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 10L container.

Concentration of A = Molar concentration of A
= Molar of A = Active mass of
= $[A] = \frac{5}{10}$ molL^{-1} = 0.5(M)

Molarity of substance =

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

$$A \longrightarrow B$$

At t=0   5m   0m

After 10sec   (5-2)m   2m

= 3M

r_A = rate of dispperance of A
r_B is rate of formation of B

www.PMTmentor.com

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

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

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

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

$$r_A = r_B$$

$$r_A = r_B$$

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

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

Rate is always positive

www.PMTmentor.com

$$A \longrightarrow 2B$$

At t=0 $\quad 8\,m \qquad 0\,m$

20 sec $\quad (8-2)\,m \qquad 4\,m$

$= 6$

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

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

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

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

$$r_B = 2 \times r_A$$

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

$$r_B = 2 \times r_A$$

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

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

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

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

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

www.PMTmentor.com

$$A \longrightarrow 6B$$

At $t=0$ $5m$ $0m$

$20 sec$ $(5-2)m$ $12m$

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

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

$$r_B = 6 \times r_A$$

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

$$r_B = 6 \times r_A$$

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

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

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

www.PMTmentor.com

For the reaction

$aA + bB \longrightarrow cC + dD$

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

Q. Choose the Correct option for the reaction

$aA + bB \longrightarrow cC + dD$

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

$3A + 8B \longrightarrow 10C$

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

www.PMTmentor.com

Choose the correct option

$N_2 + 3H_2 \longrightarrow 2NH_3$

rav. Can be expressed by

(a) $\frac{-\Delta[H_2]}{\Delta t}$ (b) $\frac{\Delta[NH_3]}{\Delta t}$

(c) $\frac{-1}{3}\left[\frac{\Delta[H_2]}{\Delta t}\right]$ (d) None

$A + 2B \longrightarrow 4C$

$r_A = 3.2 \times 10^{-2}\ ms^{-1}$

$r_B = 2 \times r_A$

$r_B = 2 \times r_A$

$r_B = 2 \times 3.2 \times 10^{-2}\ ms^{-1}$

$r_C = 4 r_A$

$r_C = 4 \times r_A$

$r_C = 4 \times 32 \times 10^{-2}\ ms^{-1}$

www.PMTmentor.com

Q. For the reaction

$$4A + 8B \longrightarrow 20C + 40D$$

$rA = 5\times10^{-2}\ ms^{-1}$

$rB = 2\times\ rA$

$= 2\times5\times10^{-2}\ ms^{-1}$

$rC = 5\times rA$

$= 5\times\ 5\times10^{-2}\ Ms^{-1}$

$rD = 10\times rA$

$= 10\times5\times10^{-2}\ ms^{-1}$

Q. $4A + 12B \longrightarrow 16C$

$rB = 8\times10^{-2}\ ms^{-1}$

$rA = \frac{4}{12}\times rA$

Q. For the reaction

$$2A + 6B \longrightarrow 8C$$

$rA = -\frac{\Delta[A]}{\Delta t} = 4\times10^{-2}\ ms^{-1}$

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

$= \frac{1}{2}\times4\times10^{-2}\ ms^{-1}$

$= 2\times10^{-2}\ ms^{-1}$

www.PMTmentor.com

$4A + 12B \longrightarrow 16C$

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

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

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

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

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

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

www.PMTmentor.com

Instantaneous rate

$$A \longrightarrow B$$

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

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

for the reaction

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

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

Simple reaction

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

$$O_3 \longrightarrow O_2 + O$$

www.PMTmentor.com

Complex reaction

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

$H_2O_2 \longrightarrow H_2O + O$

$H_2O_2 + O \longrightarrow H_2O + O_2$

Adding $2H_2O_2 \longrightarrow 2H_2O + O_2$

Law of mass action

This law was given by Guldberge & Wage.

for the reaction.

$aA + bB \longrightarrow cC + dD$

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

$2A + 3B \longrightarrow 4C + 8D$

$A + A + B + B + B \longrightarrow 4C + 8D$

www.PMTmentor.com

www.PMTmentor.com

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

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

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

Molecularity of simple reaction

Molecularity of simple reaction is equal to sum of no. of molecules of reactents involved in balanced stoichimetric equation.

$A + B \longrightarrow C + D$ (simple reaction)

Molecularity = 1+1
= 2

$O_3 \longrightarrow O_2 + O$ (molecularity = 1)

$O + O_3 \longrightarrow 2O_2$ (molecularity = 2)

$2NO + O_2 \longrightarrow 2NO_2$ (molecularity = 3)

www.PMTmentor.com

Important Points

(i) Molecularity is a theoretical concept.

(ii) Molecularity can not be negative, Zero, Fractional, infinite and imaginary.

(iii) Molecularity Can not 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 stage involve has its own molecularity.

Theortical
Matha होता है।
Molecularity

www.PMTmentor.com

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

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

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

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.

www.PMTmentor.com

By experimental observation

$[H_2O_2]$	Rate
xM	r'
$2x$M	$2r'$

According to experimental observation

$$H_2O_2 \longrightarrow H_2O + O \quad [\text{slow}]$$

$$H_2O_2 + O \longrightarrow H_2O + O_2 \quad (\text{fast})$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

So, order of reaction = 1

** slow step rate determining step because reaction spends most of it's time in slow type.

www.PMTmentor.com

VVI

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

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

$$K[A]^{l} \times [B]^{m}$$

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

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

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.

www.PMTmentor.com

Units of rate constants

$r = K[A]^n$ (n is order of reaction)

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

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

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

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

→ for Zero order reaction

$n = 0$

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

→ for 1st order rK.

Unit of K = s^{-1}

www.PMTmentor.com

→ for 2nd order reaction

$n = 2$

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

→ for 3rd order rxn

$n = 3$

unit of K = $mol^{-2}\ L^{2}\ s^{-1}$

for concept.

for Zero order reaction

$r = k[A]^0$

$r = K$

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

www.PMTmentor.com

for 1st order

$r = K[A]^1$

initial concentration of $A = [A]_0 = aM$

$r_1 = K \times a$ (r_1 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

$r = K[A]^2$

$[A]_0 = aM$

$r_1 = K \times a^2$

suppose concentration of A becomes n times

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

~~$r_n = n^2 r_1$~~

www.PMTmentor.com

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

Problem:- For a gaseous reaction

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

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

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

$= 3$ $H_2 = 3$

Key concept:-

For concepts

Concentration change rate unchanged → zero order rxn

concentration become n time, rate also become n times. → 1st order rxn

Concentration n time rate become n^2 times. → 2nd order rxn

www.PMTmentor.com

Very Important reaction

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

Problem:- for the reaction

$$2A + B + C \xrightarrow{(\text{excess})} \text{Products}$$

Calculate

(a) rate law equation

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

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

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

www.PMTmentor.com