

For two different concentration  $C_1$  and  $C_2$

We have  $\frac{dC_1}{dt} = k C_1^m$

and  $\frac{dC_2}{dt} = k C_2^m$

Thus,  $\frac{dC_1/dt}{dC_2/dt} = \left(\frac{C_1}{C_2}\right)^m$

Taking logarithm

$\log \frac{dC_1/dt}{dC_2/dt} = \log \left(\frac{C_1}{C_2}\right)^m$

$\Rightarrow \log \frac{dC_1}{dt} - \log \frac{dC_2}{dt} = m \log \frac{C_1}{C_2}$

$\Rightarrow \log \frac{dC_1}{dt} - \log \frac{dC_2}{dt} = m(\log C_1 - \log C_2)$

$\Rightarrow \left[ \begin{matrix} m = \frac{\log \frac{dC_1}{dt} - \log \frac{dC_2}{dt}}{\log C_1 - \log C_2} \end{matrix} \right]$

The values of  $\frac{dC_1}{dt}$  and  $\frac{dC_2}{dt}$  can be determined by graphical method as mentioned in 3rd method.

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3 Graphical method:

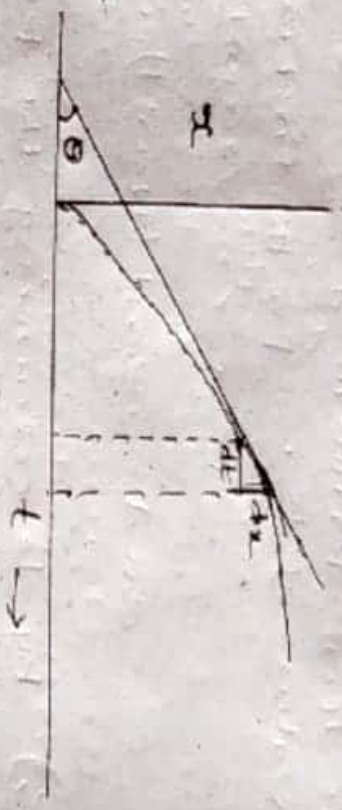
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In this method, the rate of reaction  $\frac{dx}{dt}$  and the existing concentration of reactants  $(a-x)$  are determined at various time intervals, value of  $(a-x)$  can be determined by analysis of the reaction mixture and the value of  $\frac{dx}{dt}$  is determined graphically as follows:

Values of  $x$  (i.e. amount of reactant) are plotted against  $t$  (time) and the curve is plotted. Now tangents are drawn at several points on the curve making angle  $\theta$  with the abscissa which is measured.

At any time  $\frac{dx}{dt} = \tan \theta$

For a 1st order reaction, the plot of various values of  $\frac{dx}{dt}$  against the corresponding values of  $(a-x)$  is a straight line.



If the straight line is obtained by plotting  $\frac{dx}{dt}$  against  $(a+x)^2$  or  $(a-x)^2$ , the reaction is of 2nd (second) order or 3rd (third order) respectively.

4 Van't Hoff's differential method:

At any concentration  $(c)$  of the reactant

$$\frac{dx}{dt} \propto c^n$$

$$\text{or } \frac{dx}{dt} = k c^n$$

where  $n =$  order of reaction and  $k =$  velocity constant



Experimental determination of order of reaction:

① Integration method: known quantities (a) of reactants are taken in a reaction vessel and their amounts reacted (x) at different time intervals (t) are determined by analysing the reaction mixture. The data are then substituted in the various equation for the velocity constants of first, second and third order reactions. The order of reaction is then known by the equation which gives the constant value of K.

For the first order reaction  $K = \frac{1}{t} \ln \frac{a}{a-x}$

For 2nd (second) order reaction  $K = \frac{x}{t \cdot a(a-x)}$

and 3rd (third) order reaction  $= \frac{x(2a-x)}{2ta^2(a-x)^2}$

② By determining the period of half change :->

The time ( $t_{1/2}$ ) taken in completing half of the reaction is determined experimentally and the experiment is repeated with different initial concentrations (a) of the reactants.

Now if the value of  $t_{1/2}$  is independent of the initial concentration of the reactant, the reaction is of first order.

If  $t_{1/2}$  is proportional to  $\frac{1}{a}$ , the reaction is of 2nd order and  $t_{1/2}$  is proportional to  $\frac{1}{a^2}$ , the reaction is of 3rd order.