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Rate of reaction.

In unit times, decrease in concentration of reactants or increase in concentration of product is called rate of a reaction

$$\text{Rate of a reaction} = \frac{\text{change in concentration}}{\text{Time}}$$

$$= \frac{x}{t}$$

But a rate of reaction is not uniform as time passes, the concentration of reactant decreases and hence according to law of mass action, rate of reaction decreases with time.

At any instant, rate of reaction $= \frac{dx}{dt}$

When dx is small change in concentration in small time interval.

Reaction $A + B \longrightarrow C + D$

Reactants (A + B), products (C + D)

Rate of reaction =

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[C]}{dt} = +\frac{d[D]}{dt}$$

$-\frac{d}{dt}$ rate decreases and

$+\frac{d}{dt}$ rate increases

Let us consider,

$$aA + bB \longrightarrow \text{Product}$$

and let the rate ~~is~~ law of this reaction be given as

$$\text{Rate} \propto [A]^a \times [B]^b$$

$$\text{order of } rx^n = a + b$$

MOLECULARITY :

Molecularity of a reaction is the number of molecules involved in the reaction ~~or~~

or

the number of molecules required for its reaction to take place.

Thus, when only one molecule is involved in the reaction which is known as unimolecular reaction.

Example:-

(i) Decomposition of H_2O_2 (Hydrogen peroxide)

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$$

(ii) Dissociation of Bromine molecules into atoms

$$Br_2 \longrightarrow 2 Br$$

{order = 1st with respect to ~~water~~ ester and order = 0 (zero) with respect to water } because rate of reaction depends upon concentration of one molecule only.

Mathematically, it can be proved from Law of mass action.

$$\text{Rate} \propto [\text{Ester}][\text{water}]$$

$$= k[\text{Ester}][\text{water}]$$

where k = rate constant

Since [water] = constant

$$\text{Rate} = k'[\text{ester}], \quad k' = k \cdot [\text{water}] = \text{a new const.}$$

Hence, $\text{Rate} \propto [\text{ester}]$ ---- (i)

order = 1

The above reaction is called pseudo unimolecular rxn and k is called pseudo rate const.

~~The order of reaction wa~~

"The number of molecules of this reaction whose concentration determine the rate of chemical reaction is called the order of reaction or

The sum of power of concentration terms appearing in the experimentally rate data is called the order of chemical reaction.

Rate of reaction is affected by following factors

(i) Ionic reaction are very fast

$$H^+Cl^- + Ag^+NO_3^- \rightarrow AgCl\downarrow + HNO_3$$

(ii) concⁿ of reactants (

(iii) Temperature → Rate of rxⁿ decrease double or triple when tempʳ raises to 10°c

(iv) Presence of catalyst

(v) Light

Order of Reaction :

The total number of molecules, atoms or ions of the reactants whose concⁿ alters as a result of chemical change is called order of reaction

e.g. Hydrolysis of ester in presence of acid (HCl)

$$\underset{\text{Ester (ethyl acetate)}}{CH_3COOC_2H_5} + H_2O \xrightarrow[\text{acid}]{H^+} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

Although, the above reaction is bimolecular it behaves kinetically as that of First order

Second Order of the reaction.

It is that type of a reaction in which the rate of a chemical reaction is directly proportional to the double power of the concentration of the reactant.

>>> Second order reaction are of two types –

(i) When the initial concn of reactants are same

(ii) when the initial concn of reactants are different.

(i) When the initial concentration of reactants are same.

$$A + B \longrightarrow \text{Product}$$

Let the initial concn of the reactants A and B be a gm mole per litre and after time t second, its x gm mole per litre is decomposed. Hence in equilibrium, the concn of A and B will be (a-x) gm mole per litre

Now according to the law of mass action

$$\frac{dx}{dt} \propto (a-x)^2$$

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

where k is the rate constant for second order reaction, when the initial concn of the reactants are same.

· upon rearranging:–

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

on Integrating both sides, we have

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

or, $$\frac{1}{a-x} = kt + C \quad ------ (i)$$

where C is integration constant

When $t=0$, $x=0$

Thus from equ^n- (i)

$$\frac{1}{a} = C$$

Put the value of C in equ^n (i)

$$\frac{1}{(a-x)} = kt + \frac{1}{a}$$

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

or $$kt = \frac{a-a+x}{a(a-x)}$$

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

or $$k = \frac{1}{t} \times \frac{x}{a(a-x)} \quad ------ (ii)$$

This expression (ii) gives the value of rate constant for second order reaction when the initial conc^n of reactants are same.

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(ii) When the initial concn of the reactants are different :-

Let us consider a reaction takes place according to the following equation(i)

$$A + B \longrightarrow \text{Product} \quad (1)$$

Initial	a	b	0
After time t	(a-x)	(b-x)	after time 't' second sec

Let the initial concn of A be a gm mole per litre and that of B be 'b' gm mole per litre. After time t second its x gm mole per litre is decomposed, hence in equilibrium the concn of A and B will be (a-x) gm mole per litre and (b-x) gm mole per litre respectively.

According to Law of mass action,

$$\frac{dx}{dt} \propto (a-x)(b-x)$$

or, $$\frac{dx}{dt} = K(a-x)(b-x) \quad \ldots (ii)$$

Where K is the rate constant for second order reaction when the initial concn of reactants are different.

Upon rearranging of eqn (ii)

$$\frac{dx}{(a-x)(b-x)} = K\,dt \quad \text{———} (iii)$$

Integrating both sides

$$\int \frac{dx}{(a-x)(b-x)} = K\int dt \quad \ldots (iv)$$

$$= K.t + C \quad \ldots (ii)$$

This eqn (iv) gives the value of rate constant for second order reaction when the initial concn of reactants are different.

Half Life Period of Second Order rxn when the initial concn is the same.

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

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

When $t = t_{1/2}$ then $x = \frac{a}{2}$

Therefore,

$$t_{1/2} = \frac{1}{k} \times \frac{a/2}{a(a-a/2)}$$

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

$$= \frac{1}{k} \times \frac{1}{a}$$

$$t_{1/2} \propto \frac{1}{a}$$

Half life period of 2nd order rxn when the initial concn to be same are inversely proportional to the initial concn of reactants.

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

Thus from equ^n. (ii),

$$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = kt + C \quad \text{------ (iii)}$$

where C = integration constant.

When $t=0$, $x=0$

Thus from equ^n. (iii), we get

$$\frac{1}{(a-b)} \ln \frac{a}{b} = C$$

or, $$C = \frac{1}{(a-b)} \ln \frac{a}{b}$$

Put the value of C in equ^n. (iii), we get

$$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = kt + \frac{1}{(a-b)} \ln \frac{a}{b}$$

~~or, $\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)}$ [illegible] $\frac{1}{(a-b)} \ln \frac{a}{}$~~

$$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} - \frac{1}{(a-b)} \ln \frac{a}{b} = kt$$

or, $$kt = \frac{1}{(a-b)} \left[\ln \frac{(a-x)}{(b-x)} - \ln \frac{a}{b} \right]$$

or $$kt = \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

or $$\boxed{k = \frac{1}{t} \times \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)}} \quad \text{--- (iv)}$$

$$\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)}$$

or, $$\frac{1}{(a-x)(b-x)} = \frac{A(b-x)+B(a-x)}{(a-x)(b-x)}$$

$$\therefore \quad A(b-x) + B(a-x) = 1$$

When $x = a$, then $A(b-a) = 1$

$$\therefore \quad A = \frac{1}{(b-a)}$$

When $x = b$, then $B(a-b) = 1$

$$\therefore \quad B = \frac{1}{(a-b)}$$

$$\therefore \int \frac{dx}{(a-x)(b-x)} = \int \frac{A\,dx}{(a-x)} + \int \frac{B\,dx}{(b-x)}$$

Put the value of A and B

$$\int \frac{dx}{(a-x)(b-x)} = \int \frac{dx}{(b-a)(a-x)} + \int \frac{dx}{(a-b)(b-x)}$$

$$= \frac{1}{(b-a)} \int \frac{dx}{(a-x)} + \frac{1}{(a-b)} \int \frac{dx}{b-x}$$

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

$$= +\frac{1}{(a-b)} \ln(a-x) - \frac{1}{(a-b)} \ln(b-x)$$

$$= \frac{1}{(a-b)} \left[\ln(a-x) - \ln(b-x)\right]$$