

Paper : Physical Chemistry

Topic : Chemical Kinetics

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Kinetics of nth Order Reactions :-

Consider a reaction of nth order which takes place as follows :



In this reaction, all the reactants are at the same concentration. Suppose 'a' is the initial concentration of A in g moles/litre. Let x g moles/litre decomposes in time 't'. Then the concentration of A at that time will be (a-x) g moles/litre. According to the law of mass action, the rate of nth order is given by

$$\frac{dx}{dt} \propto (a-x)^n \quad \text{--- (1)}$$

$$\text{or, } \frac{dx}{dt} = k_n (a-x)^n \quad \text{--- (2)}$$

where k_n is the rate constant for the nth order reaction. Separating the variables, equation (2) may be put as

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

and integration of this leads to

$$\frac{1}{(n-1)(a-x)^{n-1}} = k_n t + C_n \quad \text{--- (3)}$$

where C_n is the integration constant.

When $t = 0$, $x = 0$; equation (3) then becomes as

$$\frac{1}{(n-1) a^{n-1}} = C_n \quad \text{--- (4)}$$

substituting this value in equation (3), we get (8)

$$\frac{1}{(n-1)(a-x)^{n-1}} = k_m \cdot t + \frac{1}{(n-1)a^{n-1}}$$

$$\text{or, } k_m \cdot t = \frac{1}{(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

$$\text{or, } k_m = \frac{1}{t \cdot (n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right] \quad \text{--- (5)}$$

This is the kinetic equation of the n th order reaction.

Half-life of n th Order Reaction :-

when $t = t_{1/2}$, $x = a/2$ so that from equation (5) we have

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

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

$$\text{or, } t_{1/2} = \frac{1}{k_m \cdot (n-1)} \cdot \frac{(2^{n-1} - 1)}{a^{n-1}} \quad \text{--- (6)}$$

$$\text{or, } t_{1/2} \propto \frac{1}{a^{n-1}} \quad \text{--- (7)}$$

It is easy to see from equation (7) that for a first order reaction ($n=1$), $t_{1/2}$ is independent of the initial concentration (a); for a second order reaction ($n=2$), $t_{1/2} \propto \frac{1}{a}$; for a third order reaction ($n=3$), $t_{1/2} \propto \frac{1}{a^2}$, and so on.

Similarly, it can be proved that-

$$t_{3/4} \propto \frac{1}{a^{n-1}} \quad \text{--- (8)}$$

Thus, the time required to complete a definite fraction of the reaction of n th order is inversely proportional to the initial concentra-

tion raised to the power which is one less than the order of reaction.

Units of n th Order Reaction :-

The rate constant for the n th order reaction is

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

$$= \frac{1}{\text{time}} \times \frac{1}{(\text{concentration})^{n-1}}$$

$$= \frac{1}{\text{time}} \times \frac{1}{(\text{mol/litre})^{n-1}}$$

Thus, the units of k_n for the n th order reaction is $\text{mol}^{1-n} \text{litre}^{n-1} \text{time}^{-1}$.

Methods of Determination of Order of a Reaction:

Essentially, the order of a reaction is determined by finding a rate expression which fits observed data over a wide range of conditions. This is simple enough statement, but carrying out the procedure is not always easy or obvious. Several special procedures used in determining such consistency are very much worth mentioning explicitly, as are some pitfalls of which to be aware.

The various methods of determining the order of a reaction are :

1. Differential Method :- The differential method was first suggested by van't Hoff in 1884. According to this method, the rate of an n th-order reaction is given by

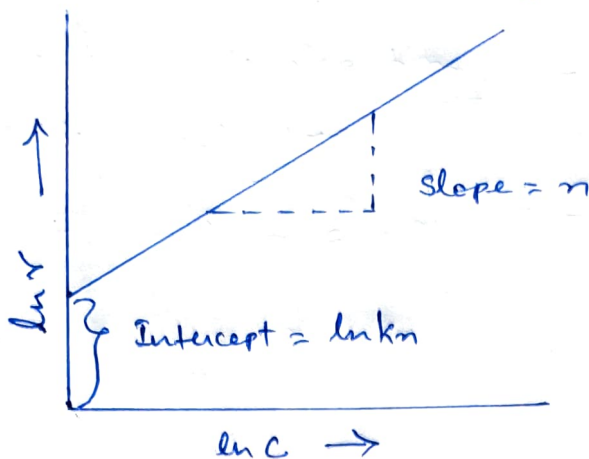
$$\text{Rate, } r = - \frac{dc}{dt} = k_n c^n \quad \text{--- (1)}$$

On taking logs, we have

$$\ln r = \ln k_n + n \ln c \quad \text{--- (2)}$$

Thus, if the double logarithmic plot of rate versus concentration gives a straight line, then the slope

gives the value of n and the intercept gives the value of $\ln k_n$, as shown in figure given below



Also, if r_1 and r_2 are the rates at two different concentrations C_1 and C_2 , then

$$\frac{r_1}{r_2} = \frac{-dc_1/dt}{-dc_2/dt} = \frac{k_n C_1^n}{k_n C_2^n}$$

or,
$$\frac{r_1}{r_2} = \left(\frac{C_1}{C_2}\right)^n$$

Taking logs, we get

$$\ln \frac{r_1}{r_2} = n \cdot \ln \frac{C_1}{C_2}$$

or,
$$n = \frac{\ln (r_1/r_2)}{\ln (C_1/C_2)} \quad \text{--- (3)}$$

Thus we can determine the order (i.e. n) of a chemical reaction.

2. Integration Method or Hit and Trial Method :-

This is a very simple procedure to calculate the rate constant. In this method, known quantities of the reactants are mixed in a reaction vessel and the progress of the reaction can be noted by determining the amount of reactant consumed after different intervals of time. These values are then substituted in the equations for the first-order, second order and third order reactions. The order of the reaction corresponds to that equation which

gives the constant value of k . In this method, one equation after the other undergoes trial till the correct equation is known.

Limitations of the Method :- Two main limitations are

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

3. Half-life Method or Fractional Change Method:-

The half-life, $t_{1/2}$ of an n th order reaction when all the reactants present are in the same molar concentrations is given by

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

If two experiments are carried out at different initial molar concentrations, then

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

On taking logs we get-

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

$$\text{or, } n = 1 + \frac{\ln(t_{1/2})_1 / \ln(t_{1/2})_2}{\ln(a_2/a_1)} \quad \text{--- (4)}$$

This method was suggested by Ostwald. The determination of half-lives of a reaction at two different initial concentrations leads to the determination of n .

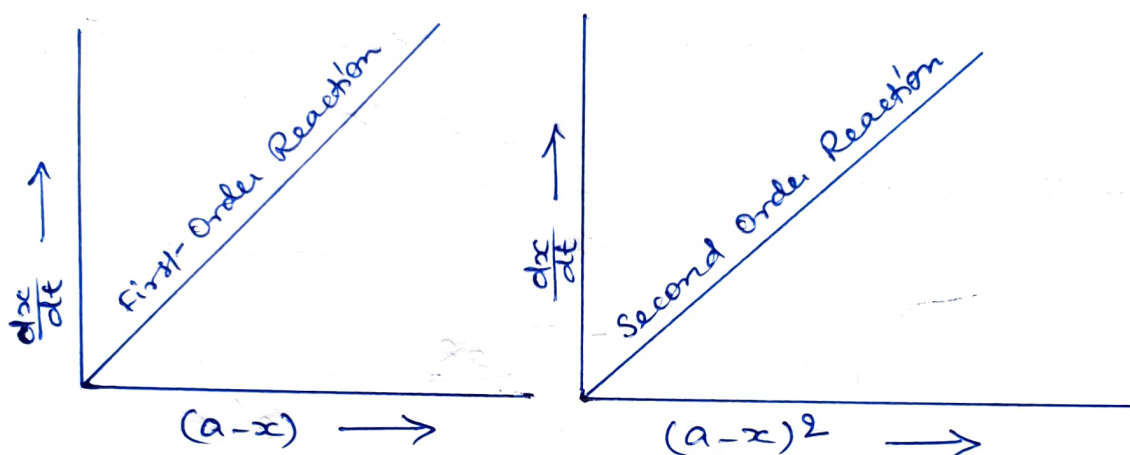
4. Graphical Method :- According to the law of mass action, the rate of n th order reaction is given by as

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

This is only true when all the reactants taking part in the reaction are at the same initial concentration.

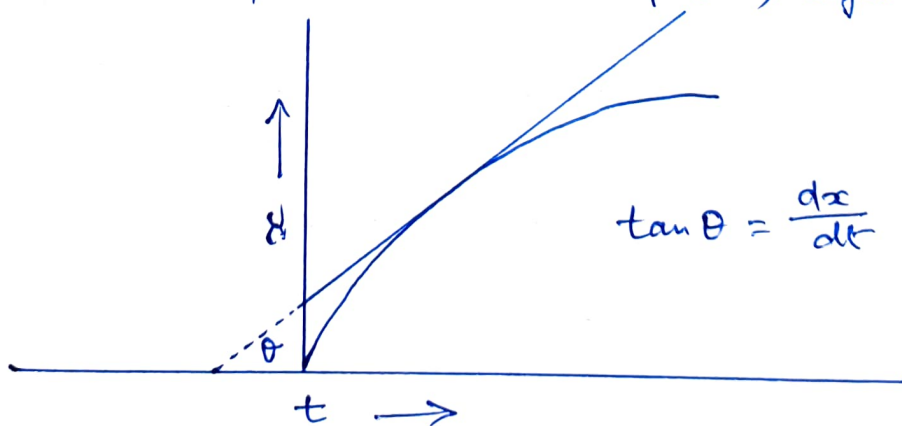
Thus, for a first order reaction it can be written as $\frac{dx}{dt} = k_1 (a-x)^1$; for a second order reaction, $\frac{dx}{dt} = k_2 (a-x)^2$; for a third order reaction it will be $\frac{dx}{dt} = k_3 (a-x)^3$; and so on.

Now, if a curve is plotted between dx/dt and $(a-x)$ at different-time intervals, a straight line is obtained for the first-order reaction. But if a straight-line is obtained by plotting dx/dt against $(a-x)^2$, then the reaction is said to be of second order.



Similarly, if a straight-line is obtained by plotting dx/dt against $(a-x)^n$, then the reaction is of the n th order.

In this method, the value of dx/dt at different-time intervals can be obtained by plotting 'x' (i.e. the amount of substance decomposed) against time t .



The value of $\tan \theta$ (tangent) at any time will give the value of $\frac{dx}{dt}$ at that-time.

5. Isolation Method :- This method was suggested

by Ostwald in 1902. In this method, all the reactants except one are taken in large excess so that ^{their} concentrations remain constant throughout this change. Thus, the order of the reaction is determined with respect to the reactant whose concentration is changing significantly. 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.

This can be seen by considering the following general reaction



The reaction rate is given by

$$\frac{dx}{dt} = k C_A^{n_1} C_B^{n_2} C_C^{n_3}$$

In the first experiment, the reactants B and C are taken in large excess and the order of the reaction is to be determined with respect to A. Let this order be n_1 with respect to A.

In the second experiment, the reactants A and C are taken in large excess and the order of the reaction is to be determined with respect to B. Let this order be n_2 .

In the third experiment, the reactants A and B are taken in large excess and the order of this reaction is determined with respect to C. Let this order be n_3 .

Now the total order of the reaction will be equal to $n_1 + n_2 + n_3$.

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