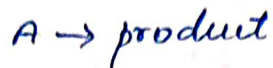


First order reaction :

A reaction whose rate depends on the reactant concentration raised to the first power is called a first order reaction. Let us consider the following first order reaction.



Rate law can be expressed as

$$\text{Rate} = k[A]^1$$

where  $k$  is the first order rate constant.

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

$$-\frac{d[A]}{[A]} = k dt \quad \text{--- (1)}$$

Integrate the above equation between the limits of time  $t=0$  and time equal to  $t_1$  while the concentration varies from the ~~for~~ initial concentration  $[A_0]$  to  $[A]$  at the later time

$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]} = k \int_0^t dt$$

$$[-\ln [A]]_{[A_0]}^{[A]} = k(t)_0^t$$

$$-\ln [A] - (-\ln [A_0]) = k(t-0)$$

$$-\ln [A] + \ln [A_0] = kt$$

$$\ln \left( \frac{[A_0]}{[A]} \right) = kt \quad \text{--- (2)}$$

This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303

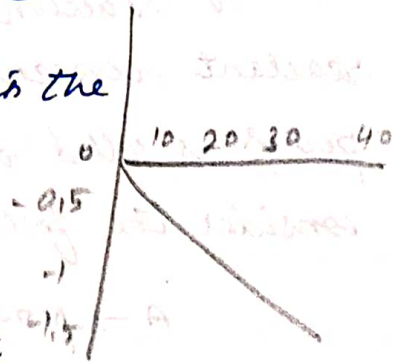
$$2.303 \log \left( \frac{[A_0]}{[A]} \right) = kt$$

$$k = \frac{2.303}{t} \log \left( \frac{[A_0]}{[A]} \right) \quad \text{--- (2)}$$

eq (2) can be written in the form  $y = mx + c$

$$\ln [A_0] - \ln [A] = kt$$

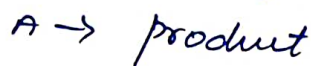
$$\ln [A] = \ln [A_0] - kt$$



If we follow the reaction by measuring the concentration of the reactant at regular time interval 'A' a plot of  $\ln [A]$  against 't' yields a straight line with a negative slope. From this the rate constant is calculated.

Zeroth Order Reaction:

A reaction in which the rate is independent of the concentration of the reactant "over a wide range of concentration. Is called as zero order reaction. Such reactions are rare. Let us consider the following hypothetical zero order reaction



The rate law can be written as

$$\text{Rate} = k[A]^0$$

$$-\frac{d[A]}{dt} = k(1) \quad [\because [A]^0 = 1]$$

$$\Rightarrow -d[A] = k dt$$

Integrate the above equation between the limits of  $[A_0]$  at zero time and  $[A]$  at some later time 't'

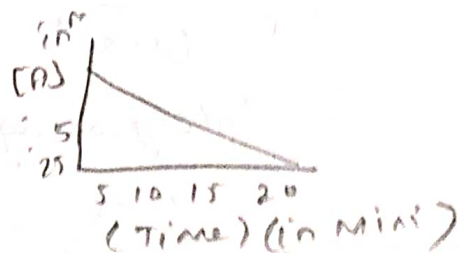
$$-\int_{[A^0]}^{[A]} d[A] = k \int_0^t dt$$

$$-\frac{[A] - [A^0]}{[A^0]} = k(t) \frac{[A] - [A^0]}{[A^0]}$$

$$-[A] - [A^0] = kt$$

$$[A^0] - [A] = kt$$

$$k = \frac{[A^0] - [A]}{t}$$



Let us calculate the half 'life' period for a zero order reaction.

$$\text{Rate constant } k = \frac{[A^0] - [A]}{t}$$

at  $t = t_{1/2}$   $[A] = [A^0]_{1/2}$

$$k = \frac{[A^0] - [A^0]_{1/2}}{t_{1/2}}$$

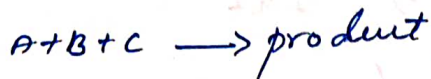
$$k = \frac{[A^0]}{2t_{1/2}}$$

$$t_{1/2} = \frac{[A^0]}{2k}$$

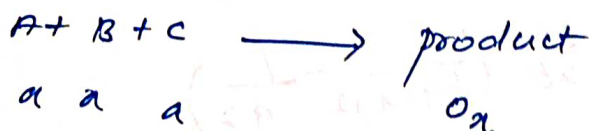
Hence in contrast to the half life of a first order reaction the half life of a zero order reaction is directly proportional to the initial concentration of the reactant.

Third order Reaction:

Rate of the reaction is determined by the variation of 3 concentration of all the reactants are same.



$$\text{Rate} = k [A]^1 [B]^1 [C]^1$$



$$(a-x)(a-x)(a-x)$$

$$\text{Rate} = k [A]^1 [B]^1 [C]^1$$

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

$$\boxed{\frac{dx}{dt} = k(a-x)^3} \quad \text{--- ①}$$

$$\frac{dx}{(a-x)^3} = k dt \quad \text{--- ②}$$

Integrating on both side

$$\int \frac{dx}{(a-x)^3} = k \int dt$$

$$\frac{1}{2(a-x)^2} = kt + c \quad \text{--- ③}$$

$$t=0, x=0$$

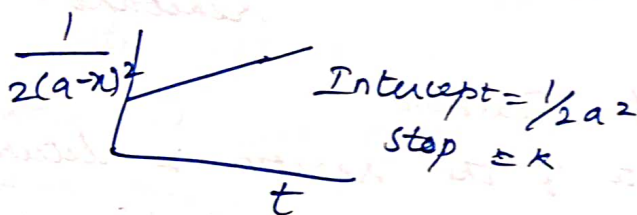
$$\frac{1}{2(a-0)^2} = k(0) + c$$

$$\frac{1}{2a^2} = c$$

Substitute in equation ③

$$\frac{1}{2(a-x)^2} = kt + \frac{1}{2a^2} \quad \text{--- ④}$$

$$y = mx + c$$



$$kt = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$$

$$k = \frac{1}{t} \left( \frac{1}{2(a-x)^2} - \frac{1}{2a^2} \right)$$

$$k = \frac{1}{2t} \left( \frac{1}{(a-x)^2} - \frac{1}{a^2} \right)$$

$$k = \frac{1}{2t} \left( \frac{x(2a-x)}{a^2(a-x)^2} \right)$$

Third order reaction rate expression.

## Order of a reaction:

"The order of a reaction is defined as the sum of the powers of concentrations in the rate law." Let us consider the example of a reaction which has the rate law

$$\text{rate} = k[A]^m[B]^n$$

The order of such a reaction is  $(m+n)$

The order of a reaction can also be depended with respect to the single reactant. Thus the reaction order with respect to A is  $m$  and with respect to B it is  $n$ . The overall order of reaction  $(m+n)$  may range from 1 to 3 and can be fractional

Rate law	Reaction order
----------	----------------

$\text{rate} = k[N_2O_5]$	1
---------------------------	---

$\text{rate} = k[H_2][I_2]$	$1+1=2$
-----------------------------	---------

$\text{rate} = k[NO_2]^2$	2
---------------------------	---

$\text{rate} = k[H_2][NO]^2$	$1+2=3$
------------------------------	---------

$\text{rate} = k[CHCl_3][Cl_2]^{1/2}$	$1+1/2=1\frac{1}{2}$
---------------------------------------	----------------------

$m+n=1$ , it is first order reaction

$m+n=2$ , it is second order reaction

$m+n=3$ , it is third order reaction.

## Order of a reaction

## Molecularity of a reaction

1. It is the sum of powers of the concentration of the terms in the rate law expression

It is number of reacting species undergoing simultaneous collision in the elementary or simple reactions.

2. It is an experimentally determined value

It is a theoretical concept

3. It can have fractional value

It is always a whole number.

4. It can assume zero value

It can not have zero value.

5. Order of a reaction can change with the concentration such as pressure temperature concentration.

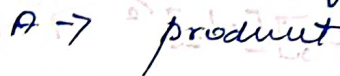
Molecularity is invariant for a chemical equation.

Rate law of Second order reaction:

Second order reaction can be defined as chemical reaction where in the sum of the exponents in corresponding rate law of the chemical reaction is equal to two. The rate of such a reaction can be written either as

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

Consider the following equation



Rate can be expressed as

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

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

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

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

$$\int_a^b \frac{-d[A]}{[A]^2} = k \int_0^t dt$$

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

$$k = \frac{1}{t} \left[ \frac{1}{a-x} - \frac{1}{a} \right]$$

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

Half life time: The half life is inversely proportional to the concentration of the reactant

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

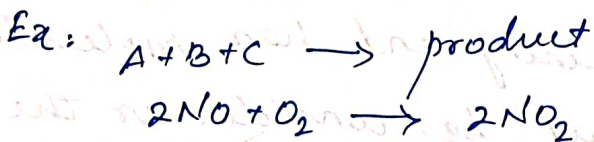
Molecularity:

The number of reactant molecules involved in a reaction is known as molecularity. Chemical reactions may be classified into two types.

i) Elementary reaction

ii) complex reaction.

i) An elementary reaction is a simple reaction which occurs in a single step.



The molecularity of the above reaction is 3, thus the sum of the number of reactant molecules involved in the reaction.

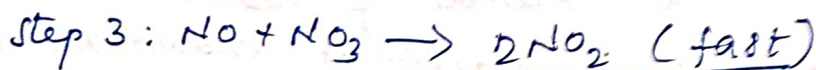
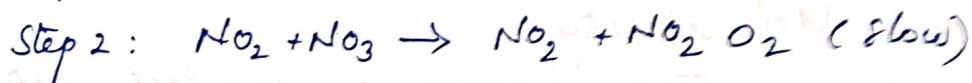
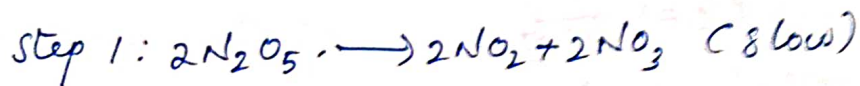
ii) Most chemical reactions are complex reactions. They occur in a series of steps.

Each step is an elementary reaction. The stepwise sequence of elementary reactions that convert reactants to products is called the mechanism of the reaction. In any mechanism, some of the steps will be fast

others will be slow. Thus the slowest step is the rate determining step of the reaction Ex:

The Decomposition of  $N_2O_5$

$2N_2O_5 \rightarrow 4NO_2 + O_2$  is an example of complex reaction. It occurs by the following steps.



The molecularity of above reaction is the number of molecules or atoms taking part in the rate determining step.

Thus step 2: in the above mechanism is rate-determining and has molecularity '2' which could be considered as the molecularity of the decomposition reaction of  $N_2O_5$ .

Polarimetry:

In measuring optical rotation plane-polarized light travels down a long tube containing the sample. If it is a liquid, the sample may be placed in the tube as a pure liquid. Usually the sample is dissolved in a solvent and the



resulting solution is placed in the tube.

In summary:

$$[\alpha]_p^t = \frac{\alpha}{c \times l}$$

\*  $\alpha$  is the measured optical rotation  
\*  $c$  is the sample concentration in grams per deciliter ( $1 \text{ dl} = 10 \text{ ml}$ )

\* That is  $c = m/v$  (mass in g = m, volume in dl)

\*  $l$  is the cell length in decimeters ( $1 \text{ dm} = 10 \text{ cm} = 100 \text{ mm}$ )

\* The square brackets means the optical rotation has been corrected for these variables.

Methods for Determination of <sup>Order</sup> area of reaction

1. Integration method using characteristic equation:

(In this method the initial concentration of all the reactant taking part are determined) (The concentration of the reacting substance at different intervals of time are also determined) (Thus different values of  $x$  are determined these values are then substituted in the different) which gives the most constant value of velocity constant for a series of interval of time will give the order of the reaction.

As this method involves the trial different equation it is usually called the hit and trail method.

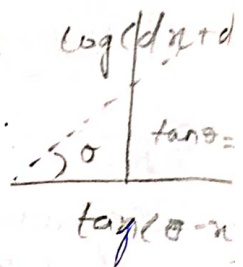
### Limitation:

1. This method can be used for simple reactions only and not for complex reaction.
2. In this method the reaction should be studied over wide time interval.

### 2. Differential method (Vant' Hoff)

We know that  $(dx/dt) = k(a-x)^n$ . Taking logarithm on both sides  $\log(dx/dt) = \log k + n \log(a-x)$ . A graph is drawn with  $\log(dx/dt)$  against  $\log(a-x)$  (that is the graph is drawn with the logarithm of concentration). A curve as shown in figure is obtained.

The slope of the curve is found. The slope gives the order of the reaction.

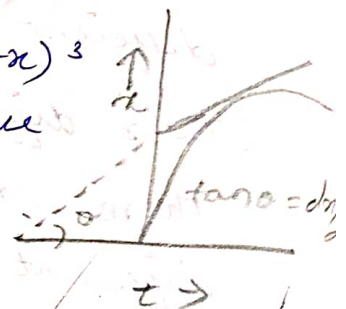


### B. Graphical methods:

As we have seen earlier the velocity of a first order reaction  $(dx/dt) = k(a-x)$ , a second order reaction  $(dx/dt) = k(a-x)^2$  and a third order reaction  $(dx/dt) = k(a-x)^3$ .

In general for an  $n$ th order one

$$(dx/dt) = k(a-x)^n$$



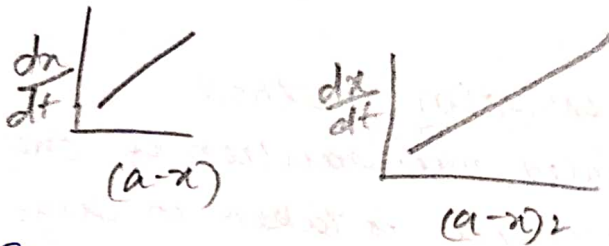
### To find $(dx/dt)$ :

The value of  $(dx/dt)$  at different intervals of time can be determined by plotting a curve between the amount of the substance decomposed and time  $t$ .

The nature of the curve obtained is shown in figure. The slope of the curve gives the value of  $(dx/dt)$ . Slope is nothing but  $\tan \theta$  value.

### Determination of order:

The various value of  $(dx/dt)$  thus obtained are plotted against the corresponding concentration  $[(a-x)$  or  $(a-x)^2$  or  $(a-x)^3]$



If a straight line is obtained by plotting  $(dx/dt)$  against  $(a-x)$  as shown figure. the reaction is first order. If a straight  $(dx/dt)$  against  $(a-x)^2$  as shown in figure the reaction is second order so on.

### 4. Half life method:

(we have already seen that the time required for the completion of half the reaction is independent of initial concentration for a first order reaction) (It is inversely proportional to the concentration for a second order reaction) (It is inversely proportional to the square of the concentration for a third order reaction) (In general the time required for half the change in any order is inversely proportional to the initial concentration raised to the power which is one less than the order of the reaction)

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

(where  $n$  is the order) thus if  $t_1$  and  $t_2$  are the time intervals for half change of a particular reaction (where the initial concentrations are  $a_1$  and  $a_2$  then)

$$\frac{t_1}{t_2} = \left[ \frac{a_2}{a_1} \right]^{n-1}$$

Since all the quantities except  $n$  are known - the order of the reaction can be calculated.

### Ostwald's isolation method:

He pointed out isolation of one of the reacting substances is taken in large excess so concentration does not change appreciably. It can be taken as constant. All reactions except one are taken in large excess and the order of the reaction is determined by any one of the above methods. The process is repeated with each of the reactants in turn. The sum of all these gives the total order of the reaction.

### Advantage:

The mode of action of each component can be determined separately and disturbing factors can be traced to the origin.

1. photochemical reaction between hydrogen and chlorine to form hydrogen chloride.
2. Thermal decomposition of  $H_2$  on a gold surface.
2. Some enzyme catalyzed reactions.

### CHARACTERISTICS:

#### Zero order reaction:

↳ The rate of the reaction does not depend on any concentration term. i.e. the concentration term of the reactants do not change with time.

↳ The sum of the powers of the concentration terms that occur in the rate equation is zero.

↳ The half-life period of a zero order reaction is directly proportional to the initial concentration of the reactant.

### First order reaction:

↳ The rate of the reaction depends of one concentration term only

↳ The rate of the reaction is proportional to the concentration of the reactants

↳ The sum of the powers of the concentration terms that occur in the rate equation is one

↳ The rate constant  $k$  will be independent of the units in which the concentration of the reactant is expressed.

↳ The half-life period of a first order reaction is independent of the initial concentration of the reactant.

### Second order reaction:

↳ The rate of the reaction depends on two concentration terms.

↳ The sum of the powers of the concentration terms that occur in the rate equation is two

↳ The half-life period of a second order reaction is inversely proportional to the initial concentration of the reactant.

## Theories of Reaction Rates:

The ultimate goal of theoretical chem. kinetics is the calculation of the rate of any reaction from a knowledge of the fundamental properties of the reacting molecules; properties such as the mass, diameter, moment of inertia, vibrational frequencies, binding energies and so on. Two approaches are given, here for this purpose.

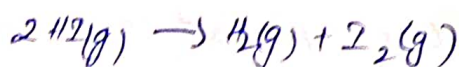
### Collision theory:

postulates:

- i) The reactant molecules collide before they react.
- ii) When molecules possessing energy is equal to or greater than the activation energy required for the reaction, collide with each other, an activated complex is formed, the activated complex then gives products.
- iii) The activated complex then gives products.

### Explanation with illustration:

Let us consider the decomposition of gaseous hydrogen iodide.



According to simple collision theory two HI molecules possessing energy equal to or greater than the energy of activation for this reaction collide and give the

activated complex. This activated complex decompose to  $H_2(g)$  and  $I_2(g)$

Derivation of rate constant of a bimolecular reaction from collision theory.

The rate constant

$$k = Zf \quad \text{--- (1)}$$

$\therefore Z$  = no of molecules colliding

$f$  = no of molecules activated

Total no of molecules -

Maxwell's distribution law

$$n' = n e^{-E_a/RT}$$

$\therefore n$  = total no of molecules.

$n'$  no. of molecules with  $E_a$

$$f = \frac{n'}{n} = e^{-E_a/RT} \quad \text{--- (2)}$$

put equ (2) in (1)

$$k = Zf$$

$$= Z e^{-E_a/RT}$$

$$k = Z e^{-E_a/RT} \quad \text{--- (3)}$$

Arrhenius equation

$$k = A e^{-E_a/RT} \quad \text{--- (4)}$$

from (3) and (4)

$$Z = A$$

Merits of the simple collision theory:

Collision theory predicts the value of the rate constant satisfactorily for reaction which involve relatively simple molecules if the activation  $E_a$  is known.

## Limitation of the collision theory

The collision theory of reaction rates is logical and correct.

↳ The theory applied to simple gaseous reactions only. It is also valid for solutions in which the reacting species exist as simple molecules.

↳ For reactions involving complex molecules, the experimental rate constants are quite different from the calculated values.

↳ There is no method for determining the steric effect ( $p$ ) for has not been determined experimentally.

↳ In the collision theory it is supposed that only the kinetic energy of the colliding molecules contributes to the energy required for surmounting the energy barrier. There is no reason why the rotational and vibrational energies of molecules should be ignored.

Q9/13/23  
↳ The collision theory is silent on the cleavage and formation of bonds involved in the reaction.