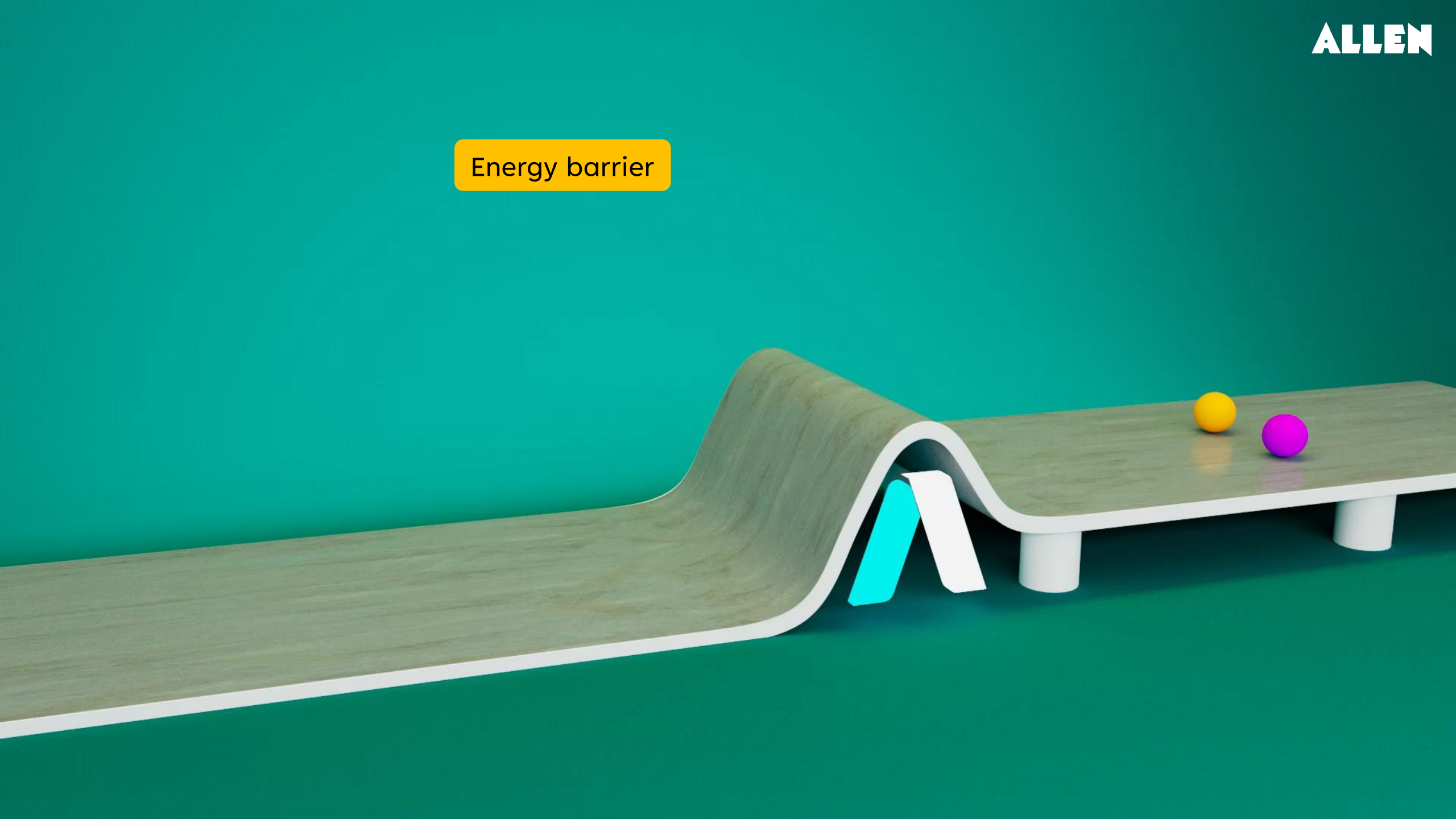
Ans. $\sqrt{8}$

COLLISION THEORY OF REACTION RATE

Ineffective collision

Effective collision




Energy barrier

COLLISION THEORY OF REACTION RATE

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.

Passive molecules ⇌ Active molecules, ΔH = +ve

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

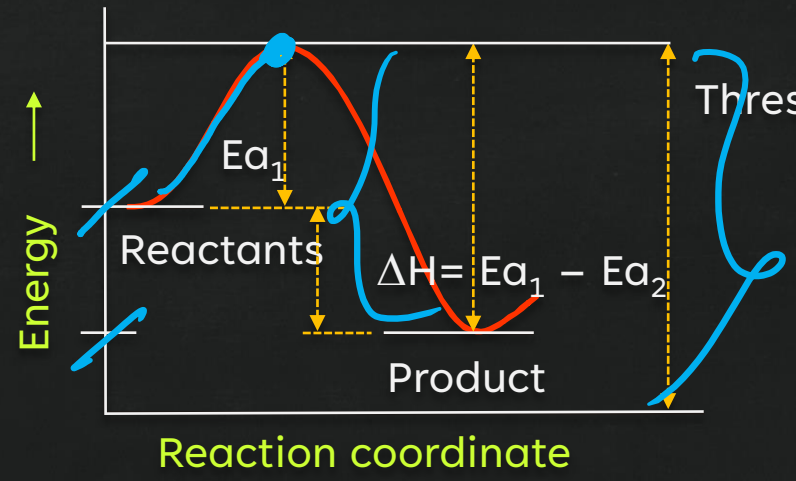
CONCEPT OF ENERGY OF ACTIVATION (E_a)

E_a = Threshold energy – Actual average energy of reactants

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

$\Delta H = Ea_1 - Ea_2$

CONCEPT OF ENERGY OF ACTIVATION (E_a)



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

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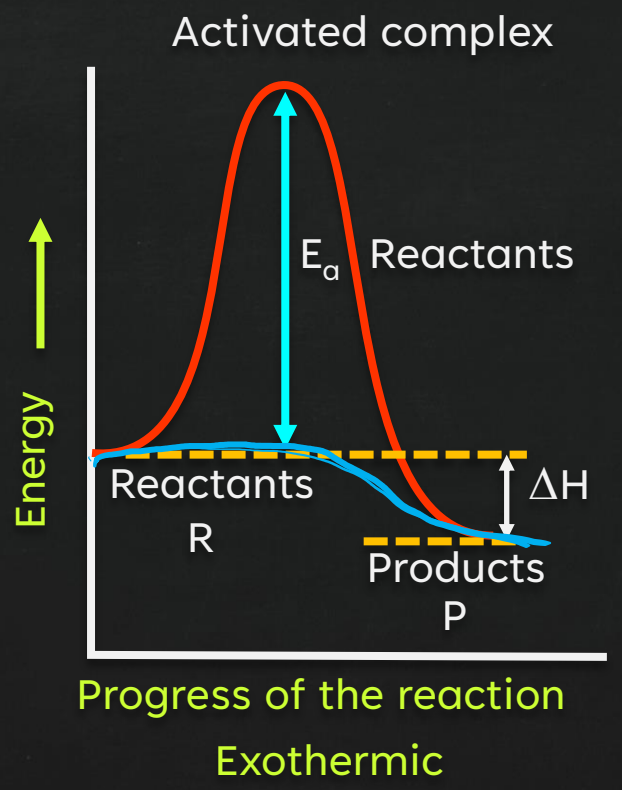
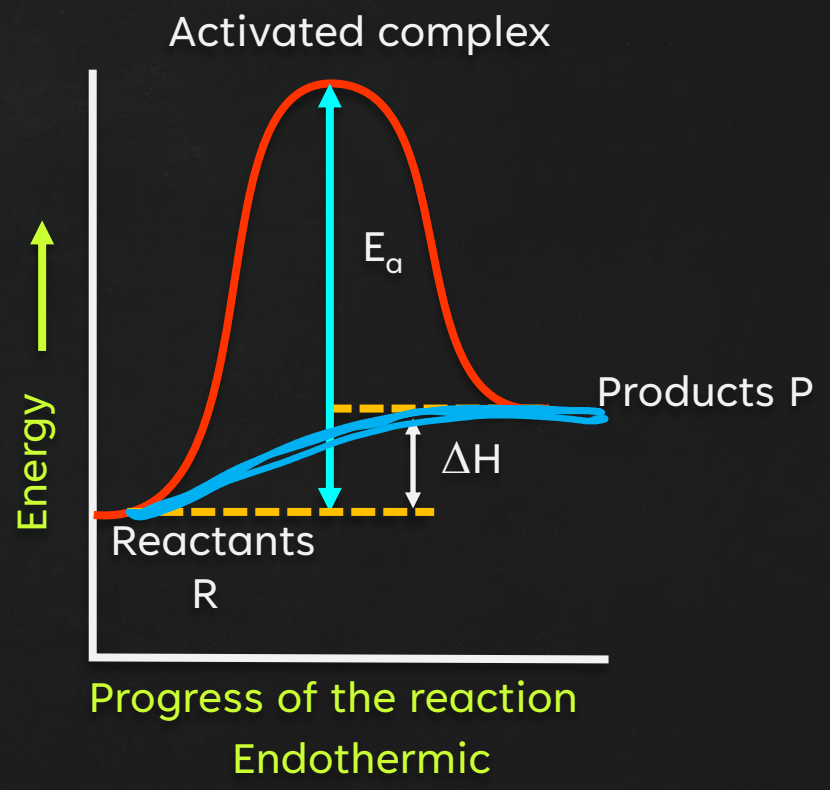
ΔH = +ve → endo → $(E_a)_{min} = \Delta H_r$

ΔH = -ve → exo

$E_{a\,min} = 0$

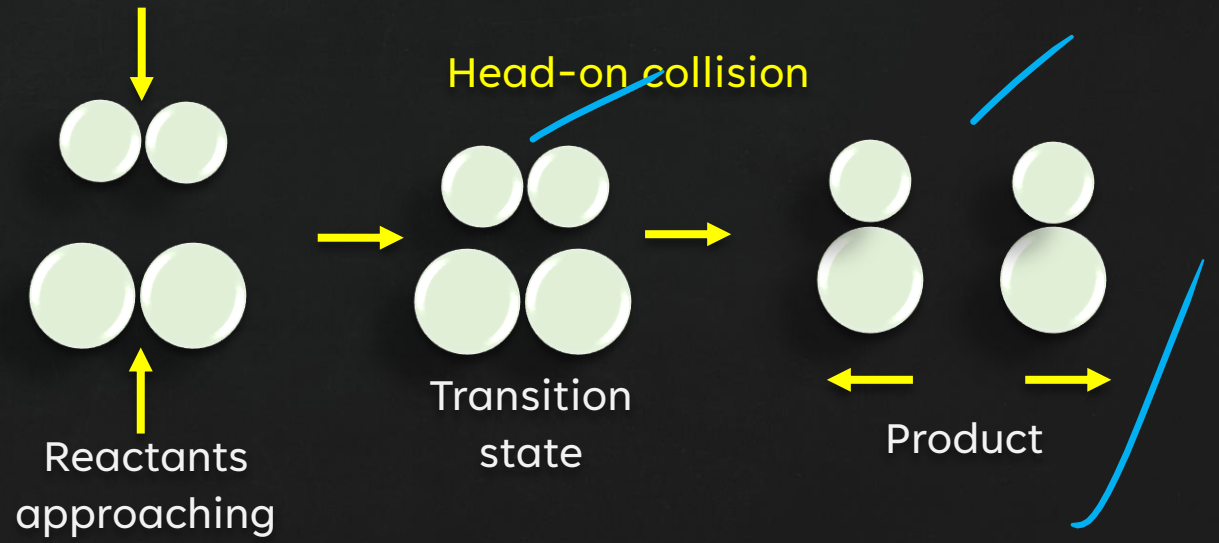
CONCEPT OF ENERGY OF ACTIVATION (E_a)



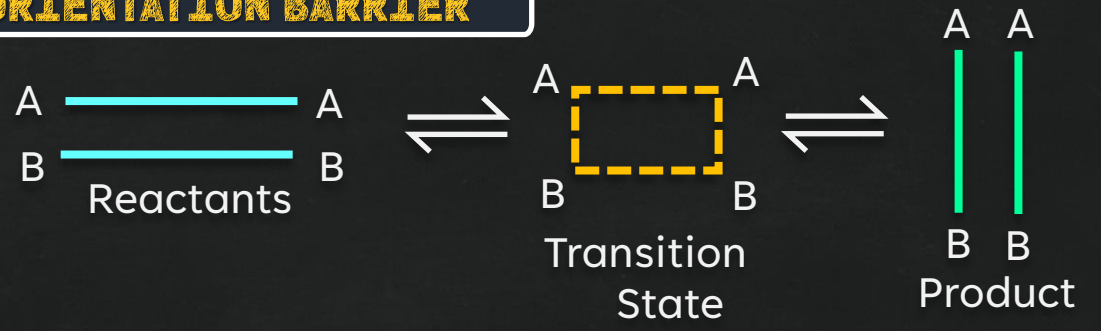


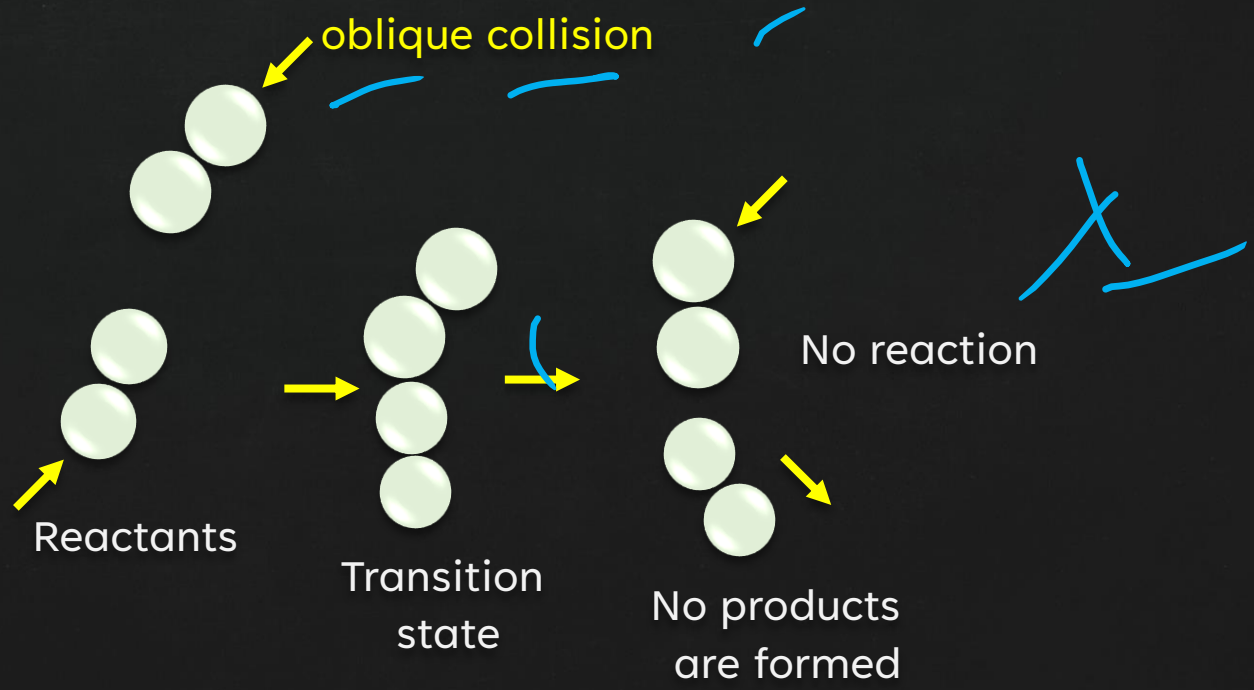
ORIENTATION BARRIER

Following diagrams can explain importance of suitable direction for collision. Consider reaction : $A_2 + B_2 \rightarrow 2AB$



ORIENTATION BARRIER





steric factor (P) = $\frac{A_{actual}}{A_{theoretical}}$ ⇒ Ea remains same

ORIENTATION BARRIER

- $e^{-E_a/RT}$ Represents fraction of molecules having K.E. greater than or equal to E_a.

$$\text{Rate} \propto e^{-E_a/RT}$$

- Dependence of rate on temperature is due to dependence of k on temperature.

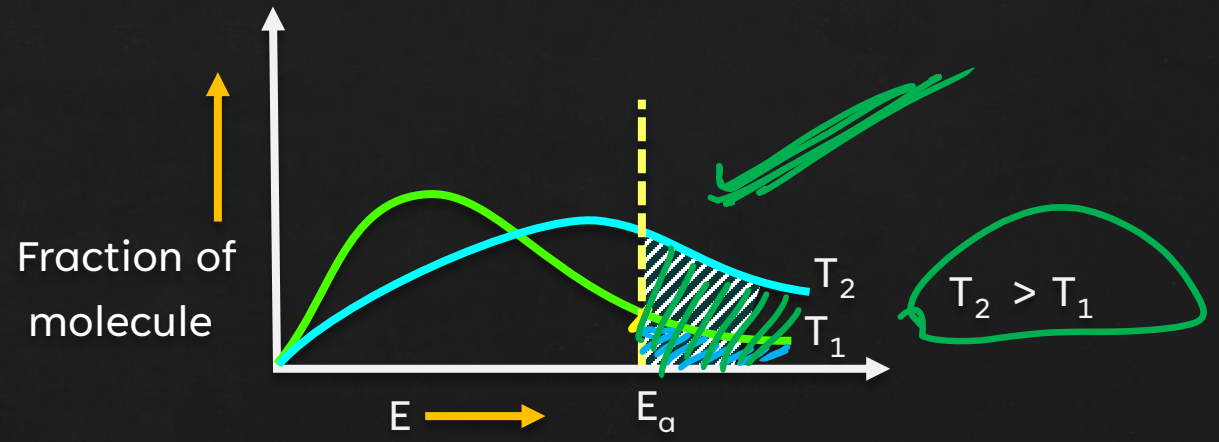
theoretical $k \propto e^{-E_a/RT}$

$$k = Ae^{-E_a/RT}$$ [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.

ORIENTATION BARRIER

From Maxwellian distribution, it is found that fraction of molecules having excess energy greater than threshold energy lead to the formation of product.



CALCULATION OF ACTIVATION ENERGY BY ARRHENIUS EQUATION

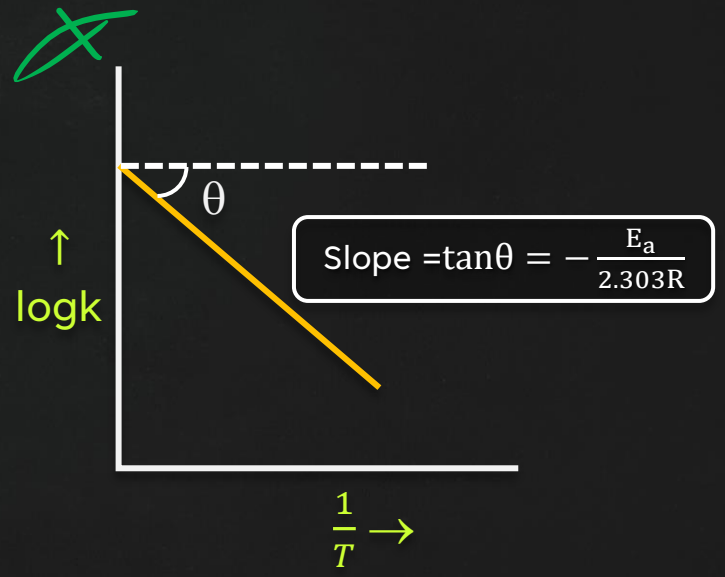
$$k = Ae^{-E_a/RT}$$

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

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

As $T \to \infty$, $k \to A$

Unit of k = Unit of A



If $E_a \to$ Cal/mole $\quad R = 2Cal/mole/K$

$E_a \to$ J/mole $\quad R = 8.314J/mole/K$

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CALCULATION OF ACTIVATION ENERGY BY ARRHENIUS EQUATION

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

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

At temperature T_1, Rate constant = k_1

At temperature T_2, Rate constant = k_2

$$\ell nk_1 = \ell nA - \frac{E_a}{RT_1}$$

$$\ell nk_2 = \ell nA - \frac{E_a}{RT_2}$$

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

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Example

In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are) : [JEE-2017]

(A) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

(B) The activation energy of the reaction is unaffected by the value of the steric factor

(C) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used.

(D) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation.

Solution

$P = 4.5 = \frac{A_{actual} \rightarrow \text{exp.}}{A_{theoritical} \rightarrow \text{Arrhenius}}$

$A_{actual} > A_{theoritical}$

Ans. (B,D)

REVERSIBLE REACTIONS

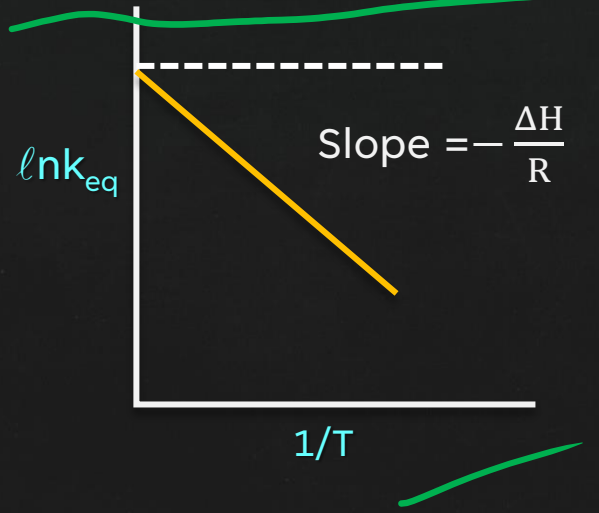
$$k_f = A_f\, e^{-(E_a)_f/RT}$$

$$k_b = A_b\, e^{-(E_a)_b/RT}$$

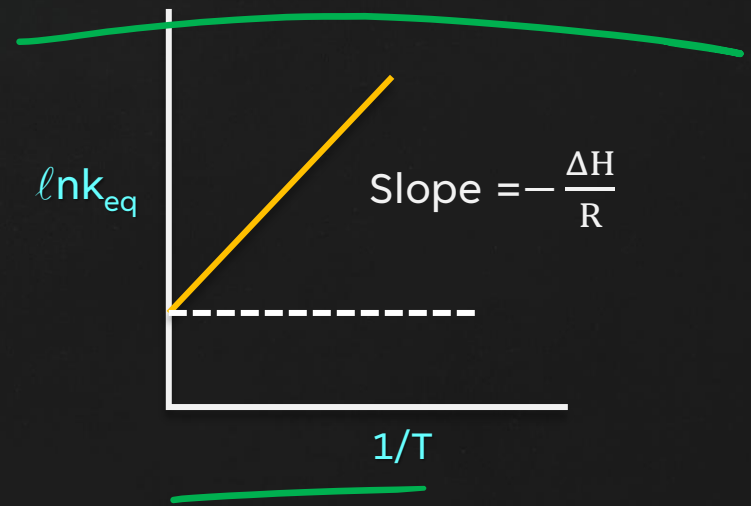
$$k_{eq} = \frac{k_f}{k_b} = \frac{A_f e^{-(E_a)_f/RT}}{A_b e^{-(E_a)_b/RT}} = \left(\frac{A_f}{A_b}\right) e^{-\{(E_a)_f - (E_a)_b\}/RT}$$

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

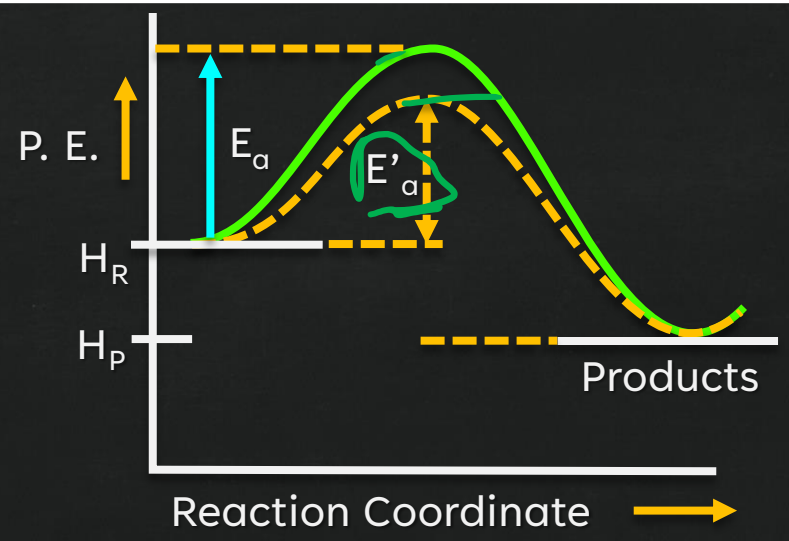
Endothermic reaction (ΔH = +ve)



Exothermic reaction (ΔH = -ve)



GENERAL CHARACTERISTICS OF CATALYST



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.

GENERAL CHARACTERISTICS OF CATALYST

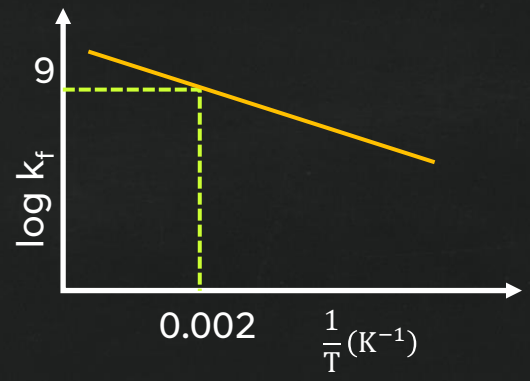
The rate of reaction in the presence of catalyst at any temperature T_1 may be made equal to the rate of reaction in absence of catalyst but for this sake we will have to raise the temperature. Let this temperature be T_2.

Then

$$e^{-\frac{E'a}{RT_1}} = e^{-\frac{E_a}{RT_2}} \quad or \quad \frac{E'a}{T_1} = \frac{E_a}{T_2}$$

Example

The plot of log k_f versus $\frac{1}{T}$ for a reversible reaction A (g) $\rightleftharpoons$ P (g) is shown.



[JEE (Advanced) 2023]

Pre-exponential factors for the forward and backward reactions are 10^{15} s^{-1} and 10^{11} s^{-1}, respectively. If the value of log K for the reaction at 500 K is 6, the value of | log k_b | at 250 K is _____.

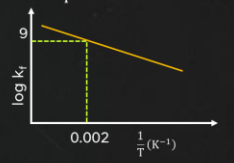
[K = equilibrium constant of the reaction
k_f = rate constant of forward reaction
k_b = rate constant of backward reaction]

Solution

ALLEN

Solution

The plot of log k_f versus $\frac{1}{T}$ for a reversible reaction A (g) $\rightleftharpoons$ P (g) is shown.



[JEE (Advanced) 2023]

Pre-exponential factors for the forward and backward reactions are 10^{15} s^{-1} and 10^{11} s^{-1}, respectively. If the value of log K for the reaction at 500 K is 6, the value of | log k_b | at 250 K is _____.

[K = equilibrium constant of the reaction
k_f = rate constant of forward reaction
k_b = rate constant of backward reaction]

Ans. (5)