

Ans. (i) **1st order reaction :**

If the rate of the reaction is varied by the variation of only one concentration term of the reactant then such type of reaction is called the 1st order reaction.

—Order of reaction is known by the adding of the powers of the concentration terms of the reactant. It is obvious that the sum of the powers of the concentrations of the reactant of the 1st order reaction is one.

—Let us suppose that 'A' is a reactant which is converted into the product 'B' i.e.



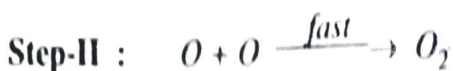
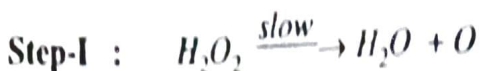
$$\text{then, the rate, } r = \frac{dx}{dt} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt} = K[A]$$

Here, the power of $[A] = 1$

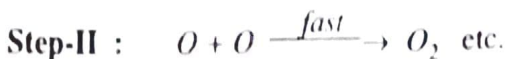
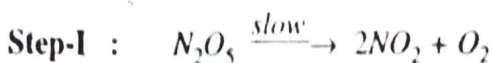
Thus, it is a 1st order reaction.

Example : (a) Decomposition of H_2O_2 :

It decomposes into the following two steps. 1st step is the slowest one whereas the 2nd step is the fast. Since the slowest step is the rate determining step, hence according to this 1st step, its order is determined, which follows the 1st order :

**(b) Decomposition of N_2O_5 :**

This is an another example of 1st order reaction which also involves into the following two steps in which 1st step is slow whereas the 2nd step is fast. Since we know that the slowest step is the rate determining step and hence since the 1st step is the slowest one, thus it also follows the 1st order kinetics.



Ans. (ii) **Rate expression for the 1st order reaction :**

Let us suppose that following is the 1st order reaction—



$$\text{Rate, } r = \frac{dx}{dt} = -\frac{dC_A}{dt} \propto C_A \quad \text{Where } C_A = \text{concentration of 'A'}$$

$$\text{or, } -\frac{dC_A}{dt} = kC_A$$

$$\text{or, } -\frac{dC_A}{C_A} = kdt$$

After the integration of the both sides by C_0 to C in the L.H.S. and $t = 0$ to ' t ' in the R.H.S., we get—

$$-\int_{C_0}^C \frac{dC_A}{C_A} = k \int_0^t dt$$

$$\text{or, } -\ln \frac{C}{C_0} = kt$$

$$\text{or, } -\ln \frac{C_0}{C} = kt$$

$$\text{or, } K = \frac{1}{t} \ln \frac{C_0}{C}$$

By converting 'ln' into 'log'

$$\text{or, } K = \frac{2.303}{t} \log \frac{C_0}{C}$$

Where $\left\{ \begin{array}{l} k = \text{rate constant} \\ C_0 = \text{concentration of the reactant when the time 't' = 0 and} \\ C = \text{concentration of the reactant after time 't'} \end{array} \right.$

Ans. (iii) **Unit for the rate constant of the 1st order reaction :**

$$\begin{aligned} \text{Since, rate constant, } k &= \frac{2.303}{t} \log \frac{C_0}{C} \\ &= 2.303 \times \frac{1}{\text{time}} \log \frac{\text{moles/litre}}{\text{moles/litre}} \\ &= \frac{1}{\text{time}} \\ &= \text{time}^{-1} \end{aligned}$$

Thus, the unit of the rate constant, k of the 1st order reaction is time^{-1} . If we express time in second then its unit will be in sec^{-1} and similarly if we express time in minute, then the unit of the 1st order reaction will be in min^{-1} .

It is evident that ' C_0 ' and ' C ' are the two concentration terms which are involved as a ratio in the above expression and are cancelled out by their own units respectively. Thus it is clear that the rate constant of the 1st order reaction is independent of the unit of the concentration terms of the reactant.

Ans. (iv) **Half life period :**

—It is denoted by ' $t_{1/2}$ '

—It is a such type of time in which the concentration of the reactant becomes to half to its initial concentrations.

Expression of the half life period of the 1st order reaction—

Since, we know that—

$$k = \frac{2.303}{t} \log \frac{C_0}{C}$$

$$\text{or, } t = \frac{2.303}{k} \log \frac{C_0}{C} \quad \dots (2)$$