goes on changing since D-glucose rotates the plane of polarised light to the right and D-fructose to the left. **The change in rotation is proportional to the amount of sugar decomposed.**

Let the final rotation be r_∞, the initial rotation r_0 while the rotation at any time t is r_t

The initial concentration, a is ∞ $(r_0 - r_\infty)$.

The concentration at time t, $(a - x)$ is $\propto (r_t - r_\infty)$

Substituting in the first order rate equation,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x}$$

we have

$$k = \frac{2.303}{t} \log_{10} \frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$$

If the experimental values of t $(r_0 - r_\infty)$ and $(r_t - r_\infty)$ are substituted in the above equation, a constant value of k is obtained.

SOLVED PROBLEM. The optical rotation of sucrose in 0.9N HCl at various time intervals is given in the table below.

time (min)	0	7.18	18	27.1	∞
rotation (degree)	+24.09	+21.4	+17.7	+15	–10.74

Show that inversion of sucrose is a first order reaction.

SOLUTION

The available data is substituted in the first order rate equation for different time intervals.

$$k = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

$r_0 - r_\infty = 24.09 - (-10.74) = 34.83$ for all time intervals. Thus, the value of rate constant can be found.

time (t)	$r_t = r_\infty$	$k = \frac{1}{t} \log \frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$
7.18	32.14	$k = \frac{1}{7.18} \log \frac{34.83}{32.14} = 0.0047$
18	28.44	$k = \frac{1}{18} \log \frac{34.83}{28.44} = 0.0048$
27.1	25.74	$k = \frac{1}{27.1} \log \frac{34.83}{25.74} = 0.0048$

Since the value of k comes out to be constant, the inversion of sucrose is a **first order reaction**.

SECOND ORDER REACTIONS

Let us take a second order reaction of the type

$$2\text{A} \longrightarrow \text{products}$$

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,

$$\frac{dx}{dt} = k(a - x)^2 \qquad \text{...(1)}$$

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

$$\frac{dx}{(a-x)^2} = k\,dt \qquad ...(2)$$

On integration, it gives

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

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

$$I = \frac{1}{a} \qquad ...(4)$$

Substituting for I in equation (3)

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$kt = \frac{1}{a-x} - \frac{1}{a}$$

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.

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow CH_3COONa + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

The reaction is carried in a vessel at a constant temperature by taking. equimolar amounts of ethyl acetate and NaOH. Measured volumes of the reaction mixture (say, 25 ml) are withdrawn at various times and titrated against a standard acid. The volume of the acid used is a measure of the concentration of NaOH or ester. Thus the volume of the acid used when $t = 0$, gives the initial concentration (a) of the reactants. The volume of acid consumed at any other time t gives $(a - x)$. The value of x can be calculated. The rate constant k can be determined by substituting values in the second order integrated rate equation.

SOLVED PROBLEM. Hydrolysis of ethyl acetate by NaOH using equal concentration of the reactants, was studied by titrating 25ml of the reaction mixture at different time intervals against standard acid. From the data given below, establish that this is a second order reaction.

t (mts)	0	5	15	25
ml acid used	16.00	10.24	6.13	4.32

SOLUTION

The second order integrated rate equation is

$$k = \frac{1}{at} \cdot \frac{x}{a(a-x)} \qquad ...(1)$$

The volume of acid used at any time is a measure of concentration of the unreacted substances at that time.

Therefore,

a, initial concentration = 16.00

after 5 mts $(a - x) = 10.24$ and $x = 5.76$

after 15 mts $(a-x) = 6.13$ and $x = 9.85$
after 25 mts $(a-x) = 4.32$ and $x = 11.68$

Substituting values in the rate equation (1), we have

$$k = \frac{1}{16 \times 5} . \frac{5.76}{10.24} = 0.0070$$

$$k = \frac{1}{16 \times 15} . \frac{9.85}{6.13} = 0.0067$$

$$k = \frac{1}{16 \times 25} . \frac{11.68}{4.32} = 0.00675$$

The values of k being fairly constant, this reaction is of the second order.

THIRD ORDER REACTIONS

Let us consider a simple third order reaction of the type

$$3\text{A} \longrightarrow \text{products}$$

Let the initial concentration of A be a moles litre^{-1} and after time t, x, moles have reacted. Therefore, the concentration of A becomes $(a-x)$. The rate law may be written as :

$$\frac{dx}{dt} = k\,(a-x)^3 \qquad \text{...(1)}$$

Rearranging equation (1), we have

$$\frac{dx}{(a-x)^3} = k\,dt \qquad \text{...(2)}$$

On integration, it gives

$$\frac{1}{2\,(a-x)^2} = k\,t + I \qquad \text{...(3)}$$

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

$$I = \frac{1}{2a^2}$$

By substituting the value of I in (3), we can write

$$k\,t = \frac{1}{2\,(a-x)^2} - \frac{1}{2a^2}$$

Therefore,

$$k = \frac{1}{t} . \frac{x\,(2a-x)}{2a^2\,(a-x)^2}$$

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

Examples of Third order Reactions

There are not many reactions showing third order kinetics. A few of the known examples are :

(*i*) $2\text{FeCl}_3(aq) + \text{SnCl}_2(aq) \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$

(*ii*) $2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g)$

(*iii*) $2\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\text{NOCl}(g)$

UNITS OF RATE CONSTANT

The units of rate constant for different orders of reactions are different.

Units of Zero order Rate constant

For a zero order reaction, the rate constant k is given by the expression

$$k = \frac{d[\mathrm{A}]}{dt} = \frac{\mathrm{mol}}{\mathrm{litre}} \times \frac{1}{\mathrm{time}}$$

Thus the units of k are

$$\mathbf{mol\ l^{-1}\ time^{-1}}$$

Time may be given in seconds, minutes, days or years.

Units of First order Rate constant

The rate constant of a first order reaction is given by

$$k = \frac{2.303}{t} \log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}$$

Thus the rate constant for the first order reaction is independent of the concentration. It has the unit

$$\mathbf{time^{-1}}$$

Units of Second order Rate constant

The rate constant for a second order reaction is expressed as

$$k = \frac{1}{t} \times \frac{x}{[\mathrm{A}]_0\,([\mathrm{A}]_0 - x)}$$

or

$$= \frac{\mathrm{concentration}}{\mathrm{concentration} \times \mathrm{concentration}} \times \frac{1}{\mathrm{time}}$$

$$= \frac{1}{\mathrm{concentration}} \times \frac{1}{\mathrm{time}}$$

$$= \frac{1}{\mathrm{mole/litre}} \times \frac{1}{\mathrm{time}}$$

$$= \mathrm{mol^{-1}\ l\ time^{-1}}$$

Thus the units for k for a second order reactions are

$$\mathbf{mol^{-1}\ 1\ time^{-1}}$$

Units of Third order Rate constant

The rate constant for a third order reaction is

$$k = \frac{1}{t} . \frac{x(2a - x)}{2a^2\,(a - x)^2}$$

or

$$k = \frac{\mathrm{concentration} \times \mathrm{concentration}}{(\mathrm{concentration})^2 \times (\mathrm{concentration})^2} \times \frac{1}{\mathrm{time}}$$

$$= \frac{1}{(\mathrm{concentration})^2} \times \frac{1}{\mathrm{time}}$$

$$= \frac{1}{(\mathrm{mol/litre})^2} \times \frac{1}{\mathrm{time}}$$

Thus the units of k for third order reaction are

$$\mathbf{mol^{-2}\ l^2\ time^{-1}}$$

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.**

In other words, half-life is the time required for one-half of the reaction to be completed. It is represented by the symbol $t_{1/2}$ or $t_{0.5}$.

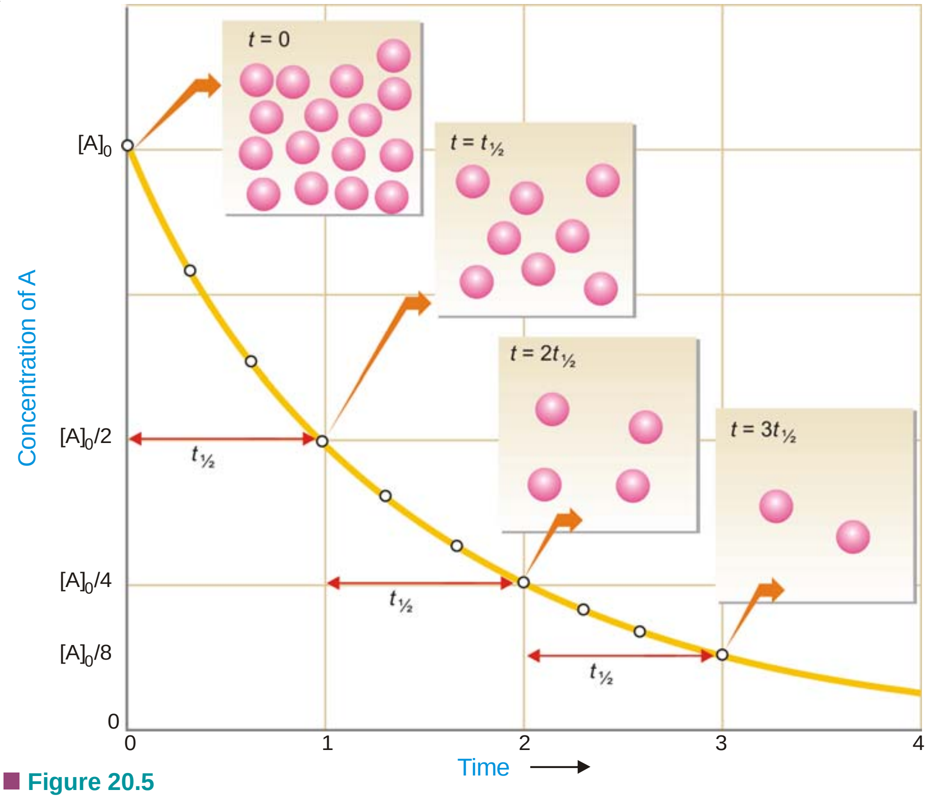

Figure 20.5
First-order half-life. Concentration of a reactant A as a function of time for a first-order reaction. The concentration falls from its initial value, $[A]_0$, to $[A]_0/2$ after one half-life, to $[A]_0/4$ after a second half-life, to $[A]_0/8$ after a third half-life, and so on. For a first-order reaction, each half-life represents an equal amount of time.

Calculation of Half-life of a First order Reaction

The integrated rate equation (4) for a first order reaction can be stated as :

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

where $[A]_0$ is initial concentration and [A] is concentration at any time t. Half-life, $t_{1/2}$, is time when initial concentration reduces to $\frac{1}{2}$ *i.e.*,

$$[A] = \frac{1}{2}[A]_0$$

Substituting values in the integrated rate equation, we have

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A]_0}{1/2[A]_0} = \frac{2.303}{t_{1/2}} \log 2$$

or $$t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.3010$$

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

It is clear from this relation that :

(1) half-life for a first order reaction is **independent of the initial concentration.**

(2) it is **inversely proportional ot *k*,** the rate-constant.

Calculation of Time for Completing any Fraction of the Reaction

As for half-change, we can calculate the time required for completion of any fraction of the reaction. For illustration, let us calculate the time in which two-third of the reaction is completed. First order integrated rate equation is

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

Here, the initial concentration has $\frac{2}{3}$ reacted reducing it to $\frac{1}{3}$. Thus,

$$[A] = \frac{1}{3}[A]_0$$

Substituting values in the rate equation

$$t_{3/4} = \frac{2.303}{k} \log \frac{[A]_0}{1/3[A]_0} = \frac{2.303}{k} \log 3$$

$$= \boldsymbol{\frac{2.303}{k} \times 0.4771}$$

SOLVED PROBLEM 1. Compound A decomposes to form B and C the reaction is first order. At 25°C the rate constant for the reaction is 0.450 s^{-1}. What is the half-life of A at 25°C ?

SOLUTION

We know that for a first order reaction, half-life $t_{1/2}$, is given by the expression

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

where k = rate constant

Substituting the value of k = 0.450 s^{-1}, we have

$$t_{1/2} = \frac{0.693}{0.450\,s^{-1}} = \mathbf{1.54\ s}$$

Thus half-life of the reaction $A \longrightarrow B + C$ is 1.54 seconds.

SOLVED PROBLEM 2. The half-life of a substance in a first order reaction is 15 minutes. Calculate the rate constant.

SOLUTION

For a first order reaction

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

Putting $t_{1/2}$ = 15 min in the expression and solving for k, we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{15\,\text{min}} = \mathbf{4.62 \times 10^{-2}\ min^{-1}}$$