

SOLVED PROBLEM. From the following data for the decomposition of N_2O_5 in CCl_4 solution at 48°C , show that the reaction is of the first order

t (mts)	10	15	20	∞
Vol of O_2 evolved	6.30	8.95	11.40	34.75

SOLUTION

For a first order reaction the integrated rate equation is

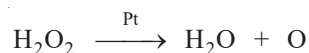
$$\frac{1}{t} \log \frac{V_\infty}{V_\infty - V_t} = k$$

In this example, $V_\infty = 34.75$

t	$V_\infty - V_t$	$\frac{1}{t} \log \frac{V_\infty}{V_\infty - V_t}$	$= k$
10	28.45	$\frac{1}{10} \log \frac{34.75}{28.45}$	$= 0.00868$
15	25.80	$\frac{1}{15} \log \frac{34.75}{25.80}$	$= 0.00862$
20	23.35	$\frac{1}{20} \log \frac{34.75}{23.35}$	$= 0.00863$

Since the value of k is fairly constant, it is a **first order reaction**.

(2) **Decomposition of H_2O_2 in aqueous solution.** The decomposition of H_2O_2 in the presence of Pt as catalyst is a first order reaction.



The progress of the reaction is followed by titrating equal volumes of the reaction mixture against standard KMnO_4 solution at different time intervals.

SOLVED PROBLEM. A solution of H_2O_2 when titrated against KMnO_4 solution at different time intervals gave the following results :

t (minutes)	0	10	20
Vol KMnO_4 used for 10 ml H_2SO_4	23.8 ml	14.7 ml	9.1 ml

Show that the decomposition of H_2O_2 is a first order reaction.

SOLUTION

The integrated rate equation for first order reaction is

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

Since volume of KMnO_4 used in the titration is measure of concentration of H_2O_2 in solution,

$$\begin{aligned} a &= 23.8 \text{ ml} \\ (a-x) &= 14.7 \quad \text{when } t = 10 \text{ mts} \\ (a-x) &= 9.1 \quad \text{when } t = 20 \text{ mts} \end{aligned}$$

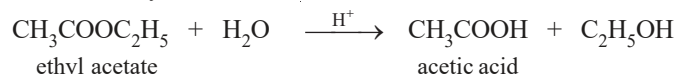
Substituting these values in the rate equation above, we have

$$\begin{aligned} k &= \frac{2.303}{10} \log \frac{23.8}{14.7} \\ &= 0.2303 (\log 23.8 - \log 14.7) \end{aligned}$$

$$\begin{aligned}
 &= 0.2303 (1.3766 - 1.1673) \\
 &= 0.04820 \\
 \text{and} \quad k &= \frac{2.303}{20} \log \frac{23.8}{9.1} \\
 &= 0.10165 (\log 23.8 - \log 9.1) \\
 &= 0.10165 (1.3766 - 0.9595) = 0.04810
 \end{aligned}$$

Since the value of k is almost constant, the decomposition of H_2O_2 is a **first order reaction**.

(3) **Hydrolysis of an Ester.** The hydrolysis of ethyl acetate or methyl acetate in the presence of a mineral acid as catalyst, is a first order reaction.



For studying the kinetics of the reaction, a known volume of ethyl acetate is mixed with a relatively large quantity of acid solution, say N/2 HCl. At various intervals of time, a known volume of the reaction mixture is titrated against a standard alkali solution. Hydrolysis of the ester produces acetic acid. Therefore as the reaction proceeds, the volume of alkali required for titration goes on increasing.

SOLVED PROBLEM. The following data was obtained on hydrolysis of methyl acetate at 25°C in 0.35N hydrochloric acid. Establish that it is a first order reaction.

t (secs)	0	4500	7140	∞
ml alkali used	24.36	29.32	31.72	47.15

SOLUTION

For a first order reaction,

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

At any time, the volume of alkali used is needed for the acid present as catalyst and the acid produced by hydrolysis.

The volume of alkali used for total change from t_0 to t_∞ gives the initial concentration of ester. Thus,

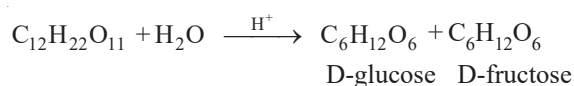
$$\begin{aligned}
 a &= 47.15 - 24.36 = 22.79 \text{ ml} \\
 (a-x) \text{ after } 4500 \text{ sec} &= 47.15 - 29.32 = 17.83 \text{ ml} \\
 (a-x) \text{ after } 7140 \text{ sec} &= 47.15 - 31.72 = 15.43 \text{ ml}
 \end{aligned}$$

Substituting values in the rate equation above, we have

$$\begin{aligned}
 k &= \frac{2.303}{4500} \log \frac{22.79}{17.83} = 0.00005455 \\
 k &= \frac{2.303}{7140} \log \frac{22.79}{15.43} = 0.0000546
 \end{aligned}$$

Since the values of k in the two experiments are fairly constant, the reaction is of the first order.

(4) **Inversion of Cane sugar (sucrose).** The inversion of cane sugar or sucrose catalyzed with dil HCl,



follows the first order kinetics. The progress of the reaction is followed by noting the optical rotation of the reaction mixture with the help of a polarimeter at different time intervals. The optical rotation

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 $\propto (r_0 - r_\infty)$.

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.

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

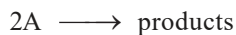
$r_0 - r_\infty = 24.09 - (-10.74) = 34.83$ for all time intervals. Thus, the value of rate constant can be found.

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



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,

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

Units of Zero order Rate constant

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

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

Thus the units of k are

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

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

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

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

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

Units of Second order Rate constant

The rate constant for a second order reaction is expressed as

$$\begin{aligned} k &= \frac{1}{t} \times \frac{x}{[A]_0 ([A]_0 - x)} \\ &= \frac{\text{concentration}}{\text{concentration} \times \text{concentration}} \times \frac{1}{\text{time}} \\ &= \frac{1}{\text{concentration}} \times \frac{1}{\text{time}} \\ &= \frac{1}{\text{mole/litre}} \times \frac{1}{\text{time}} \\ &= \text{mol}^{-1} \text{ l time}^{-1} \end{aligned}$$

Thus the units for k for a second order reactions are

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

Units of Third order Rate constant

The rate constant for a third order reaction is

$$\begin{aligned} k &= \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2 (a - x)^2} \\ \text{or } k &= \frac{\text{concentration} \times \text{concentration}}{(\text{concentration})^2 \times (\text{concentration})^2} \times \frac{1}{\text{time}} \\ &= \frac{1}{(\text{concentration})^2} \times \frac{1}{\text{time}} \\ &= \frac{1}{(\text{mol/litre})^2} \times \frac{1}{\text{time}} \end{aligned}$$

Thus the units of k for third order reaction are

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

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.**

SOLVED PROBLEM. The values of the rate constant (k) for the reaction $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ were determined at several temperatures. A plot of $\ln k$ versus $1/T$ gave a straight line of which the slope was found to be $-1.2 \times 10^4 \text{ K}$. What is the activation energy of the reaction ?

SOLUTION

We know that

$$\text{Slope} = -\frac{E_a}{R}$$

$$E_a = -R \times (\text{slope})$$

Substituting the values, we have

$$E_a = (-8.314 \text{ JK}^{-1} \text{ mol}^{-1})(-1.2 \times 10^4 \text{ K})$$

$$= 1.0 \times 10^5 \text{ J mol}^{-1}$$

Thus the activation energy for the reaction is $1.0 \times 10^5 \text{ J mol}^{-1}$

Calculation of E_a from the Values of k at Two Temperatures

The rate constant, k , is measured at two temperatures. E_a , is then calculated using the formula that can be derived as follows from equation (3) above.

At temperature T_1 , where the rate constant is k_1 ,

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \dots(1)$$

At temperature T_2 , where the rate constant is k_2 ,

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \quad \dots(2)$$

Subtracting the equation (1) from the equation (2), we have

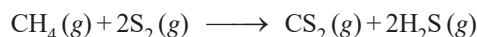
$$\ln k_2 - \ln k_1 = \left(-\frac{E_a}{RT_2} + \ln A \right) - \left(-\frac{E_a}{RT_1} + \ln A \right)$$

$$= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

or
$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Thus the values of k_1 and k_2 measured at T_1 and T_2 can be used to find E_a .

SOLVED PROBLEM. The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the equation



At 550°C the rate constant for this reaction is $1.1 \text{ l mol}^{-1} \text{ sec}$ and at 625°C the rate constant is $6.4 \text{ l mol}^{-1} \text{ sec}$. Calculate E_a for this reaction.

SOLUTION

Here

$$k_1 = 1.1 \text{ litre mol}^{-1} \text{ sec.} \quad T_1 = 550 + 273 = 823 \text{ K}$$

$$k_2 = 6.4 \text{ litre mol}^{-1} \text{ sec.} \quad T_2 = 625 + 273 = 898 \text{ K}$$

Substituting the values in the equation

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}} \right)$$

Solving for E_a , gives

$$E_a = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)} = 1.4 \times 10^5 \text{ J/mol}$$

SIMULTANEOUS REACTIONS

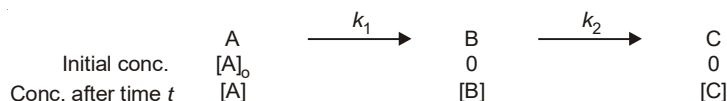
Sometimes there are some side reactions accompanying the main chemical reaction. Such reactions are known as **complex reactions** as these do not take place in a single step. In other words, such complex reactions proceed in a series of steps instead of a single step and the rate of overall reaction is in accordance with the stoichiometric equation for that reaction. Generally, following types of complications occur.

- (1) **Consecutive reactions**
- (2) **Parallel reactions**
- (3) **Reversible or opposing reactions**

These are discussed as follows :

(1) Consecutive Reactions

The reactions in which the final product is formed through one or more intermediate steps are called **consecutive reactions**. These are also known as **sequential reactions**. In such reactions the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. Various step reactions can be written for the overall reaction as shown below :



In the above reaction the product C is formed from the reactant A through intermediate B. In this reaction each stage has its own different rate constants k_1 for the first step and k_2 for the second step. The net or overall rate of reaction depends upon the magnitude of these two rate constants. The initial concentration and concentration after time t are shown below each species in above reaction under consideration.

It is clear that

$$[\text{A}]_0 = [\text{A}] + [\text{B}] + [\text{C}]$$

The differential rate expressions are

$$-\frac{d[\text{A}]}{dT} = k_1 [\text{A}]$$

$$\frac{d[\text{B}]}{dT} = k_1 [\text{A}] - k_2 [\text{B}]$$

and

$$\frac{d[\text{C}]}{dT} = k_2 [\text{B}]$$

During the course of the reaction the concentration of A, B and C vary as shown in the Fig. 20.12