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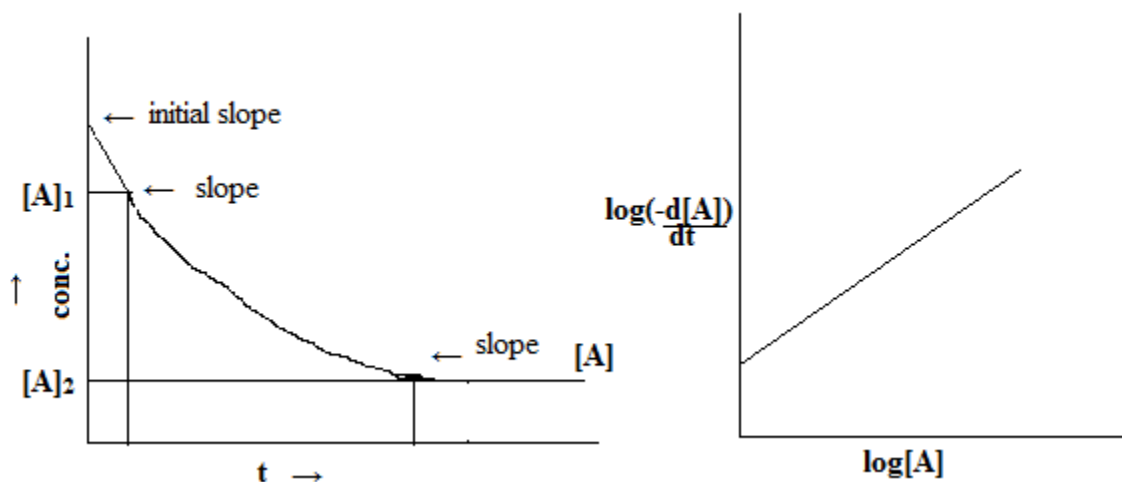
Figure 6: Plot of (-d[A]/dt) vs time and log(-d[A]/dt) vs for log[A] for differential method

(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 ,

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

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

$$CH_3COOC_2H_5 + H_2O \underset{}{\overset{H_3O^+}{\rightleftharpoons}} CH_3COOH + C_2H_5OH$$
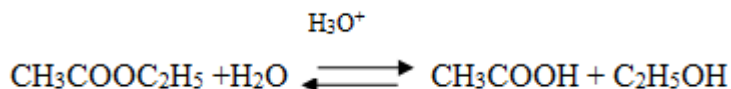
The simplest process is that of a reversible or opposing reaction where the reaction is 1st orderin both the directions. The reactions considered are simple except this complication so that it may be written as

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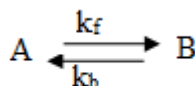
The reactant A changes to B with a specific rate k_f and B changes to A with a specific rate k_b. Let only A be present initially and let the initial concentration a gm moles/l. x gm moles/l be converted into B at time t, then the net rate of production of B is

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

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

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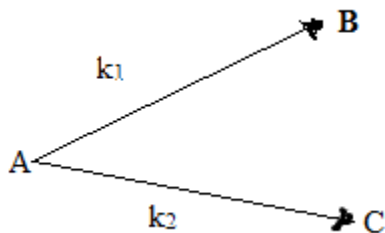
So,
$$k_f = \frac{x_e}{at} \ln \frac{x_e}{x_e-x}$$

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)

ii) **Parallel reactions :** If reacting substances follow more than one path to give different products, then the different paths are termed as parallel or concurrent reactions. A general simple case containing two parallel first order reactions is depicted below.

Here k_1 is the specific rate of conversion of A→B and k_2 is the specific rate of conversion of A→C. The reactions are taken as one way elementary reaction. Let the initial concentration of A be a, and let x be the concentration of A spent at time t, then

$dx/dt = k_1(a-x) + k_2(a-x)$ .... (53)

$dx/dt = (k_1+k_2)(a-x)$

Consequently $k = k_1+k_2 = 1/t \ln(a/a-x)$ .... (54)

Hence $(a-x) = a.e^{-(k_1+k_2)t}$ ....(55)

So, $dC_B/dt = k_1 a.e^{-(k_1+k_2)t}$

Integrating, $C_B = -\{k_1/ k_{1+} k_2\} a.e^{-(k_1+k_2)t} + I_c$

When t=0, $C_B = 0$

So, $I_c = (k_1/ k_{1+} k_2)a$

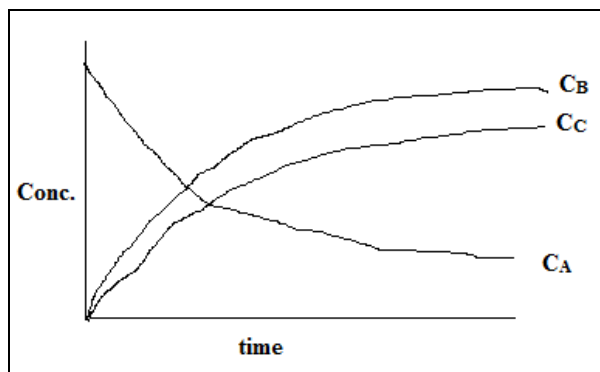So, $C_B = (k_1 a / k_{1+} k_2)[1 - e^{-(k_1+k_2)t}]$ ……………………(56)

Similarly, $C_c = (k_2 a / k_{1+} k_2)[1 - e^{-(k_1+k_2)t}]$ …………………(57)

So, $(C_B/C_c) = k_1/k_2$ ……………………(58)

The plot of C_A, C_B and C_C versus t is depicted below (assuming $k_1 > k_2$)

Figure7: The plot of C_A, C_B and C_C versus t

Nitration of phenol involves three parallel reactions of 1st order, the products being ortho, meta and para nitrophenol respectively. The ratio of the amounts of three isomers remain constant during the course of the experiment as predicted by eq (58).

If the parallel reaction are reversible, the proportion of B and C in the product may be different.
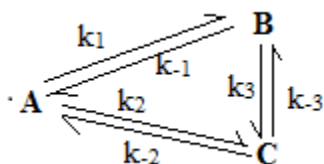
Let B also react to give C, and let the general sequence be k_{-1}, and k_{-2} are the specific rates of the backward reactions B→A and C→A and k_3 and k_{-3} are the specific rates of B→C and C→B reactions respectively. Then, since the reactions are elementary, the equilibrium constant for A→B is

$K_1 = k_1/k_{-1}$ and A→C is $K_2 = k_2/k_{-2}$

If we wait for equilibrium to be attained, the ratio $C_B/C_C = K_1/K_2$. This is thermodynamic control of reactions; the product with most negative ΔG^0 is favoured. However, during early stages the ratio of C_B/C_C will follow rq (58). This is kinetic control of reaction. Again, if k_1 and k_2 are much greater than k_{-1}, k_{-2} and k_{-3}, the product will be kinetically controlled even when A has been nearly completely consumed. It frequently happens that $K_1/K_2 >> 1$ and $k_1/k_2 << 1$. Then C is

favoured kinetically and B is favoured thermodynamically. Examples are many in organic chemistry. The relative yield depends on whether there is kinetic or thermodynamic control.

iii) Consecutive reactions: There are reactions which proceed from reactants to products through one or more intermediate steps. Consider a simple first order consecutive reaction scheme

$$A \xrightarrow{k_1} B \xrightarrow{k'_1} C$$

	A	B	C
Initial Concentration	a	0	0
Concentration After time t	x	y	z
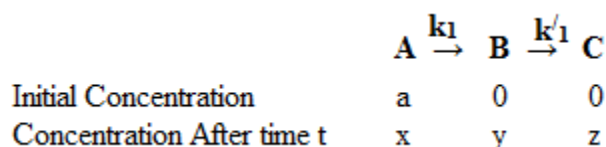
In the above reaction each stage has its own rate constant given by k_1 and k'_1 as shown. The overall rate of the reaction will depend upon the relative magnititudes of these rate constants. If $k_1 \gg k'_1$ –conversion of B to C is slow step and will determine the rate of formation of the products. On the other hand, if $k'_1 \gg k_1$ – formation of B from A will control the overall rate of the reaction. However, if the two rate constants are of comparable magnitudes, the overall rate of the reaction will depend on both the rate constants and the problem becomes more complicated.

The rate of disappearance of A, $-d[A]/dt = -dx/dt = k_1 x$ ……………….. (59)

The rate of formation of B, $d[B]/dt = dy/dt = k_1 x - k'_1 y$ ………………… (60)

The rate of formation of C, $d[C]/dt = dz/dt = k'_1 y$ …………………. …….(61)

Eq.(59) on integration in the limits x=a, t=x to t=t, gives

$$k_1 t = \ln(a/x)$$

or, $\quad x = ae^{-k_1 t}$ …………………………………………….. (62)

The concentration of A decreases exponentially with time as happens in any first order reaction. Substituting this value of x in Eq. (60) gives

$$dy/dt = k_1 ae^{-k_1 t} - k'_1 y$$

This is a linear first order differential equation whose solution is

$$y = \frac{k_1 a}{k'_1 - k_1} [e^{-k_1 t} - e^{-k'_1 t}]$$

…………………………………(63)

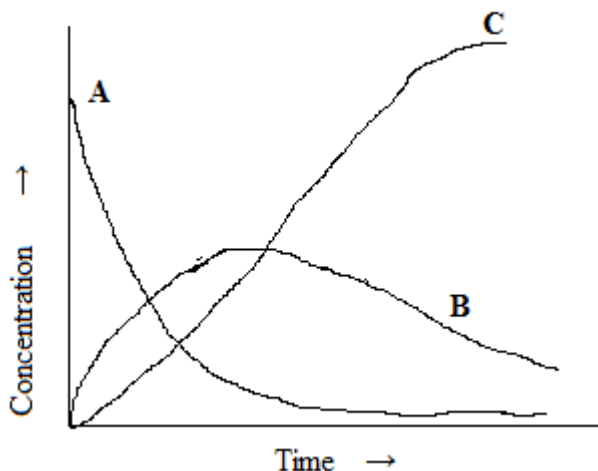During the reaction there is no change in the number of moles, i.e.,

$$x + y + z = a$$

or, $\quad z = a - (x+y)$

$$= a - \frac{k_1 a}{k'_1 - k_1} [e^{-k_1 t} - e^{-k'_1 t}] - ae^{-k_1 t}$$

$$z = \frac{a}{k'_1 - k_1} [(k'_1 - k'_1 e^{-k_1 t}) - (k_1 - k_1 e^{-k'_1 t})]$$

…………………….(64)

Figure8: Concentration changes in a consecutive first order reaction

If $k'_1 \gg k_1$ in the eq.(63), then $e^{-k'_1 t}$ is much less than $e^{-k_1 t}$ and eq (63) reduces to

$$y = \frac{k_1 a}{k'_1 - k_1} e^{-k_1 t}$$

Since $x = a e^{-k_1 t}$

$$\frac{y}{x} = \frac{k_1}{k'_1 - k_1}$$

i.e, the ratio of the amounts of B and A formed in a definite interval of time after the start of the reaction becomes constant. The amounts of A and B falls to the same extent. Such a state is called the transient equilibrium. If $k'_1 \gg k_1$ then,

$$\frac{y}{x} = \frac{k_1}{k'_1}$$

For a first order reaction

$$\frac{y}{x} = \frac{(t_{1/2})_B}{(t_{1/2})_A}$$
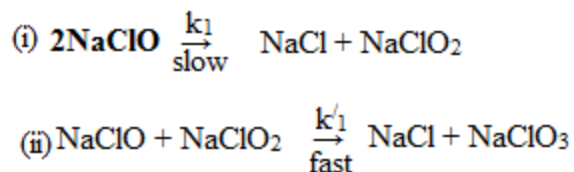
This equation is called secular equilibrium.

The formation of C therefore involves only the smaller rate constant k'_1 and is therefore, the rate determining step. Similarly, when $k'_1 \gg k_1$ (64) reduces to

$$z \approx a(1-e^{-k_1 t})$$

which again involves the rate constant of the slower step.

Example of Consecutive reactions:

a) Decomposition of sodium hypochlorite takes place in two steps as

(i) $2NaClO \xrightarrow[\text{slow}]{k_1} NaCl + NaClO_2$

(ii) $NaClO + NaClO_2 \xrightarrow[\text{fast}]{k'_1} NaCl + NaClO_3$

Steady State approximation

In the preceding section we have seen that the concentration of the intermediate B grows up to a certain small and fixed value. At this stage the rates of formation of the intermediate and its disappearance are equal, i.e.

$$d[B]/dt = 0$$

This fact of constant concentration of an unstable intermediate species is called the principle of *steady state approximation.*

From equation (63), we have

$$y = \frac{k_1 a}{k'_1 - k_1} [e^{-k_1 t} - e^{-k'_1 t}]$$

From the principle of steady state,

$$\frac{dy}{dt} = \frac{k_1 a}{k'_1 - k_1} [-k_1 e^{-k_1 t} + k'_1 e^{-k'_1 t}] = 0$$

Therefore, $k'_1 e^{-k'_1 t} = k_1 e^{-k_1 t}$

$$\frac{k_1}{k_1'} = \frac{e^{-k_1't}}{e^{-k_1t}}$$

Replacing t by t_{max}, we have
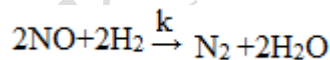
$$\ln \frac{k_1}{k_1'} = (k_1 - k_1') t_{max}$$

$$t_{max} = \frac{1}{(k_1 - k_1')} \ln \frac{k_1}{k_1'}$$

The maximum concentration of B (y_{max}) is given by

$$y_{max} = a \left[\frac{k_1'}{k_1} \right]^{\frac{k_1'}{(k_1 - k_1')}}$$
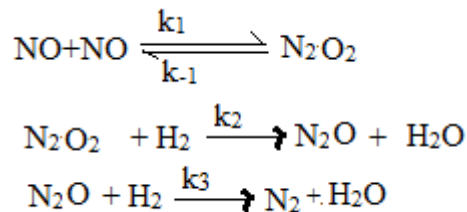
The maximum amount of the intermediate B depends not on the absolute values of the rate constants k_1 and k_1' but only on the ratio k_1' / k_1

By the use of this principle it is possible to obtain the overall rate equation of complex reactions.

$$2NO + 2H_2 \xrightarrow{k} N_2 + 2H_2O$$

The overall rate of the equation is given by $k[NO]^2[H_2]$

The following mechanism may be proposed:

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$$

$$N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$$

The rate for the intermediates N_2O_2 and N_2O are

$$\frac{d[N_2O_2]}{dt} = k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][H_2]$$

and
$$\frac{d[N_2O]}{dt} = k_2[N_2O_2][H_2] - k_3[N_2O]H_2$$

Using steady state approximation, we get

$$k_1[NO]^2 = k_{-1}[N_2O_2] + k_2[N_2O_2][H_2]$$

$$[N_2O_2] = \frac{k_1[NO]^2}{k_{-1} + k_2[H_2]}$$

and $\quad k_2[N_2O_2][H_2] - k_3[N_2O][H_2] = 0$

or $\quad [N_2O] = \frac{k_2[N_2O_2]}{k_3}$

Substituting the value of $[N_2O_2]$ in the above equation, we get

$$[N_2O] = \frac{k_2 k_1[NO]^2}{k_3 (k_{-1} + k_2[H_2])}$$

The overall rate of the reaction can be expressed as

$$d[N_2]/dt = k_3[N_2O][H_2]$$

$$= k_3 \left(\frac{k_2}{k_3}\right) \frac{k_1[NO]^2 [H_2]}{(k_{-1} + k_2[H_2])}$$

$$= \frac{k_2 k_1[NO]^2 [H_2]}{(k_{-1} + k_2[H_2])}$$

If $k_{-1} \gg k_2$, then $k_2[H_2]$ can be neglected, and the rate becomes

$$\frac{d[N_2]}{dt} = \frac{k_2 k_1[NO]^2 [H_2]}{k_{-1}}$$