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CHEMICAL KINETICS

Introduction

Chemical kinetics is a branch of physical chemistry, which deals with the study of the rate of chemical reactions and the various factors affecting it. Such studies also enable us to elucidate the mechanism by which a reaction occurs.

Depending on the speed, the reactions are mainly of three types.

1) Fast reactions: These reactions occur instantaneously and in some cases it is not easy to measure their rates. Special techniques have been devised to study their kinetics.

Eg., many ionic and explosive reactions.

2) Slow reactions: These are reactions are so slow that it is difficult to observe the appreciable changes in concentrations at room temperature even after months or years.

3) Moderate reactions: For these reactions, it is easy to determine their rates.

Eg., The gaseous reactions like decomposition of HI or N₂O₅, the reactions in liquid phase like the hydrolysis of ester, sugar etc. come under this category.

Rate of reaction

The rate of reaction is defined as the change in the concentration of any one of the reactants or products per unit time. It is usually denoted by $\frac{dx}{dt}$.

The molar concentration (mol L⁻¹) of a substance is represented by putting the symbol of the substance in a square bracket, [].

For the reaction, R → P, the $\frac{dx}{dt}$ is given by,

$$\begin{aligned} \frac{dx}{dt} &= \frac{\text{decrease in concentration of any reactant}}{\text{time taken}} = -\frac{d[R]}{dt} \\ &= \frac{\text{increase in concentration of any product}}{\text{time taken}} = +\frac{d[P]}{dt} \end{aligned}$$

Unit for the rate of reaction: Since concentration is expressed in mol L⁻¹ and time seconds, the unit of rate will be mol L⁻¹ s⁻¹ or mol dm⁻³ s⁻¹.

Rate expressions

Consider the reaction, A + B → P + Q

The different rate expressions for this reaction are:

$$\frac{dx}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[P]}{dt} = +\frac{d[Q]}{dt}$$

or
$$\frac{dx}{dt} = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = +\frac{dC_P}{dt} = +\frac{dC_Q}{dt}$$

where [A] or C_A represents the molar concentration (mol L⁻¹) of a substance A.

Consider another reaction, 2A + B → 3P + 2Q

In this reaction, the stoichiometric coefficients of reactants and products are different. It is to be remembered that the rate of a particular reaction must remain constant irrespective

of the reactant or product taken for its determination. So, in order to get the same value for rate constant, we should write the rate expressions per unit mole of any reactant or product. Thus the different rate expressions for this reaction are:

$$\frac{dx}{dt} = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{1}{3} \frac{d[P]}{dt} = +\frac{1}{2} \frac{d[Q]}{dt}$$

Problems based on rate expressions: Refer Text Book

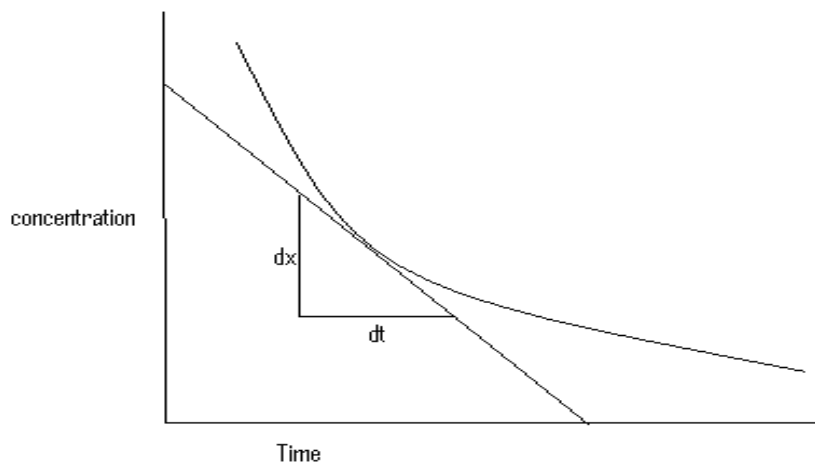
Average rate and Instantaneous rate

The rate measured during a time interval is called **average rate**. This because the rate of a reaction goes on decreasing with progress of time due to decrease in concentration of the reactants with time. Thus during a given time interval, the reaction goes through different rates and the rate measured is only an average rate. It is denoted by $\frac{\Delta x}{\Delta t}$.

The rate of a reaction at any instant or moment is called the instantaneous rate. It is obtained from the average rate, when the time interval tends to approach zero. It is denoted by $\frac{dx}{dt}$.

$$\frac{dx}{dt} = \left(\frac{\Delta x}{\Delta t} \right)_{\Delta t \rightarrow 0}$$

The instantaneous rate is determined from the concentration versus time graph. For this, a tangent drawn to the curve at a particular instant and the slope of this tangent will give the instantaneous rate.



Factors affecting the rate of reactions

1. Concentration of reactants
2. Temperature
3. Catalyst
4. Radiation

I. Rate and concentration of reactants

Rate law gives the dependence of the rate of reaction with concentration of the reactants. This law states that at constant temperature, the rate of a reaction is directly proportional to the reactant concentration, each concentration being raised to some power.

Consider the reaction, $A + B \rightarrow P + Q$

$$\begin{aligned}\frac{dx}{dt} &\propto [A]^x [B]^y \\ &= k[A]^x [B]^y\end{aligned}$$

where k is rate constant.

This expression is called rate equation or rate law. Thus rate equation gives the relationship between the rate of reaction and the concentration of reactants in a chemical reaction.

The powers of concentration terms, i.e. m and n in the rate equation are determined by experiment. The values of m and n may or may not be equal to the stoichiometric coefficients of the given chemical equation.

Definition of rate constant

In the above equation, suppose $[A] = [B] = 1 \text{ mol L}^{-1}$, then $\frac{dx}{dt} = k$

Hence the rate constant or specific reaction rate is defined as the rate of the reaction when the concentration of each reactant is taken as unity.

Order of reaction

The order of reaction is defined as the sum of exponents to which the concentration terms of reactants in the rate law are raised to express the observed rate of reaction.

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

The overall order of reaction, $n = x + y$

The order of reaction with respect to $A = x$

The order of reaction with respect to $B = y$

The order of reaction is an experimentally measured value and may be a whole number or a fractional number.

Reactions of different orders

If $n = 0$, it is the zero order reaction.

If $n = 1$, it is the first order reaction.

If $n = 2$, it is the second order reaction

If $n = 3$, it is the third order reaction.

If $n = \frac{1}{2}, \frac{3}{2}, \frac{5}{4}$, etc., it is the fractional order reaction

If $n > 3$, it is the higher order reaction

And Pseudo-order reactions

Unit of specific reaction rate, k

Consider an n^{th} reaction,

	A	\longrightarrow	Products
Initial conc. (mol L^{-1})	a		0
Conc. after a time, t	$(a-x)$		x

Then the rate of n^{th} order reaction at time t is given by

$$\frac{dx}{dt} \propto [A]^n$$

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

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

$$= \text{mol L}^{-1} \text{ s}^{-1} / (\text{mol L}^{-1})^n$$

$$= (\text{mol L}^{-1})^{(1-n)} \text{ s}^{-1} \quad \text{or} \quad \text{mol}^{(1-n)} \text{ L}^{(n-1)} \text{ s}^{-1}$$

Order of reaction	Unit of k , $\text{mol}^{(1-n)} \text{ L}^{(n-1)} \text{ s}^{-1}$
zero	$\text{mol L}^{-1} \text{ s}^{-1}$
First	s^{-1}
Second	$\text{L mol}^{-1} \text{ s}^{-1}$
Third	$\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$
Fraction (Say 3/2)	$\text{L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$

Zero order reactions

A reaction is said to be of zero order if the rate of the reaction is independent of the concentration of all reactants.

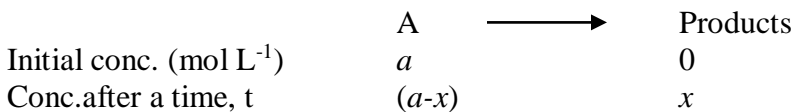
For such reactions, the rate remains constant throughout irrespective of the change in concentration..

Examples

1. Photochemical reactions eg., $\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl}$
2. The decomposition of HI on the surface of gold. $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$
3. The decomposition of NH_3 on the surface of tungsten. $2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$

Derivation of integrated rate equation for zero order reactions

Consider a zero-order reaction of the type,



At the beginning of the reaction ($t = 0$), the concentration of the reactant A is $a \text{ mol L}^{-1}$. If after a time t , x moles of A has changed, the concentration of A is $(a-x) \text{ mol L}^{-1}$. Then the rate of reaction at time t is given by,

$$\frac{dx}{dt} \propto [\text{A}]^0 \qquad x = kt$$

$$\begin{aligned}\frac{dx}{dt} &\propto (a-x)^0 \\ &= k(a-x)^0 \\ &= k\end{aligned}\quad (1)$$

where k is called rate constant of the reaction.

On rearranging Eq. 1,

$$dx = kdt$$

On integration,

$$\int dx = \int kdt$$

$$x = kt + I \quad (2)$$

where I is integration constant and x is the number of moles the substance reacted.

When $t = 0$, $x = 0$, therefore $I = 0$

Substituting for I in Eq.2,

$$x = kt \quad (3)$$

This is the integrated rate expression for zero order reaction

Half-life period:

The half-life period of a reaction is defined as the time taken for half of the reaction to be completed.

$$\text{When } t = t_{1/2}, \quad x = a/2$$

Substituting these values in eqn. (3),

$$\frac{a}{2} = kt_{1/2}$$

$$t_{1/2} = \frac{a}{2k} \quad (4)$$

Therefore the half life period of a zero-order reaction is directly proportional to the initial concentration of the reactants.

First order reactions

A reaction is said to be of first order if the rate of the reaction depends upon the first power of one reactant concentration only.

Examples

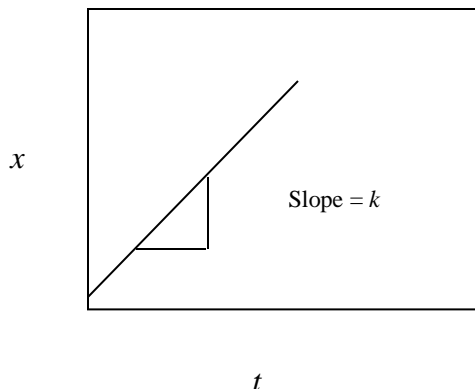
- i) Decomposition of nitrogen pentoxide in carbon tetrachloride solution

$$\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$$
- ii) Decomposition of hydrogen peroxide in aqueous solution.

$$\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}$$
- iii) Radioactivity

Derivation of integrated rate equation for first order reactions

Consider a first order reaction of the type,



Initial conc. (mol L ⁻¹)	a	0
Conc. after a time, t	$(a-x)$	x

At the beginning of the reaction ($t=0$), the concentration of the reactant A is a mol L⁻¹. If after a time t , x moles of A have changed, the concentration of A is $(a-x)$ mol L⁻¹. Then the rate of reaction at time t is given by,

$$\frac{dx}{dt} \propto [A]$$

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

Where k is called rate constant of the reaction.

On rearranging Eq. 1,

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

On integration,

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

$$-\ln(a-x) = kt + I \quad (2)$$

When $t = 0$, $x = 0$ Therefore $I = -\ln a$

Substituting for I in Eq.2,

$$-\ln(a-x) = kt - \ln a$$

$$kt = \ln a - \ln(a-x)$$

$$kt = \ln \frac{a}{a-x}$$

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

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad (3)$$

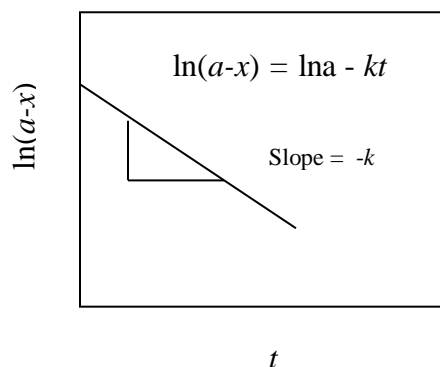
This is the integrated rate expression for the first order reaction.

Sometimes the integrated rate law in the following form is also used:

Half-life period

When $t = t_{1/2}$, $x = a/2$

Substituting these values in eqn. (3),



On rearranging,

$$\frac{dx}{(a-x)^2} = kdt$$

On integration,

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

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

When $t = 0$, $x = 0$ Therefore $I = 1/a$

Substituting for I in Eq. (2)

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

$$kt = \frac{1}{a-x} - \frac{1}{a} \quad (3)$$

$$= \frac{a - (a-x)}{a(a-x)} = \frac{x}{a(a-x)} \quad (4)$$

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad (5)$$

OR from eqn. (3)

$$k = \frac{1}{t} \cdot \left[\frac{1}{a-x} - \frac{1}{a} \right] \quad (6)$$

This is the integrated rate expression for the second order reaction.

Half-life period

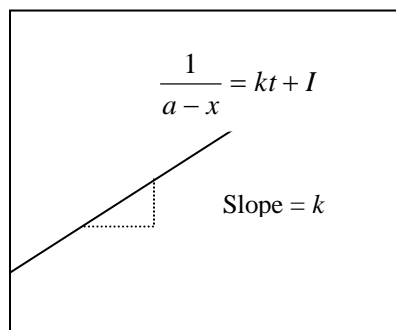
When $t = t_{1/2}$, $x = a/2$

Substituting these values in eqn. (5),

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

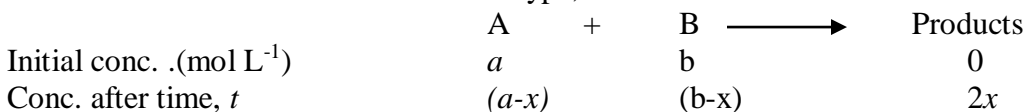
$$t_{1/2} = \frac{1}{k} \cdot \frac{1}{a} \quad (7)$$

Therefore the half-life period of a second order reaction is inversely proportional to the initial concentration of the reactants.



Derivation of integrated rate equation for second order reactions involving two different reactants with different initial concentration.

Consider a second order reaction of the type,



At the beginning of the reaction (t=0), the concentration of the reactant A is a mol L⁻¹ and concentration of reactant B is b mol L⁻¹. If after a time t , x moles of A has changed, then the amount of B that would react in the same time would also be x mol L⁻¹. So the concentration of A and B at time t would become $(a-x)$ mol L⁻¹ and $(b-x)$ mol L⁻¹ respectively.. Then the rate of reaction at time t is given by,

$$\frac{dx}{dt} \propto [A][B]$$

$$\frac{dx}{dt} = k(a-x)(b-x) \quad (1)$$

On rearranging,

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

Resolving the left hand side into partial fractions,

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

On integration,

$$\frac{1}{(a-b)} \left[\int \frac{dx}{(b-x)} - \int \frac{dx}{(a-x)} \right] = \int k dt$$

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

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

$$\frac{1}{(a-b)} \left[\ln \frac{a-x}{b-x} \right] = kt + I \quad (2)$$

when $t = 0$, $x = 0$ Therefore $I = \frac{1}{(a-b)} \left[\ln \frac{a}{b} \right]$

Substituting for I in Eq. (2)

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

$$\begin{aligned}
 kt &= \frac{1}{a-b} \ln \frac{a-x}{b-x} - \frac{1}{(a-b)} \ln \frac{a}{b} \\
 &= \frac{1}{a-b} \left[\ln \frac{a-x}{b-x} - \ln \frac{a}{b} \right] \\
 &= \frac{1}{(a-b)} \ln \left[\frac{a-x}{b-x} \times \frac{b}{a} \right] \\
 k &= \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}
 \end{aligned}$$

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

(3)

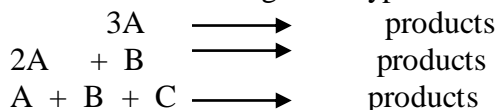
This is the integrated rate expression for the second order reaction.

Third order reactions

A reaction is said to be of third order if the rate of the reaction depends upon the product of three concentration terms or the third power of one reactant concentration.

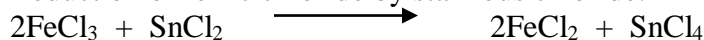
The third order reactions are rare compared to first order and second order reactions.

These reactions are of the following three types:



Examples.

i) Reduction of ferric chloride by stannous chloride.

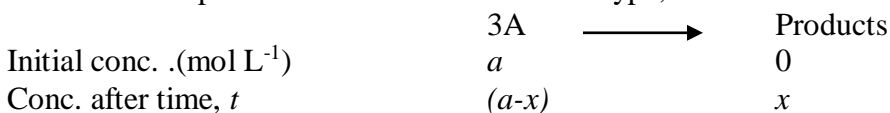


ii) Combination of nitric oxide and chlorine to form nitrosyl chloride.



Derivation of integrated rate equation for third order reactions involving one reactant only

Consider a simplest third order reaction of the type,



At the beginning of the reaction ($t=0$), the concentration of the reactant A is a mol L⁻¹. If after a time t , x moles of A have reacted, the concentration of A is $(a-x)$ mol l⁻¹. Then the rate of reaction at time t is given by,

$$\begin{aligned}
 \frac{dx}{dt} &\propto [A]^3 \\
 \frac{dx}{dt} &\propto (a-x)^3 \\
 &= k(a-x)^3 \qquad (1)
 \end{aligned}$$

On rearranging,

$$\frac{dx}{(a-x)^3} = kdt$$

On integration,

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

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

When $t = 0$, $x = 0$ Therefore $I = \frac{1}{2a^2}$

Substituting for I in Eq. (2)

$$\begin{aligned} \frac{1}{2(a-x)^2} &= kt + \frac{1}{2a^2} \\ kt &= \frac{1}{2(a-x)^2} - \frac{1}{2a^2} \\ &= \frac{a^2 - (a-x)^2}{2a^2(a-x)^2} = \frac{x(2a-x)}{2a^2(a-x)^2} \end{aligned}$$

$$k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2} \quad (3)$$

OR from eqn. (11),

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

The eqn. (13) is the integrated rate expression for the third order reaction.

Half-life period

When $t = t_{1/2}$, $x = a/2$

Substituting these values in eqn. (3),

$$k = \frac{1}{t_{1/2}} \cdot \frac{\frac{a}{2} \left(2a - \frac{a}{2} \right)}{2a^2 \left(a - \frac{a}{2} \right)^2}$$

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

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

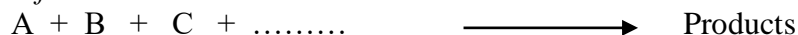
$$t_{1/2} = \frac{1}{2k} \cdot \frac{3}{a^2}$$

Then, $t_{1/2} \propto 1/a^{1/2}$ (4)

Therefore the half-life period of a third order reaction is inversely proportional to the square of the initial concentration of the reactants.

Higher order reactions (nth order reactions)

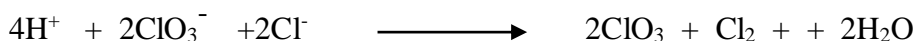
A reaction is said to be of higher order if the rate of the reaction depends upon the product of more than three concentration terms.



The reactions of higher order are very rare. The reason for this may be explained by the collision theory. According to this theory, a reaction takes place only when the reactant molecules come together simultaneously to collide with each other. The possibility of three molecules colliding simultaneously to each other is less than for two molecules and hence the reactions of third order are fewer than those of second order. Similarly, the chances of four molecules to come together simultaneously and collide are still less. Hence reactions of fourth order or higher order are very rare.

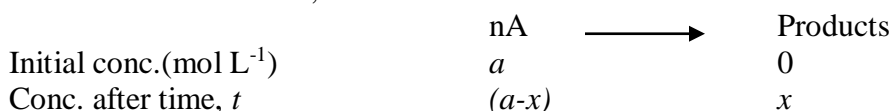
Examples.

The action of HCl on HClO₃ in aqueous solution is of eighth order.



Derivation of integrated rate equation for nth order reactions

Reactions of fourth or higher order seem to be improbable. In general, consider a reaction of the nth order, where all the initial concentrations are the same:



At the beginning of the reaction ($t=0$), the concentration of the reactant A is a mol L⁻¹. If after a time t , x moles of A have reacted, the concentration of A is $(a-x)$ mol L⁻¹. Then the rate of reaction at time t is given by,

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

$$= k(a-x)^n \quad (1)$$

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

On integration,

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

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

When $t = 0$, $x = 0$ Therefore $I = \frac{1}{(n-1)a^{(n-1)}}$

Substituting for I in Eq. (2),

$$\begin{aligned} \frac{1}{(n-1)(a-x)^{(n-1)}} &= kt + \frac{1}{(n-1)a^{(n-1)}} \\ kt &= \frac{1}{(n-1)(a-x)^{(n-1)}} - \frac{1}{(n-1)a^{(n-1)}} \\ kt &= \frac{1}{(n-1)} \left[\frac{1}{(a-x)^{(n-1)}} - \frac{1}{a^{(n-1)}} \right] \\ k &= \frac{1}{t(n-1)} \left[\frac{1}{(a-x)^{(n-1)}} - \frac{1}{a^{(n-1)}} \right] \quad (3) \end{aligned}$$

This is the integrated rate expression for the n^{th} order reaction.

[*NOTE This equation is applicable for all orders except when $n = 1$]

Half-life period

When $t = t_{1/2}$, $x = a/2$

Substituting these values in eqn. (3),

$$\begin{aligned} k &= \frac{1}{t_{1/2}(n-1)} \left[\frac{1}{(a-a/2)^{(n-1)}} - \frac{1}{a^{(n-1)}} \right] \\ k &= \frac{2^{(n-1)} - 1}{t_{1/2}(n-1)} \cdot \frac{1}{a^{(n-1)}} \\ t_{1/2} &= \frac{2^{(n-1)} - 1}{k(n-1)} \cdot \frac{1}{a^{(n-1)}} \quad (4) \end{aligned}$$

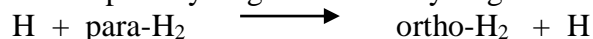
Thus the half-life period of n^{th} order reaction is inversely proportional to the $(n-1)^{\text{th}}$ power of the initial concentration.

Fractional order reactions

A reaction is said to be of fractional order if the rate of the reaction depends upon the fractional power of the reactant concentration.

Examples.

Conversion of para-hydrogen to ortho-hydrogen is of the order 1.5



The integrated rate equation for fractional order reactions

The integrated rate expression for the n^{th} order reaction is applicable to the of fractional order reactions.

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

when $n = 3/2$,

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

when $n = 5/2$,

$$k = \frac{2}{3t} \left[\frac{1}{(a-x)^{3/2}} - \frac{1}{a^{3/2}} \right] \quad \text{etc.}$$

•Time for fractional change:

The integrated rate expression for the n^{th} order reaction

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

Suppose it is required to calculate the time for the completion of half of the reaction.

i.e., $t = t_{1/2}$, $x = a/2$

Substituting these values in the above eqn.

$$k = \frac{1}{t_{1/2}(n-1)} \left[\frac{1}{(a-a/2)^{(n-1)}} - \frac{1}{a^{(n-1)}} \right]$$

$$k = \frac{2^{(n-1)} - 1}{t_{1/2}(n-1)} \cdot \frac{1}{a^{(n-1)}}$$

$$t_{1/2} = \frac{2^{(n-1)} - 1}{k(n-1)} \cdot \frac{1}{a^{(n-1)}}$$

or $t_{1/2} \alpha \frac{1}{a^{(n-1)}}$

Similarly, it can be proved that $t_{3/4} \alpha \frac{1}{a^{(n-1)}}$

Thus, the time required to complete a definite fraction of the n^{th} order is inversely proportional to the $(n-1)^{\text{th}}$ power of the initial concentration.

SUMMARY

Order of reactions	Integrated rate equation	Half-life period
Zero	$K = x/t$	$t_{1/2} = \frac{a}{2k}$
First	$k = \frac{2.303}{t} \log \frac{a}{a-x}$ $k = \frac{2.303}{t_2 - t_1} \log \frac{a-x_1}{a-x_2}$	$t_{1/2} = \frac{0.693}{k}$
Second	$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$ OR $k = \frac{1}{t} \cdot \left[\frac{1}{a-x} - \frac{1}{a} \right]$	$t_{1/2} = \frac{1}{k} \cdot \frac{1}{a}$

	$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$	
Third	$k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2} \quad \text{OR}$ $k = \frac{1}{2t} \cdot \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$	$t_{1/2} = \frac{1}{2k} \cdot \frac{3}{a^2}$
n th	$k = \frac{1}{t(n-1)} \left[\frac{1}{(a-x)^{(n-1)}} - \frac{1}{a^{(n-1)}} \right]$	$t_{1/2} = \frac{2^{(n-1)} - 1}{k(n-1)} \cdot \frac{1}{a^{(n-1)}}$

• Elementary and complex reactions

Elementary reactions (or isolated reactions) are simple reactions in which the reactants are directly transformed into products without any intermediate step.

Complex reactions do not occur in a single step, but complicated by intermediate stages or by side and reverse reactions.

• Molecularity of reaction

The molecularity of a reaction is defined as the number of molecules, atoms or ions that must collide with one another simultaneously so as to result into a chemical reaction.

(a) For relatively simple reactions: Earlier, no distinction was made between molecularity and order of a reaction. Reactions of first, second and third order were called unimolecular, bimolecular and trimolecular reactions. This practice is, however, not followed now. The molecularity is simply the sum of the molecules of different reactants as represented by the balanced chemical equation.

Examples:

- (i) Decomposition of F₂O₂

$$\text{F}_2\text{O}_2 \longrightarrow \text{F}_2 + \text{O}_2 \quad \text{Unimolecular}$$
- (ii) Dissociation of HI

$$2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2 \quad \text{Bimolecular}$$
- (iii) Oxidation of nitric oxide to nitrogen dioxide

$$2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2 \quad \text{Trimolecular}$$

In several reactions, the order of reaction is different from molecularity.

Eg., Pseudo-order reactions (Pseudo-molecular reactions)

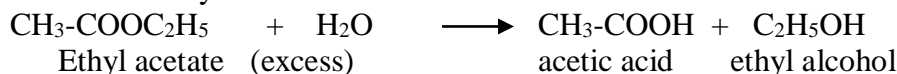
A reaction in which one of the reactants is present in large excess, showing an order different from the actual order is called pseudo-order reaction. (Such reactions in old days are mentioned as pseudo-molecular reactions, since molecularity and order are same for elementary reactions).

(i) Pseudo- first order reactions (Pseudo-unimolecular reactions)

A reaction in which one of the reactants is present in large excess, showing first order kinetics different from the actual order is called pseudo- first order reaction. Actually, more than one molecule is involved in the chemical reaction.

Examples:

(a) **Hydrolysis of an ester:** Ethyl acetate upon hydrolysis in aqueous solution forms acetic acid and ethyl alcohol.



Since it is an elementary reaction, the rate law can be written as,

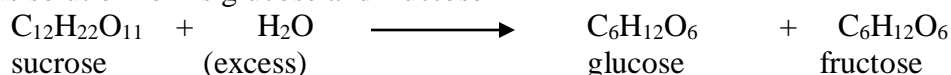
$$\text{Rate} = k[\text{CH}_3\text{-COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

As H_2O is present in large excess, its concentration remains practically constant in the course of reaction.

$$\text{Then, Rate} = k'[\text{CH}_3\text{-COOC}_2\text{H}_5] \quad \text{where } k' = k[\text{H}_2\text{O}]$$

Therefore the reaction is said to have a pseudo-first order, but the reaction is bimolecular.

(b) **Hydrolysis of sucrose (Inversion of cane sugar):** Sucrose upon hydrolysis in aqueous solution forms glucose and fructose



Since it is an elementary reaction, the rate law can be written as,

$$\text{Rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}] [\text{H}_2\text{O}]$$

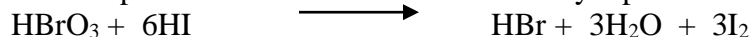
As H_2O is present in large excess, its concentration remains practically constant in the course of reaction.

$$\text{Then, Rate} = k'[\text{C}_{12}\text{H}_{22}\text{O}_{11}] \quad \text{where } k' = k[\text{H}_2\text{O}]$$

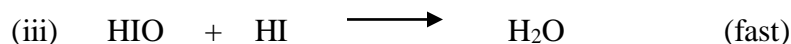
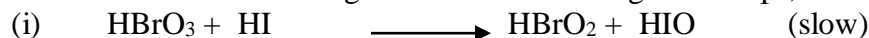
Experimentally this reaction will be first- order. Therefore it is a pseudo-first order reaction, but it is bimolecular.

(b) **For complex reactions:** Those reactions which occur in two or more steps are called complex reactions. The molecularity of the overall reaction has no significance. But every step or elementary process involved in a complex reaction has its own molecularity. The stepwise sequence of 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. The slowest step is the rate-determining step of the reaction and it determines the order of the reaction.

. The reduction of bromic acid to hydrobromic acid by hydriodic acid is an example of complex reaction. It is stoichiometrically represented as:



It is believed to have the following mechanism involving three steps,



The molecularities of steps (i), (ii) and (iii) are 2, 5 and 2 respectively. It is not desirable to express molecularity for the overall reaction. Steps (ii) and (iii) are fast while step (i) is slow. According to the step (i), the reaction is of second order.

Thus there is also no correlation between the order and molecularity of a reaction.

Differences between order and molecularity

	Order	Molecularity
1	It is the sum of the powers of concentration terms in the rate law expression	It is the number of molecules, atoms or ions that must collide with one another simultaneously so as to result into a chemical reaction.
2	It is an experimentally determined value.	It is theoretical concept.
3	It can have fractional number and zero values besides whole number values	It can have only whole number values.
4	It is always same for the overall reaction, whether the reaction is complex or simple.	It has no significance for a complex reaction and can be expressed for each step in case of complex reaction.
5	Order of a reaction can change with the conditions such as pressure, temp. and concentration.	Molecularity is invariant for a chemical equation.

Methods of determining the order of a reaction.

There are various methods for determining the order of a reaction.

1. Integration method
 - a. Analytical or integrated rate equation method
 - b. Graphical method
2. Half-life method
3. Van't Hoff Differential method
4. Ratio variation method
5. Ostwald's Isolation method

1. Integration method

a. Analytical or integrated rate equation method

In this method the initial concentration of all the reactants taking part are determined. The progress of the reaction can be noted by determining the concentration of the reacting substances at different intervals of time. These values are then substituted into the integrated equations for the first, second, third order reactions etc.

For zero order reaction , $k = x/t$

For first order reaction, $k = \frac{2.303}{t} \log \frac{a}{a-x}$

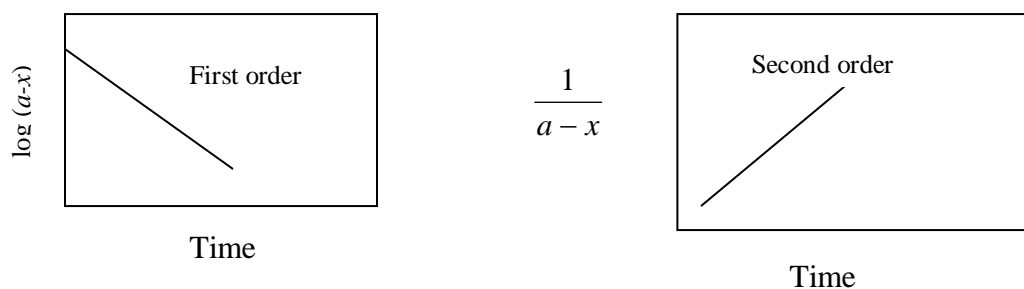
For Second order reaction, $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$

For Third order reaction, $k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$

The rate equation which yields a constant value of the rate constant for a series of intervals of time gives the correct order of the reaction. As this method involves of the trial of different equations, it is usually called as the **hit and trial** method.

b. Graphical method using integrated rate equation

In this method the initial concentration of all the reactants taking part are determined. The progress of the reaction can be noted by determining the concentration of the reacting substances at different intervals of time. Then the suitable concentration function for the first, second, third order reactions etc is plotted against time. The graph, which gives a straight line, corresponds to the correct order of the reaction.



- If the plot of $\log(a-x)$ against time is a straight line, the reaction is of the first order.
- If the plot of $1/(a-x)$ against time is a straight line, the reaction is of the second order, and so on.

2. Half-life method (Fractional change method)

The time taken for half of the reaction to be completed is called half-life period. It is found that the half life period or any fractional change is a constant for first order reaction, inversely proportional to the initial concentration for the second order reaction and inversely proportional to square of the initial concentration and so on. In general, the half life period of an n^{th} order reaction is inversely proportional to the $(n-1)^{\text{th}}$ power of the initial concentration.

Thus for the n^{th} order reaction, $t_{1/2}$ is given by

$$t_{1/2} \propto \frac{1}{a^{(n-1)}}$$

Consider two separate experiments with different initial concentration. Let a_1 and a_2 . let $(t_{1/2})_1$ and $(t_{1/2})_2$ are their respective half-life periods.

$$(t_{1/2})_1 \propto \frac{1}{a_1^{(n-1)}} \quad (1)$$

$$(t_{1/2})_2 \propto \frac{1}{a_2^{(n-1)}} \quad (2)$$

On dividing,

$$\begin{aligned}\frac{(t_{1/2})_1}{(t_{1/2})_2} &= \frac{a_2^{(n-1)}}{a_1^{(n-1)}} \\ &= \left(\frac{a_2}{a_1}\right)^{(n-1)}\end{aligned}$$

Taking logarithm,

$$\log \frac{(t_{1/2})_1}{(t_{1/2})_2} = (n-1) \log \frac{a_2}{a_1}$$

$$\log((t_{1/2})_1) - \log((t_{1/2})_2) = (n-1)(\log a_2 - \log a_1)$$

$$n-1 = \frac{\log((t_{1/2})_1) - \log((t_{1/2})_2)}{(\log a_2 - \log a_1)}$$

$$n = 1 + \frac{\log((t_{1/2})_1) - \log((t_{1/2})_2)}{(\log a_2 - \log a_1)}$$

By substituting the experimental data in this equation, the order of the reaction can be calculated.

3. Van't Hoff Differential method

The rate of the reaction of n^{th} order is proportional to the n^{th} power of concentration.

$$-\frac{dC}{dt} = C^n, \text{ where } c \text{ is the concentration of the reactant.}$$

On taking logarithm,

$$\log\left(-\frac{dC}{dt}\right) = \log k + n \log C$$

Consider two separate experiments with different initial concentrations, C_1 and C_2 .

Then we can write,

$$\log\left(-\frac{dC_1}{dt}\right) = \log k + n \log C_1$$

$$\log\left(-\frac{dC_2}{dt}\right) = \log k + n \log C_2$$

On subtraction,

$$\log\left(-\frac{dC_1}{dt}\right) - \log\left(-\frac{dC_2}{dt}\right) = n (\log C_1 - \log C_2)$$

$$n = \frac{\log\left(-\frac{dC_1}{dt}\right) - \log\left(-\frac{dC_2}{dt}\right)}{(\log C_1 - \log C_2)}$$

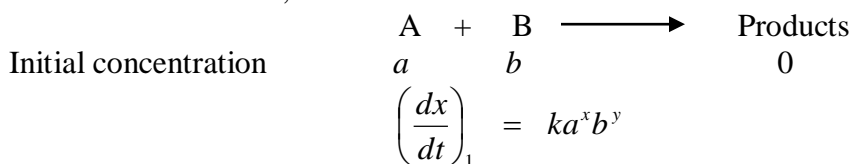
The values of $\frac{dC_1}{dt}$ and $\frac{dC_2}{dt}$ can be determined by plotting the concentration of reactants against time and then taking the slope of the straight line. By substituting these values in the above equation, the order of the reaction can be calculated.

4. Ratio variation method (Initial rate method)

In this method, the rate at the beginning of the reaction (i.e., initial rate) is measured. Then the initial concentration of only one of the reactants is varied by a known factor while keeping the concentrations of the other reactants constant. The reaction rate is measured again. From the reaction rates, the order with respect to this particular reactant is calculated. The procedure is repeated with respect to every other reactant and thus the order with respect to each of them is calculated. Then the sum of the individual orders gives the overall order of the reaction.

This method can be illustrated as follows,

Consider the reaction,



If the concentration of A is doubled, keeping that of B constant

$$\left(\frac{dx}{dt}\right)_2 = k(2a)^x b^y$$

Dividing, we get

$$\frac{\left(\frac{dx}{dt}\right)_1}{\left(\frac{dx}{dt}\right)_2} = 2^x$$

On taking logarithm,

$$\log \frac{\left(\frac{dx}{dt}\right)_1}{\left(\frac{dx}{dt}\right)_2} = x \log 2$$

$$x = \frac{1}{\log 2} \times \log \frac{\left(\frac{dx}{dt}\right)_1}{\left(\frac{dx}{dt}\right)_2}$$

Thus the order, x with respect to reactant A is calculated. The procedure is repeated with the other reactant B to calculate its order, y . then the overall order of the reaction is given by, $n = x + y$.

5. Ostwald's Isolation method

In this method, all the reactants except one are taken in large quantities so that the concentrations of these reactants remain constant throughout the reaction. Thus the order of the reaction with respect to that isolated reactant, which is not taken in large quantity. The experiment is repeated by isolating each reactant in turn. The total order of the reaction will be given by the sum of the order of isolated reactions.

For example, suppose a reaction involves three reactants A, B and C. In the first case B and C are taken in excess so that A is isolated. The order thus observed is the order with respect to A. Similarly by taking A and C in excess, the order with respect to B can be found and by taking A and B in excess, the order with respect to C can be found. If n_A , n_B and n_C are the orders with respect to A, B and C respectively, then the overall order of the reaction n will be given by the expression:

$$n = n_A + n_B + n_C.$$