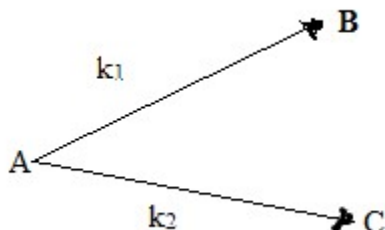


- ii) **Parallel reactions** : If reacting substances follow more than one path to give different products, then the different paths are termed as parallel or concurrent reactions. A general simple case containing two parallel first order reactions is depicted below.



Here k_1 is the specific rate of conversion of $A \rightarrow B$ and k_2 is the specific rate of conversion of $A \rightarrow C$. 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

$$\frac{dx}{dt} = k_1(a-x) + k_2(a-x) \quad \dots\dots\dots (53)$$

$$\frac{dx}{dt} = (k_1 + k_2)(a-x)$$

$$\text{Consequently } k = k_1 + k_2 = 1/t \ln(a/a-x) \quad \dots\dots\dots (54)$$

$$\text{Hence } (a-x) = a \cdot e^{-(k_1 + k_2)t} \quad \dots\dots\dots (55)$$

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

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

$$\text{When } t=0, C_B = 0$$

$$\text{So, } I_c = (k_1 / k_1 + k_2) a$$

$$\text{So, } C_B = (k_1 a / k_1 + k_2) [1 - e^{-(k_1 + k_2)t}] \quad \dots\dots\dots (56)$$

$$\text{Similarly, } C_C = (k_2 a / k_1 + k_2) [1 - e^{-(k_1 + k_2)t}] \quad \dots\dots\dots (57)$$

$$\text{So, } (C_B/C_C) = k_1/k_2 \quad \dots\dots\dots (58)$$

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

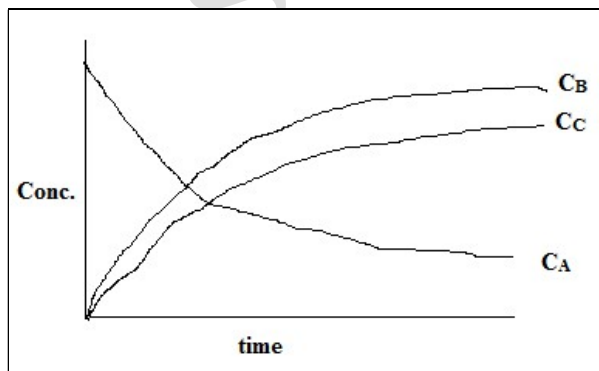
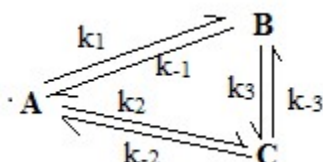


Figure7: The plot of C_A , C_B and C_C versus t

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.

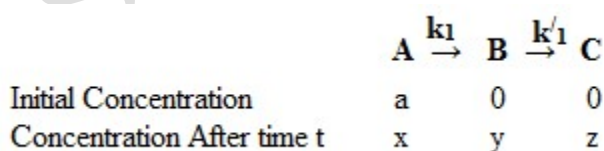


Let B also react to give C, and let the general sequence be k_1 and k_{-1} are the specific rates of the backward reactions $B \rightarrow A$ and $C \rightarrow A$ and k_3 and k_{-3} are the specific rates of $B \rightarrow C$ and $C \rightarrow B$ reactions respectively. Then, since the reactions are elementary, the equilibrium constant for $A \rightarrow B$ is

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

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 eq (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 $K_1/K_2 \gg 1$ and $k_1/k_2 \ll 1$. 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



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 magnitudes 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

Chemical Kinetics

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, $-d[A]/dt = -dx/dt = k_1x$ (59)

The rate of formation of B, $d[B]/dt = dy/dt = k_1x - k'_1y$ (60)

The rate of formation of C, $d[C]/dt = dz/dt = k'_1y$ (61)

Eq.(59) on integration in the limits $x=a$, $t=0$ to $t=t$, gives

$$\begin{aligned} k_1t &= \ln(a/x) \\ \text{or, } x &= ae^{-k_1t} \end{aligned} \quad \text{..... (62)}$$

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

$$dy/dt = k_1 ae^{-k_1t} - k'_1y$$

This is a linear first order differential equation whose solution is

$$y = \frac{k_1a}{k'_1 - k_1} [e^{-k_1t} - e^{-k'_1t}] \quad \text{..... (63)}$$

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

$$x + y + z = a$$

or,

$$z = a - (x + y)$$

$$= a - \frac{k_1a}{k'_1 - k_1} [e^{-k_1t} - e^{-k'_1t}] - ae^{-k_1t}$$

$$z = \frac{a}{k'_1 - k_1} [(k'_1 - k_1)e^{-k_1t} - (k_1 - k'_1)e^{-k'_1t}] \quad \text{..... (64)}$$

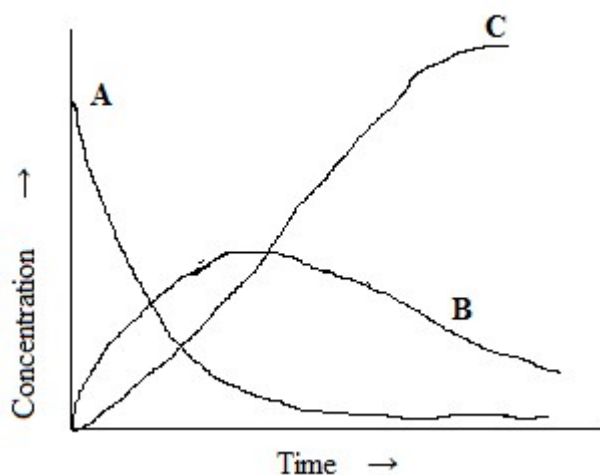


Figure8: Concentration changes in a consecutive first order reaction

Chemical Kinetics

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 $x = ae^{-k'_1 t}$

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

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.

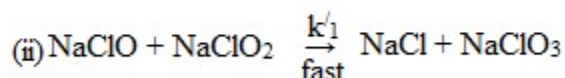
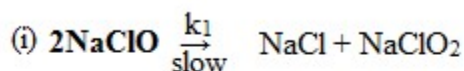
The formation of C therefore involves only the smaller rate constant k'_1 and is therefore, the rate determining step. Similarly, when $k'_1 \gg k_1$ (64) reduces to

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

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



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

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

Replacing t by t_{\max} , we have

$$\ln \frac{k_1}{k'_1} = (k_1 - k'_1) t_{\max}$$

$$t_{\max} = \frac{1}{(k_1 - k'_1)} \ln \frac{k_1}{k'_1}$$

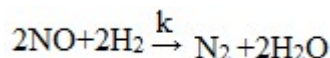
The maximum concentration of B (y_{\max}) is given by

$$y_{\max} = a \left[\frac{k'_1}{k_1} \right] \frac{k_1}{(k_1 - k'_1)}$$

Chemical Kinetics

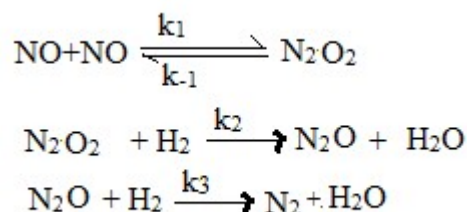
The maximum amount of the intermediate B depends not on the absolute values of the rate constants k_1 and k'_1 but only on the ratio k'_1 / k_1

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



The overall rate of the equation is given by $k[\text{NO}]^2[\text{H}_2]$

The following mechanism may be proposed:



The rate for the intermediates N_2O_2 and N_2O are

$$\frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2] - k_2[\text{N}_2\text{O}_2][\text{H}_2]$$

$$\frac{d[\text{N}_2\text{O}]}{dt} = k_2[\text{N}_2\text{O}_2][\text{H}_2] - k_3[\text{N}_2\text{O}][\text{H}_2]$$

and

Using steady state approximation, we get

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2] + k_2[\text{N}_2\text{O}_2][\text{H}_2]$$

$$[\text{N}_2\text{O}_2] = \frac{k_1[\text{NO}]^2}{k_{-1} + k_2[\text{H}_2]}$$

$$\text{and } k_2[\text{N}_2\text{O}_2][\text{H}_2] - k_3[\text{N}_2\text{O}][\text{H}_2] = 0$$

$$\text{or } [\text{N}_2\text{O}] = \frac{k_2[\text{N}_2\text{O}_2]}{k_3}$$

Substituting the value of $[\text{N}_2\text{O}_2]$ in the above equation, we get

Chemical Kinetics

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

The overall rate of the reaction can be expressed as

$$\begin{aligned} \frac{d[N_2]}{dt} &= k_3 [N_2O] [H_2] \\ &= k_3 \left(\frac{k_2}{k_3} \right) \frac{k_1 [NO]^2 [H_2]}{(k_{-1} + k_2 [H_2])} \\ &= \frac{k_2 k_1 [NO]^2 [H_2]}{(k_{-1} + k_2 [H_2])} \end{aligned}$$

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

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