

# Chemical Kinetics

## Chemical Kinetics :-

It deals with the rate of chemical reaction & the mechanism by which the chemical reaction take place:

5 mole of substance A are present in 10 L container.

$$\begin{aligned}\text{Concentration of A} &= \text{Molar concentration of A} \\ &= \text{Molar of A} = \text{Active mass of} \\ &= [A] = \frac{5 \text{ mol}}{10} = 0.5 \text{ (M)}\end{aligned}$$

Molarity of substance =

$$\frac{\text{Moles of substance}}{\text{Volume of container in L}}$$



At  $t=0$  5m      0m

After 10sec (5-2)m      2m

= 3m

$r_A$  = rate of disappearance of A

$r_B$  is rate of formation of B

$$r_A = - \left( \frac{3-5}{10} \right) \text{ms}^{-1} = \frac{2}{10} \text{ms}^{-1}$$

$$r_A = \frac{-\Delta[A]}{\Delta t}$$

$$r_B = \frac{2-0}{10} \text{ms}^{-1} = \frac{2}{10} \text{ms}^{-1}$$

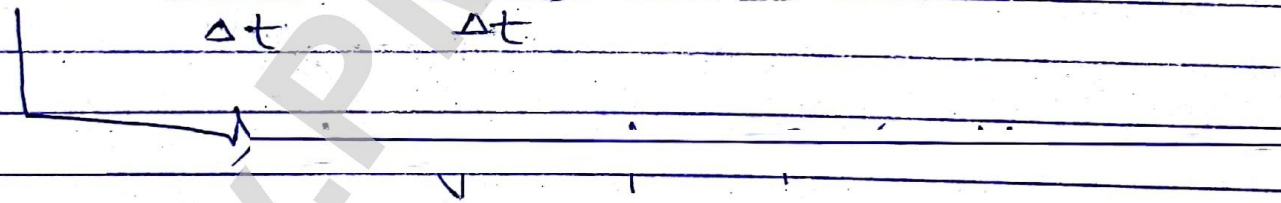
$$r_B = \frac{\Delta[B]}{\Delta t}$$

$$r_A = r_B$$

$$r_A = r_B$$

$$\frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

$$r_{av} = \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$



Rate is always positive





$$\text{At } t=0 \quad 8 \text{ m} \quad 0 \text{ m}$$

$$20 \text{ sec} \quad (8-2) \text{ m} \quad 4 \text{ m}$$

$$= 6$$

$$r_A = -\left(\frac{6-8}{20}\right) \text{ ms}^{-1} = \frac{2}{10} \text{ ms}^{-1}$$

$$r_A = -\frac{\Delta[A]}{\Delta t}$$

$$r_B = \frac{4-0}{20} \text{ ms}^{-1} = \frac{4}{20} \text{ ms}^{-1}$$

$$r_B = \frac{\Delta[B]}{\Delta t}$$

$$r_B = 2 \times r_A$$

$$r_B = \frac{4}{20} \text{ ms}^{-1} = 2 \times \frac{2}{20} \text{ ms}^{-1}$$

$$r_B = 2 \times r_A$$

$$r_A = \frac{1}{2} r_B$$

$$-\frac{1}{1} \frac{\Delta[A]}{\Delta t} = \frac{1}{2} \frac{\Delta[B]}{\Delta t}$$

$$r_{AV} = -\frac{1}{1} \frac{\Delta[A]}{\Delta t} = \frac{2}{20} \text{ ms}^{-1}$$

$$r_{AV} = \frac{1}{2} \times \frac{\Delta[B]}{\Delta t} = \frac{1}{2} \times \frac{4}{20} \text{ ms}^{-1}$$

$$r_{AV} = \frac{2}{20} \text{ ms}^{-1}$$

A  $\longrightarrow$  6B

At  $t=0$  5m 0m

20 sec (5-2)m 12m

$$r_A = \frac{-\Delta[A]}{\Delta t} = -\frac{(3-5)}{20} \text{ ms}^{-1}$$

$$r_B = \frac{\Delta[B]}{\Delta t} = \frac{12-0}{20} \text{ ms}^{-1}$$

$$r_B = 6 \times r_A$$

$$r_B = \frac{12}{20} \text{ ms}^{-1} = 6 \times \frac{2}{20} \text{ ms}^{-1}$$

$$r_B = 6 \times r_A$$

$$r_A = \frac{1}{6} \times r_B$$

$$\frac{-\Delta[A]}{\Delta t} = \frac{1}{6} \times \frac{\Delta[B]}{\Delta t}$$

$$r_{av} = -\frac{1}{1} \frac{\Delta[A]}{\Delta t} = -\frac{1}{6} \frac{\Delta[B]}{\Delta t}$$



For the reaction



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

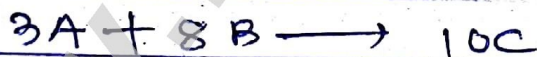
Q. Choose the correct option for the reaction



average rate of reaction can be expressed by

(a)  $-\frac{\Delta[A]}{\Delta t}$  (b)  $-\frac{\Delta[B]}{\Delta t}$  (c)  $\frac{1}{c} \frac{\Delta[C]}{\Delta t}$  (d) None

for the reaction



$$r_{av} = -\frac{1}{3} \frac{\Delta[A]}{\Delta t} = -\frac{1}{8} \frac{\Delta[B]}{\Delta t} = \frac{1}{10} \frac{\Delta[C]}{\Delta t}$$

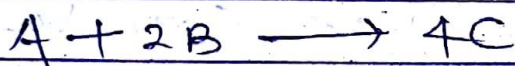
Choose the correct option



$r_{\text{av}}$  can be expressed by

(a)  $-\frac{\Delta[\text{H}_2]}{\Delta t}$  (b)  $\frac{\Delta[\text{NH}_3]}{\Delta t}$

✓ (c)  $-\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t}$  (d) None



$$r_{\text{A}} = 3.2 \times 10^{-2} \text{ ms}^{-1}$$

$$r_{\text{B}} = 2 \times r_{\text{A}}$$

$$r_{\text{B}} = 2 \times r_{\text{A}}$$

$$r_{\text{B}} = 2 \times 3.2 \times 10^{-2} \text{ ms}^{-1}$$

$$r_{\text{C}} = 4 \times r_{\text{A}}$$

$$r_{\text{C}} = 4 \times r_{\text{A}}$$

$$r_{\text{C}} = 4 \times 3.2 \times 10^{-2} \text{ ms}^{-1}$$



Q. For the reaction



$$r_A = 5 \times 10^{-2} \text{ ms}^{-1}$$

$$r_B = 2 \times r_A$$

$$= 2 \times 5 \times 10^{-2} \text{ ms}^{-1}$$

$$r_C = 5 \times r_A$$

$$= 5 \times 5 \times 10^{-2} \text{ ms}^{-1}$$

$$r_D = 10 \times r_A$$

$$= 10 \times 5 \times 10^{-2} \text{ ms}^{-1}$$



$$r_B = 8 \times 10^{-2} \text{ ms}^{-1}$$

$$r_A = \frac{4}{12} \times r_B$$

Q. For the reaction



$$r_A = -\frac{\Delta[A]}{\Delta t} = 4 \times 10^{-2} \text{ ms}^{-1}$$

$$r_{av} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t}$$

$$= \frac{1}{2} \times 4 \times 10^{-2} \text{ ms}^{-1}$$

$$= 2 \times 10^{-2} \text{ ms}^{-1}$$



$$r_{AV} = 3 \times 10^{-2} \text{ ms}^{-1}$$

$$r_B = -\frac{\Delta[B]}{\Delta t} = ?$$

$$r_{AV} = -\frac{1}{4} \frac{\Delta[A]}{\Delta t} = -\frac{1}{12} \frac{\Delta[B]}{\Delta t}$$

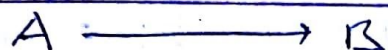
$$r_{AV} = -\frac{1}{12} \frac{\Delta[B]}{\Delta t}$$

$$3 \times 10^{-2} = -\frac{1}{12} \cdot \frac{\Delta[B]}{\Delta t}$$

$$-\frac{\Delta[B]}{\Delta t} = 12 \times 3 \times 10^{-2} \text{ ms}^{-1}$$



## Instantaneous Rate



$$r_{\text{inst}} = \lim_{\Delta t \rightarrow 0} \frac{-\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}$$

$$r_{\text{inst}} = \lim_{\Delta t \rightarrow 0} \frac{\Delta[B]}{\Delta t} = \frac{d[B]}{dt}$$

for the reaction



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

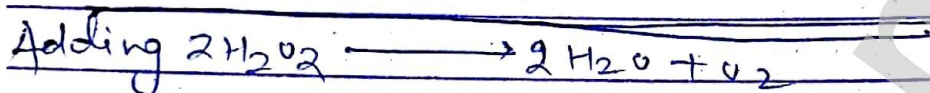
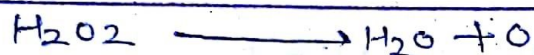
## Simple reaction

The reaction which takes place in one step is called simple reaction.



## Complex reaction

The reaction which take place in two or more steps is called complex reaction.



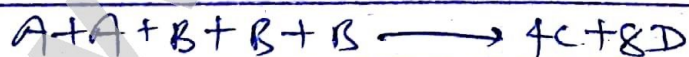
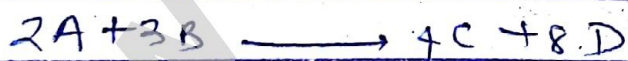
## Law of mass action

This law was given by Guldberg & Wage.

for the reaction,



$$r \propto [A]^a [B]^b$$





$$r \propto [A]$$

$$r \propto [A]$$

$$r \propto [B]$$

$$r \propto [B]$$

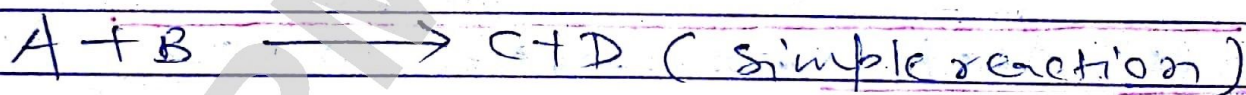
$$r \propto [B]$$

$$r \propto [A] \times [A] \times [B] \times [B] \times [B]$$

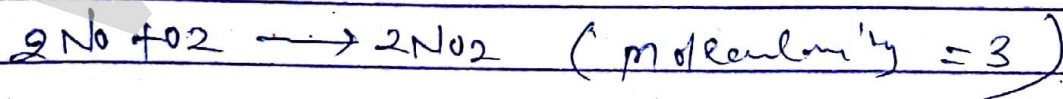
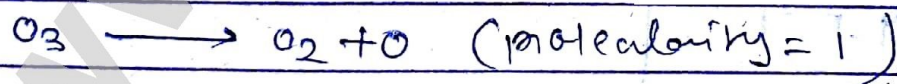
$$r \propto [A]^2 [B]^3$$

### Molecularity of Simple reaction

molecularity of simple reaction is equal to sum of no. of molecules of reactants involved in balanced stoichiometric equation.



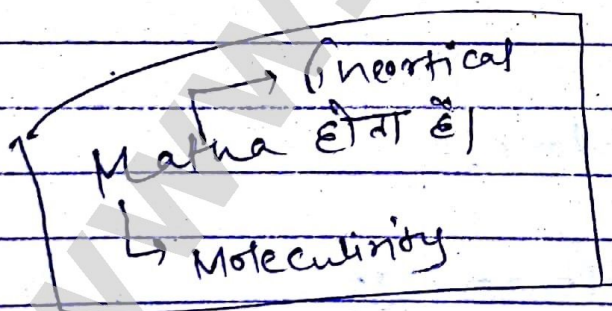
$$\begin{aligned} \text{molecularity} &= 1 + 1 \\ &= 2 \end{aligned}$$





## Important Points

- (i) Molecularity is a theoretical concept.
- (ii) molecularity can not be negative, zero, fractional, infinite and imaginary.
- (iii) Molecularity cannot be greater than three (3) because more than three molecules may not mutually collide with each other.
- (iv) The concept of molecularity has no significance in case of complex reaction, because in case of complex reaction, each step involve has its own molecularity.





## Order of reaction

order of reaction is defined as the no. of molecules whose concentrations determine the rates of a chemical reaction.

for the reaction



$$r = k[A]^l \times [B]^m$$

$l$  is order of reaction with respect to A.

$m$  is order of reaction with respect to B.

$$\boxed{\text{Order of reaction} = l + m}$$

$k$  is known as rate constant.

$k$  is also called specific rate constant.

By experimental observation

$[H_2O_2]$

Rate

$xM$

$x'$

$2xM$

$2x'$

According to experimental observation



So, order of reaction = 1

\*\*

Slow step rate determining  
step because reaction  
spends most of its  
time in slow type.



VVI



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

$$K[A]^x[B]^y$$

$$-\frac{d[A]}{dt} = a \times r$$

$$\frac{d[C]}{dt} = c \times r$$

$$-\frac{d[B]}{dt} = b \times r$$

$$\frac{d[D]}{dt} = d \times r$$

Important points

(i) order of reaction is an experimentally determined quantity.

(ii) order of reaction can be 0, negative and fractional.

Infinite & imaginary values are not possible.

## Units of rate constants

$$r = K[A]^n \quad (n \text{ is order of reaction})$$

$$K = \frac{r}{[A]^n}$$

$$\text{Unit of } K = \frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})^n}$$

$$= \frac{\text{mol}^{1-n} \text{ s}^{-1}}{\text{L}^{1-n}}$$

$$\boxed{\text{Unit of } K = \text{mol}^{1-n} \text{ L}^{n-1} \text{ s}^{-1}}$$

→ for Zero order reaction

$$n = 0$$

$$\text{Unit of } K = \text{mol L}^{-1} \text{ s}^{-1}$$

→ for 1st order rxn.

$$\text{Unit of } K = \text{s}^{-1}$$



→ for 2nd order reaction

$$n = 2$$

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

→ for 3rd order reaction

$$n = 3$$

$$\text{Unit of } k = \text{mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

for Zero order reaction

$$r = k [A]^0$$

$$r = k$$

with change in concentration of A rate remains unchanged for Zero order reaction.

for 1st order

$$r = k[A]^1$$

initial concentration of A =  $[A]_0 = a \text{ M}$

$$r_1 = k \times a \quad (r_1 \text{ is initial rate})$$

concentration of A becomes  $n$  times

$$r_n = k \times na = n \times k \times a$$

$$r_n = n \times r_1$$

for first order reaction if  
concentration of A becomes  $n$   
times, rate also becomes  $n$  times.

for 2nd order reaction

$$r = k[A]^2$$

$$[A]_0 = a \text{ M}$$

$$r_1 = k \times a^2$$

suppose concentration of A becomes  
 $n$  times

$$r_n = k \times (na)^2 = n^2 \times k \times a^2$$

$$r_n = n^2 \times r_1$$



for 2nd order reaction when concentration of A becomes  $n$  times, rate becomes  $n^2$  times

Problem:- For a gaseous reaction

$A_2 + 2B \rightarrow 2AB$ , then following rate data were obtained at 300K.

$[A_2]$	$[B]$	Rate of disappearance of $A_2$
0.1 M	0.01	$1.5 \times 10^{-3} \text{ ms}^{-1}$
0.1 M	0.04	$6 \times 10^{-3} \text{ ms}^{-1}$
0.2 M	0.01	$5 \times 10^{-3} \text{ ms}^{-1}$

$$r = [A]^1 [B]^2$$

$$= 3$$

$$H_2 = 3$$

Key concept:-

Concentration change rate unchanged



Zero order  $r_k$

Concentration become  $n$  times, rate also become  $n$  times.



1st order  $r_k$

Concentration  $n$  times rate become  $n^2$  times.

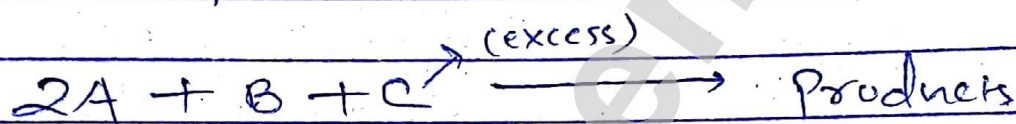


2nd order  $r_k$

## Very Important Reaction

order of reaction with respect to a reactant which is in excess is "Zero"

Problem:- for the reaction



Calculate

(a) rate law equation

(b) effect on rate if concentration of A is doubled & B is tripled

$$r = k[A]^2[B]^1[C]^0$$

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