

Paper : Physical Chemistry

Topic : Chemical Kinetics

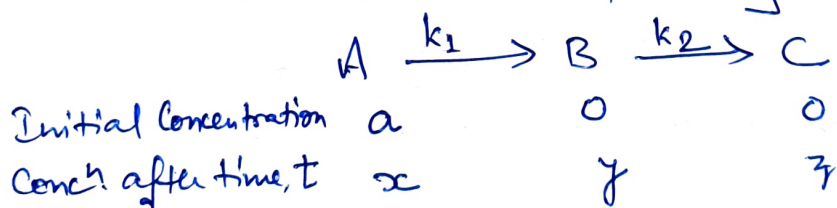
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2. Consecutive Reactions :-

consecutive reactions are defined as that reactions which proceed from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive (or consecutive) steps. These are also known as sequential reactions. In such reactions the products obtained in first step react with each other or with the original reactants to produce new products. It is important to remark that the velocity coefficient is being determined by such a stage which is the lowest.

Let us consider the following consecutive reaction:



In this reaction the product C is formed from the reactant A through intermediate B. Each stage has its own different rate constants, k_1 for the first step and k_2 for the second step. The net or overall rate of reaction depends upon the magnitude of these two rate constants.

Let 'a' is the initial concentration of A and x, y and z are the concentrations of A, B and C resp. at time t. Therefore we can write

$$x + y + z = a \quad \text{--- (1)}$$

The rate of disappearance (or consumption) of A is

$$- \frac{dx}{dt} = k_1 \cdot x \quad \text{--- (2)}$$

Separating the variables, we get

$$- \frac{dx}{x} = k_1 \cdot dt \quad \text{--- (3)}$$

Integrating this, we get

$$- \ln x = k_1 \cdot t + C \quad \text{--- (4)}$$

where C is the integration constant. When $t=0, x=a$, and equation (4) becomes as

$$- \ln a = C \quad \text{--- (5)}$$

Substituting the value of C in equation (4), we get

$$- \ln x = k_1 \cdot t - \ln a$$

$$\text{or, } \ln a - \ln x = k_1 \cdot t$$

$$\text{or, } - \ln x - \ln a = -k_1 t$$

$$\text{or, } \ln(x/a) = -k_1 t$$

$$\text{or } \frac{x}{a} = e^{-k_1 t}$$

$$\text{or } x = a \cdot e^{-k_1 t} \quad \text{--- (6)}$$

Equation (6) states that the concentration of A falls off exponentially with time.

Now,

$$\text{Rate of formation of B} = k_1 \cdot x$$

$$\text{Rate of consumption of B} = k_2 \cdot y$$

The net rate of consumption of B

$$= \text{Rate of consumption of B} - \text{Rate of formation of B.}$$

$$\text{i.e. } - \frac{dy}{dt} = k_2 \cdot y - k_1 \cdot x \quad \text{--- (7)}$$

On putting the value of x from equation (6), we get

$$- \frac{dy}{dt} = k_2 \cdot y - k_1 \cdot a \cdot e^{-k_1 t} \quad \text{--- (8)}$$

Equation (8) is a linear differential equation of

the first order, whose solution is

$$y = \frac{k_1 a}{(k_2 - k_1)} \left[e^{-k_1 t} - e^{-k_2 t} \right] \quad \text{--- (9)}$$

Since, from equation (1)

$$x + y + z = a$$

$$\therefore z = a - x - y \quad \text{--- (10)}$$

Putting the values of x and y from equations (6) and (9) respectively in equation (10), we get-

$$z = a - a \cdot e^{-k_1 t} - \frac{k_1 a}{(k_2 - k_1)} \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

$$\text{or, } z = a \left[1 - \frac{k_2}{(k_2 - k_1)} e^{-k_1 t} + \frac{k_1}{(k_2 - k_1)} e^{-k_2 t} \right] \quad \text{--- (11)}$$

Now the following cases arise :

Case I :- When $k_1 < k_2$, then

$$e^{-k_2 t} \ll e^{-k_1 t}$$

Hence, the equation (9) becomes

$$y = \frac{k_1 a}{(k_2 - k_1)} \cdot e^{-k_1 t}$$

But since $x = a \cdot e^{-k_1 t}$ (equation (6)), we have

$$y = \frac{k_1 x}{(k_2 - k_1)}$$

$$\text{or } \frac{y}{x} = \frac{k_1}{(k_2 - k_1)} \quad \text{--- (12)}$$

Since k_1 and k_2 are constants, hence

$$\frac{y}{x} = \text{constant} \quad \text{--- (13)}$$

This equation states that - the ratio of amount B and A present at any interval of time after the start of reaction becomes constant. In other words, the amounts of A and B diminish to

the same extent. Such a state is called the transient equilibrium.

Case II :- When $k_1 \ll k_2$, then from equation (12) we have

$$\frac{y}{x} = \frac{k_1}{k_2} \quad \text{--- (14)}$$

For first-order reaction

$$k = \frac{0.693}{t_{1/2}}$$

$$\text{or } k \propto \frac{1}{t_{1/2}}$$

$$\therefore k_1 \propto \frac{1}{(t_{1/2})_A} \quad \text{and } k_2 \propto \frac{1}{(t_{1/2})_B}$$

Hence equation (14) becomes

$$\frac{y}{x} = \frac{(t_{1/2})_B}{(t_{1/2})_A} \quad \text{--- (15)}$$

The equilibrium corresponding to equation (15) is called secular equilibrium.

Case III :- When $k_1 \ll k_2$, then equation

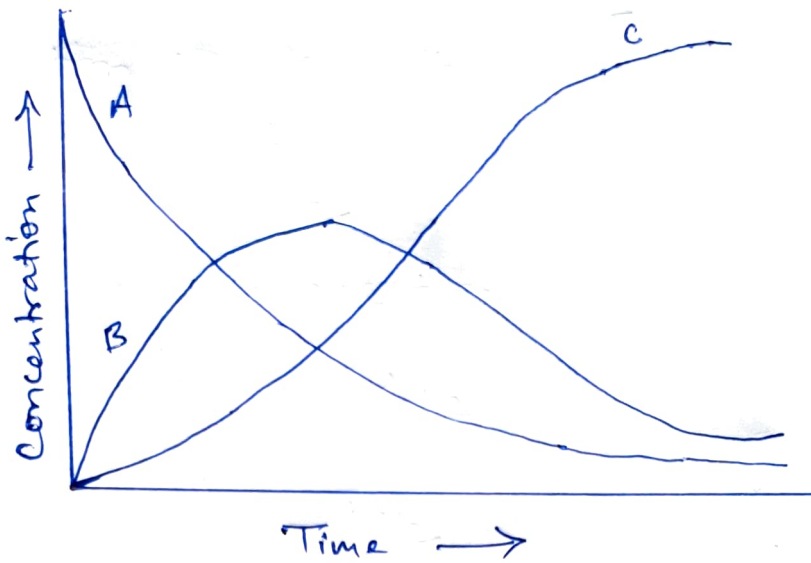
(11) becomes

$$z = a(1 - e^{-kt}) \quad \text{--- (16)}$$

The equation (16) shows the first order kinetics. However, in the very beginning of the reaction, the concentration 'z' remains very low and can not be detected analytically. The value of z remains almost constant over a certain period of time. This interval of time is called induction period.

Variation of concentration with Time in the Consecutive Reaction :-

During the course of the consecutive reaction, the concentrations of A, B and C vary as shown in the figure given below:

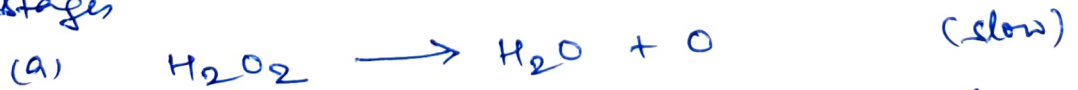


From the figure, the following conclusions have been drawn:

- (a) The concentration of A falls continuously (i.e. decreases exponentially).
- (b) The concentration of B first increases, rises to a maximum and then falls with time. This behaviour is the characteristic of consecutive reactions with comparable values of velocity constants and may be used to identify such reactions.
- (c) The concentration of C increases (from zero in the beginning) with time and finally attains the value equal to the initial concentration of A when all A has changed into the final product C.

Example :-

(i) Decomposition of H_2O_2 occurs in two stages



(ii) Thermal decomposition of ~~acet~~ acetone :



(ii') Decomposition of dimethyl ether in gaseous phase :



(iv) Any radioactive decay of the type



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