



# Topics to be covered

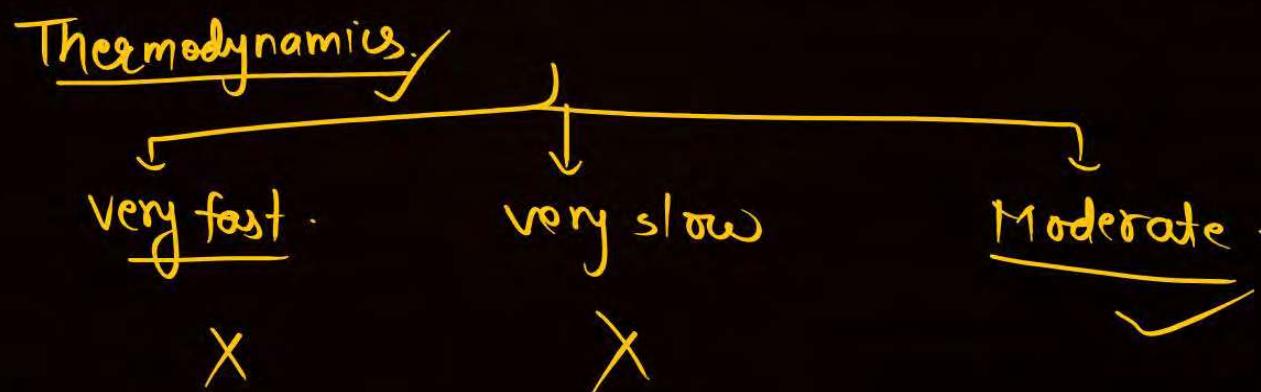
- 1) Rate of Reaction and rate law
  - 2) Order of Reaction and Molecularity of Reaction
  - 3) Integrated rate equations
  - 4) Collision Theory
- A yellow bracket is drawn under the last three items (2), (3), and (4).



## Definition



- The branch of chemistry, which deals with the study of reaction rates , their mechanisms and Factors affecting rate of reaction, is called chemical kinetics.





# **Rate of Reaction**



## Rate of Reaction



- It can be defined as the change in concentration of reactants and products in unit time.



$$t=t_1 \quad [R_1]$$

$$[P_1]$$

$$t=t_2 \quad [R_2]$$

$$[P_2]$$

$$\left\{ \begin{array}{l} R_2 < R_1 \\ P_2 > P_1 \end{array} \right\}$$

$$* \text{Rate of disappearance of } R = - \frac{[R_2] - [R_1]}{t_2 - t_1} = - \frac{\Delta[R]}{\Delta t}$$

$$* \text{Rate of appearance of } P = \frac{[P_2] - [P_1]}{t_2 - t_1} = \frac{\Delta[P]}{\Delta t}$$

$$\text{Rate of } R^\uparrow = - \frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$



## Rate of Reaction

\* Unit of Rate :-

$$\text{Rate} = \frac{\text{Concentration}}{\text{time}}$$

$$\text{Rate} = \frac{\text{mol litre}^{-1}}{\text{Sec}}$$

$$\begin{aligned}\text{Rate} &= \text{mol litre}^{-1} \text{ sec}^{-1} \\ &= \text{M sec}^{-1}\end{aligned}$$



\* for gases:-

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$\underline{P} = C R T$$

$$\text{Rate} = \frac{\text{Change in pressure}}{\text{time taken.}}$$

$$\text{Rate} = \text{atm s}^{-1}$$



## Rate of Reaction



$$\text{Rate of disappearance of H}_2 = -\frac{\Delta [\text{H}_2]}{\Delta t}$$

$$\text{Rate of disappearance of I}_2 = -\frac{\Delta [\text{I}_2]}{\Delta t}$$

$$\text{Rate of appearance of HI} = \frac{\Delta [\text{HI}]}{\Delta t}$$

Ans

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



$$*\text{ Rate of disappearance of N}_2 = -\frac{\Delta [\text{N}_2]}{\Delta t}$$

$$*\text{ Rate of disappearance of H}_2 = -\frac{\Delta [\text{H}_2]}{\Delta t}$$

$$*\text{ Rate of appearance of NH}_3 = \frac{\Delta [\text{NH}_3]}{\Delta t}$$

$$\text{Rate of Rx} = -\frac{1}{3} \frac{\Delta [\text{H}_2]}{\Delta t} = -\frac{\Delta [\text{N}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta [\text{NH}_3]}{\Delta t}$$



## Rate of Reaction



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

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

$$\text{Rate of app. of C} = \frac{\Delta [C]}{\Delta t}$$

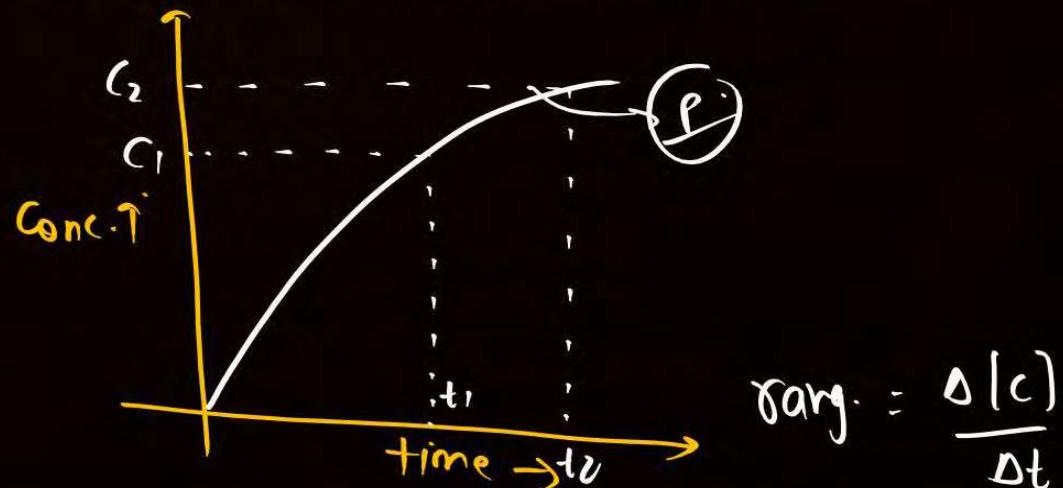
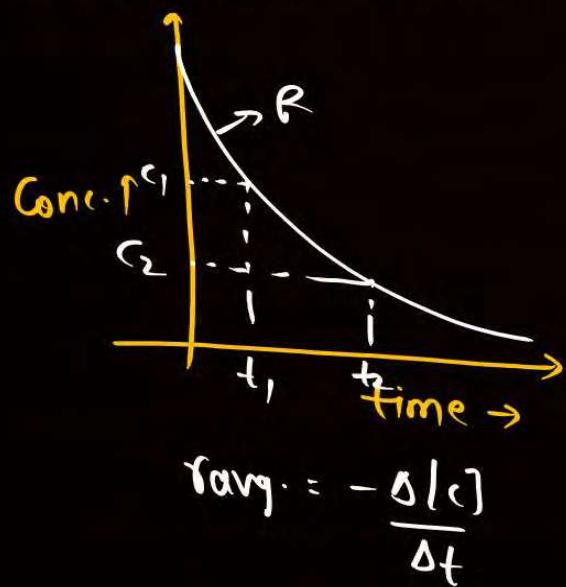
$$\text{Rate of R} \hat{x} = -\frac{1}{a} \frac{\Delta [A]}{\Delta t} = -\frac{1}{b} \frac{\Delta [B]}{\Delta t} = \frac{1}{c} \frac{\Delta [C]}{\Delta t} = \frac{1}{d} \frac{\Delta [D]}{\Delta t}$$



## Average and Instantaneous Rate

### Average Rate :

- The Rate Measured over a long time interval is called average rate.

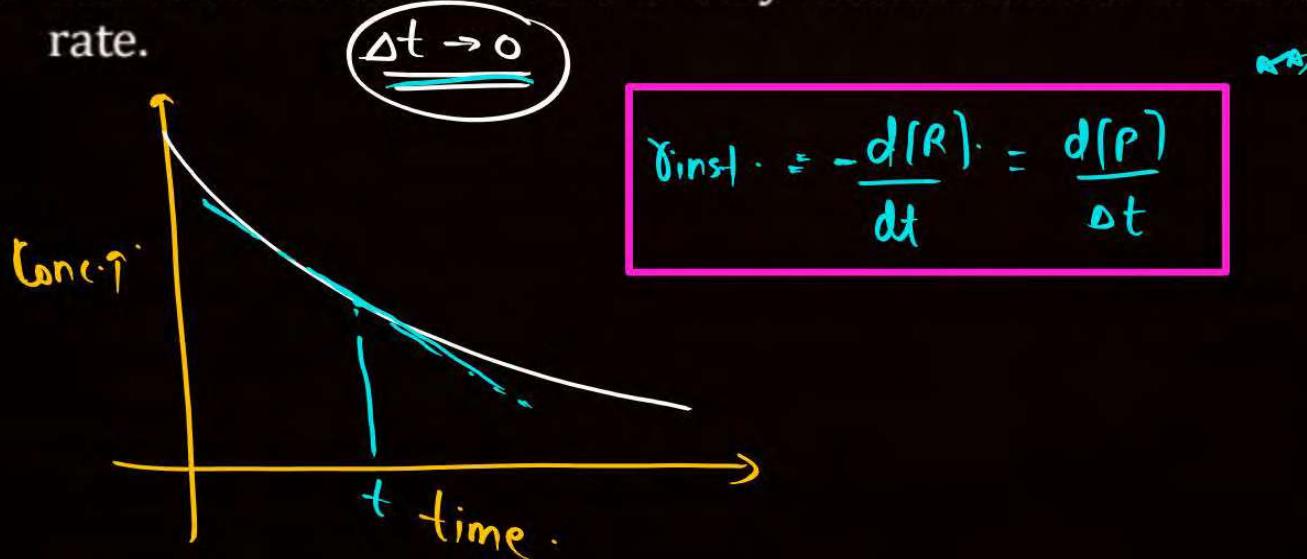




## Average and Instantaneous Rate

### Instantaneous Rate :

- The Rate Measured over a very small interval of time, is called instantaneous rate.



## Question



For the reaction  $R \rightarrow P$ , the concentration of reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

$$\begin{aligned} \text{Ans : } \text{Avg. rate} &= -\frac{(C_2 - C_1)}{t_2 - t_1} \\ &= -\frac{(0.02 - 0.03)}{25} \\ &= \underline{\underline{\frac{0.01}{25} \text{ mol litre}^{-1} \text{ min}^{-1}}} \end{aligned}$$
$$\Rightarrow \frac{0.01}{25 \times 60} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

## Question



In a reaction,  $2A \rightarrow \text{Products}$ , the concentration of A decreases from  $0.5 \text{ mol L}^{-1}$  to  $0.4 \text{ mol L}^{-1}$  in 10 minutes. Calculate the rate during this interval?

$$\underline{\text{Ans}} : -\frac{\Delta[A]}{\Delta t} = -\frac{(C_2 - C_1)}{t_2 - t_1} = \frac{0.1}{10} \text{ mol litr}^{-1} \text{ min}^{-1}.$$



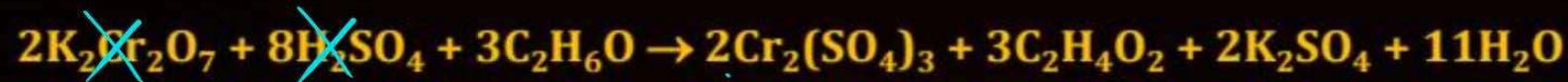
$$\text{Rate of Rx} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t}$$

$$\Rightarrow \frac{1}{2} \times \frac{0.1}{10} \text{ M min}^{-1}$$

Ans

## Question

The reaction that occurs in a breath analyser, a device used to determine the alcohol level in a person's blood stream is



If the rate of appearance of  $Cr_2(SO_4)_3$  is  $2.67 \text{ mol min}^{-1}$  at a particular time, the rate of disappearance of  $C_2H_6O$  at the same time is \_\_\_\_  $\text{mol min}^{-1}$ . (Nearest integer)

Ans.  $\Rightarrow \frac{\Delta [Cr_2(SO_4)_3]}{\Delta t} = 2.67 \text{ mol min}^{-1} \rightarrow -\frac{\Delta [C_2H_6O]}{\Delta t} = ?$  [27 Aug (2021)]

$$\begin{aligned} \text{Rate of } R^2 &= -\frac{1}{3} \frac{\Delta [C_2H_6O]}{\Delta t} = \frac{1}{2} \frac{\Delta [Cr_2(SO_4)_3]}{\Delta t} \\ &= -\frac{\Delta [C_2H_6O]}{\Delta t} = 3.2 \times 2.67 \quad \text{Ans. (4)} \end{aligned}$$

Ans. (4)

## Question



For a chemical reaction  $A \rightarrow B$ , it was found that concentration of B is increased by  $0.2 \text{ mol L}^{-1}$  in 30 min. The average rate of the reaction is     $\times 10^{-1} \text{ mol L}^{-1} \text{ h}^{-1}$ . (in nearest integer) [25 July (2021)]

Ans:

$$\begin{aligned}\text{Ans.} &= \frac{\Delta[B]}{\Delta t} \\ &= \frac{0.2}{30} \times 60 \\ &= 0.4 \\ &\approx 4 \times 10^{-1} \\ &\text{(Ans)}$$

Ans. (4)

## Question

For the reaction  $2A + 3B + \frac{3}{2}C \rightarrow 3P$ , which statement is correct?

- A**  $\frac{dn_A}{dt} = \frac{3}{2} \frac{dn_B}{dt} = \frac{3}{4} \frac{dn_C}{dt}$
- B**  $\frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dn_C}{dt}$
- C**  $\frac{dn_A}{dt} = \frac{2}{3} \frac{dn_B}{dt} = \frac{4}{3} \frac{dn_C}{dt}$
- D**  $\frac{dn_A}{dt} = \frac{2}{3} \frac{dn_B}{dt} = \frac{3}{4} \frac{dn_C}{dt}$

Rate of Rxn  $\Rightarrow -\frac{1}{2} \frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} = -\frac{2}{3} \frac{d[C]}{dt} = \frac{1}{3} \frac{d[P]}{dt}$

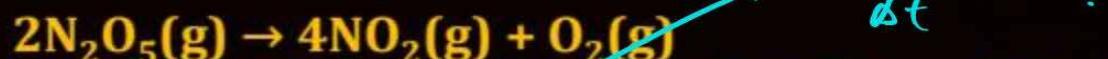
$$\frac{d[A]}{dt} : \frac{2}{3} \frac{d[B]}{dt}$$

Ans. (C)

## Question



$\text{NO}_2$  required for a reaction is produced by the decomposition of  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  as per the equation,



The initial concentration of  $\text{N}_2\text{O}_5$  is  $3.00 \text{ mol L}^{-1}$  and it is  $2.75 \text{ mol L}^{-1}$  after 30 minutes. The rate of formation of  $\text{NO}_2$  is [2019 Main, 12 April II]

- A  $4.167 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$
- B  ~~$1.667 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$~~
- C  $8.333 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$
- D  $2.083 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$

$$-\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{3 - 2.75}{30} = \frac{0.25}{30} \text{ M min}^{-1}$$

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

$$\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{1}{4} \times \frac{0.25}{30} \Rightarrow \frac{0.5}{30}$$

Ans. (B)

## Question

In the following reaction;  $xA \rightarrow yB$

$$\log_{10} \left[ \frac{d[A]}{dt} \right] = \log_{10} \left[ \frac{d[B]}{dt} \right] + 0.3010$$

A and B respectively can be

- A n-butane and iso-butane
- B  $C_2H_2$  and  $C_6H_6$
- C  $C_2H_4$  and  $C_4H_8$   $\xrightarrow{C_2Hg} 2(C_2H_4)$
- D  $N_2O_4$  and  $NO_2$   $\frac{x}{y} = 2$   $x = 2y$

[2019 Main, 12 April I]

$$\text{Rate of } Rx = -\frac{1}{x} \frac{d[A]}{dt} = \frac{1}{y} \frac{d[B]}{dt}$$

$$-\frac{d[A]}{dt} = \frac{x}{y} \left( \frac{d[B]}{dt} \right)$$

$$\log \left\{ -\frac{d[A]}{dt} \right\} = \log \left( \frac{x}{y} \right) + \log \frac{d[B]}{dt}$$

$$\log \left( \frac{x}{y} \right) = 0.3010$$

$$\Rightarrow \frac{x}{y} = 2$$

Ans. (C)

**Question**

Consider the chemical reaction,



The rate of this reaction can be expressed in terms of time derivatives of concentration of  $\text{N}_2(\text{g})$ ,  $\text{H}_2(\text{g})$  or  $\text{NH}_3(\text{g})$ . Identify the correct relationship amongst the rate expressions

[2002, 3M]

CH

**A** Rate =  $-\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$

**B** Rate =  $-\frac{d[\text{N}_2]}{dt} = -3 \frac{d[\text{H}_2]}{dt} = 2 \frac{d[\text{NH}_3]}{dt}$

**C** Rate =  $\frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$

**D** Rate =  $-\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$

**Ans. (A)**



# Rate Law or Rate Equation



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## Rate Law



- Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.



$$\text{Rate of Rx} \propto [A]^x [B]^y \rightarrow \text{Rate law}$$

$$\underbrace{\text{Rate of Rx}}_{\substack{\rightarrow \\ \text{Rate Constant}}} = K [A]^x [B]^y$$

↳ Rate Constant / Velocity

Specific Rate or Reaction Constant

$$[A] = [B] = 1 \text{ M}$$

$$\underline{\text{Rate of Rx} = K}$$



## Rate Law



### Characteristic of Rate Constant:

- Larger the value of K, faster is the reaction.
- At a particular temperature, value of K is constant for a reaction.
- It is independent of initial concentration of reactants and products.

## Question



The specific rate constant of a first order reaction depends on the

[1983, 1M]

- A Concentration of the reactant
- B Concentration of the product
- C Time
- D Temperature

Ans. (D)



# **Order of a Reaction**



## Order of Reaction



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



Rate of Rx  $\propto$  [A]<sup>x</sup> [B]<sup>y</sup>

Rate =  $k[A]^x[B]^y \rightarrow$  Rate law.

Order of  $R^{\alpha}(n) = x + y$

Order w.r.t.  $A \rightarrow x$

$\beta \rightarrow y$ .

Overall order of Rx (n) = x+y.



## Order of Reaction

Unit of Rate Constant:

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

$$\text{Rate} = K (\text{concentration})^{x+y}$$

$$\text{mol liter}^{-1} \text{ sec}^{-1} = K (\text{mol liter}^{-1})^n$$

Unit of  $K = \text{mol}^{-n} \text{ liter}^{n-1} \text{ sec}^{-1}$

\*  $n=0$  (zero order Rx)  
=  $\text{mol liter}^{-1} \text{ sec}^{-1}$

\*  ~~$n=1$~~  (first order Rx)  
=  $\text{sec}^{-1}$

\*  $n=2$  (second order Rx)  
=  $\text{mol}^{-1} \text{ liter}^{-1} \text{ sec}^{-1}$





## Order of Reaction :

### Note :

- ✓ 1. Order of a reaction can be zero, negative, positive or fraction.
- ✓ 2. It can be derived experimentally.
- ✓ 3. It is defined for both elementary as well as complex reactions.

## Order of Reaction :

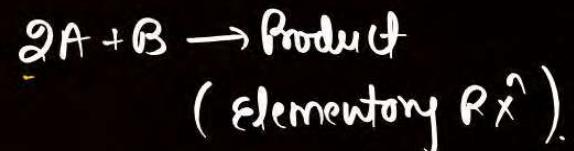
### Elementary Reactions :

- ❖ Reactions taking place in a single step.
- ❖ Rate Law is given according to law to mass action.



$$\text{Rate of Rxn} \propto [A]^1 [B]^1$$

Order = 1+1 = 2.



$$\text{Rate of Rxn} \propto [A]^2 [B]^1$$

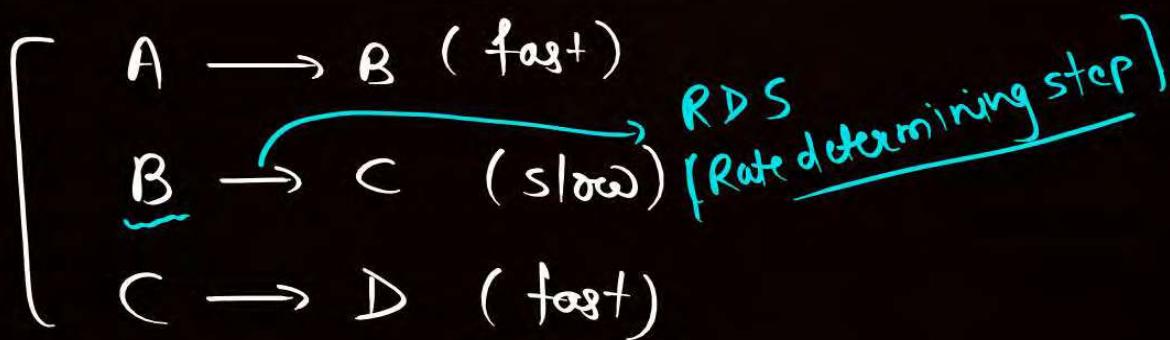
$$\text{order} = 1+2 = 3$$


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## Order of Reaction :

## Complex Reactions :

→ Takes place in more than one steps.



## Question



Calculate the overall order of a reaction which has the rate expression

(a) Rate =  $k [A]^{1/2} [B]^{3/2}$  order =  $1/2 + 3/2 = \textcircled{2}$

(b) Rate =  $k [A]^{3/2} [B]^{-1}$

order =  $3/2 + (-1) = 1/2$ .

## Question



The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?



$$\text{Rate of } R_x \propto [X]^2$$

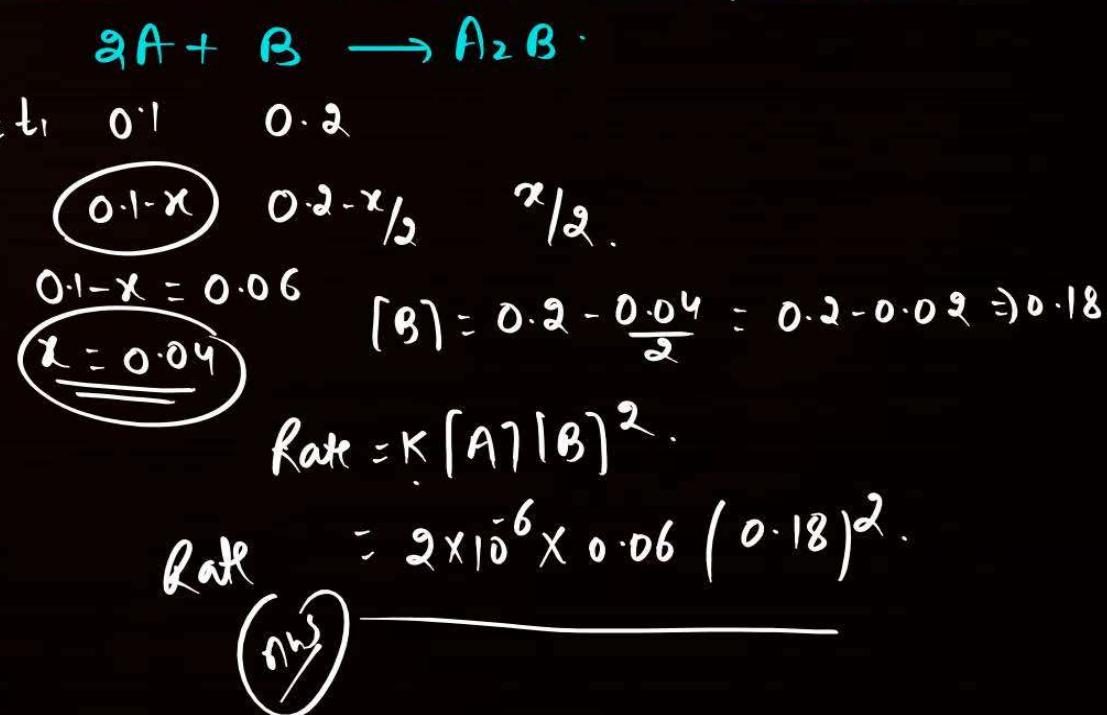
9 times

## Question



For the reaction,  $2A + B \rightarrow A_2B$ , the reaction rate =  $k [A][B]^2$  with  $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ . Calculate the initial rate of the reaction when  $[A] = 0.1 \text{ mol L}^{-1}$ ;  $[B] = 0.2 \text{ mol L}^{-1}$ . Also calculate the reaction rate when  $[A]$  is reduced to  $0.06 \text{ mol L}^{-1}$ .

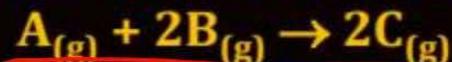
$$\begin{aligned} \text{Ans.} & \rightarrow \boxed{\text{Rate} = k[A][B]^2} \\ \text{Rate} &= 2 \times 10^{-6} (0.1)(0.2)^2 \\ &= 2 \times 10^{-6} \times 10^{-1} \times 4 \times 10^{-2} \\ \text{Rate.} &\Rightarrow 8 \times 10^{-9} \end{aligned}$$



## Question



Compounds 'A' and 'B' react according to the following chemical equation



Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. The following results were obtained. Choose the correct option for the rate equations for this reaction.

<u>Experiment</u>	1	2	3
Initial concentration of [A]/mol L <sup>-1</sup>	0.30	0.30	0.60
Initial concentration of [B]/mol L <sup>-1</sup>	0.30	0.60	0.30
Initial rate of formation of [C]/mol L <sup>-1</sup> s <sup>-1</sup>	0.10	0.40	0.20

Rate law

$$\text{Rate of R} \propto [A][B]^2$$

$$\text{Rate} = k[A][B]^2$$

$$\text{Rate} \propto [B]^2$$

$$\text{Rate} \propto [A]$$

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

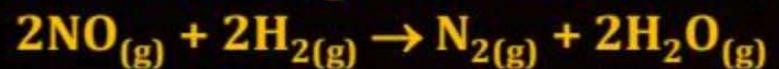
**B** Rate =  $k[A][B]^2$

**C** Rate =  $k[A][B]$

**D** Rate =  $k[A]^2[B]^2$

## Question

The following data was obtained for chemical reaction given below at 975 K.



[NO] mol L <sup>-1</sup>	[H <sub>2</sub> ] mol L <sup>-1</sup>	Rate mol L <sup>-1</sup> s <sup>-1</sup>
(A) $8 \times 10^{-5}$	$8 \times 10^{-5}$	$7 \times 10^{-9}$
(B) $24 \times 10^{-5}$	$8 \times 10^{-5}$	$2.1 \times 10^{-8}$
(C) $24 \times 10^{-5}$	$32 \times 10^{-5}$	$8.4 \times 10^{-8}$

Let  $\rightarrow \text{Rate} = k [ \text{NO} ]^x [ \text{H}_2 ]^y$

The order of the reaction with respect to NO is \_\_\_\_\_. [Integer answer]

Ans: →

Rate  $\propto [\text{NO}]^1$

[26 Aug (2021)]

**Ans. (1)**

## Question

The reaction  $2A + B_2 \rightarrow 2AB$  is an elementary reaction.

For a certain quantity of reactants, if the volume of the reaction vessel is reduced by a factor of 3, the rate of the reaction increases by a factor of \_\_\_\_\_ (Round off to the Nearest Integer).

$$\text{Ans. : } (n) \text{ Rate of } R_2 = K [A]^2 [B_2]^{1/2}$$

$$R_2 = K [3A]^2 [3B_2]^{1/2}$$

$$= 9 \times 3 K [A]^2 [B_2]^{1/2}$$

$$\therefore 27 K [A]^2 [B_2]^{1/2}$$

$$\therefore 27 (R_1)$$

[17 March (2021)]

$$V_2 = \frac{V_1}{3}$$

$$C_2 = \underline{\underline{3C_1}}$$

27

Ans. (27)

## Question



For a reaction of order n, the unit of the rate constant is: [27 Jul (2021)]

- A  $\text{mol}^{1-n} \text{L}^{1-n} \text{s}$
- B  $\text{mol}^{1-n} \text{L}^{2n} \text{s}^{-1}$
- C  $\text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$
- D  $\text{mol}^{1-n} \text{L}^{1-n} \text{s}^{-1}$



Ans. (C)

## Question

For the reaction,  $2A + B \rightarrow C$ , the values of initial rate at different reactant concentrations are given in the table below.

The rate law for the reaction is

[2019 Main, 8 April I]

~~A~~  $\text{rate} = k [A][B]^2$

Rate  $\propto [A]$

Rate  $\propto [B]$

~~B~~  $\text{rate} = k [A]^2[B]^2$

~~C~~  $\text{rate} = k [A][B]$

~~D~~  $\text{rate} = k [A]^2[B]$

<u>[A] (mol L<sup>-1</sup>)</u>	<u>[B] (mol L<sup>-1</sup>)</u>	<u>Initial rate (mol L<sup>-1</sup>s<sup>-1</sup>)</u>
0.05	0.05	0.045
0.10	0.05	0.090
0.20	0.10	0.72

~~(x 8)~~



**Ans. (A)**

## Question



For the reaction,  $2A + B \rightarrow \text{products}$ , When concentration of both (A and B) becomes double, then rate of reaction increases from  $0.3 \text{ mol L}^{-1} \text{ s}^{-1}$  to  $2.4 \text{ mol L}^{-1} \text{ s}^{-1}$ . When concentration of only A is doubled, the rate of reaction increases from  $0.3 \text{ mol L}^{-1} \text{ s}^{-1}$  to  $0.6 \text{ mol L}^{-1} \text{ s}^{-1}$ .

Which of the following is true?

[2019 Main, 9 Jan II]

- A The whole reaction is of 4th order
- B The order of reaction w.r.t. B is one
- C The order of reaction w.r.t. B is 2
- D The order of reaction w.r.t. A is 2

Ans. (C)

## Question

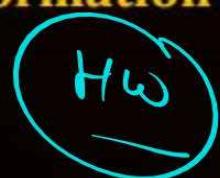
For the non-stoichiometric reaction,  $2A + B \rightarrow C + D$ , the following kinetic data were obtained in three separate experiments, all at 298 K.

	Initial concentration [A]	Initial concentration [B]	Initial rate of formation of C (mol L <sup>-1</sup> s <sup>-1</sup> )
(i)	0.1 M	0.1 M	$1.2 \times 10^{-3}$
(ii)	0.1 M	0.2 M	$1.2 \times 10^{-3}$
(iii)	0.2 M	0.1 M	$2.4 \times 10^{-3}$

The rate law for the formation of C is

[2014 Main]

**A**  $\frac{dC}{dt} = k[A][B]$



**C**  $\frac{dC}{dt} = k[A][B]^2$

**B**  $\frac{dC}{dt} = k[A]^2[B]$

**D**  $\frac{dC}{dt} = k[A]$

Ans. (D)

## Question



Consider a reaction,  $aG + bH \rightarrow$  products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is [2007, 3M]

- A 0
- B 1
- C 2
- D 3



Ans. (D)

## Question



**Which one of the following statement(s) is incorrect about order of reaction?**  
**[2005, 1M]**

- A** Order of reaction is determined experimentally
- B** Order of reaction is equal to sum of the power of concentration terms in differential rate law
- C** It is not affected with stoichiometric coefficient of the reactants
- D** Order cannot be fractional

**Ans. (D)**



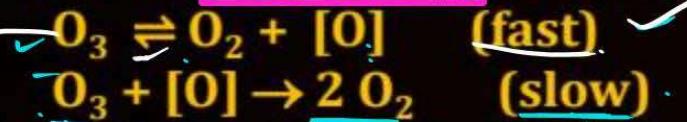
## Order of Reaction from Reaction Mechanism

Complex  
Reaction

Question :

## Question

The reaction  $2O_3 \rightarrow 3O_2$  Proceeds as follows



Find out the rate law for this reaction.

Ans :- Rate of Rxn  $\propto [O_3][O]$

$$\text{Rate} = k [O_3] [O]$$

$$k_{eq} = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \frac{k_{eq}[O_2]}{[O_3]}$$

$$\text{Rate} = k' [O_3] K_{eq} [O_3] [O_2]^{-\frac{1}{2}}$$

$$\text{Rate} = k' [O_3]^2 [O_2]^{-\frac{1}{2}}$$

Rate Law

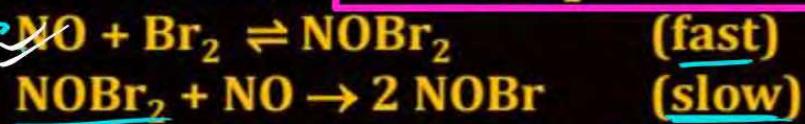
$$\text{order of Rxn} = 2 + (-\frac{1}{2}) = \frac{3}{2}$$

Order w.r.t  $O_3 = 2$ .

$O_2 \rightarrow -\frac{1}{2}$

## Question

The reaction  $2 \text{NO} + \text{Br}_2 \rightarrow 2 \text{NOBr}$  Proceeds as follows



Find out the rate law for this reaction.

$$\text{Ans: } \text{Rate} = k \underbrace{[\text{NOBr}_2]}_{X} [\text{NO}]$$

$$K_q = \frac{[\text{NOBr}_2]}{[\text{NO}] [\text{Br}_2]}$$

$$[\text{NOBr}_2] = K_q [\text{NO}] [\text{Br}_2]$$

$$\text{Rate} = k' K_q [\text{NO}] [\text{Br}_2] [\text{NO}]$$

$$\text{Rate} = k' [\text{NO}]^2 [\text{Br}_2]$$

→ Rate  
Law

order w.r.t  $\text{NO} \rightarrow 2$   
 $\text{Br}_2 \rightarrow 1$

overall order of Rx =  $2+1=3$

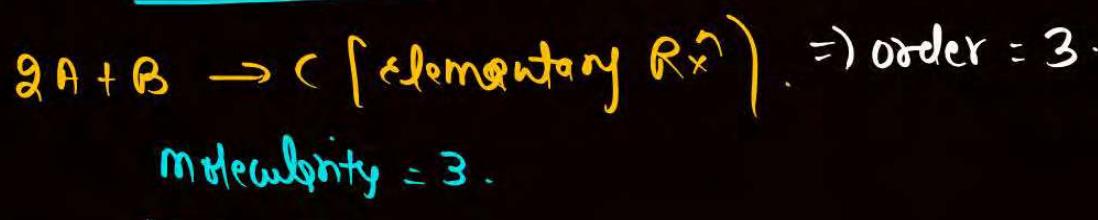


# Molecularity



## Molecularity

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.



for Elementary Rxn :-

order = Molecularity



## Molecularity



- It can't be zero, negative or non- integer.
- For elementary reactions, molecularity is equal to the sum of stoichiometry coefficients of reactant molecules in a balanced reaction.



## Molecularity



- The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed.



## Difference Between Molecularity and Order

- ❖ Order of a reaction is an experimental quantity. It can be zero and even a fraction.
- ❖ Order is applicable to elementary as well as complex reactions.
- ❖ For complex reaction, order is given by the slowest step.

- ❖ Molecularity cannot be zero or a non integer and it is a theoretical concept.
- ❖ Molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.
- ❖ ~~Molecularity of the slowest step is same as the order of the overall reaction.~~

## Question



The rate law has the form,  $\text{rate} = K[A][B]^{3/2}$ , can this reaction be an elementary reaction?

Ans :- .

$$\text{order} = \frac{1+3}{2} = \frac{5}{2}$$

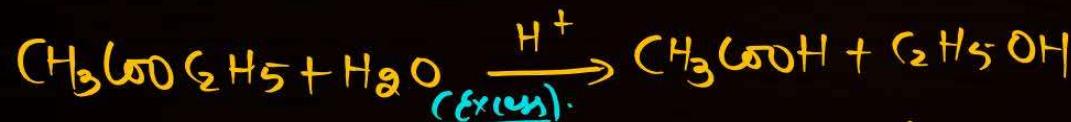




## Pseudo First Order Chemical Reactions

- Those reactions which are not of 1<sup>st</sup> order but approximated or appears to be of 1<sup>st</sup> order due to higher concentration of the reactant/s than other reactant are known as pseudo first order reactions.

Ex. Acid catalysed Hydrolysis of ester :-



$$\underbrace{\text{Order of Rx} = 1}_{\downarrow}$$

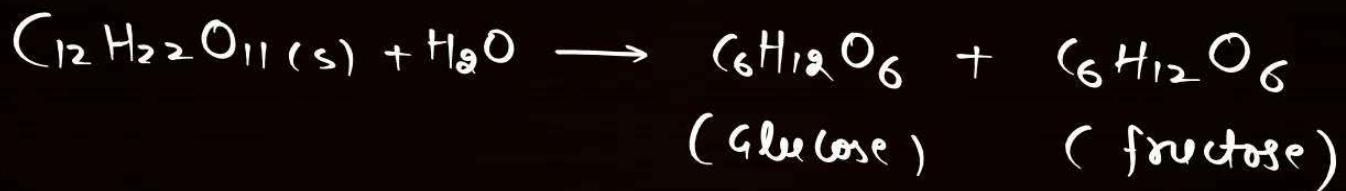
Pseudo first order Rx.



## Pseudo First Order Chemical Reactions

\*

Hydrolysis of sucrose :-



$$\text{Rate of Rx} \propto [C_{12}H_{22}O_{11}]^{\perp} [H_2O]^0$$

$$\text{Rate of Rx} = k [C_{12}H_{22}O_{11}]^{\perp}$$

order = 1.

Pseudo first order Rx.

## Question



**Highest order ( $> 3$ ) reactions are rare due to**

**[2015 Main]**

- A** low probability of simultaneous collision of all the reacting species
- B** increase in entropy and activation energy as more molecules are involved
- C** shifting of equilibrium towards reactants due to elastic collisions
- D** loss of active species on collision

**Ans. (A)**

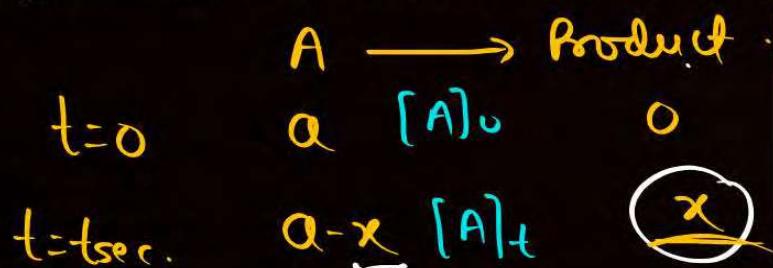


# Integrated Rate Equations



## Zero Order Reaction

- Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants.



$$\text{Rate} \propto [A]^0$$

$$\text{Rate} = K$$

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

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

$$[A]_0 \quad [A]_t \quad \xrightarrow{\text{Rate}}$$

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

$$a-x = a-Kt$$

$$x = Kt$$

Dissociation of A  
Formation of Product



## Zero Order Reaction



**Half Life Period:** ( $t_{1/2}$ )

- Time required for 50 % completion of a reaction, is known as half life period.

$$\alpha = kt$$

$$At \ t = t_{1/2} \Rightarrow \alpha = \alpha_{1/2}$$

∴

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

$$t_{1/2} \propto [A]_0$$

$$At \ t = t_{1/2} \Rightarrow \alpha = \alpha_{1/2}$$

$$\alpha = \frac{3a}{4}$$

$$t_{1/2} = \frac{3a}{4k}$$

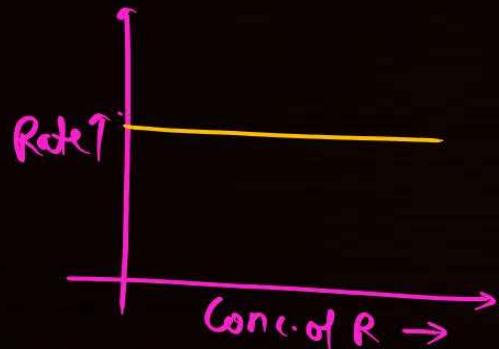
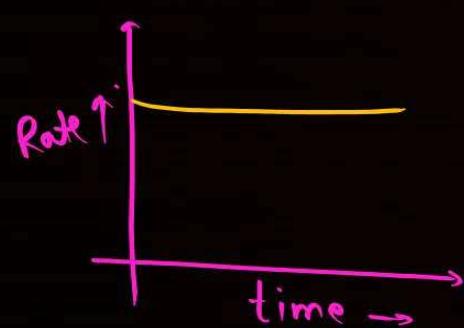
$$\frac{3[A]_0}{4k}$$



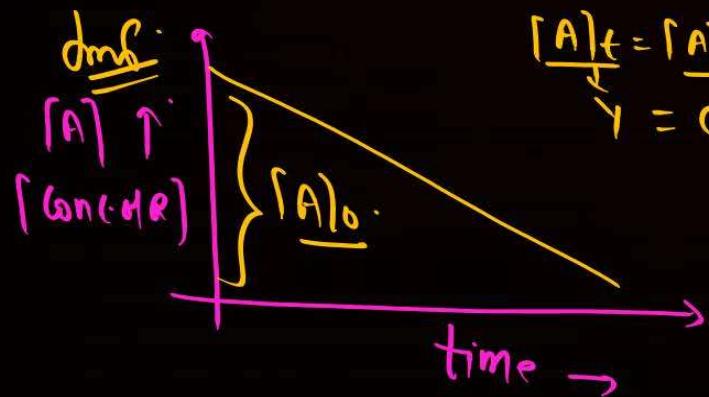
## Graphical Representation



Zero Order Reaction:

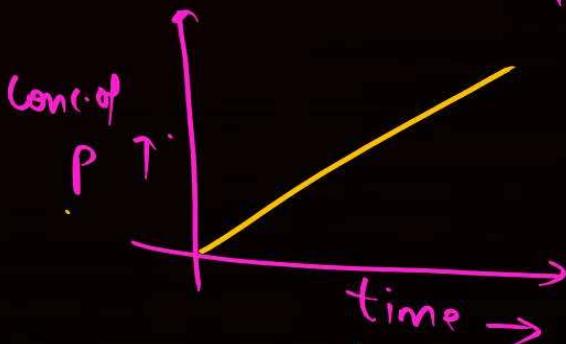


$$\text{Rate} = k.$$



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

$$y = c - mx$$



$$t_{1/2} \propto [A]_0$$

$$\alpha = kt$$

$$\alpha t$$



## Examples of Zero Order Reaction

❖ Photochemical reactions :



❖ Surface Catalyzed reactions :



❖ Enzyme catalyzed reactions :

## Question



The decomposition of  $\text{NH}_3$  on platinum surface is zero order reaction. What are the rates of production of  $\text{N}_2$  and  $\text{H}_2$  if  $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ Ls}^{-1}$ .



$$\text{Rate} = -\frac{1}{2} \frac{\Delta [\text{NH}_3]}{\Delta t} = \frac{\Delta [\text{N}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta [\text{H}_2]}{\Delta t}$$

$$\text{Rate} = k = 2.5 \times 10^{-4}$$

$$\frac{\Delta [\text{N}_2]}{\Delta t} = 2.5 \times 10^{-4}$$

$$\frac{\Delta [\text{H}_2]}{\Delta t} = 3 \times (2.5 \times 10^{-4})$$

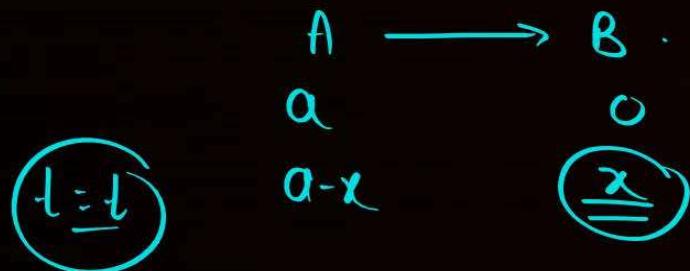
## Question



The rate constant of the reaction  $A \rightarrow B$  is  $0.6 \times 10^{-3}$  mole L<sup>-1</sup>s<sup>-1</sup>. If the concentration of A is 5 M, then concentration of B after 20 minutes is:

Ans :-

Zero order Rx :-



$$x = kt$$

## Question



The reaction,  $2X \rightarrow B$  is a zero<sup>th</sup> order reaction. If the initial concentration of X is 0.2 M, the half-time is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be

- A** 7.2 h
- B** 18.0 h
- C** 12.0 h
- D** 9.0 h

Case - 1

$$[A]_0 = 0.2$$

$$t_{1/2} = 6 \text{ h.}$$

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

$$k = \frac{[A]_0}{2 \times t_{1/2}} = \frac{0.2}{2 \times 6}$$

Case - 2

$$[A]_0 = 0.5$$

$$[A]_t = 0.2$$

$$t = ?$$

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

[2019 Main, 11 Jan II]

$$t = ?$$

Ans

Ans. (B)

$A \rightarrow B$

The above reaction is of zero order. Half life of this reaction is 50 min. The time taken for the concentration of A to reduce to one-fourth of its initial value is \_\_\_\_\_ min. (Nearest integer)

Ans :  $\Rightarrow t_{1/2} = 50 \text{ min}$

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

$$t_{3/4} = -\ln(75\%) = \frac{3[\text{A}]_0}{4k} \Rightarrow \frac{3}{2} \left( \frac{[\text{A}]_0}{2k} \right)$$

$$\Rightarrow \frac{3}{2} \times 50 \Rightarrow 75 \quad (\text{Ans})$$

At 345 K, the half life for the decomposition of a sample of a gaseous compound initially at 55.5 kPa was 340 s. When the pressure was 27.8 kPa, the half life was found to be 170 s. the order of the reaction is 0.  
(integer answer)

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

for gases.

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

$$P_1 = 55.5, (t_{1/2})_1 = 340 \text{ sec.}$$

$$P_2 = 27.8, (t_{1/2})_2 = 170 \text{ sec}$$

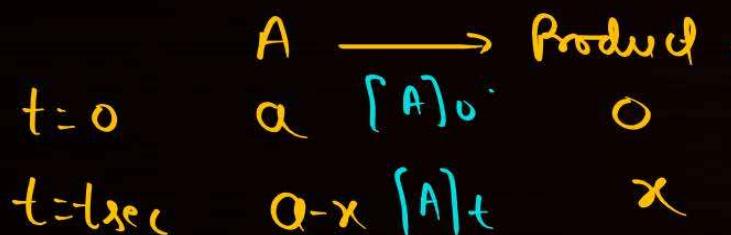
$$\cancel{t_{1/2}}(P),$$





## First Order Reaction

- Reactions whose rate depends on the first power of the reaction, are called as first order reaction.



Rate  $\propto [A]^1$ .

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

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



$$\begin{aligned} K &= \frac{2.303}{t} \log_{10} \left( \frac{a}{a-x} \right) \\ &= \frac{2.303}{t} \log_{10} \left\{ \frac{[A]_0}{[A]_t} \right\} \end{aligned}$$

..



## First Order Reaction



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



## First Order Reaction



Half Life Period:

$$\tau = \frac{\alpha}{2} = \frac{[A]_0}{2}$$

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

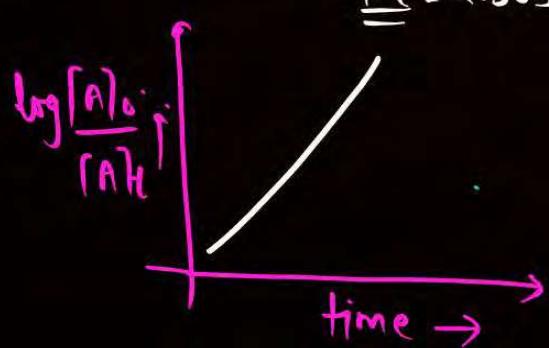
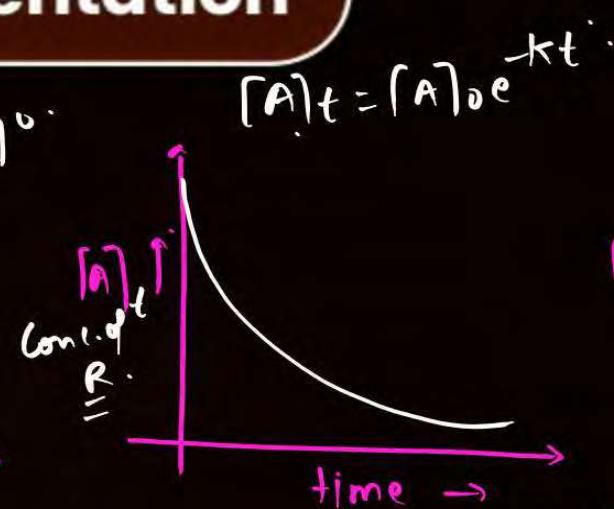
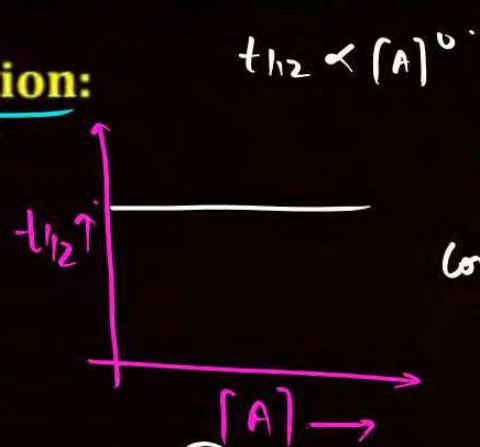
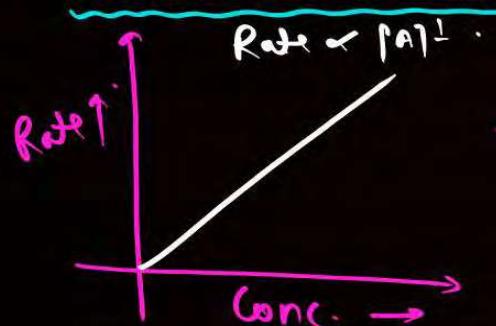
~~t<sub>1/2</sub>~~  $t_{1/2} \propto [A]_0$



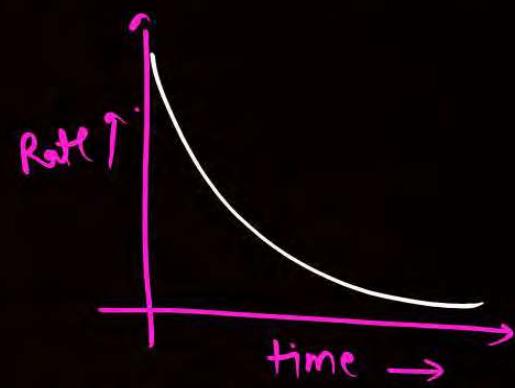
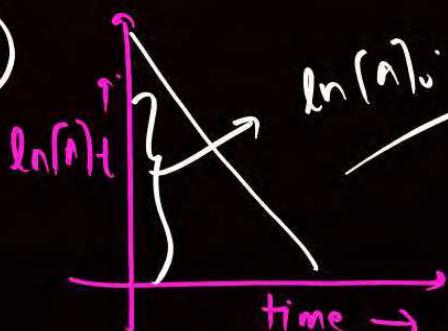
## Graphical Representation



### First Order Reaction:



$$\frac{k}{t} = 2.303 \log_{10} \frac{[\text{A}]_0}{[\text{A}]_t}$$



$$K = \frac{2.303}{t} \log_{10} \frac{[\text{A}]_0}{[\text{A}]_t}$$

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

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

$$\frac{\ln[\text{A}]_t}{y} = \frac{\ln[\text{A}]_0}{C} - mx$$

$$\left. \begin{array}{l} \text{Rate} = K[\text{A}]t \\ \text{Rate} = K[\text{A}]e^{-kt} \end{array} \right\}$$



## Examples of First Order Reaction

1. All radioactive decay reaction.

2. Decomposition of  $\text{N}_2\text{O}_5$



3. Decomposition of  $\text{H}_2\text{O}_2$



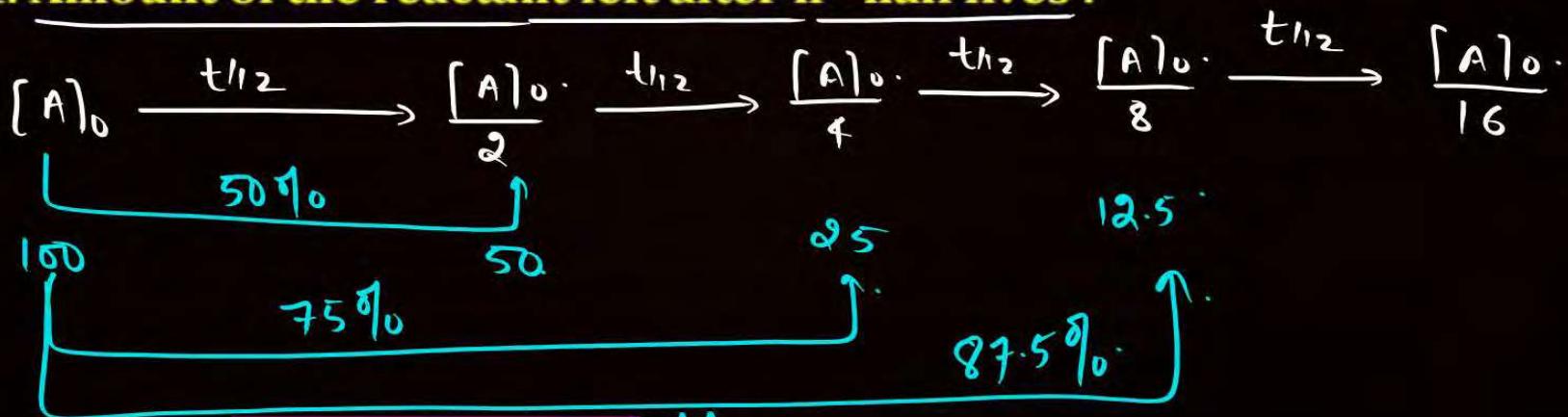
~~4. Hydrogenation of ethene~~



## First Order Reaction :

NOTE :

1. Amount of the reactant left after n - half lives :



$$\frac{[A]_0}{2^n}$$

AN

n :- no. of Half  
lives

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

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

$$t_{99.99\%} = 10 t_{1/2}$$

## First Order Reaction :

**NOTE :**

2. Degree of dissociation : ( $\alpha$ ) .

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

$$(a-\alpha) = a e^{-kt}$$

$$\frac{\alpha}{a} - \frac{x}{a} = e^{-kt}$$

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

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

$$\alpha = 1 - e^{-kt}$$

## First Order Reaction :

NOTE :

3. Average life :

$t_{avg}$

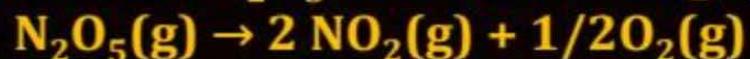
- It is the time in which 63.21% of the reactant is converted into products.
- It is equal to the reciprocal of rate constant.

$$t_{avg} = \frac{1}{K} = 1.44 t_{1/2}$$

## Question



The initial concentration of  $\text{N}_2\text{O}_5$  in the following first order reaction



was  $1.24 \times 10^{-2} \text{ mol L}^{-1}$  at 318 K. The concentration of  $\text{N}_2\text{O}_5$  after 60 minutes was  $0.20 \times 10^{-2} \text{ mol L}^{-1}$ . Calculate the rate constant of the reaction at 318 K.

$$\text{Ans} \rightarrow [\text{A}]_0 = 1.24 \times 10^{-2}$$

$$t = 60 \text{ min}$$

$$[\text{A}]_t = 0.2 \times 10^{-2}, k = ?$$

$$(k) \frac{2.303}{t} \log \frac{[\text{A}]_0}{[\text{A}]_t}$$

## 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.

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

## Question



The rate constant for a first order reaction is  $60 \text{ s}^{-1}$ . How much time will it take to reduce the initial concentration of the reactant to its  $1/16^{\text{th}}$  value?

Ans :-  $K = 60 \text{ s}^{-1}$   $\rightarrow$  1<sup>st</sup> order Rxn.

$$[A]_0$$

$$[A]_t = \frac{[A]_0}{16}$$

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

$$t = \frac{2.303}{60} \cdot \log(2)^4$$

$$t = \frac{2.303}{60} \cdot 4 \log 2 \xrightarrow{0.3010} 15\text{s}$$

## Question

A. For a reaction  $A + B \rightarrow P$ , the rate is given by Rate =  $k [A][B]^2$

(i) How is the rate of reaction affected if the concentration of B is doubled?

4 times

2

(ii) What is the overall order of reaction if A is present in large excess?

B. A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction

$$\text{Ans} : \rightarrow t_{1/2} = 30 \text{ mins}$$

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

$$K = \frac{0.693}{30}$$

$$\alpha = 100$$

$$\alpha = 90 \quad (\alpha - x) = 10$$

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

$$\frac{0.693}{30} = \frac{2.303}{t} \log 10 \rightarrow 2$$

$$t = ?$$

$t_{87.5}$  is the time required for the reaction to undergo 87.5% completion and  $t_{50}$  is the time required for the reaction to undergo 50% completion. The relation between  $t_{87.5}$  and  $t_{50}$  for a first order reaction is  $t_{87.5} = x \times t_{50}$ . The value of x is \_\_\_\_ (Nearest integer)

$$\Rightarrow 3 \times t_{50}$$

Ans : -

3

?

**Question**

For a first order reaction, the ratio of the time for 75% completion of a reaction to the time for 50% completion is 2. (Integer answer)

[31<sup>st</sup> Aug (2021)]

$$\frac{t_{75\%}}{t_{50\%}} = 2 \times (50\%)$$

**Ans. (2)**

## Question



The inactivation rate of a viral preparation is proportional to the amount of virus. In the first minute after preparation, 10% of the virus is inactivated. The rate constant for viral inactivation is \_\_\_\_\_  $\times 10^{-3}$  min $^{-1}$ . (Nearest integer)

[Use :  $\ln 10 = 2.303$ ;  $\log_{10} 3 = 0.477$ ; property of logarithm:  $\log xy = y \log x$ ]

[20 July (2021)]

Hω

Ans. (106)

## Question



A reaction has a half life of 1 min. the time required for 99.9% completion of the reaction is \_\_\_\_\_ min. (Round off to the Nearest integer).

[Use :  $\ln 2 = 0.69$ ;  $\ln 10 = 2.3$ ]

[18 March (2021)]

$$10 \text{ } t_{1/2}$$

$$\underline{10 \times 1 = 10}$$

Ans. (10)

## Question



Decomposition of X exhibits a rate constant of  $0.05 \text{ } \mu\text{g/year}$ . How many years are required for the decomposition of  $5 \text{ } \mu\text{g}$  of X into  $2.5 \text{ } \mu\text{g}$ ?

1st order

[2019 Main, 12 Jan I]

$$\frac{(A)}{(A)_0} = e^{(0-n)t}$$

A 20

B 25

C 40

D 50

Hw

$$k = \frac{2.303}{t} \log \frac{(A)_0}{(A)_t}$$

Ans. (D)

## Question



Under the same reaction conditions, initial concentration of  $1.386 \text{ mol dm}^{-3}$  of a substance becomes half in 40 s and 20 s through first order and zero order kinetics respectively. Ratio  $\left(\frac{k_1}{k_0}\right)$  of the rate constants for first order ( $k_1$ ) and zero order ( $k_0$ ) of the reaction is [2008, 3M]

A  $0.5 \text{ mol}^{-1} \text{ dm}^3$

B  $1.0 \text{ mol dm}^{-3}$

C  $1.5 \text{ mol dm}^{-3}$

D  $2.0 \text{ mol}^{-1} \text{ dm}^3$

~~MW~~

Ans. (A)

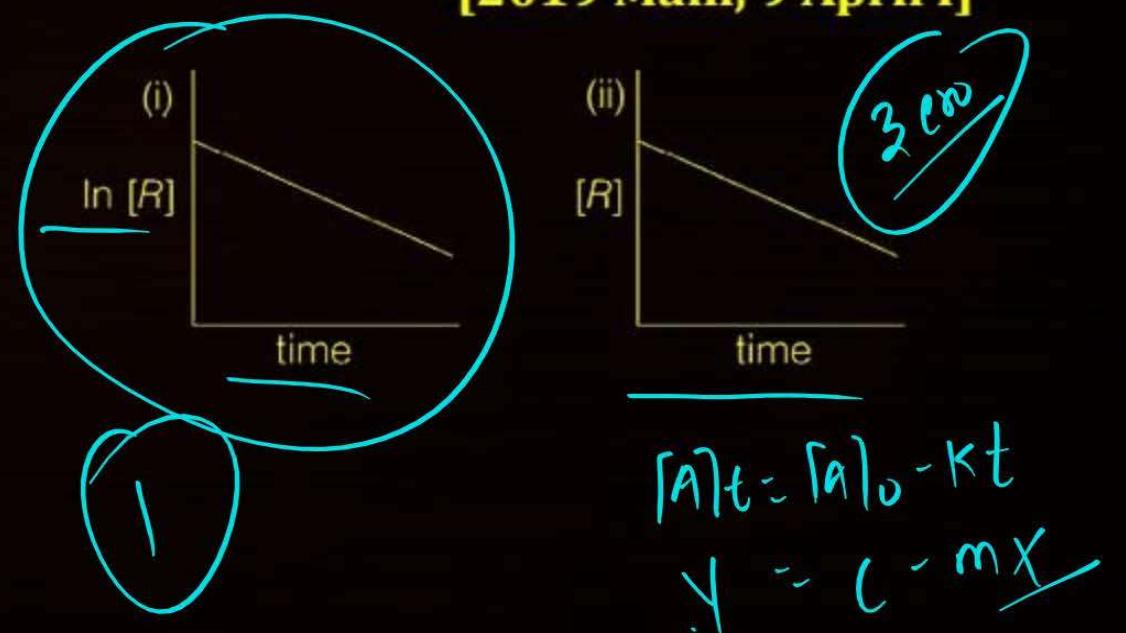
## Question



The given plots represent the variation of the concentration of a reaction R with time for two different reactions (i) and (ii). The respective orders of the reactions are:

[2019 Main, 9 April I]

- A 1, 1
- B 0, 2 ~~X~~
- C 0, 1 ~~X~~
- D 1, 0 ~~X~~



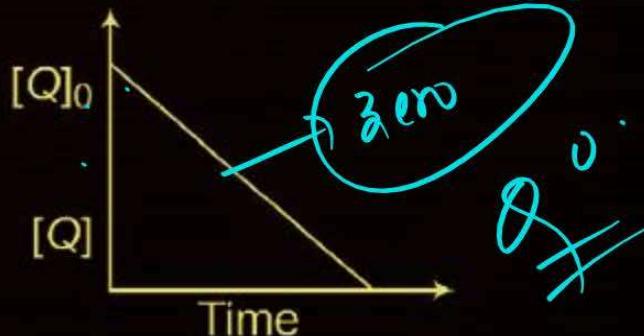
Ans. (D)

**Question***1st order*

In the reaction  $P + Q \rightarrow R + S$ , 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

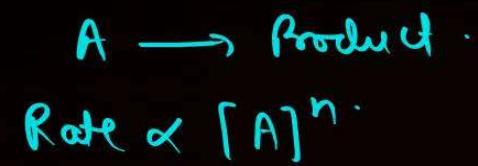
**A** 2

$$t_{75\%} = 2 \times t_{50\%}$$

**B** 3**C** 0**D** 1**[2013 Adv.]****Ans. (D)**



## N<sup>th</sup> Order Reaction



$$-\frac{d[A]}{dt} = K [A]^n$$

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

$n \geq 2$

$$K = \frac{1}{(n-1)t} \left[ \frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$$

$$t^{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

\*  $n=2$  (2<sup>nd</sup> order Rxn).

$$K = \frac{1}{t} \left[ \frac{1}{[A]_t} - \frac{1}{[A]_0} \right]$$

$$t^{1/2} \propto \frac{1}{[A]_0}$$

$n=3$  (3<sup>rd</sup> order Rxn).

$$K = \frac{1}{2t} \left[ \frac{1}{[A]_t^2} - \frac{1}{[A]_0^2} \right]$$

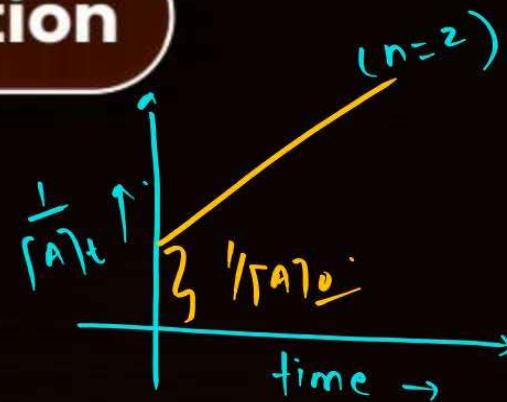
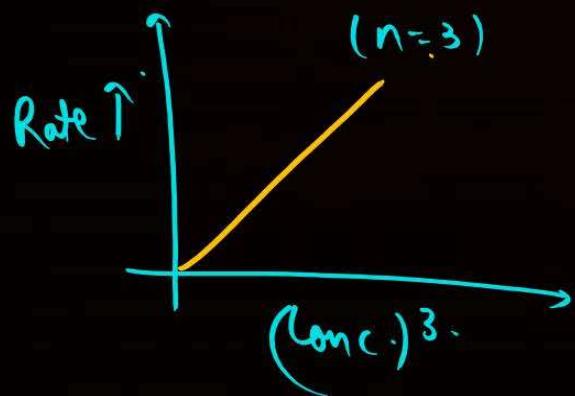
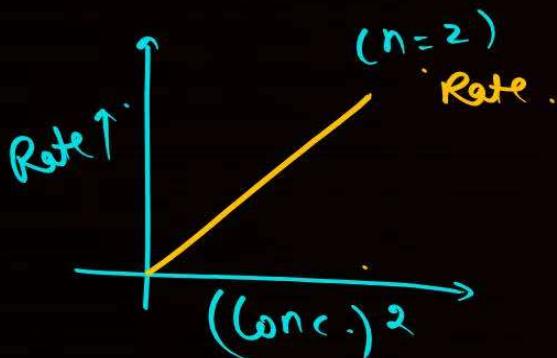
$$t^{1/2} \propto \frac{1}{[A]_0^2}$$





## N<sup>th</sup> Order Reaction

\* Graphical Representation:

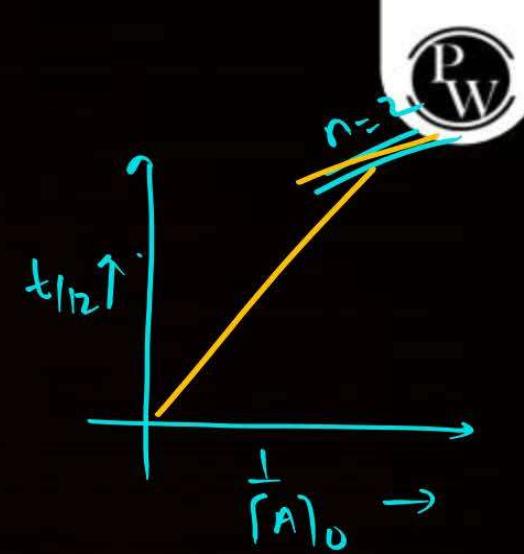


$$K = \frac{1}{t} \left( \frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} \right) \quad (n=2)$$

$$Kt = \frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0}$$

$$\left( \frac{1}{[\text{A}]_t} \right) = \left( \frac{1}{[\text{A}]_0} \right) + Kt$$

$$Y = C + mx$$



$$t_{1/2} \propto \frac{1}{[\text{A}]_0^{n-1}}$$

$$t_{1/2} \propto \frac{1}{[\text{A}]_0}$$



## Question

The half life of reaction was doubled when initial concentration was doubled. Find the order of reaction.

$$\text{Ans :- } t_{1/2} = \frac{a}{2k}$$

(Zero order Rxn)

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{([A]_0^{n-1})_2}{([A]_0^{n-1})_1}$$

## Question

Consider the following reactions



The order of the above reactions are (i), (ii), (iii), and (iv), respectively. The following graph is obtained when  $\log [\text{rate}]$  vs.  $\log [\text{conc.}]$  are plotted. Among the following, the correct sequence for the order of the reaction is:

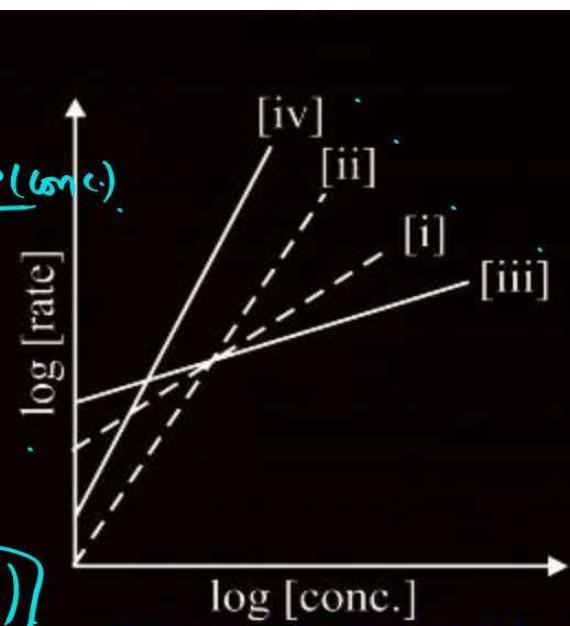
$$\text{Rate} \propto (\text{conc.})^n$$

$$\text{Rate} = k (\text{conc.})^n$$

$$\log(\text{Rate}) = \log k + n \log(\text{conc.})$$

$$Y = C + mx$$

$$\text{Slope} = n \text{ (order)}$$



[6 Sept (2020-I)]

- A** (iv) > (i) > (ii) > (iii)
- C** (iii) > (i) > (ii) > (iv)

- B** (i) > (ii) > (iii) > (iv)
- D** (iv) > (ii) > (i) > (iii)

Ans. (D)



## Numericals in Terms of Pressure

(1<sup>st</sup> order Rx).

A)  $\rightarrow$  Product . (1<sup>st</sup> order Rx).

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

$$K = \frac{2.303}{t} \log \left( \frac{P_0}{P(t)} \right) \xrightarrow{\text{Reactant}}$$



## Question



$A(g) \rightarrow B(g) + C(g)$  is a first order reaction.

Time	0	t
Partial pressure of A	$P_1$	$P_2$

Calculate rate constant for the reaction.

Ans :-

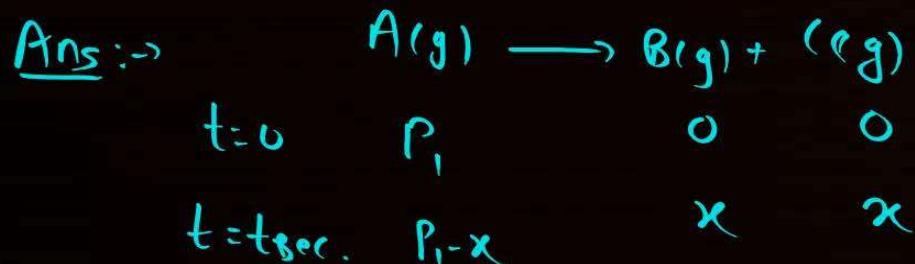
$$K = \frac{2.303}{t} \log\left(\frac{P_1}{P_2}\right)$$



**Question** $A(g) \rightarrow B(g) + C(g)$  is a first order reaction.

Time	0	t
Total pressure (A + B + C)	P <sub>1</sub>	P <sub>2</sub>

Calculate rate constant.



$$\text{Total pressure at time } t = P_1 - x + x + x \\ = P_1 + x = P_2$$

$$\underline{x = P_2 - P_1}$$

$$K = \frac{2.303}{t} \log \frac{P_1}{(P_1 - x)} \\ = \frac{2.303}{t} \log \frac{P_1}{P_1 - (P_2 - P_1)}$$

$$\underline{K = \frac{2.303}{t} \log \left( \frac{P_1}{2P_1 - P_2} \right)}.$$

## Question

$A(g) \rightarrow B(g) + C(g)$  is a first order reaction.



Time	t	$\infty$
Total pressure (A + B + C)	$P_2$	$P_3$

Calculate rate constant?

Ans :-

$$t=0$$



$$P_1$$

$$0$$

$$0$$

$$t=t$$

$$P_1 - x$$

$$x$$

$$x$$

$$t=\infty$$

$$0$$

$$P_1$$

$$P_1$$

$$\begin{aligned} P_3 &= 2P_1 \\ P_1 &= P_3/2 \end{aligned}$$

$$P_2 = (P_1 - x) + x + x$$

$$P_2 = P_1 + x$$

$$P_2 = \frac{P_3}{2} + x$$

$$x = P_2 - \frac{P_3}{2}$$

$$K = \frac{2.303}{t} \log \left( \frac{P_1}{P_1 - x} \right)$$

$$K = \frac{2.303}{t} \log \frac{P_3/2}{\frac{P_3}{2} - (P_2 - \frac{P_3}{2})}$$

$$K = 1$$

## Question



Decomposition of  $N_2O_5$  follows first order kinetics. After 30 minutes, the total pressure was found to be 284.5 mm Hg and on completion, total pressure was found to be 584.5 mm Hg. Calculate the rate constant for the reaction.

Ans:-



$t=0$	$P_1$	0	0
$t=t$	$P_1-x$	$2x$	$\frac{x}{2}$
$t=\infty$	0	$2P_1$	$\frac{P_1}{2}$

$$\text{Total Pressure at time } t \Rightarrow P_1 - x + 2x + \frac{x}{2} = 284.5$$

$$\Rightarrow P_1 + \frac{3x}{2} = 284.5$$

$x = ?$

$$2P_1 + \frac{P_1}{2} = 584.5$$

$$\frac{5P_1}{2} = 584.5$$

$$P_1 = ?$$

$$K = \frac{2.303}{t} \log \frac{P_1}{P_1 - x}$$

## Question



The reaction given below, involving the gases is observed to be first order with rate constant  $7.48 \times 10^{-3} \text{ sec}^{-1}$ . Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm.





# **Factors Affecting Rate of Reaction**



## Factors Affecting Rate of Reaction

### 1. Concentration of reactants:

$$\text{Rate of Rx} \propto (\text{Conc})^n$$

### 2. Exposure to light: (for photochemical Rx)

$$\text{Rate of Rx} \propto \text{Intensity of light}$$

### 3. Nature of reactants and products:

- Reactions which involve complex reactants and products occur at slow rate.



## Factors Affecting Rate of Reaction



### 1. Temperature:

- For most of the reactions, rate of reaction increases 2 or 3 times when the temperature is increased by 10 units.

$K_T$  → Rate Constant at temp.  $T$

$K_{T+10}$  :-  $\frac{\text{Rate at } T+10}{\text{Rate at } T} = u$

$$u = \frac{K_{T+10}}{K_T} \approx 2 \text{ or } 3$$

Temp. Coefficient.

$$\frac{K_{T_2}}{K_{T_1}} = u = e^{\frac{E_a}{R} \frac{1}{T_1} - \frac{1}{T_2}}$$

$K_{T_2}$  :- Rate Constant at temp.  $T_2$

$K_{T_1}$  :-

$\Delta T$  :-  $T_2 - T_1$



## Factors Affecting Rate of Reaction

- The dependence of rate constant on temperature is given by Arrhenius Equation.

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

Rate constant

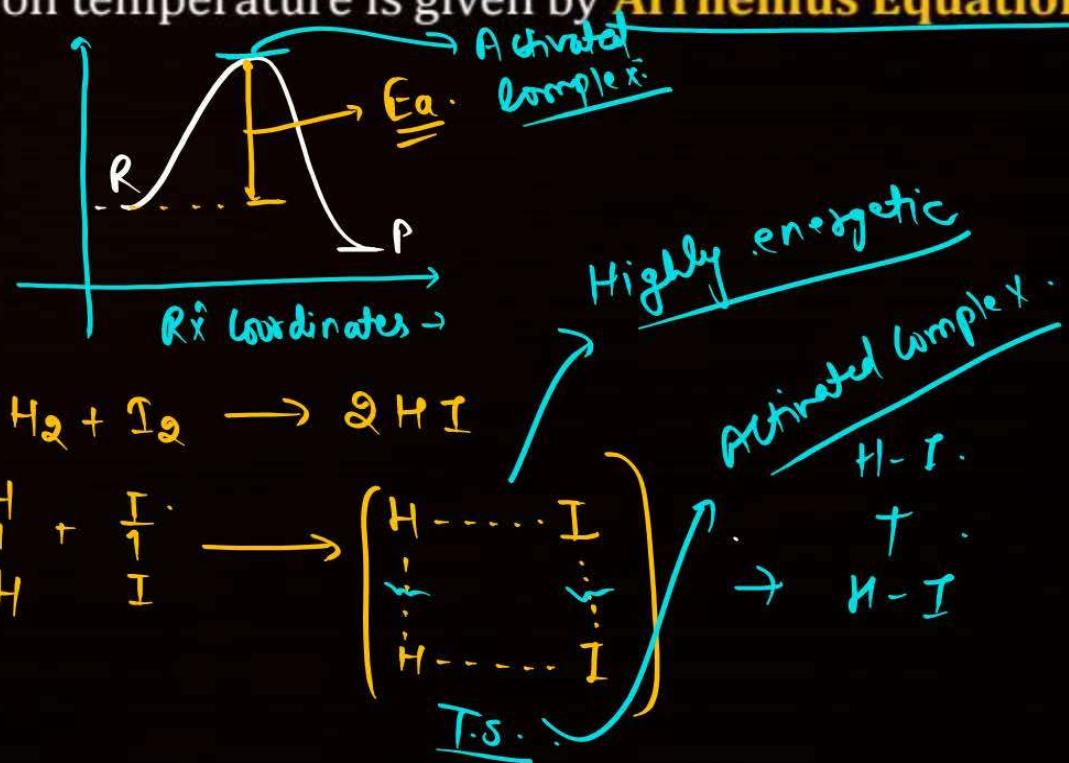
Arrhenius constant

or

Pre-exponential factor

$E_a$ : Activation energy.

T : Temp.



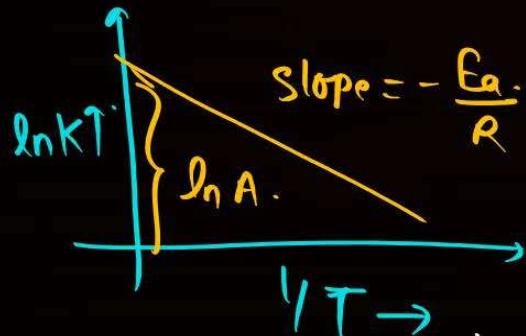


## Factors Affecting Rate of Reaction

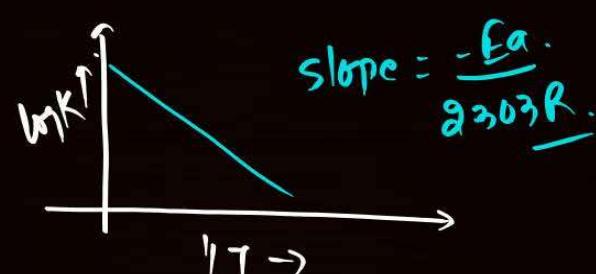
$$K = A e^{-\frac{E_a}{RT}}$$

$$\ln K = \ln \left( A e^{-\frac{E_a}{RT}} \right)$$

$$\frac{\ln K}{T} = \ln A - \frac{E_a}{R T}$$



$$\log K = \log A - \frac{E_a}{2.303R} \left[ \frac{1}{T} \right]$$



$$\log K_1 = \log A - \frac{E_a}{2.303R} \left( \frac{1}{T_1} \right)$$

$$\log K_2 = \log A - \frac{E_a}{2.303R} \left( \frac{1}{T_2} \right)$$

$$\log \left( \frac{K_2}{K_1} \right) = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$K_2$  : Rate constant at temp  $T_2$ .

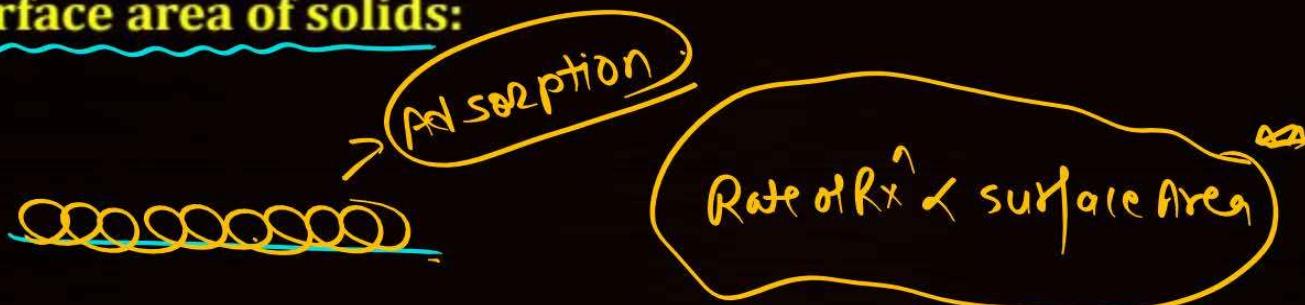
$K_1$  :-

$$T_2 > T_1$$



## Factors Affecting Rate of Reaction

### 5. Surface area of solids:





## Factors Affecting Rate of Reaction

### 6. Effect of Catalyst:

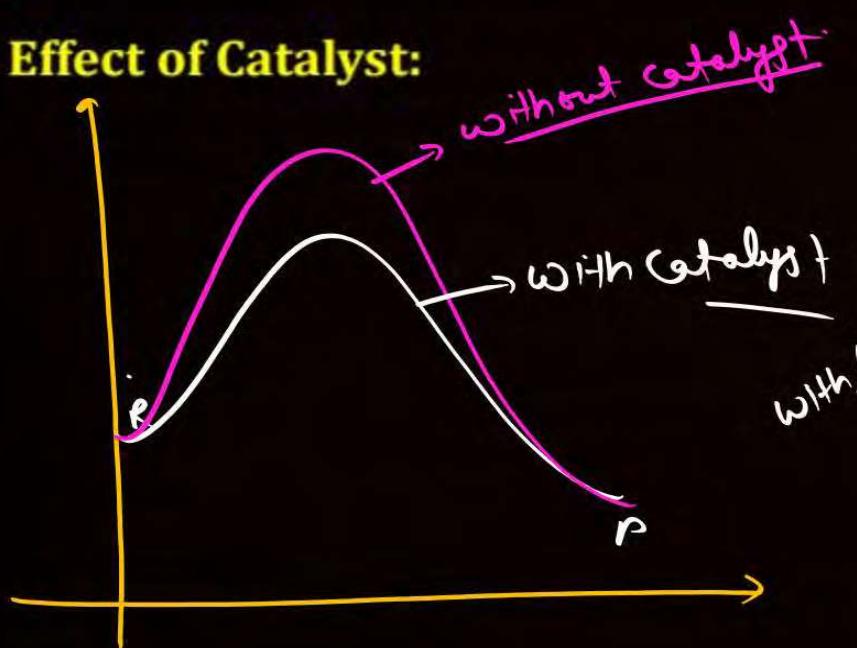
A substance that alters the rate of reaction without changing its mass and chemical composition, is known as catalyst.

- It does not alter Gibb's energy of reaction.
- It does not catalyse non spontaneous reaction.  $\Delta G = +ve$
- A small amount of catalyst can catalyse a large amount of reactants.
- It does not alter equilibrium state. It reduces the time to achieve the equilibrium state.
- It decreases the activation energy of the reaction.



## Factors Affecting Rate of Reaction

### 6. Effect of Catalyst:



$$E_a > E_{ac}$$

with catalyst.

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

$$(K_c) = A e^{-\frac{E_{ac}}{RT}}$$

$$\frac{K_c}{K} = e^{\frac{E_a - E_{ac}}{RT}}$$

$$\boxed{\frac{K_c}{K} = e^{\frac{\Delta E}{RT}}}$$

$$\log \left( \frac{K_c}{K} \right) = \frac{\Delta E}{2.303RT}$$

$$\Delta E = (E_a) - (E_a)_c$$

**Question**



$K_1$ .

At 1085 K, specific rate constant of a reaction is  $3.76 \times 10^3 \text{ min}^{-1}$ . At what temperature will it be  $1.16 \times 10^4 \text{ min}^{-1}$  if the activation energy is 68400 cal.

$\overline{K_2}$

$T_2 = ?$



The rate constants of the above reaction at 200 K and 300 K are  $0.03 \text{ min}^{-1}$  and  $0.05 \text{ min}^{-1}$  respectively. The activation energy for the reaction is \_\_\_\_ J  
 (Nearest Integer)

(Given:  $\ln 10 = 2.3$   
 $R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$

$$\log 5 = 0.70$$

$$\log 3 = 0.48$$

$$\log 2 = 0.30$$

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

$E_a = ?$



## Question

For the reaction  $A \rightarrow B$ , the rate constant  $k$ (in  $s^{-1}$ ) is given by

$$\log_{10} k = 20.35 - \frac{(2.47 \times 10^3)}{T}$$

The energy of activation in  $\text{kJ mol}^{-1}$  is \_\_\_\_\_. (Nearest integer)

[Given:  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ]

[31<sup>st</sup> Aug (2021)]

Ans.  $\log k = \log A - \frac{E_a}{2.303R} \left( \frac{1}{T} \right)$

$$\log A = 20.35$$

$$\frac{E_a}{2.303R} = 2.47 \times 10^3$$

$$2.303R \rightarrow 8.314$$

$$E_a = ?$$

Ans. (47)

## Question



The first order rate constant for the decomposition of  $\text{CaCO}_3$  at 700 K is  $6.36 \times 10^{-3} \text{ s}^{-1}$  and activation energy is 209 kJ mol $^{-1}$ . Its rate constant (in  $\text{s}^{-1}$ ) at 600 K is  $x \times 10^{-6}$ . The value of x is \_\_\_\_\_. (Nearest integer)  
[Given  $R = 8.31 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $\log 6.36 \times 10^{-3} = -2.19$ ,  $10^{-4.79} = 1.62 \times 10^{-5}$ ]

[27 Aug (2021)]



Ans. (16)

## Question



For the reaction of  $\text{H}_2$  with  $\text{I}_2$ , the rate constant is  $2.5 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $327^\circ\text{C}$  and  $1.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $527^\circ\text{C}$ . The activation energy for the reaction, in  $\text{kJ mol}^{-1}$  is ( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )

[2019 Main, 10 April II]

**A** 59



**B** 72

**C** 150

**D** 166

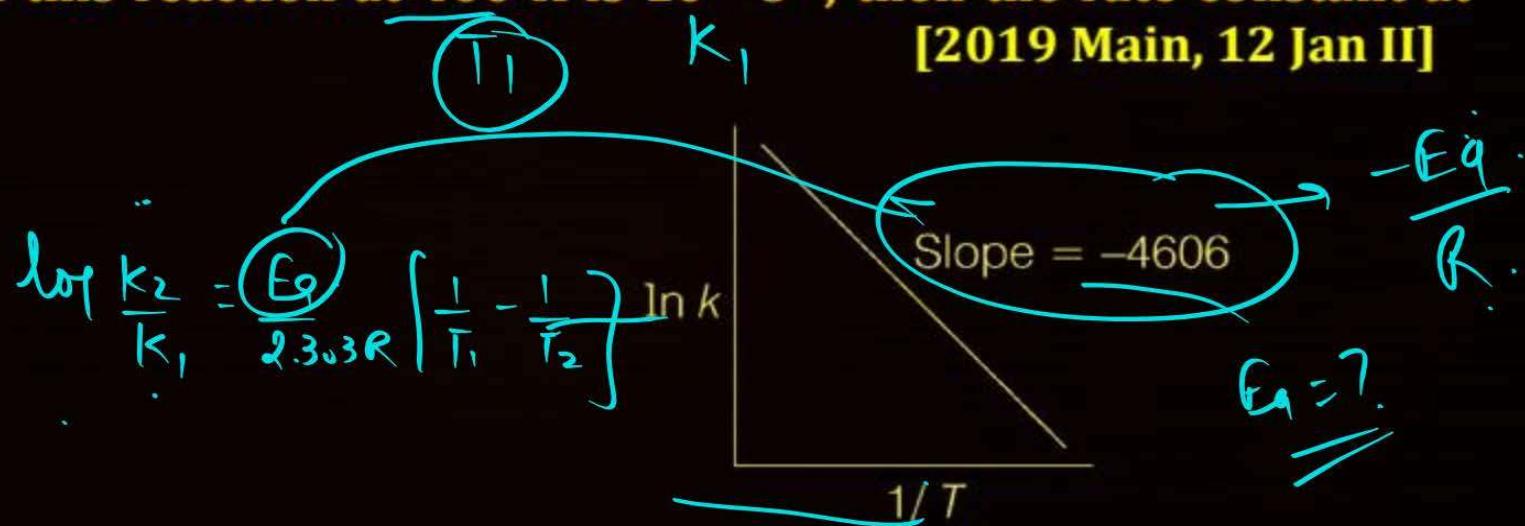
Ans. (D)

## Question

For a reaction, consider the plot of  $\ln k$  versus  $1/T$  given in the figure. If the rate constant of this reaction at 400 K is  $10^{-5} \text{ s}^{-1}$ , then the rate constant at 500 K is  $\boxed{12}$

[2019 Main, 12 Jan II]

- A**  $4 \times 10^{-4} \text{ s}^{-1}$
- B**  $10^{-6} \text{ s}^{-1}$
- C**  $10^{-4} \text{ s}^{-1}$
- D**  $2 \times 10^{-4} \text{ s}^{-1}$



Ans. (C)

**Question**

If a reaction follows the Arrhenius equation, the plot  $\ln k$  vs  $1/(RT)$  gives straight line with a gradient  $(-y)$  unit.

The energy required to activate the reactant is:

[2019 Main, 11 Jan I]

A  $\frac{y}{R}$  unit

B  $-y$  unit

C  $yR$  unit

D  $y$  unit

$$\ln K = \ln A - \frac{E_a}{RT}$$
$$Y = C - m(X)$$
$$m = -y$$
$$y = m$$

**Ans. (D)**

**Question**

Two reactions  $R_1$  and  $R_2$  have identical pre-exponential factors. Activation energy of  $R_1$  exceeds that of  $R_2$  by  $10 \text{ kJ mol}^{-1}$ . If  $k_1$  and  $k_2$  are rate constants for reaction  $R_1$  and  $R_2$ , respectively at  $300 \text{ K}$ , then

$$\ln\left(\frac{k_2}{k_1}\right) \text{ is equal to } (R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$$

[2017 Main]

- (A) 8
- (C) 6

- (B) 12
- (D) 4

$\hbar\omega$

**Ans. (D)**

## Question



The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be ( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $\log 2 = 0.301$ ) [2013 Main]

- A  $53.6 \text{ kJ mol}^{-1}$
- B  $48.6 \text{ kJ mol}^{-1}$
- C  $58.5 \text{ kJ mol}^{-1}$
- D  $60.5 \text{ kJ mol}^{-1}$

$$K_2 = 2K_1$$

$$E_a = ?$$

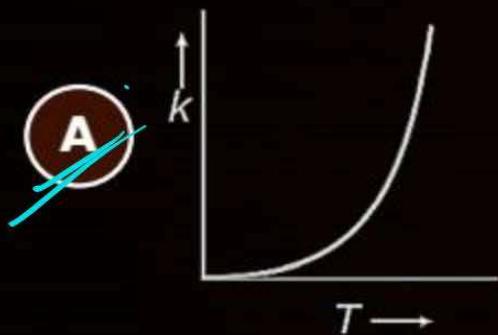
$$\log\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$E_a = ?$$

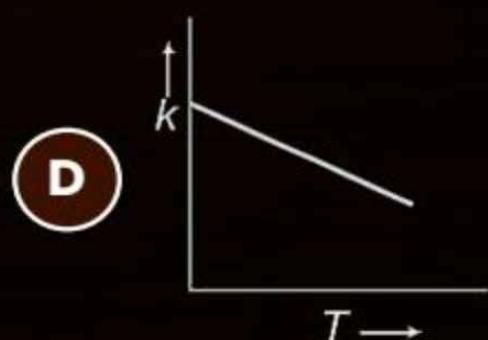
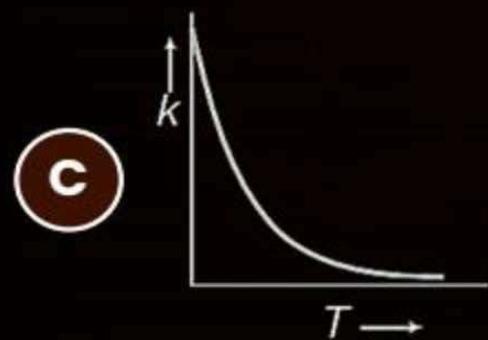
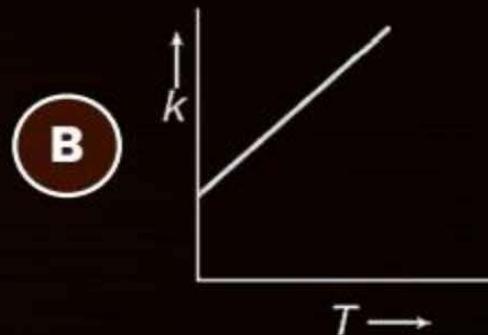
Ans. (A)

## Question

Plots showing the variation of the rate constant ( $k$ ) with temperature ( $T$ ) are given below. The plot that follows Arrhenius equation is [2010]



$$K = Ae^{-\frac{E_a}{RT}}$$



Ans. (A)

**Question**

For a first order reaction,  $A \rightarrow P$ , the temperature (T) dependent rate constant (k) was found to follow the equation:

$$\log k = \frac{2000}{T} + 6.0$$

the pre-exponential factor A and the activation energy  $E_a$ , respectively, are

[2009]

- A**  $1.0 \times 10^6 \text{ s}^{-1}$  and  $9.2 \text{ kJ mol}^{-1}$

Hω

- B**  $6.0 \text{ s}^{-1}$  and  $16.6 \text{ kJ mol}^{-1}$

- C**  $1.0 \times 10^6 \text{ s}^{-1}$  and  $16.6 \text{ kJ mol}^{-1}$

- D**  $1.0 \times 10^6 \text{ s}^{-1}$  and  $38.3 \text{ kJ mol}^{-1}$

**Ans. (D)**



# Collision Theory

10 mins

21:20 ✓

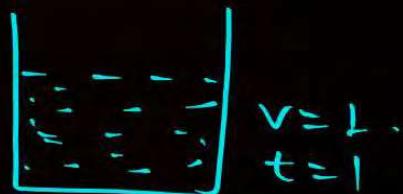


## Collision Theory



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

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



- Every collision does not bring a chemical change. The number of collisions with sufficient energy and proper orientation that actually produce the products , are called as **effective collisions.**



## Collision Theory



- For a collision to be effective the following two factors are to be cleared:

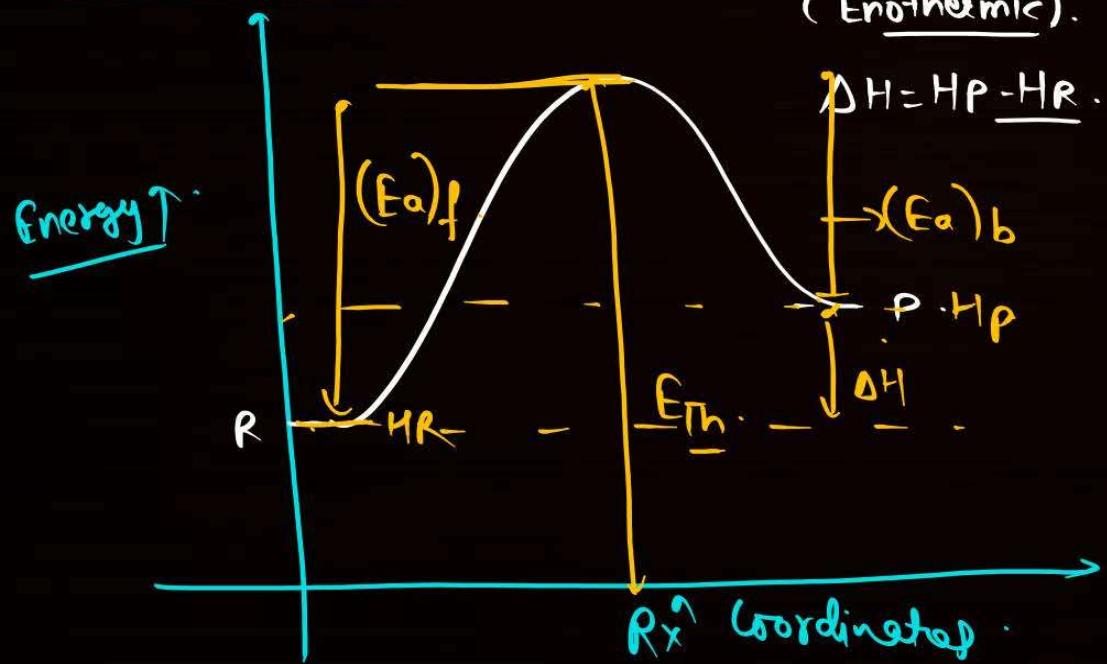
1. Energy Barrier ✓
2. Orientation Barrier ✓



## Collision Theory



### Energy Barrier:



$$\Delta H = +ve .$$

(Endothermic) .

$$\Delta H = H_P - H_R .$$

$$\Delta H = H_P - H_R .$$

$$E_{Th} = H_R + (E_a)_f .$$

$$= H_P + (E_a)_b .$$

$$\Delta H = (E_a)_f - (E_a)_b .$$





## Collision Theory



### Energy Barrier:

➤ **Activation Energy**: The minimum amount of energy required to make active participate (transition state).

**NOTE :** The activation energy depends on the nature of chemical bonds undergoing rupture and is independent of reactants and products.

➤ **Threshold Energy**: Minimum amount of energy which the colliding molecules must possess in order to make the chemical reaction to occur.

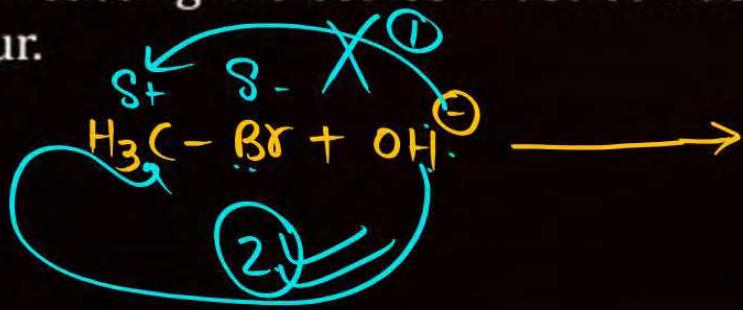


## Collision Theory



### Orientation Barrier:

- Energy alone does not determine the effectiveness of the collision.
- The reacting molecules must collide in proper manner if the reaction is to occur.



$$K = P \cdot Z \left( e^{-\frac{E_a}{RT}} \right)$$

collision frequency.

Steric factor  
(It considers orientation)

$$K = A \left( e^{-\frac{E_a}{RT}} \right)$$

$$A = P \cdot Z$$

$$P = \frac{A}{Z}$$

\*  $e^{-\frac{E_a}{RT}}$  :- fraction of molecules having Energy  $> E_a$ .

Unit of A = Unit of K

*order dependent*

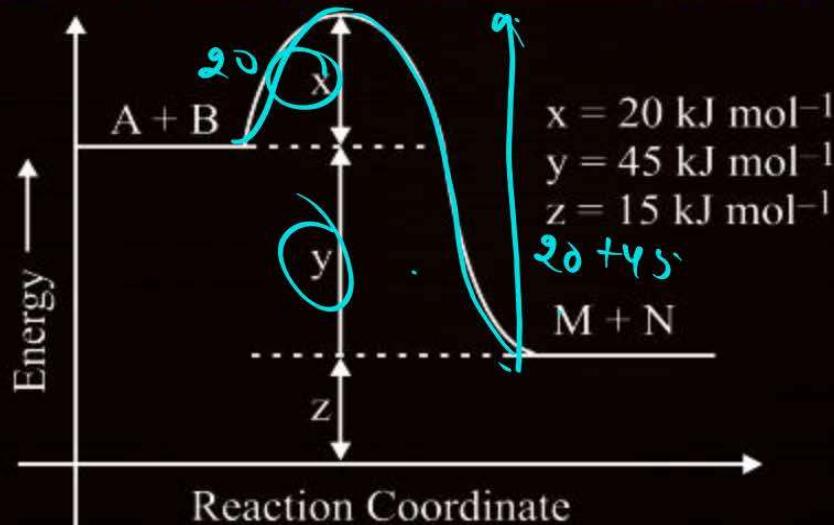


## Question



According to the following figure, the magnitude of the enthalpy change of the reaction  $\Delta H = ?$ .

$A + B \rightarrow M + N$  in  $\text{kJ mol}^{-1}$  is equal to \_\_\_\_\_. (Integer answer)



$$\begin{aligned}\Delta H &= (E_f) - (E_i) \\ &= \underline{\underline{45}}\end{aligned}$$

[31<sup>st</sup> Aug (2021)]

Ans. (45)

## Question



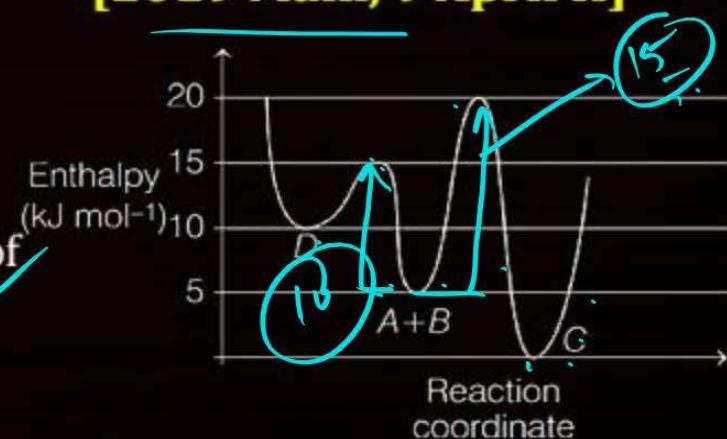
Consider the given plot of enthalpy of the following reaction between A and B.



Identify the incorrect statement.

- A D is kinetically stable product
- B Formation of A and B from C has highest enthalpy of activation
- C C is the thermodynamically stable product
- D Activation enthalpy to form C is 5 kJ mol<sup>-1</sup> less than that to form D.

[2019 Main, 9 April II]



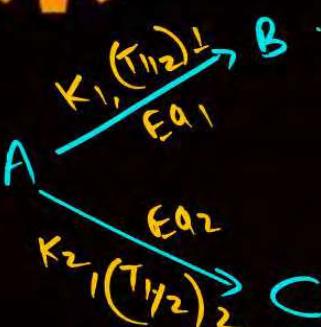
Ans. (D)



# First Order Parallel Reactions

Competing

## First Order Parallel Reactions



$$\text{Rate} = k_1[A]_t + k_2[A]_t$$

$$-\frac{d[A]}{dt} = \frac{(k_1 + k_2)}{K_{eff}} [A]_t$$

$$k_{eff} = k_1 + k_2$$

$$\frac{0.693}{(t_{1/2})_{eff}} = \frac{0.693}{(t_{1/2})_1} + \frac{0.693}{(t_{1/2})_2}$$

$$\frac{1}{(t_{1/2})_{eff}} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2}$$

$$At = A_0 e^{-kt}$$

$$[A]_t = [A]_0 e^{-(k_1 + k_2)t}$$

$$\frac{d[B]}{dt} = k_1 [A]_t = k_1 [A]_0 e^{-(k_1 + k_2)t}$$

$$[B]_t = \frac{k_1}{k_1 + k_2} [A]_0 \left[ 1 - e^{-(k_1 + k_2)t} \right]$$

$$[C]_t = \frac{k_2}{k_1 + k_2} [A]_0 \left[ 1 - e^{-(k_1 + k_2)t} \right].$$

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$



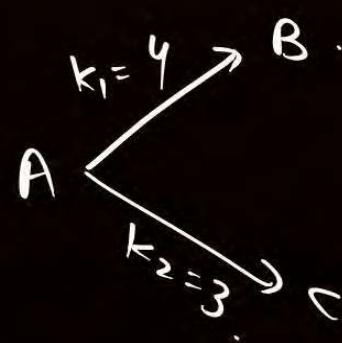
## First Order Parallel Reactions

$$\eta_0(B) = \left( \frac{k_1}{k_1+k_2} \right) \times 100\% .$$

$$\eta_0(C) = \left( \frac{k_2}{k_1+k_2} \right) \times 100\% .$$

$$\begin{aligned} &= [A]_0 - [A]_t \\ &= [A]_0 - [A]_0 e^{-(k_1+k_2)t} \\ &= [A]_0 \left[ 1 - e^{-(k_1+k_2)t} \right]. \end{aligned}$$

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$



$\eta_0$  distribution of B and C ?

$$\begin{aligned}\eta_0(B) &= \frac{4}{4+3} \times 100\% \\ \eta_0(C) &= \frac{3}{4+3} \times 100\%.\end{aligned}$$



# **First Order Sequential Reactions**



## First Order Sequential Reactions :



Rate of disappearance of A

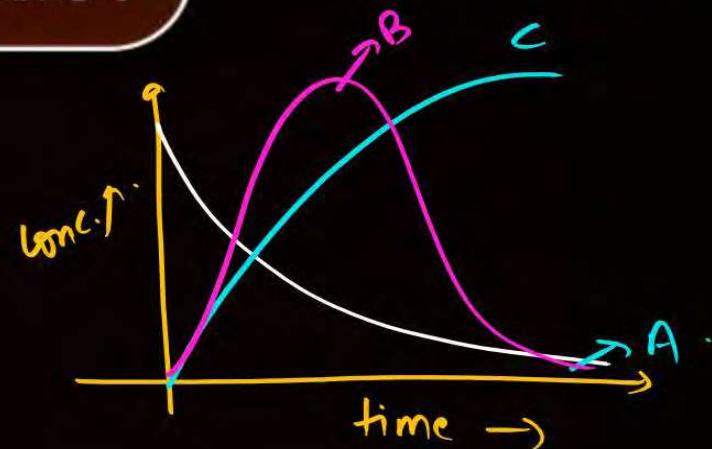
$$\left( -\frac{d[A]}{dt} \right) = k_1 [A]_t$$

Rate of appearance of C

$$\frac{d[C]}{dt} = k_2 [B]_t$$

Rate of disappearance of B

$$\frac{d[B]}{dt} = \underline{k_1 [A]_t - k_2 [B]_t}$$



## Question



For a reaction scheme,  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ , if the rate of formation of B is set to be zero then the concentration of B is given by [2019 Main, 8 April II]

**A**  $k_1 k_2 [A]$

**B**  $\left(\frac{k_1}{k_2}\right) [A]$

**C**  $(k_1 - k_2)[A]$

**D**  $(k_1 + k_2)[A]$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] = 0$$

$$k_1[A] = k_2[B]$$

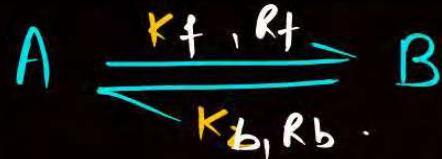
$$[B] = \frac{k_1}{k_2} [A]$$



# **First Order Reversible Reactions**



## First Order Reversible Reactions:



$$R_f \propto [A]$$

$$R_f = k_f [A]$$

$$R_b \propto [B]$$

$$R_b = k_b [B]$$

$$\text{Overall Rate} = R_f - R_b$$

$$\text{Rate.} = k_f [A] - k_b [B]$$

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$



$$R_f \propto [A] \Rightarrow R_f = k_f [A]$$

$$R_b \propto [B]^2 \Rightarrow R_b = k_b [B]^2$$

$$\text{Rate} = R_f - R_b$$

$$\text{Rate.} = k_f [A] - k_b [B]^2$$

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

Rate.

[2019 Main, 10 Shift III]



For an elementary chemical reaction,  $A_2 \xrightleftharpoons[k_{-1}]{k_1} 2A$ , the expression for  $\frac{d[A]}{dt}$  is

**A**

$$2k_1[A_2] - k_{-1}[A]^2$$

**C**

$$2k_1[A_2] - 2k_{-1}[A]^2$$

**B**

$$k_1[A_2] - k_{-1}[A]^2$$

**D**

$$k_1[A_2] + k_{-1}[A]^2$$

**Ans. [C]**