and we have

$$k\,t_{1/2} = \frac{1}{\frac{1}{2}[\mathrm{A}]_0} - \frac{1}{[\mathrm{A}]_0}$$

or
$$k\,t_{1/2} = \frac{2}{[\mathrm{A}]_0} - \frac{1}{[\mathrm{A}]_0}$$

Solving for $t_{1/2}$ we find that

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

As in case of a first order reaction, half-life for a second order reaction is inversely proportional to rate constant ***k***. While half-life of a first order reaction is independent of initial concentration, **half-life of a second order reaction depends on initial concentration.** This fact can be used to distinguish between a first order and a second order reaction.

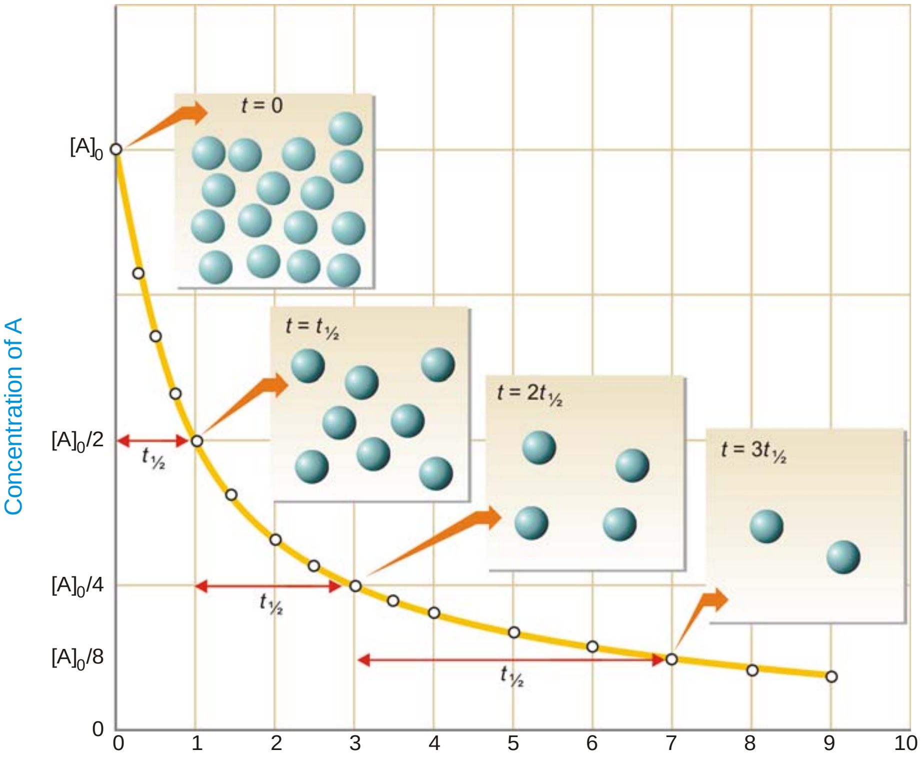

Figure 20.6

Second-order half-life. Concentration of a reactant A as a function of time for a second-order reaction. Note that each half-life is twice as long as the preceding one because $t_{1/2} = 1/k[A]_0$ and the concentration of A at the beginning of each successive half-life is smaller by a factor of 2.

HOW TO DETERMINE THE ORDER OF A REACTION

There are at least four different methods to determine the order of a reaction.

(1) Using integrated rate equations

The reaction under study is performed by taking different initial concentrations of the reactant (a) and noting the concentration ($a - x$) after regular time intervals (t). The experimental values of a,

$(a - x)$ and t are then substituted into the integrated rate equations for the first, second and third order reactions. **The rate equation which yields a constant value of *k* corresponds to the correct order of the reaction.** This method of ascertaining the order of a reaction is essentially a method of hit-and-trial but was the first to be employed. It is still used extensively to find the order of simple reactions.

(2) Graphical method

For reactions of the type A ⟶ products, we can determine the reaction order by seeing whether a graph of the data fits one of the integrated rate equations.

In case of First order

We have already derived the integrated rate equation for first order as

$$1\text{n}\,\frac{a}{a-x} = kt$$

Simplifying, it becomes

$$\begin{array}{ccccc} 1\text{n}\,(a-x) & = & -\,kt & + & 1\text{n}\,a \\ \uparrow & & \uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$

Thus the two variables in the first order rate equation are :

$$1\text{n}\,\frac{a}{a-x} \text{ and } t$$

Hence, if $1\text{n}\,\dfrac{a}{a-x}$ is plotted against t and straight line results (Fig. 20.7), the corresponding reaction is of the first order. However, if a curve is obtained, the reaction is not first order.

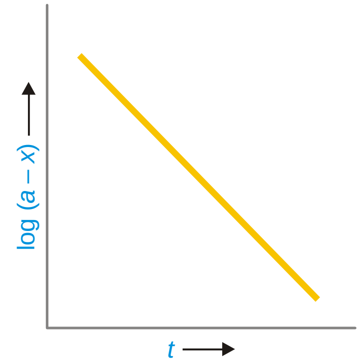

Figure 20.7
Plot of log($a - x$) against t for a first order reaction.

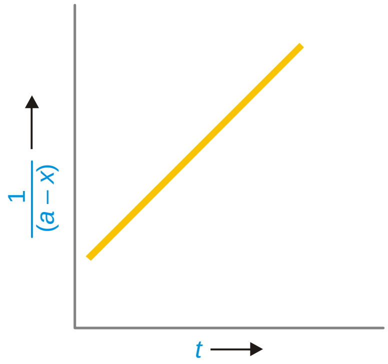

Figure 20.8
Plot of 1/($a - x$) against t for a second order reaction.

In case of Second order

We have already shown that second order rate equation can be written as

$$\begin{array}{ccccc} \dfrac{1}{a-x} & = & kt & + & \dfrac{1}{a} \\ \uparrow & & \uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$

This is the equation of a straight line, $y = mx + b$. Here the two variables are

$$\frac{1}{a-x} \text{ and } t$$

Thus when $\frac{1}{a-x}$ is plotted against t and we get a straight line (Fig. 20.8), the reaction is second order. In case a curve is obtained, the reaction is not second order.

(3) Using half-life period

Two separate experiments are performed by taking different initial concentrations of a reactant. The progress of the reaction in each case is recorded by analysis. When the initial concentration is reduced to one-half, the time is noted. Let the initial concentrations in the two experiments be $[A_1]$ and $[A_2]$, while times for completion of half change are t_1 and t_2 respectively.

Calculation of order of reaction. We know that half-life period for a first order reaction is independent of the initial concentration, [A]. We also know :

$$\text{half-life} \propto \frac{1}{[A]} \quad \text{for 2nd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^2} \quad \text{for 3rd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^{n-1}} \quad \text{for } n\text{th order reaction}$$

Substituting values of initial concentrations and half-life periods from the two experiments, we have

$$t_1 \propto \frac{1}{[A_1]^{n-1}} \qquad t_2 \propto \frac{1}{[A_2]^{n-1}}$$

and

$$\frac{t_2}{t_1} = \left[\frac{A_1}{A_2}\right]^{n-1}$$

$$(n-1) \log \left[\frac{A_2}{A_1}\right] = \log \left[\frac{t_1}{t_2}\right]$$

Solving for n, the order of reaction

$$n = 1 + \frac{\log [t_1/t_2]}{\log [A_2/A_1]}$$

SOLVED PROBLEM. In the reduction of nitric oxide, 50% of reaction was completed in 108 seconds when initial pressure was 336 mm Hg and in 147 seconds initial pressure was 288 mm Hg. Find the order of the reaction.

SOLUTION

We know that

$$\frac{t_2}{t_1} = \left[\frac{A_1}{A_2}\right]^{n-1} \qquad \text{...(1)}$$

where t_1 and t_2 are half-life periods and $[A_1]$ and $[A_2]$ are the corresponding initial concentrations, while n is the order of the reaction.

Taking logs of the expression (1), we have

$$n = 1 + \frac{\log [t_2/t_1]}{\log [A_1/A_2]} \qquad \text{...(2)}$$

Substituting values in expression (2),

$$n = 1 + \frac{\log 108/147}{\log 288/336}$$

$$= 1 + \frac{0.1339}{0.0669} = 1 + 2 = 3$$

Therefore, the reaction is of the **third order**.

(4) The Differential method

This method was suggested by van't Hoff and, therefore, it is also called **van't Hoff's differential method.** According to it, the rate of a reaction of the *n*th order is proportional to the *n*th power of concentration.

$$-\frac{dC}{dt} = k\,C^n$$

where C = concentration at any instant. In two experiments performed with different initial concentrations, we can write

$$-\frac{dC_1}{\mathrm{dt}} = k\,C_1^n \qquad \text{...(1)}$$

$$-\frac{dC_2}{\mathrm{dt}} = k\,C_2^n \qquad \text{...(2)}$$

Taking logs of the expression (1) and (2)

$$\log\left(-\frac{dC_1}{dt}\right) = \log k + n\log C_1 \qquad \text{...(3)}$$

$$\log\left(-\frac{dC_2}{dt}\right) = \log k + n\log C_2 \qquad \text{...(4)}$$

On substracting (4) from (3), we get

$$n = \frac{\log\left(-\frac{dC_1}{dt}\right) - \left(-\frac{dC_2}{dt}\right)}{\log C_1 - \log C_2} \qquad \text{...(5)}$$

To find $n, \left(-\frac{dC}{dt}\right)$ in the two experiments is determined by plotting concentrations against time (t). The slope, $\left(-\frac{dC}{dt}\right)$ at a given time interval is measured by drawing tangents. Using the values of slopes $\left(-\frac{dC_1}{dt}\right)$ and $\left(-\frac{dC_2}{dt}\right)$ in the equation (5), n can be calculated.

(5) Ostwald's Isolation method

This method is employed in determining the order of complicated reactions by 'isolating' one of the reactants so far as its influence on the rate of reaction is concerned. Suppose the reaction under consideration is :

$$A + B + C \longrightarrow \text{products}$$

The order of the reaction with respect to *A*, *B* and *C* is determined. For the determination of the order of reaction with respect to *A*, *B* and *C* are taken in a large excess so that their concentrations are not affected during the reaction. The order of the reaction is then determined by using any of the methods described earlier. Likewise, the order of the reaction with respect to *B* and *C* is determined. If n_A, n_B and n_C are the orders of the reaction with respect to *A*, *B* and C respectively, the order of the reaction n is given by the expression.

$$n = n_A + n_B + n_C$$