

- (iii) For complex reaction, order is given by the slowest step and molecularity of the slowest step is same as the order of the overall reaction.

### *Intext Questions*

- 4.3** For a reaction,  $A + B \rightarrow \text{Product}$ ; the rate law is given by,  $r = k [A]^{1/2} [B]^2$ . What is the order of the reaction?
- 4.4** The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

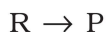
## *4.3 Integrated Rate Equations*

We have already noted that the concentration dependence of rate is called differential rate equation. It is not always convenient to determine the instantaneous rate, as it is measured by determination of slope of the tangent at point 't' in concentration vs time plot (Fig. 4.1). This makes it difficult to determine the rate law and hence the order of the reaction. In order to avoid this difficulty, we can integrate the differential rate equation to give a relation between directly measured experimental data, i.e., concentrations at different times and rate constant.

The integrated rate equations are different for the reactions of different reaction orders. We shall determine these equations only for zero and first order chemical reactions.

### **4.3.1 Zero Order Reactions**

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,



$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

As any quantity raised to power zero is unity

$$\text{Rate} = -\frac{d[R]}{dt} = k \times 1$$

$$d[R] = -k dt$$

Integrating both sides

$$[R] = -k t + I \quad (4.5)$$

where, I is the constant of integration.

At  $t = 0$ , the concentration of the reactant  $R = [R]_0$ , where  $[R]_0$  is initial concentration of the reactant.

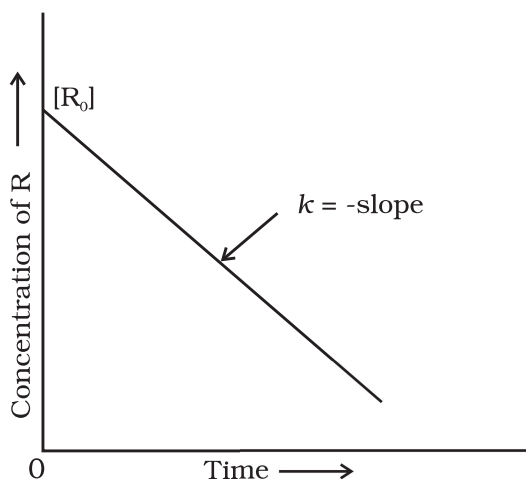
Substituting in equation (4.5)

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation (4.5)

$$[R] = -kt + [R]_0 \quad (4.6)$$



**Fig. 4.3:** Variation in the concentration vs time plot for a zero order reaction

Comparing (4.6) with equation of a straight line,  $y = mx + c$ , if we plot  $[R]$  against  $t$ , we get a straight line (Fig. 4.3) with slope =  $-k$  and intercept equal to  $[R]_0$ .

Further simplifying equation (4.6), we get the rate constant,  $k$  as

$$k = \frac{[R]_0 - [R]}{t} \quad (4.7)$$

Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions. The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

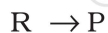


$$\text{Rate} = k [\text{NH}_3]^0 = k$$

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. The thermal decomposition of HI on gold surface is another example of zero order reaction.

#### 4.3.2 First Order Reactions

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant R. For example,



$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k[\text{R}]$$

$$\text{or } \frac{d[\text{R}]}{[\text{R}]} = -kdt$$

Integrating this equation, we get

$$\ln [\text{R}] = -kt + I \quad (4.8)$$

Again,  $I$  is the constant of integration and its value can be determined easily.

When  $t = 0$ ,  $R = [R]_0$ , where  $[R]_0$  is the initial concentration of the reactant.

Therefore, equation (4.8) can be written as

$$\ln [R]_0 = -k \times 0 + I$$

$$\ln [R]_0 = I$$

Substituting the value of  $I$  in equation (4.8)

$$\ln [R] = -kt + \ln [R]_0 \quad (4.9)$$

Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = -kt$$

or  $k = \frac{1}{t} \ln \frac{[R]_0}{[R]}$  (4.10)

At time  $t_1$  from equation (4.8)

$$*\ln[R]_1 = -kt_1 + *\ln[R]_0$$
 (4.11)

At time  $t_2$

$$\ln[R]_2 = -kt_2 + \ln[R]_0$$
 (4.12)

where,  $[R]_1$  and  $[R]_2$  are the concentrations of the reactants at time  $t_1$  and  $t_2$  respectively.

Subtracting (4.12) from (4.11)

$$\ln[R]_1 - \ln[R]_2 = -kt_1 - (-kt_2)$$
$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$
$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2}$$
 (4.13)

Equation (4.9) can also be written as

$$\ln \frac{[R]}{[R]_0} = -kt$$

Taking antilog of both sides

$$[R] = [R]_0 e^{-kt}$$
 (4.14)

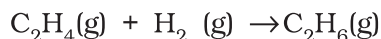
Comparing equation (4.9) with  $y = mx + c$ , if we plot  $\ln [R]$  against  $t$  (Fig. 4.4) we get a straight line with slope =  $-k$  and intercept equal to  $\ln [R]_0$

The first order rate equation (4.10) can also be written in the form

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$
 (4.15)
$$*\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between  $\log [R]_0/[R]$  vs  $t$ , (Fig. 4.5), the slope =  $k/2.303$

Hydrogenation of ethene is an example of first order reaction.

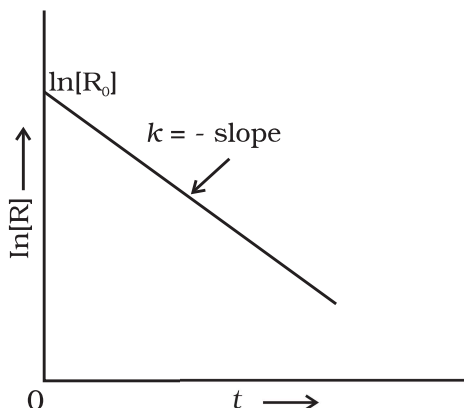


$$\text{Rate} = k [C_2H_4]$$

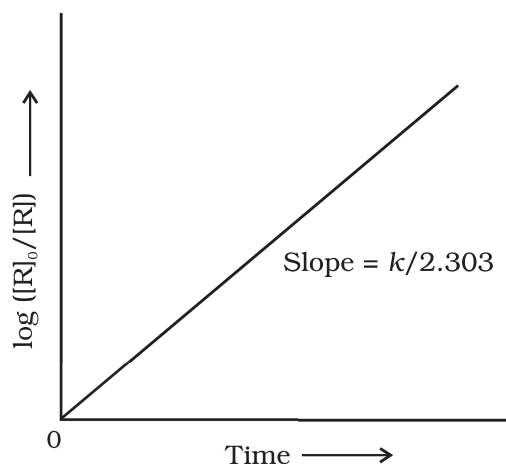
All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

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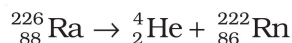
\* Refer to Appendix-IV for  $\ln$  and  $\log$  (logarithms).



**Fig. 4.4:** A plot between  $\ln[R]$  and  $t$  for a first order reaction



**Fig. 4.5:** Plot of  $\log [R]_0/[R]$  vs time for a first order reaction



$$\text{Rate} = k [\text{Ra}]$$

Decomposition of  $\text{N}_2\text{O}_5$  and  $\text{N}_2\text{O}$  are some more examples of first order reactions.

**Example 4.5** The initial concentration of  $\text{N}_2\text{O}_5$  in the following first order reaction  $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$  was  $1.24 \times 10^{-2} \text{ mol L}^{-1}$  at 318 K. The concentration of  $\text{N}_2\text{O}_5$  after 60 minutes was  $0.20 \times 10^{-2} \text{ mol L}^{-1}$ . Calculate the rate constant of the reaction at 318 K.

**Solution** For a first order reaction

$$\begin{aligned} \log \frac{[R]_1}{[R]_2} &= \frac{k(t_2 - t_1)}{2.303} \\ k &= \frac{2.303}{(t_2 - t_1)} \log \frac{[R]_1}{[R]_2} \\ &= \frac{2.303}{(60 \text{ min} - 0 \text{ min})} \log \frac{1.24 \times 10^{-2} \text{ mol L}^{-1}}{0.20 \times 10^{-2} \text{ mol L}^{-1}} \\ &= \frac{2.303}{60} \log 6.2 \text{ min}^{-1} \\ k &= 0.0304 \text{ min}^{-1} \end{aligned}$$

Let us consider a typical first order gas phase reaction

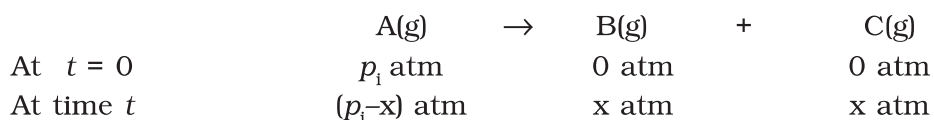


Let  $p_i$  be the initial pressure of A and  $p_t$  the total pressure at time ' $t$ '. Integrated rate equation for such a reaction can be derived as

$$\text{Total pressure } p_t = p_A + p_B + p_C \text{ (pressure units)}$$

$p_A$ ,  $p_B$  and  $p_C$  are the partial pressures of A, B and C, respectively.

If  $x$  atm be the decrease in pressure of A at time  $t$  and one mole each of B and C is being formed, the increase in pressure of B and C will also be  $x$  atm each.



where,  $p_i$  is the initial pressure at time  $t = 0$ .

$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

where,  $p_A = p_i - x = p_i - (p_t - p_i)$

$$= 2p_i - p_t$$

$$k = \left( \frac{2.303}{t} \right) \left( \log \frac{p_i}{p_A} \right) \quad (4.16)$$

$$= \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

The following data were obtained during the first order thermal decomposition of  $N_2O_5$  (g) at constant volume:

### Example 4.6

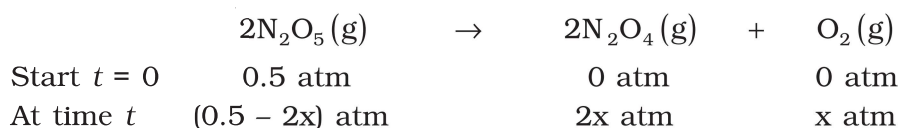


| S.No. | Time/s | Total Pressure/(atm) |
|-------|--------|----------------------|
| 1.    | 0      | 0.5                  |
| 2.    | 100    | 0.512                |

Calculate the rate constant.

Let the pressure of  $N_2O_5$ (g) decrease by  $2x$  atm. As two moles of  $N_2O_5$  decompose to give two moles of  $N_2O_4$ (g) and one mole of  $O_2$  (g), the pressure of  $N_2O_4$  (g) increases by  $2x$  atm and that of  $O_2$  (g) increases by  $x$  atm.

### Solution



$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$

$$= (0.5 - 2x) + 2x + x = 0.5 + x$$

$$x = p_t - 0.5$$

$$p_{N_2O_5} = 0.5 - 2x$$

$$= 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$$

At  $t = 100$  s;  $p_t = 0.512$  atm

$$p_{\text{N}_2\text{O}_5} = 1.5 - 2 \times 0.512 = 0.476 \text{ atm}$$

Using equation (4.16)

$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{p_i}{p_A} = \frac{2.303}{100 \text{ s}} \log \frac{0.5 \text{ atm}}{0.476 \text{ atm}} \\ &= \frac{2.303}{100 \text{ s}} \times 0.0216 = 4.98 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

### 4.3.3 Half-Life of a Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as  $t_{1/2}$ .

For a zero order reaction, rate constant is given by equation 4.7.

$$k = \frac{[\text{R}]_0 - [\text{R}]}{t}$$

$$\text{At } t = t_{1/2}, [\text{R}] = \frac{1}{2} [\text{R}]_0$$

The rate constant at  $t_{1/2}$  becomes

$$k = \frac{[\text{R}]_0 - 1/2 [\text{R}]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[\text{R}]_0}{2k}$$

It is clear that  $t_{1/2}$  for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For the first order reaction,

$$k = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]} \quad (4.15)$$

$$\text{at } t_{1/2} \quad [\text{R}] = \frac{[\text{R}]_0}{2} \quad (4.16)$$

So, the above equation becomes

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

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

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k} \quad (4.17)$$

It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.

**For zero order reaction  $t_{1/2} \propto [R]_0$ . For first order reaction  $t_{1/2}$  is independent of  $[R]_0$ .**

A first order reaction is found to have a rate constant,  $k = 5.5 \times 10^{-14} \text{ s}^{-1}$ . **Example 4.7**  
Find the half-life of the reaction.

Half-life for a first order reaction is

**Solution**

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

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14} \text{ s}^{-1}} = 1.26 \times 10^{13} \text{ s}$$

Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ( $t_{1/2}$ ) of the reaction.

When reaction is completed 99.9%,  $[R]_n = [R]_0 - 0.999[R]_0$

**Example 4.8**

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

$$= \frac{2.303}{t} \log \frac{[R]_0}{[R]_0 - 0.999[R]_0} = \frac{2.303}{t} \log 10^3$$

$$t = 6.909/k$$

**Solution**

For half-life of the reaction

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

$$\frac{t}{t_{1/2}} = \frac{6.909}{k} \times \frac{k}{0.693} = 10$$

Table 4.4 summarises the mathematical features of integrated laws of zero and first order reactions.

**Table 4.4: Integrated Rate Laws for the Reactions of Zero and First Order**

| Order | Reaction type | Differential rate law | Integrated rate law                                 | Straight line plot | Half-life  | Units of $k$  |
|-------|---------------|-----------------------|---|--------------------|------------|---|
| 0     | R → P         | $d[R]/dt = -k$        | $kt = [R]_0 - [R]$                                  | [R] vs $t$         | $[R]_0/2k$ | conc time <sup>-1</sup><br>or mol L <sup>-1</sup> s <sup>-1</sup> |
| 1     | R → P         | $d[R]/dt = -k[R]$     | $[R] = [R]_0 e^{-kt}$<br>or $kt = \ln\{[R]_0/[R]\}$ | ln[R] vs $t$       | $\ln 2/k$  | time <sup>-1</sup> or s <sup>-1</sup>                             |