CHEMICAL KINETICS

DETERMINE THE ORDER OF REACTION

Methods of determination of order of reaction: -

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Initial Rate Method

In this method initial rate of reaction is determined by varying the concentration of one of the reactants while others are kept constant

 $R = k[A]^{x}[B]^{y}[C]^{z}$

if [B] & [C] = Constant then for two different initial concentrations of A we have

 $R_{0_1} = k[A_0]_1^a$ And $R_{0_2} = k[A_0]_2^a$

$$\frac{R_{0_1}}{R_{0_2}} = (\frac{[A_0]_1}{[A_0]_2})^n$$

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Graphical Method

This method can be used when there is only one reactant.

If the plot of log [A] vs t is a straight line, the reaction follows first-order .

If the plot of 1/[A] vs t is a straight line, the reaction follows second order.

If the plot of $1/[A]^2$ is a straight line, the reaction follows third order.

Generally, for a reaction of nth order, a graph of $1/[A]^{n-1}$ vs t must be a straight line.

Here [A] is the concentration of reactant at any given time of the reaction (other t =0). [A] = (a-x) where a is the initial concentration and x is the extent of reaction at time t.

Half Life Method

This method is used only when the rate law involved by only one concentration term.

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

 $t_{(1/2)} = k' 1/a^{n-1}$

 $\log t_{(1/2)} = \log k' + (1-n)a$

Graph of logt 1/2 vs log a, gives a straight line with slope (1-n), where 'n' is the order of the reaction.

Determining the slope we can find the order n.

If half life at different concentrations is given then.

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

And

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

Taking logarithm and rearranging

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

Plots of half-lives concentration $(t_{1/2} \propto a^{1-a})$:



This relation can be used to determine order of reaction 'n'

Van't Hoff Differential Method

As we know that, the rate of a reaction varies as the nth power of the concentration of the reactant where 'n' is the order of the reaction.

Thus, for two different initial concentrations C_1 and C_2 , equations can be written in the form

$$\log\left(\frac{\mathrm{d}C_1}{\mathrm{d}t}\right) = \log k + n \log C_1 \qquad \dots (i)$$

and

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

Taking logarithms,

Subtracting Eq. (ii) from (i),

$$\log(\frac{\mathrm{d}C_1}{\mathrm{d}t}) - \log(\frac{\mathrm{d}C_2}{\mathrm{d}t}) = n(\log C_1 - \log C_2)$$

or

 $n = [\log(-(dC_1)/dt) - \log((dC_2)/dt)] \div [\log C_1 - \log C_2] \quad(iii)$

 $-dc_1/dt$ and $-dc_2/dt$ are determined from concentration vs. time graphs and the value of 'n' can be determined.

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Half-life of order of reactions:-

The half-life of a chemical reaction can be defined as the time taken for the concentration of a given reactant to reach 50% of its initial concentration (i.e. the time taken for the reactant concentration to reach half of its initial value). It is denoted by the symbol ' $t_{1/2}$ ' and is usually expressed in seconds.

Half-Life Formula

It is important to note that the formula for the half-life of a reaction varies with the order of the reaction.

For a zero-order reaction, the mathematical expression that can be employed to determine the halflife is: $t_{1/2} = [R]_0/2k$

For a first-order reaction, the half-life is given by: $t_{1/2} = 0.693/k$

For a second-order reaction, the formula for the half-life of the reaction is: $1/k[R]_0$

Were,

 $t_{1/2}$ is the half-life of the reaction (unit: seconds)

 $[R_0]$ is the initial reactant concentration (unit: mol.L⁻¹ or M)

k is the rate constant of the reaction (unit: $M^{(1-n)}s^{-1}$ where 'n' is the reaction order)

Derivation of Half-Life Formula for Zero-Order Reactions

For a zero-order reaction, the units of the rate constant are mol.L⁻¹.s⁻¹. The expression for a zero-order rate constant is:

$$k = \frac{[R]_0 - [R]}{t}$$

Substituting $t = t_{1/2}$, at which point $[R] = [R]_0/2$ (at the half-life of a reaction, reactant concentration is half of the initial concentration).

$$k = \frac{[R]_0 - [R]_0 / 2}{t_{1/2}}$$

Rearranging the equation, the expression for the half-life of a zero-order reaction is found to be:

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$$t_{1/2} = \frac{[R]_0}{2k}$$

Derivation of Half-Life Formula for First-Order Reactions

For a first-order reaction, the rate constant can be mathematically expressed as follows:

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

From the definition of reaction half-life, at $t = t_{1/2}$, $[R] = [R]_0/2$. Substituting these values in the expression for the first-order rate constant, the following equation is obtained:

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R_0]}{[R]_0/2}$$

Rearranging the expression to find the value of $t_{1/2}$:

$$t_{1/2} = \frac{2.303}{k} \log(2) = \frac{0.693}{k}$$

Thus, the half-life of a first-order reaction is given by 0.693/k.

Pseudo first order reaction:-

A Pseudo first-order reaction can be defined as a second-order or bimolecular reaction that is made to behave like a first-order reaction. This reaction occurs when one reacting material is present in great excess or is maintained at a constant concentration compared with the other substance.

In this section, we will learn about pseudo-first-order reaction and their rate equations. To begin with, reactions that appear to be second order in nature but are approximated as a first-order reaction on close analysis. For example, a second-order of the reaction is given by the equation,

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

This reaction is dependent upon the concentrations of both A and B but one of the components is present in large excess and thus its concentration hardly changes as the reaction proceeds.

So, if component B is in large excess and the concentration of B is very high as compared to that of A, the reaction is considered to be a pseudo-first-order reaction with respect to A and if component A is in large excess and the concentration of A is very high as compared to that of B, the reaction is considered to be pseudo-first order with respect to B.



Example of First-Order Reaction

Here is an example to help you understand the concept more clearly.

Consider the hydrolysis of ethyl acetate, during the hydrolysis, the concentration of ethyl acetate is 0.02 mol/L whereas the amount of water is 20 mol/L as the process of hydrolysis involves a large amount of water. Let us say, the process of hydrolysis attains completion in time t.

The reaction can be represented as

 $CH_3COOC_2H5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

(ethyl acetate)	(Water)	(Acetic acid)	(ethyl alcohol)
(000) 10000000)	((100000 0000)	(000) 1 00000000

Components	CH ₃ COOC ₂ H ₅	H ₂ O	CH ₃ COOH	C ₂ H ₅ OH
Concentration t=0	0.02	20	0	0
Concentration t	0	19.8	0.02	0.02

For the above-mentioned reaction, the rate equation can be given as,

 $Rate = k [CH_3COOC_2H_5] [H_2O]$

Here we see that the concentration of water is very high and thus does not change much during the course of the reaction. Thus the rate of the reaction can be said to be independent of the change in

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the concentration of H_2O . Putting the term for change of concentration of water in the above reaction to being zero we can write the effective rate equation as,

Rate = $k [CH_3COOC_2H_5]$

Here, the term kt takes into account the value of the constant concentration of water.

where $K = K' [H_2 O]$

We see that the reaction behaves as a first-order reaction. Such reactions are termed pseudo-firstorder reactions.

Another example of pseudo-first-order reaction is the inversion of cane sugar, given by the following reaction,

 $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

(Cane sugar) (Water) (Glucose) (Fructose)

The rate equation can be given as,

Rate = k $[C_{12}H_{22}O_{11}]$