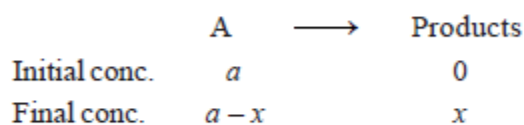


Chemical Kinetics

ZERO ORDER REACTIONS

In a zero order reaction, rate is independent of the concentration of the reactions. Let us consider a zero-order reaction of the type



$$\text{Rate of reaction} = -\frac{d[A]}{dt} = k_0[A]^0$$

or
$$\frac{dx}{dt} = \frac{-d(a - x)}{dt} = k_0(a - x)^0 = k_0$$

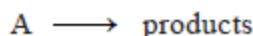
On integrating we get

$$k_0 = \frac{x}{t} \quad \text{or} \quad x = k_0 t$$

where k_0 is the rate constant of a zero-order reaction, the unit of which is concentration per unit time. In zero order reaction, the rate constant is equal to the rate of reaction at all concentrations.

FIRST ORDER REACTIONS

Let us consider a first order reaction



Suppose that at the beginning of the reaction ($t = 0$), the concentration of A is a moles litre⁻¹. If after time t , x moles of A have changed, the concentration of A is $a - x$. We know that for a first order reaction, the rate of reaction, dx/dt , is directly proportional to the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k(a - x)$$

$$\text{or} \quad \frac{dx}{a - x} = k dt \quad \dots(1)$$

Integration of the expression (1) gives

$$\int \frac{dx}{a - x} = \int k dt$$

$$\text{or} \quad -\ln(a - x) = kt + I \quad \dots(2)$$

where I is the constant of integration. The constant k may be evaluated by putting $t = 0$ and $x = 0$.

Thus,

$$I = -\ln a$$

Substituting for I in equation (2)

$$\ln \frac{a}{a - x} = kt \quad \dots(3)$$

$$\text{or} \quad k = \frac{1}{t} \ln \frac{a}{a - x}$$

Changing into common logarithms

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \quad \dots(4)$$

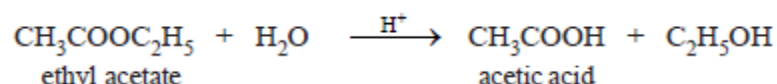
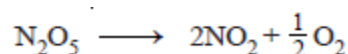
The value of k can be found by substituting the values of a and $(a - x)$ determined experimentally at time interval t during the course of the reaction.

Sometimes the integrated rate law in the following form is also used :

$$k = \frac{2.303}{t_2 - t_1} \log \frac{(a - x_1)}{(a - x_2)}$$

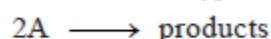
where x_1 and x_2 are the amounts decomposed at time intervals t_1 and t_2 respectively from the start.

Examples of First order Reactions



SECOND ORDER REACTIONS

Let us take a second order reaction of the type



Suppose the initial concentration of A is a moles litre⁻¹. If after time t , x moles of A have reacted, the concentration of A is $(a - x)$. We know that for such a second order reaction, rate of reaction is proportional to the square of the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k(a - x)^2 \quad \dots(1)$$

where k is the rate constant. Rearranging equation (1), we have

$$\frac{dx}{(a - x)^2} = k dt \quad \dots(2)$$

On integration, it gives

$$\frac{1}{a - x} = kt + I \quad \dots(3)$$

where I is integration constant. I can be evaluated by putting $x = 0$ and $t = 0$. Thus,

$$I = \frac{1}{a} \quad \dots(4)$$

Substituting for I in equation (3)

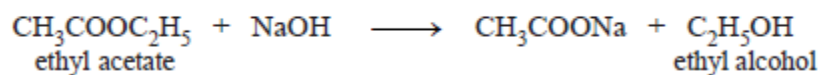
$$\begin{aligned} \frac{1}{a - x} &= kt + \frac{1}{a} \\ kt &= \frac{1}{a - x} - \frac{1}{a} \end{aligned}$$

Thus
$$k = \frac{1}{t} \cdot \frac{x}{a(a - x)}$$

This is the integrated rate equation for a second order reaction.

Examples of Second order Reaction

Hydrolysis of an Ester by NaOH. This is typical second order reaction.



HALF-LIFE OF A REACTION

Reaction rates can also be expressed in terms of **half-life** or **half-life period**. It is defined as : **the time required for the concentration of a reactant to decrease to half its initial value.**