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Determination of The Order Of Reaction

(i) The Differential Method: This method was suggested by van't Hoff and therefore it is sometimes called as van't Hoff method. According to this method the rate of a reaction of nth order is proportional to the nth power of concentration.

$$-d[A]/dt=k[A]^n$$

where [A] is the concentration at any instant. In two experiments with initial concentration $[A]_1$ and $[A]_2$

$$-d[A]_1/dt=k[A]_1^n$$

$$-d[A]_2/dt=k[A]_2^n$$

Taking logarithms, we get $\log\{-d[A]_1/dt\}=\log k+n\log[A]_1$

and $\log\{-d[A]_2/dt\}=\log k+n\log[A]_2$

Subtracting, we have,

$$n=\frac{\log\{-d[A]_1/dt\}-\log\{-d[A]_2/dt\}}{\log[A]_1-\log[A]_2}$$

An approximation method used to determine **-d[A]/dt** is as follows: This rate of change in A over and appreciable time interval, i.e, $-\Delta A/\Delta t$ is measured and assumed to be **-d[A]/dt** corresponding to the mean value of A in the interval considered.

A better method is to plot concentration versus time for two experiments with different initial concentration. The slop(**-d[A]/dt)** at a given interval is measured by drawing tangents. Using these values of slops (**-d[A]/dt)** in the above equation, n is determined.

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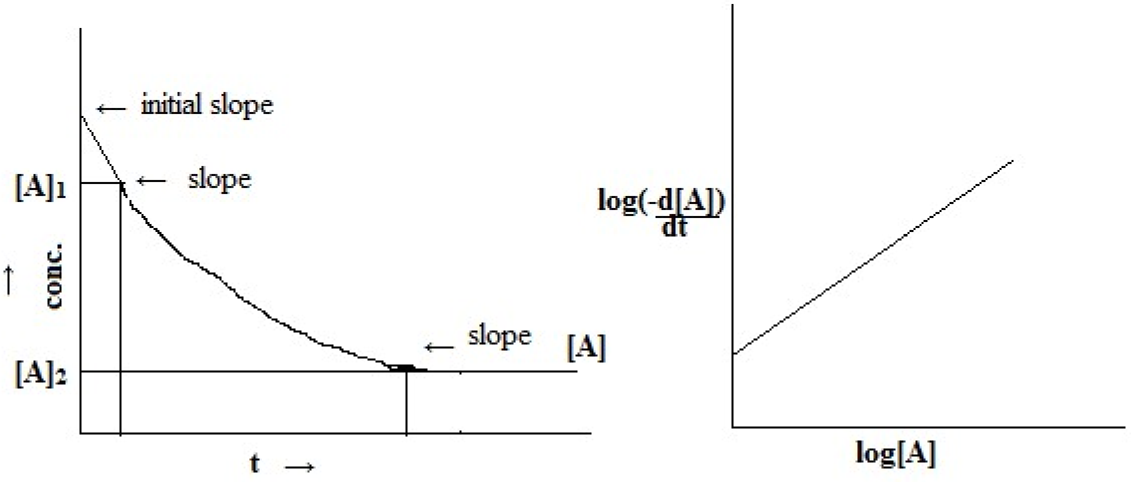

Figure 6: Plot of (-d[A]/dt) vs time and log(-d[A]/dt) vs for log[A] for differential method

(ii)Half-Life method: At the time at which half of the reactant disappear is the half-life period ($t_{1/2}$). For a first order reaction this value is constant and is independent of the initial concentration of the reactant. For a second order reaction , $t_{1/2}$ is inversely proportional to the initial concentration of the reactant. In general, for a reaction of nth order, $t_{1/2}$ is given by Eq(45),i.e ,

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

where a is the initial concentration of the reactant and n is the order of the reaction. Suppose two different experiments are carried out with initial concentrations as a_1 and a_2,then their half-life periods $(t_{1/2})_1$ and $(t_{1/2})_2$ would be related as

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

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

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

Hence n can be evaluated.

Complications in Reaction Kinetics

There are many reaction which are accompanied by side reactions in the addition to the main reaction. Such reactions do not take place in a single stage but occure ina number of well defined steps. In these cases the rate law is inconsistent with the stoichiometric equation for the reaction. The usual types of complications are:

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i) Reversible or opposing reaction

ii) Parallel reactions

iii) Consecutive reactions

i) Reversible or opposing reaction: In general it is assumed that the reactions are process in one direction only. If the products formed react to produce the reactants back, the reaction is said to be an **opposing** or a **reversible** reaction. In such instances, the ration of the reverse reaction increases as more and more of the products are formed and eventually the two rates viz., forward and reverse become equal; the overall rate is then zero. A well known example is the hydrolysis of ethyl acetate in aqueous solution

$$CH_3COOC_2H_5 + H_2O \overset{H_3O^+}{\rightleftharpoons} CH_3COOH + C_2H_5OH$$

The simplest process is that of a reversible or opposing reaction where the reaction is 1st orderin both the directions. The reactions considered are simple except this complication so that it may be written as

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

The reactant A changes to B with a specific rate k_f and B changes to A with a specific rate k_b. Let only A be present initially and let the initial concentration a gm moles/l. x gm moles/l be converted into B at time t, then the net rate of production of B is

$dx/dt=k_f(a-x)- k_b x$ ………………………………………….. (46)

Let x_e be the amount of B at equilibrium. Then

$k_f(a-x_e)= k_b x_e$

so, $k_b= k_f(a-x_e)/ x_e$ ……………………………………………….(47)

Putting eqn. (47) in (46)

$dx/dt=k_f(a-x)- k_f(a-x_e) x/ x_e$ ……………………………………….. (48)

$=k_f(x_e-x)a/x_e$ ....(49)

or, $dx/(x_e-x) = k_f adt/x_e$

Integrating

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$-\ln(x_e-x) = k_f at/x_e + I_c$

When t=0, x=0, Thus, $I_c = -\ln x_e$, consequently, $\ln x_e/(x_e-x) = k_f at/x_e$ ……..(50)

So,

$$k_f = \frac{x_e}{at}\ln\frac{x_e}{x_e-x}$$

From eq (47)

$$k_b = \frac{a-x_e}{at}\ln\frac{x_e}{x_e-x}$$

……………………… (51)

Naturally,

$$k_f + k_b = \frac{1}{t}\ln\frac{x_e}{x_e-x}$$

……………………….. (52)

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