

CHAPTER
7

CHEMICAL KINETICS

7.1.0 INTRODUCTION

Chemical kinetics is one of the most important topics of physical chemistry. It deals directly with the chemical reactions like the topics of chemical thermodynamics, chemical equilibrium and electrochemistry.

We know that chemical thermodynamics tells us whether a reaction will happen or not. Chemical equilibrium tells us the direction and extent of a reversible reaction. Electrochemistry help us to deal with the chemical reactions and the study of conversion of chemical energy into electrical energy and electrical energy into chemical energy.

Chemical kinetics deals with the chemical reactions and covers three aspects.

- (i) Rate of a chemical reaction.
- (ii) Different factors which control the rate of a chemical reaction like temperature, pressure, concentration, catalyst and solvent.
- (iii) The mechanism of reaction. The mechanism means the study of the route of the reaction and to know the nature of the intermediates.

When we study the rates of chemical reactions, then they prove to be valuable to understand the chemistry of reactions. With its help, we can select the optimum conditions for industrial process. The knowledge of optimum conditions can help the reaction to proceed at such a rate that we get the maximum yield.

7.1.1 Rate of chemical reaction:

"Rate of a chemical reaction is a speed with which a reaction proceeds." The speed of a moving body is the rate of change of distance with respect to time. Similarly the rate of chemical reaction is the change in concentration of any reactant or product per unit time.

Let us consider a simple reaction with reactant 'A' and product 'B'.



Distance + Time

The rate of reaction can be studied by noting the decrease of concentration of 'A' with respect to time. It can also be noted by measuring the increase in the concentration of 'B' with the passage of time.

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

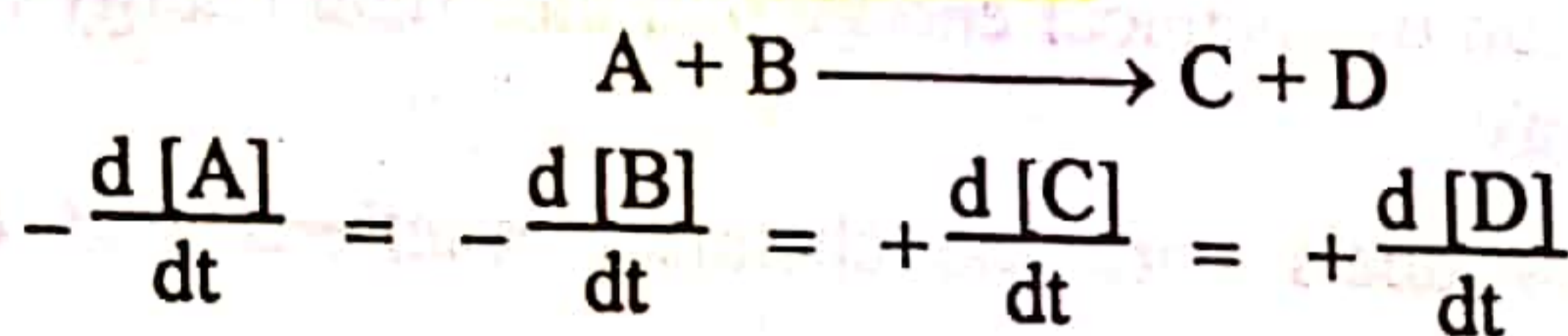
$$\text{or Rate of reaction} = \frac{+d[B]}{dt}$$

The rate with respect to reactants is given the negative sign by convention, because concentrations of reactants decrease with the passage of time (remember that rate is never negative). The rate with respect to product is positive because the concentration of 'B' is increasing every moment.

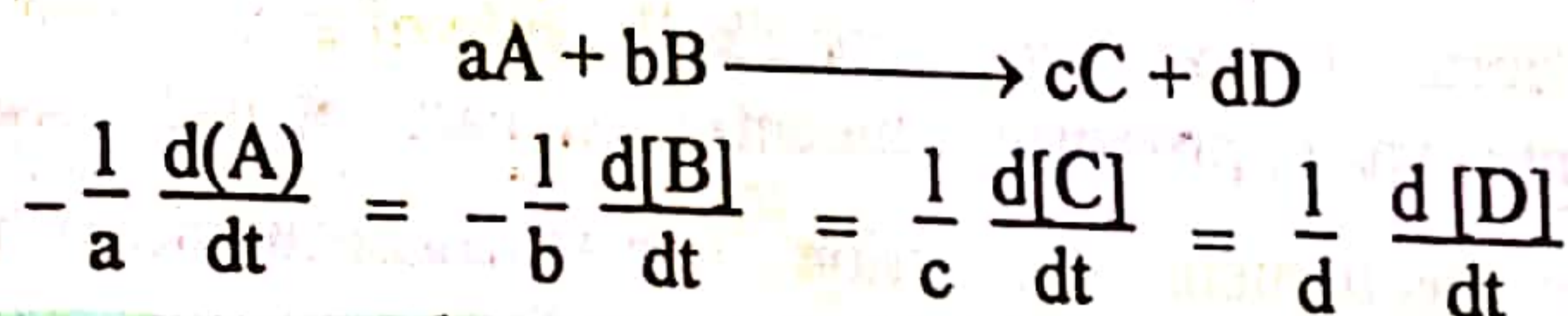
These two rates are equal, hence

$$-\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

The square brackets [], show the concentrations of 'A' and 'B' in moles dm^{-3} . 'd' represents very very small change in concentration and time $\frac{d[A]}{dt}$ is the differential of A with respect to time. For the following reaction, the rates with respect to reactants and products are given as,



Those reactions in which the reactants and products have the co-efficients other than unity, their rates can be equalized as,



The rates have been divided by coefficients to equalize the rates.

7.1.2 Units of rate of reactions:

If the concentration is expressed in moles dm^{-3} and time in seconds, then

$$-\frac{d[A]}{dt} = \frac{\text{moles} \cdot \text{dm}^{-3}}{\text{sec}} = \text{moles dm}^{-3} \text{ sec}^{-1}$$

If the time is in minutes, hours, days or years, then the units will be written accordingly and sec^{-1} will be replaced by minute^{-1} , hour^{-1} , day^{-1} , year^{-1} etc.

7.1.3 Instantaneous rate of reaction:

The rate of chemical reaction is ever changing parameter. It goes on decreasing with the passage of time. The rate at a moment is little bit smaller than the previous moment. It means that the reaction is very fast at the beginning and it is extremely slow at the end. "The rate of a chemical reaction at a specific time is called instantaneous rate of the reaction. For this purpose $d[A]$ and dt should be very very small."

Since conc. of a reactant is like the magnitude of anything & magnitude can never be zero so conc. cannot be zero at any stage

7.1.4 Average rate of a chemical reaction:

"Rate of a chemical reaction between two specific time intervals is called average rate of reaction." To denote the average rate, the change of concentration and change of time should be denoted by Δ

$$\text{The average rate of reaction} = \frac{\Delta[A]}{\Delta t}$$

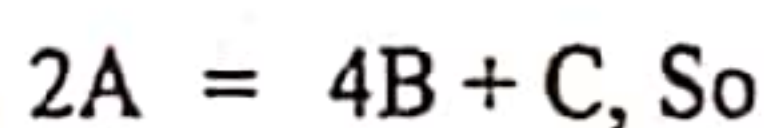
The average rate and instantaneous rate are equal for only one instant at any time interval. At the beginning of reaction, the instantaneous rate is higher than the average rate. Anyhow, the average rate becomes equal to instantaneous rate when the time interval approaches zero.

EXAMPLE (1)

A hypothetical reaction in the gas phase is, $2A = 4B + C$. The reaction is happening in a closed vessel. The conc. of B is found to increase by $8 \times 10^{-3} \text{ mol dm}^{-3}$ in 10 seconds. Calculate (i) rate of appearance of B, (ii) Rate of reaction (iii) Rate of disappearance of "A".

SOLUTION:

The reaction is



Rate of reaction

$$= -\frac{1}{2} \frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt} = + \frac{d[C]}{dt}$$

Rate of appearance of B

$$= \frac{\text{Increase in conc. of B}}{\text{Time taken}}$$

$$= \frac{8 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}}{10 \text{ sec}}$$

$$= 8 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Rate of reaction

$$= \frac{1}{4} \times \text{rate of appearance of B}$$

$$= \frac{1}{4} \times 8 \times 10^{-4} = 2 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\left(\frac{1}{2} \text{ Rate of disappearance of A}\right) = \text{Rate of reaction}$$

$$\text{Rate of disappearance of A} = 2 \times \text{rate of reaction}$$

$$= 2 \times 2 \times 10^{-4} \text{ mole dm}^{-3} \text{ s}^{-1}$$

$$= \boxed{4 \times 10^{-4} \text{ mol dm}^{-3}}$$

7.1.5 Rate law:

According to law of mass action, the rate of a given chemical reaction at a fixed temperature depends upon the concentrations of reactants. It means that there is a relationship between concentration and the rate of a reaction. This relationship is determined by measuring the reaction rate with different initial reactant concentrations. When we study a large number of reactions, then we come to know that the rate of reaction is directly proportional to the reactant concentrations and each concentration being raised to some power.

Reaction rate
→ diff. reactant
concentrations

For the reaction,



$$\text{Rate} = k[A][B]^2$$

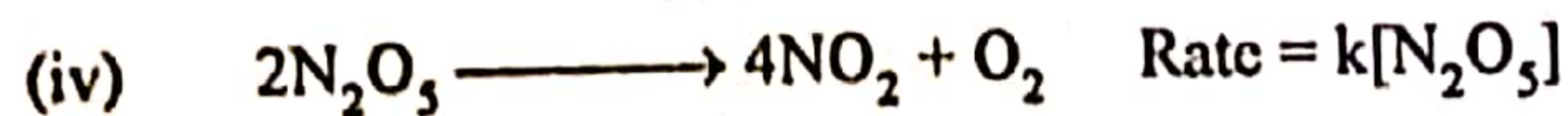
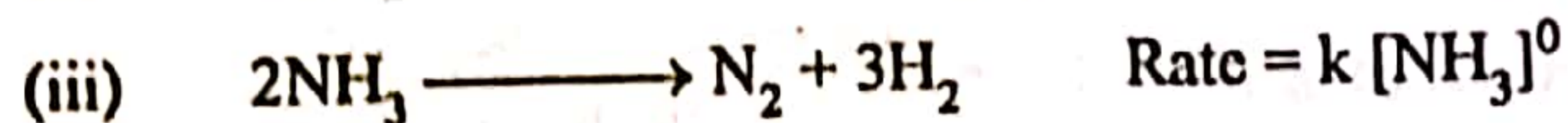
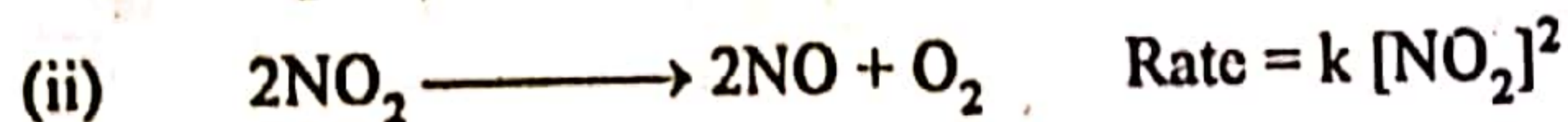
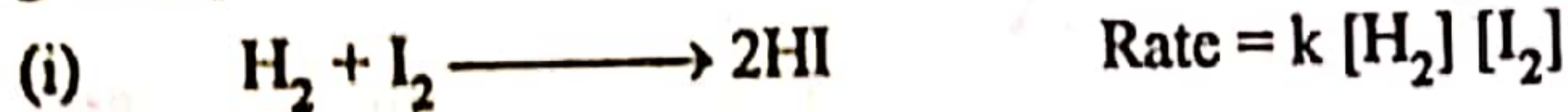
Anyhow, it is not essential that the powers in the rate expression are always equal to the co-efficients of balance chemical equations. So we can say that the rate expression of above reaction may be

$$\text{Rate} = k[A]^m [B]^n$$

where 'm' and 'n' may be 1 and 2 or some other factors. So the expression which shows, how the reaction rate is related to concentrations is called rate law. It is also called rate equation.

Rate law is determined experimentally. It can not be written by looking at the equation and making their coefficients as powers.

There are some elementary reactions in which the co-efficients of the balanced reactions become the exponents in the rate law. But, usually the powers of concentrations in the rate law are different from the co-efficients. Look at the following examples.

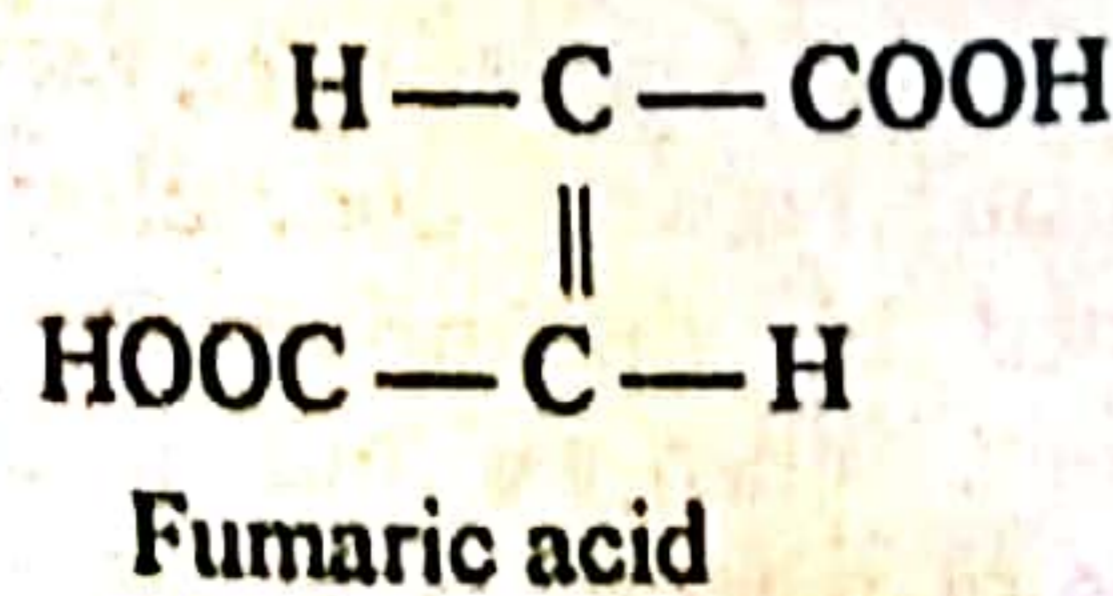
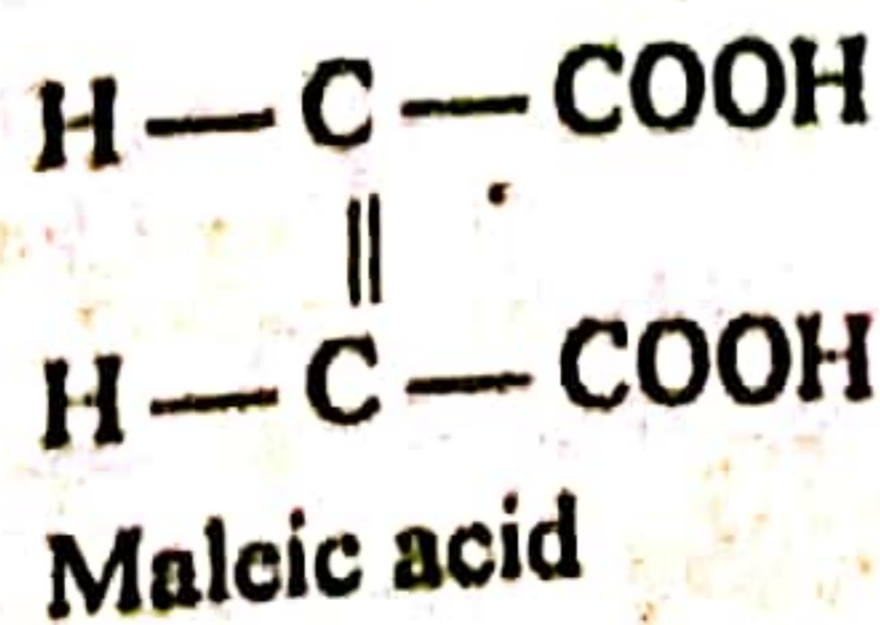


In example (iii) and (iv) the exponents in the rate expression are different from the co-efficients. These reactions are complex and they happen in more than one steps.

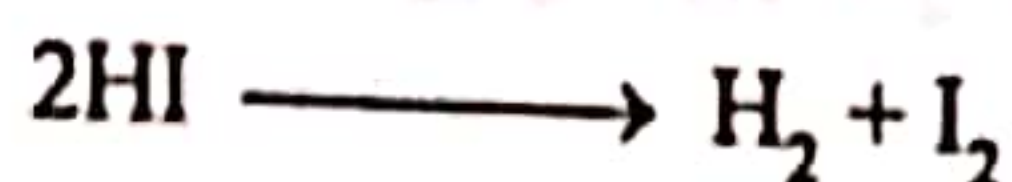
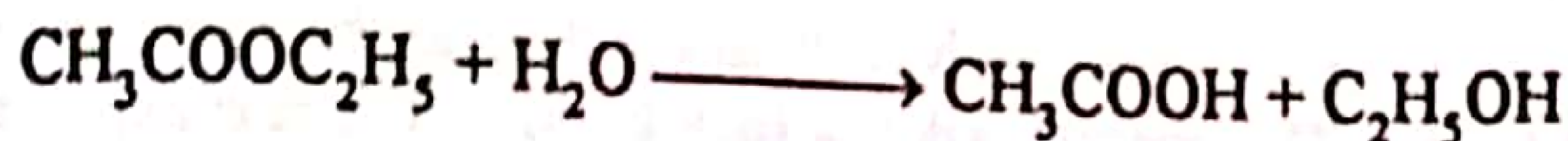
7.1.6 Molecularity of a chemical reaction:

As we mentioned above, that chemical reactions may be elementary or complex. A elementary reaction occurs in a single step while a complex reaction occurs in two or more steps.

"The molecularity of an elementary reaction is the number of reactant molecules involved in a reaction." In case one molecule takes part in elementary reaction, then it is called unimolecular. If two molecules take part, then it is bimolecular and for three molecules it is termolecular reaction. The breakage of the bromine molecule to bromine atoms and the conversions of maleic acid to fumaric acid are unimolecular reactions.



The hydrolysis of ethyl acetate and dissociation of HI to H_2 and I_2 are bimolecular reactions.



Similarly formation of NO_2 and $NOCl$ are the termolecular reactions.



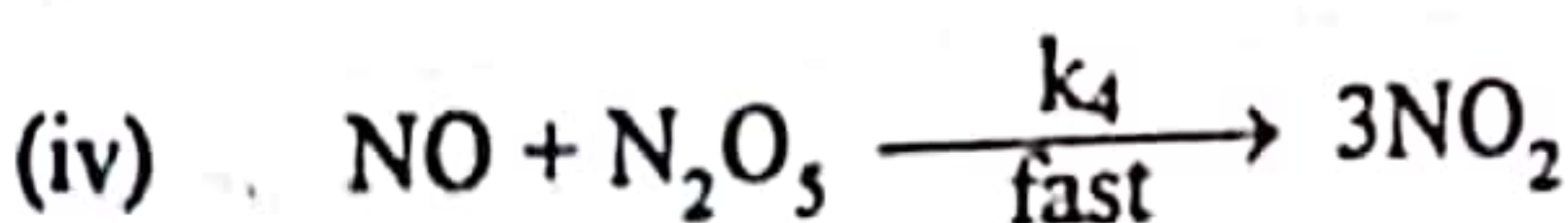
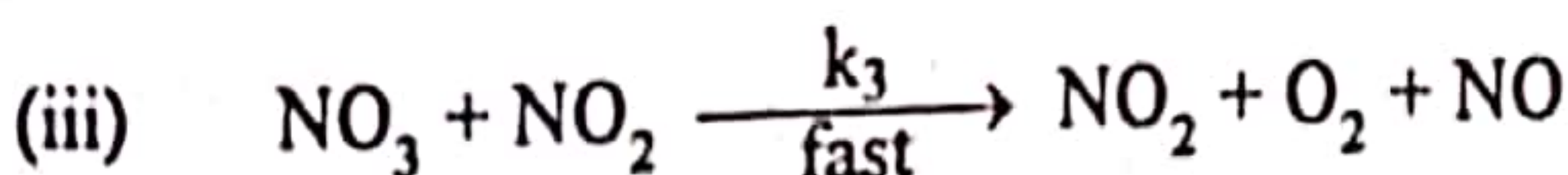
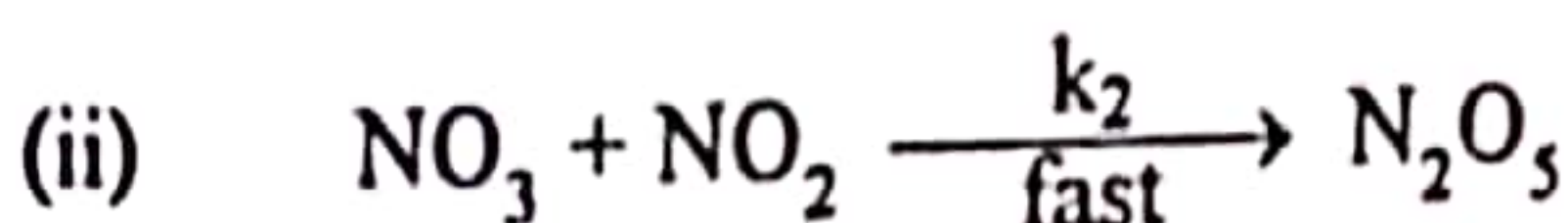
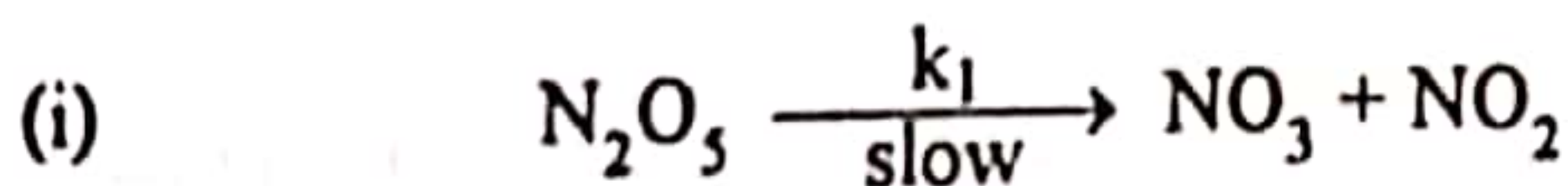
7.1.7 Reactions of high molecularity are rare:

The reactions with high molecularities are rare. This can be explained on the basis of kinetic molecular theory. Kinetic molecular theory says that the rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules.

The chances of simultaneous collisions of three or more than three molecules will go on decreasing with increase in number of molecules. The slowest step is the rate determining. In order to illustrate it, let us consider the decomposition of N_2O_5 .



It occurs in following steps, as proposed.



*1st step - slow
Rate determining step
- several elementary reactions/steps.*

The sum of these elementary processes gives the overall reaction. First step is slow and hence rate determining. That is why, it is a unimolecular reaction. It is meaningless to give molecularity of the overall reaction because it is made up of several elementary reactions. Each elementary reaction has its own molecularity.

Anyhow, we can simply say that the molecularity of this reaction is the number of molecules or atoms taking part in a rate determining step.

7.1.8 Order of reaction:

"The order of reaction is sum of the exponents of concentration terms in the rate equation." It is the number of reacting substances whose concentrations change during the chemical reaction. For the general reaction,



Let us say that the rate expression is,

$$\text{Rate} = k[A]^a [B]^b$$

The value of 'a' is the order with respect to 'A' and the value of 'b' is the order with respect to 'B'. **The overall order is (a + b).** If in the rate expression, for the above mentioned reaction,

$$\text{Rate} = k[A]^m [B]^n$$

$$\text{Then, order} = m + n$$

This situation arises when the reaction is complex, and it is taking place in more than one steps.

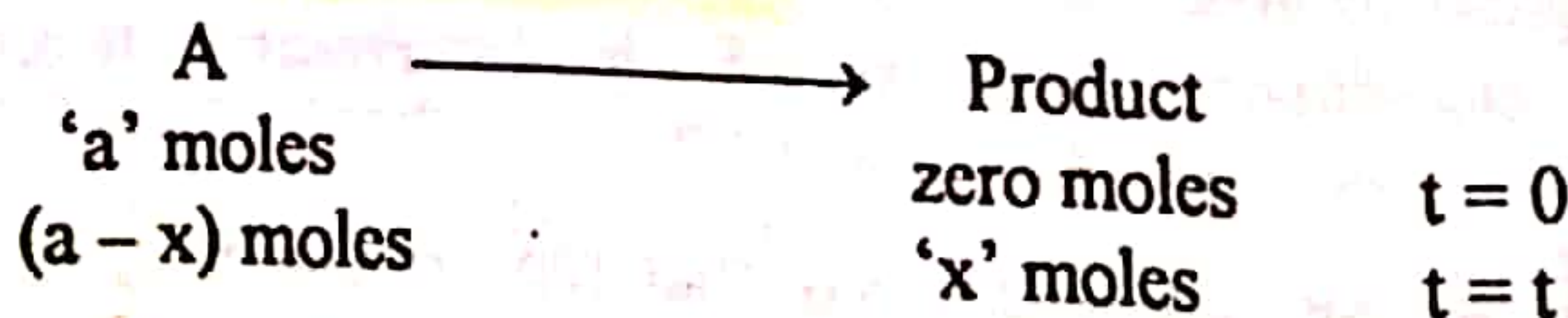
The molecularity and order of reaction are identical for elementary reactions. The comparison of order of and molecularity is as follows

| ORDER | MOLECULARITY |
|--|---|
| (1) The number of molecules whose concentration change in a chemical reaction. | (1) The number of molecules involved in a chemical reaction. |
| (2) It is the sum of exponents in the rate expression. | (2) It is sum of the moles of reactants that take part in a chemical reactions. |
| (3) It is an experimental quantity. | (3) It is a theoretical quantity. |
| (4) We get the order from the kinetic study. | (4) It is indicated from balanced equation. |
| (5) It can be fractional . | (5) It is always whole number. |
| (6) It may be equal to zero. | (6) It is never zero. |
| (7) Its maximum value may be 3. | (7) Its values may be greater than 3. |

7.2.0 ZERO ORDER REACTION

"Those chemical reactions in which the rates are independent of the concentrations of reactants are called zero order reactions."

In order to derive the kinetic equations of such reactions, consider that a substance 'A' is decomposed into products.



$$\text{Rate of reaction} = k[A]^0$$

$$\frac{dx}{dt} = k$$

Here 'k' is the rate constant for zero other reaction. It means that the rate of change of concentrations of the products is a constant quantity. In order to

Rate of Conc.
Order?
Con. change?

integrate this equation, separate the variables by taking dt on the R.H.S. and keeping dx on the L.H.S.

$$\int dx = \int dt$$

$$x = kt + c$$

where 'c' is the constant of integration. In order to determine the value of 'c', put the boundary conditions i.e.

When $t = 0, x = 0$

$$0 = k \times 0 + c$$

$$c = 0$$

Hence the final equation is

$$\boxed{x = kt} \quad \dots\dots (1)$$

This 'k' is called the rate constant for zero order reaction. If one knows the time of reaction and the rate constant k, then concentration of product x can be calculated from equation (1).

7.2.1 Units of zero order rate constant:

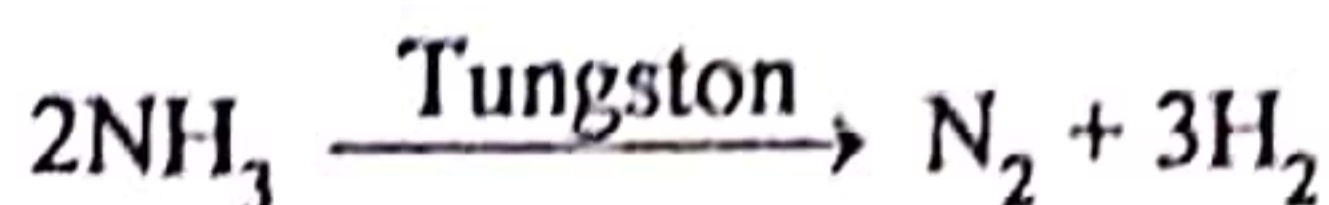
Since, $x = kt$

$$k = \frac{x}{t} = \frac{\text{mol.dm}^{-3}}{\text{sec.}} = \text{mol dm}^{-3} \text{ sec}^{-1}$$

These units of the rate constant are the same as the units of rate of a reaction. "In other words, we can say that rate constant is equal to the rate of reaction at all the concentrations."

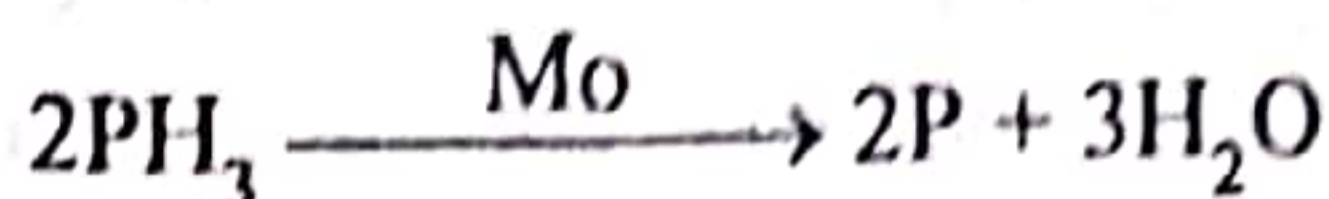
7.2.2 Examples of zero order reaction:

- (i) When ammonia is decomposed in the presence of tungsten, then it obeys the zero order mechanism.



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

- (ii) When phosphine is decomposed in the presence of Mo, then it obeys the zero order kinetics.



$$\text{Rate of reaction} = k[\text{PH}_3]^0$$

- (iii) When thermal decomposition of HI is done on gold surface, then it follows the zero order mechanism.



$$\text{Rate of reaction} = k[\text{HI}]^0$$

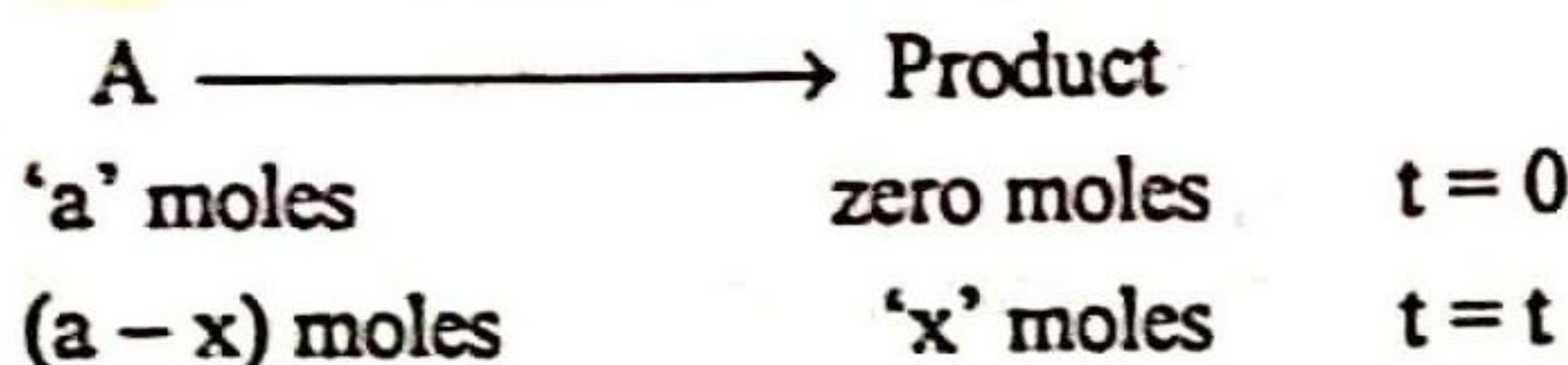
*Rate constant?
Zero order reaction?*

Zero order kinetics

- (iv) In photochemical reactions the rates are constant and they do not depend upon the concentrations of reactants. They depend upon the amount of light absorbed. Photochemical combination of H_2 and Cl_2 to give HCl , which is carried out over water saturated with the reactants is no doubt quite complex, but is of zero order.
- (v) Reactions which are catalyzed by enzymes are also zero order.

7.3.0 FIRST ORDER REACTION

Let us take a substance 'A' which decomposes, into products. Its initial concentration is 'a' moles dm^{-3} . Let after time 't' seconds the amount left behind is $(a - x)$ moles dm^{-3} and that converted into product is 'x' moles dm^{-3} .



According to law of mass action, rate of reaction at time 't' depends upon the concentration $(a - x)$ left behind.

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

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

Here 'k' is the rate constant for first order reaction. This equation (1) tells us the speed with which the substance 'A' is decomposing. Actually, we want such an equation, which can tell us the concentration of the products 'x' at any time 't'. For this purpose we have to integrate the equation (1). Before integration, separate the variables.

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

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

$$-\ln(a - x) = kt + c \quad \dots\dots (2)$$

(See Page 630 Art No. 11.7.7)

Where 'c' is integration constant. In order to determine its value we put the boundary conditions. One of the best boundary condition is the start of the chemical reaction. At the beginning of reaction,

when $t = 0$, then $x = 0$

Put these values in equation (2)

$$-\ln a = c \quad \dots\dots (3)$$

Now put this value of 'c' in eq. (2)

$$-\ln(a - x) = kt - \ln a$$

$$\ln(a - x) = -kt + \ln a \quad \dots\dots (4)$$

To integrate
Separate the
variables!

Boundary
Condition

Equation (4) is of a straight line. It has two variables, i.e. $\ln(a - x)$ and 't'. 't' is independent variable and $\ln(a - x)$ is dependent variable. When we plot a graph between independent variable 't' on x-axis and $\ln(a - x)$ on y-axis, then a straight line is obtained with the negative slope as shown in the following diagram Fig. (1).

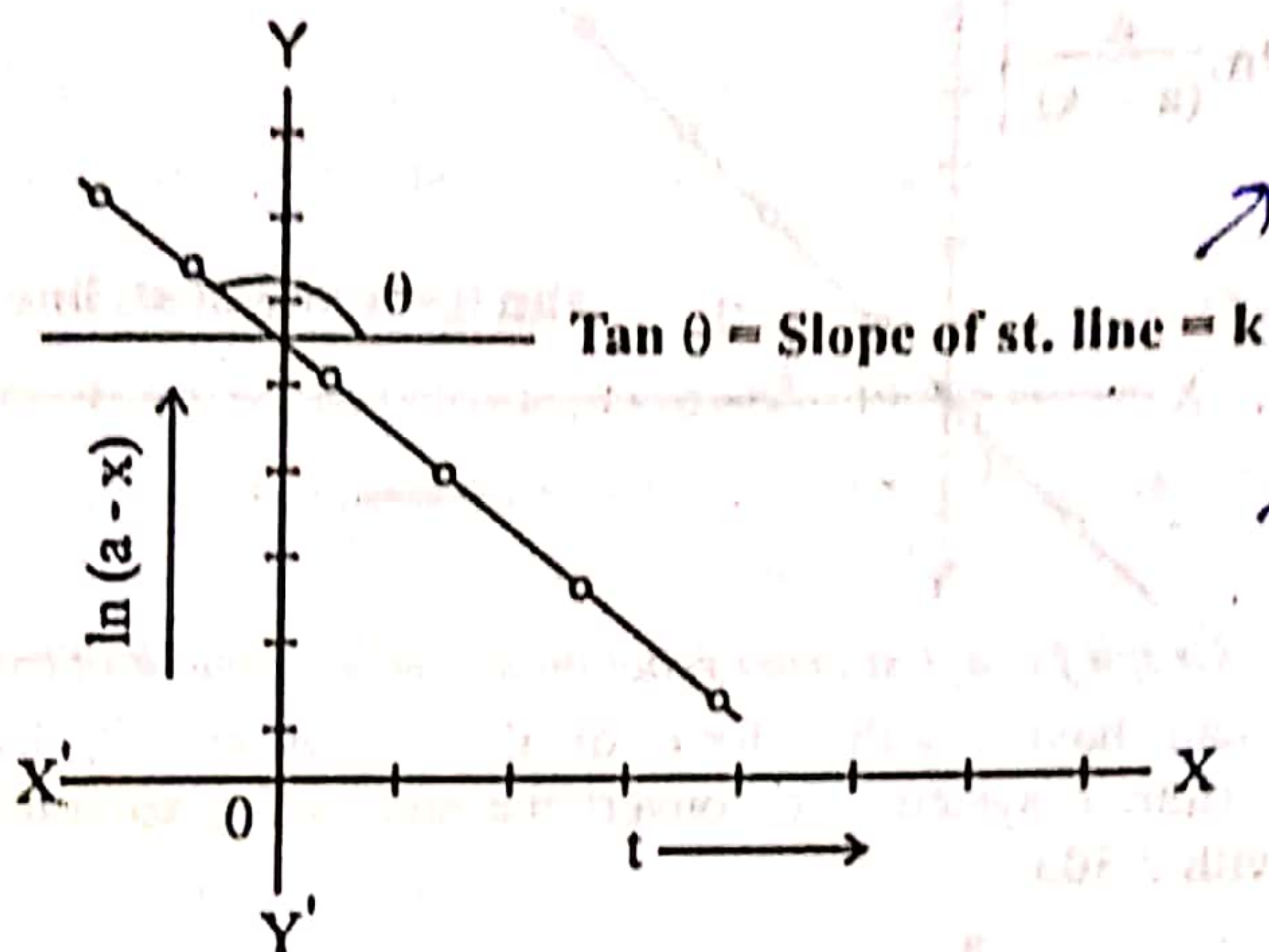


Fig. (1) Straight line graph for first order reaction.
(See Page 584 Art No. 11.2.3)

The slope of the straight line is obtained by taking the tangent of the angle which this line makes with the x-axis. This slope of straight line is equal to rate constant 'k' in equation (4).

Equation (4) can be rearranged to get another form of the first order equation

$$\ln(a - x) = -kt + \ln a \quad \dots\dots (4)$$

$$-\ln a + \ln(a - x) = -kt$$

$$\ln a - \ln(a - x) = kt$$

$$\ln \frac{a}{(a - x)} = kt \quad \dots\dots (5)$$

The equation (5) is the equation of a straight line. When a graph is plotted between time on x-axis and $\ln \frac{a}{(a - x)}$ on y-axis, then a straight line with positive slope is obtained passing through the origin. The tangent of the angle gives the value of rate constant 'k'. The line passes through the origin because there is no intercept in the equation (5). Fig. (2).

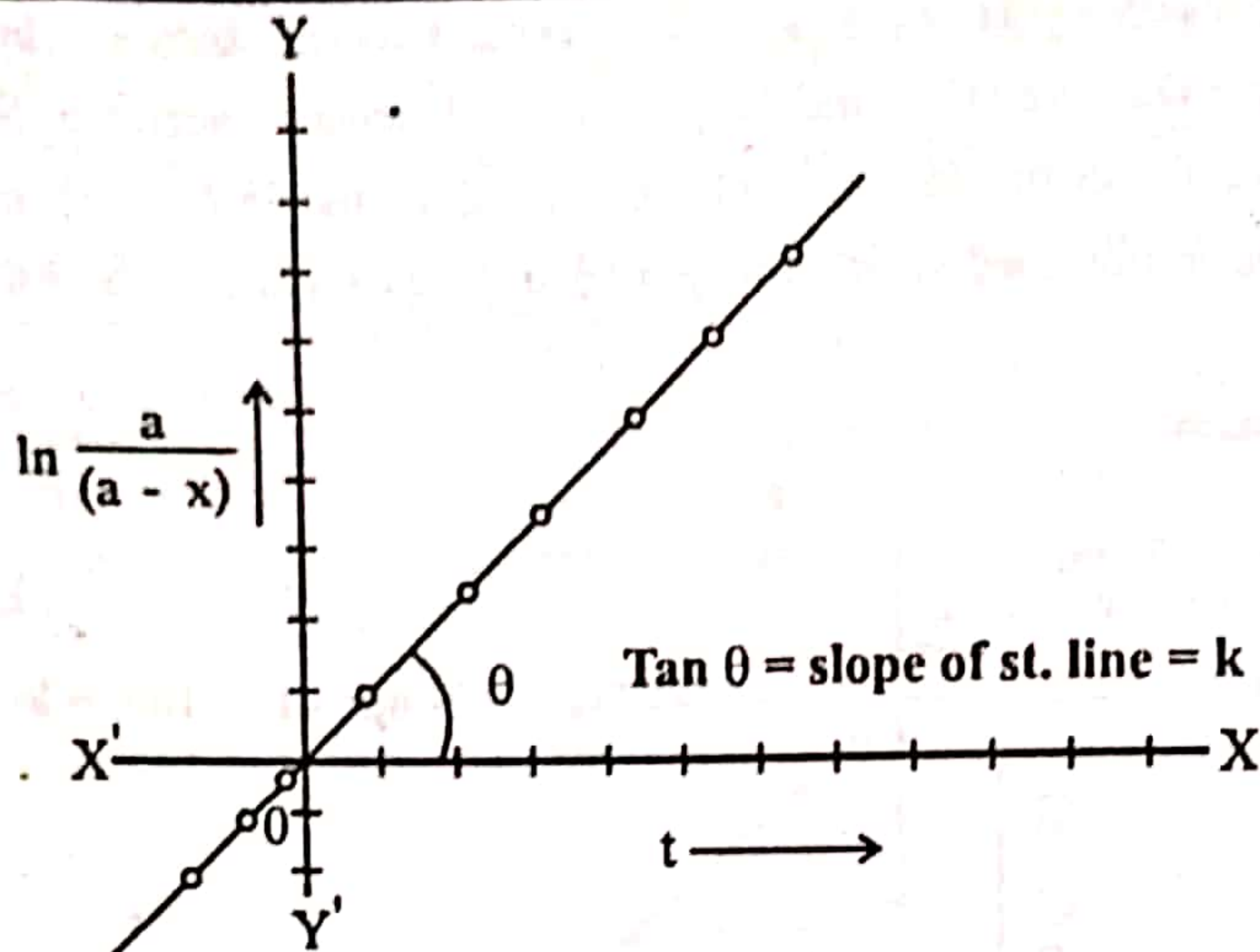


Fig. (2) Graph for a first order reaction and measurement of rate constant k .

We can have another form of this equation (5), by considering the common logarithmic system. To convert the natural log to common log, we have to multiply with 2.303.

$$2.303 \log \frac{a}{(a-x)} = kt$$

$$\log \frac{a}{(a-x)} = \frac{k}{2.303} \cdot t \quad \dots\dots (6)$$

Equation (6) is again the equation of a straight line as shown in diagram (3) and the slope of the straight line is equal to $\frac{k}{2.303}$

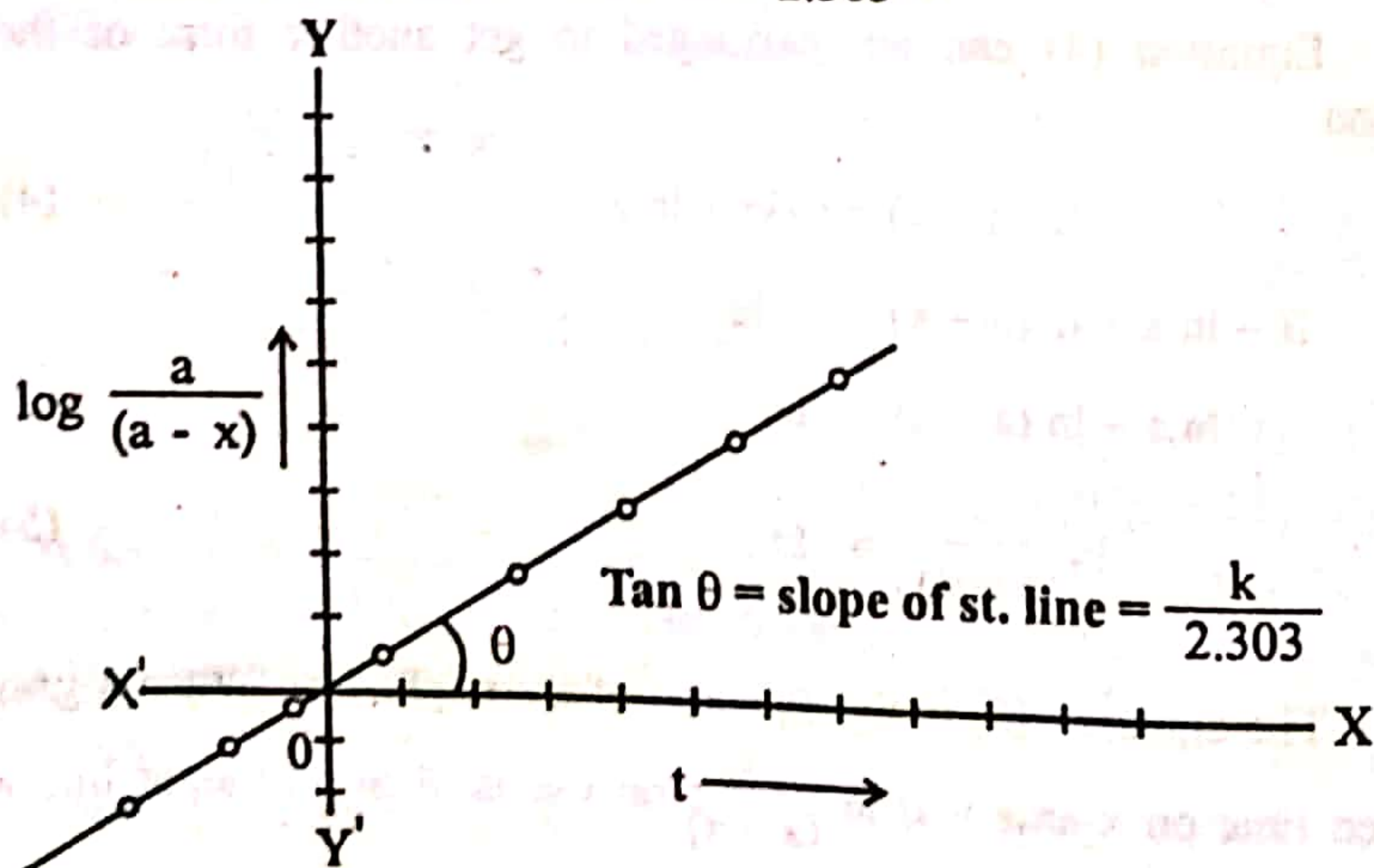


Fig. (3) Graph for a first order reaction and measurement of rate constant k .

7.3.1 Exponential form of First order equations:

The equation (5) can be converted to exponential form by taking the antilog on both sides.

$$\text{Since, } \ln \frac{a}{(a-x)} = kt$$

$$\text{So, } \frac{a}{(a-x)} = e^{kt}$$

$$\text{or } \frac{a-x}{a} = e^{-kt}$$

$$(a-x) = a e^{-kt} \quad \dots\dots (7)$$

Similarly equation (6) will have the following shape

$$(a-x) = (a e)^{-\frac{kt}{2.303}} \quad \dots\dots (8)$$

(See Chapter 11 Art No. 11.10.1)

The concentration of reactant $(a-x)$, left behind can be determined if we know initial concentration 'a' and time 't' to reach that stage.

All those chemical reactions, whose data gives the straight line, according to equation (4), (5) (6) are the first order reactions.

7.3.2 Units of first order rate constant:

The equation of first order is

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

$$\text{So, } k = \frac{1}{t} \cdot \ln \frac{a}{(a-x)}$$

'a' and $(a-x)$ have the units of mol dm^{-3} , and say the unit of time is second.

Then

$$k = \frac{1}{\text{sec.}} \ln \frac{\text{mol dm}^{-3}}{\text{mol dm}^{-3}} = \frac{1}{\text{sec.}} = \text{sec}^{-1}$$

So first order rate constant is expressed in sec^{-1} , minute^{-1} , hour^{-1} , etc. Simply, we can say that it is expressed in per unit time.

EXAMPLE (2)

H_2O_2 decomposes according to first order reaction. The reaction is studied by the noting the volume of KMnO_4 used as shown below:

| | | | | | |
|----------------------------------|----|------|------|------|-----|
| Time (minutes) | 0 | 5 | 15 | 25 | 45 |
| cm^3 of KMnO_4 | 37 | 29.8 | 19.6 | 12.3 | 5.0 |

Calculate the rate constant (k) of the reaction.

SOLUTION:

The data shows, that the titre value at zero time may be taken as initial concentration, i.e. $a = 37.0 \text{ cm}^3$. At different intervals the values of $(a-x)$ are given

Substituting the values of a , x and t in the first order rate equation as given below:

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

$$(i) \quad k = \frac{2.303}{5} \log \frac{37.0}{29.8} = 4.339 \times 10^{-2} \text{ min}^{-1}$$

$$(ii) \quad k = \frac{2.303}{15} \log \frac{37.0}{19.6} = 4.236 \times 10^{-2} \text{ min}^{-1}$$

$$(iii) \quad k = \frac{2.303}{25} \log \frac{37.0}{12.3} = 4.407 \times 10^{-2} \text{ min}^{-1}$$

$$(iv) \quad k = \frac{2.303}{45} \log \frac{37.3}{5.0} = 4.447 \times 10^{-2} \text{ min}^{-1}$$

The average value of rate constant 'k' is thus equal to $4.335 \times 10^{-2} \text{ min}^{-1}$ Ans.

EXAMPLE (3)

The decomposition of NH_4NO_2 to give N_2 gas is a first order reaction. Calculate the rate constant from the following data:

| Time (minutes) | 10 | 15 | 20 | 25 | ∞ |
|--|------|-----|------|-------|----------|
| Volume of N_2 (cm^3) | 6.25 | 9.0 | 11.4 | 13.65 | 35.05 |

SOLUTION:

The initial concentration corresponds to the maximum value of N_2 produced at infinity time

$$\text{Here } a = V_{\infty} = 35.05 \text{ cm}^3$$

The first order equation is

$$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$$

Substituting the given values of ' V_{∞} ', ' V_t ' and ' t ' from the sets given above

$$(i) \quad k = \frac{2.303}{10} \log \frac{35.05}{35.05 - 6.25} = \frac{2.303}{10} \log \frac{35.05}{28.80} = 0.01962 \text{ min}^{-1}$$

$$(ii) \quad k = \frac{2.303}{15} \log \frac{35.05}{35.05 - 9.00} = \frac{2.303}{15} \log \frac{35.05}{26.05} = 0.01976 \text{ min}^{-1}$$

$$(iii) \quad k = \frac{2.303}{20} \log \frac{35.05}{35.05 - 11.4} = \frac{2.303}{20} \log \frac{35.05}{23.65} = 0.01964 \text{ min}^{-1}$$

$$(iv) \quad k = \frac{2.303}{25} \log \frac{35.05}{35.05 - 13.65} = \frac{2.303}{25} \log \frac{35.05}{21.40} = 0.01971 \text{ min}^{-1}$$

Since the value of k is nearly the same in each case so, the reaction is first order.

EXAMPLE (4)

The hydrolysis of $\text{CH}_3\text{COOCH}_3$ was done by adding 1 cm^3 of methyl acetate to a flask containing 20 cm^3 of $\text{N}/20 \text{ HCl}$ maintained at temperature of 85°C . 2 cm^3 of the reaction mixture were withdrawn at different intervals and titrated with a standard alkali. Calculate the rate constant of this reaction: The data is as under:

| | | | | | |
|-------------------------|-------|-------|-------|-------|----------|
| Time (minutes) | 0 | 75 | 119 | 180 | ∞ |
| cm^3 of alkali | 19.24 | 24.20 | 26.60 | 29.32 | 42.03 |

SOLUTION:

Applying the first order rate equation, in which 'a' corresponds to $(V_\infty - V_0)$ and $(a - x)$ corresponds to $(V_\infty - V_t)$.

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Here $V_\infty - V_0 = 42.03 - 19.74 = 22.79$.

Substituting the values in the above equation.

$$(i) \quad k = \frac{2.303}{75} \log \frac{22.79}{42.03 - 24.20}$$

$$= \frac{2.303}{75} \log \frac{22.79}{17.83} = 0.00395 \text{ min}^{-1}$$

$$(ii) \quad k = \frac{2.303}{119} \log \frac{22.79}{42.03 - 26.60}$$

$$= \frac{2.303}{119} \log \frac{22.79}{15.43} = 0.00321 \text{ min}^{-1}$$

$$(iii) \quad k = \frac{2.303}{180} \log \frac{22.79}{42.03 - 29.30}$$

$$= \frac{2.303}{180} \log \frac{22.79}{12.73} = 0.00316 \text{ min}^{-1}$$

The mean value of $k = \boxed{0.00344 \text{ min}^{-1}}$ Ans.

EXAMPLE (5)

Benzene diazonium chloride $[\text{C}_6\text{H}_5\text{N}^\oplus \equiv \text{N}]\text{Cl}^\ominus$ decomposes to give N_2 gas. Its decomposition was studied at a constant temperature by measuring the volume of N_2 gas evolved at different intervals of time. Use the following data and show that the reaction is of the first order.

| | | | | | |
|--|---|----|----|----|----------|
| Time (minutes) | 0 | 20 | 50 | 70 | ∞ |
| Vol. of N_2 measured in (cm^3) | 0 | 10 | 25 | 33 | 162 |

SOLUTION:

When $t = 20$

$$(V_\infty - V_t) = 162 - 10 = 152$$

The expression for rate constant is as follows in which 'a' corresponds to V_{∞} and $(a - x)$ corresponds to $(V_{\infty} - V_t)$

$$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$$

Putting values from the above data

$$(i) \quad k = \frac{2.303}{20} \log \frac{162}{162 - 10} = 3.22 \times 10^{-3} \text{ min}^{-1}$$

$$(ii) \quad k = \frac{2.303}{50} \log \frac{162}{162 - 25} = 3.36 \times 10^{-3} \text{ min}^{-1}$$

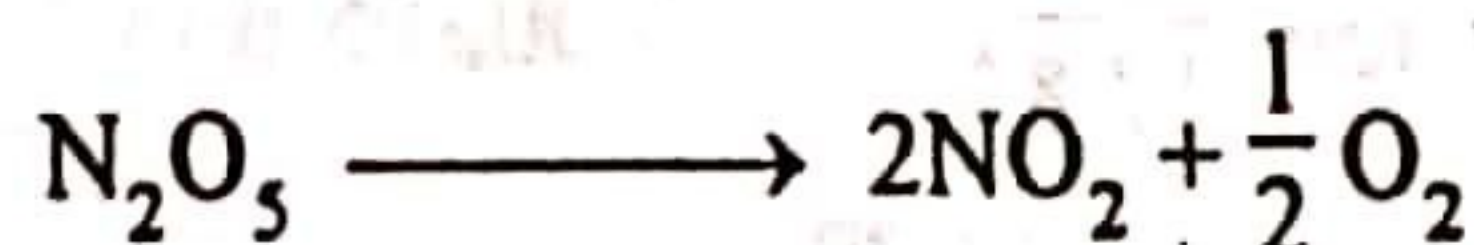
$$(iii) \quad k = \frac{2.303}{70} \log \frac{162}{162 - 33} = 3.26 \times 10^{-3} \text{ min}^{-1}$$

The fairly constant values of 'k' indicates that the reaction is of the first order.

7.3.3 Half life period of first order reaction:

Half life of a chemical reaction is the time which is required to convert half of the reactants into products. It depends upon the nature of the reactants and the conditions of the reaction.

We know that N_2O_5 decompose into NO_2 and O_2 .



If the reaction is occurring at 45°C , then 50% of the N_2O_5 is decomposed in 24 minutes. It means that 24 minutes is the half life period of N_2O_5 . Out of 1 mole of N_2O_5 , 0.5 moles is transferred to products in 24 minutes.

In the next 24 minutes, 0.25 moles is left behind. It means in 48 minutes, 75% of N_2O_5 is decomposed and 25% is left behind. In other words, it will take many days to convert N_2O_5 completely into products.

In order to derive the equation for half life period of first order reaction, we propose that when

$$t = t_{1/2}, \quad x = \frac{a}{2}$$

$$\text{Since, } kt = \ln \frac{a}{(a-x)}$$

$$\text{So, } t = \frac{1}{k} \cdot \ln \frac{a}{(a-x)}$$

$$t_{1/2} = \frac{1}{k} \cdot \ln \frac{a}{\left(a - \frac{a}{2}\right)} = \frac{1}{k} \cdot \ln \frac{a}{\frac{a}{2}} = \frac{1}{k} \ln 2$$

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

..... (9)

According to equation (9), the half life period of first order reaction $[t_{1/2}]_1$ is inversely proportional to the rate constant and is independent of initial concentration. So,

$$[t_{1/2}]_1 = 0.693 / k \quad \dots\dots (10)$$

EXAMPLE (6)

Calculate the half life period in seconds and minutes for a first order reaction, whose specific reaction rate is 10^{-3} s^{-1} .

SOLUTION:

The formula of half life period for first order reaction is

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

Since $k = 10^{-3} \text{ sec}^{-1}$

$$\text{So, } t_{1/2} = \frac{0.693}{10^{-3} \text{ sec}^{-1}} = 693 \text{ sec}$$

$$t_{1/2} = \frac{693}{60} = \frac{69.3}{6} = \boxed{11.55 \text{ minutes}} \quad \text{Ans.}$$

EXAMPLE (7)

75 % of a reaction was completed in 10 minutes. Calculate half life period of this reaction, if it follows the first order kinetics.

SOLUTION:

First of all determine the rate constant (k)

$$\text{Time (t)} = 10 \text{ minutes} = 600 \text{ seconds.}$$

So, when the reaction is 75 % completed, it means that $\frac{3}{4}$ th is converted to the products. The equation for the rate constant of a first order reaction is as follows.

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

Putting values, at $t = 600 \text{ sec}$ and $x = \frac{3}{4} a$

$$k = \frac{2.303}{600} \log \left(\frac{a}{a - \frac{3}{4}a} \right)$$

$$= \frac{2.303}{600} \log \left(\frac{a}{\frac{a}{4}} \right) = \frac{2.303}{600} \log \frac{4a}{a}$$

$$k = \frac{2.303}{600} \log 4 = \frac{2.303}{600} \times 0.6021 = 2.31 \times 10^{-3} \text{ sec}^{-1}$$

With the help of rate constant, calculate half life period. The formula for half life period of a first reaction is

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

Putting the value of k

$$t_{1/2} = \frac{0.693}{2.31 \times 10^{-3} \text{ sec}^{-1}}$$

$$t_{1/2} = \frac{0.693}{2.31} \times 10^3 \text{ sec.} = 0.3 \times 10^3 \text{ sec.} = 300 \text{ sec.}$$

$$t_{1/2} = \frac{300}{60} = \boxed{5 \text{ minutes}} \quad \text{Ans.}$$

EXAMPLE (8)

Sucrose can be hydrolysed in the presence of an acid. It is hydrolysed to 57 % in 66 minutes. Calculate the time for 75 % hydrolysis, considering that the reaction is first order.

SOLUTION:

Let us suppose that initial concentration is 100. Substituting $a = 100$; $x = 57$ at $t = 66$ minutes. In this way calculate the rate constant k , by using first order equation

$$\text{Since, } k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

Putting values

$$k = \frac{2.303}{66} \log \frac{100}{(100-57)} = \frac{2.303}{66} \log \frac{100}{43}$$

$$k = \frac{2.303}{66} \times 0.3665$$

$$k = 0.0127 \text{ min}^{-1}$$

Now use this value of rate constant (k) to get the time for 75 % completion of reaction. It means that if $a = 100$, $x = 75$

$$\text{So, } k = \frac{2.303}{t} \log_{10} \left(\frac{100}{100-75} \right)$$

$$\text{or } 0.0127 = \frac{2.303}{t} \log_{10} \left(\frac{100}{100-75} \right)$$

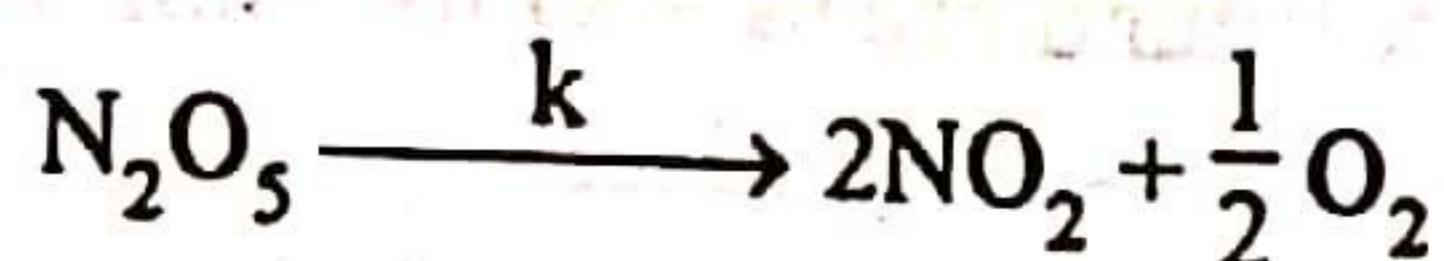
$$\text{or } t = \frac{2.303}{0.0127} \log_{10} \left(\frac{100}{100-75} \right) = \frac{2.303}{0.0127} \log \frac{100}{25} = \frac{2.303}{0.0127} \log 4$$

$$t = \frac{2.303}{0.0127} \times 0.6021$$

$$t = \boxed{109.18 \text{ minutes}} \quad \text{Ans.}$$

The reaction will take 109.18 minutes to get completed by 75 %.

7.3.4 Examples of first order reaction:

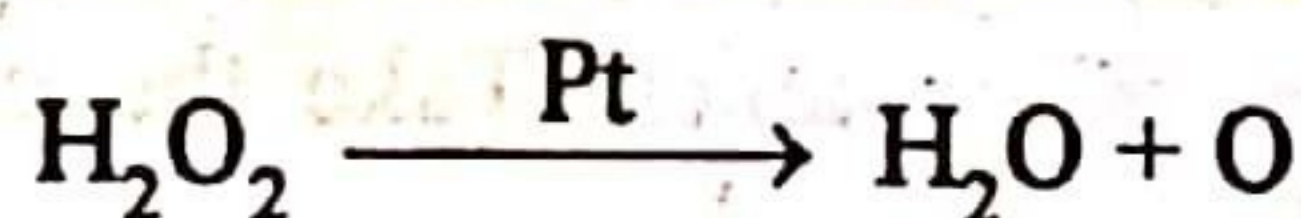
(1) Decomposition of N_2O_5 in CCl_4 solution.

The progress of this reaction can be studied by measuring the volume of oxygen from time to time.

Let ' V_t ' be the volume of oxygen at any time ' t ' and ' V_∞ ' be the final volume of oxygen when the reaction is completed, then we can say that the initial concentration ' a ' of N_2O_5 can be considered as V_∞ . $(a - x)$ will be corresponding to $(V_\infty - V_t)$. So, the first order equation for this reaction can be written as,

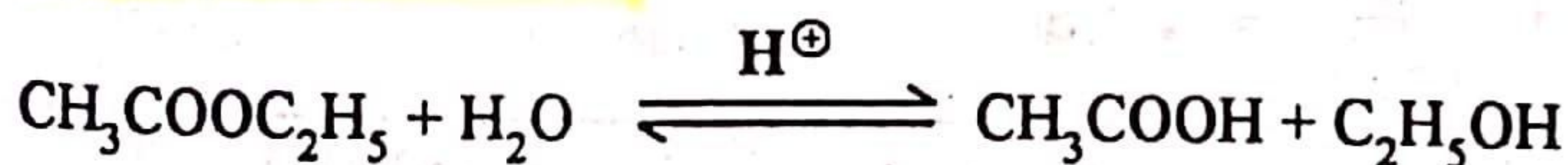
$$k = \frac{1}{t} \ln \frac{V_\infty}{(V_\infty - V_t)}$$

The values of ' V_0 ', ' V_∞ ' and ' V_t ' are determined at various time intervals and the value of rate constant ' k ' is calculated.

(2) Decomposition of H_2O_2 in aqueous solution.

The progress of this reaction is followed by volumetric analysis. H_2O_2 is titrated with standard solution of $KMnO_4$.

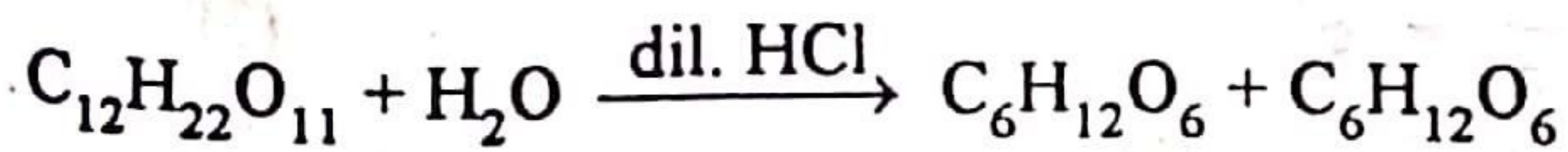
(3) Hydrolysis of an ester



The progress of this reaction is studied by volumetric analysis. i.e. acid-base titration. The greater quantity of CH_3COOH is produced with the passage of time, more and more NaOH will be used, with the passage of time.

(4) Inversion of cane sugar:

This reaction is catalyzed by dilute HCl.



The progress of reaction is followed by noting the optical rotation of the reaction mixture.

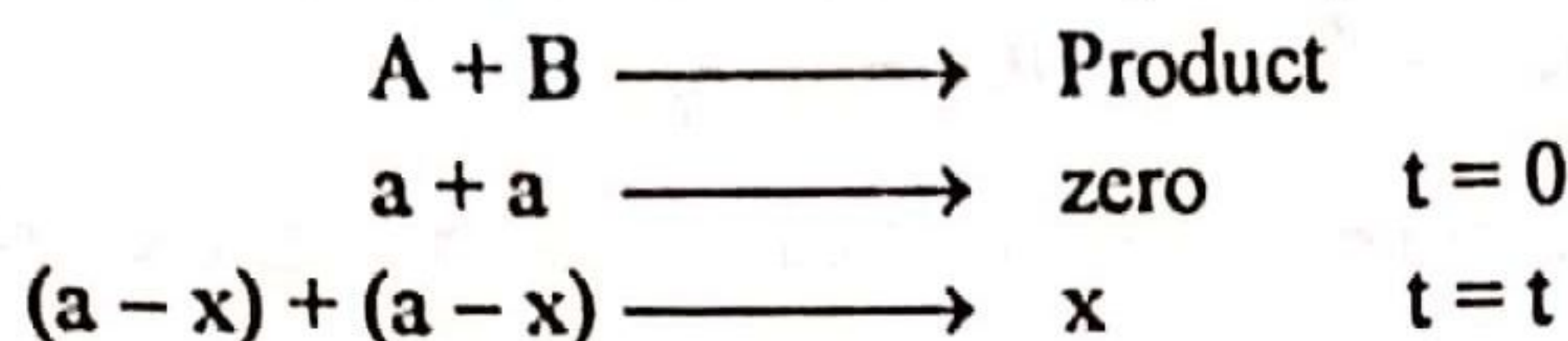
7.4.0 SECOND ORDER REACTIONS

Let us consider two substances 'A' and 'B', which react to give the products. The reaction can be carried out by

- (i) By taking equal concentrations of 'A' and 'B'
- (ii) By taking different concentrations of 'A' and 'B'

7.4.1 Second order reaction with equal concentrations of reactants:

Let the initial concentrations in moles dm^{-3} are 'a' moles dm^{-3} and after time 't' the concentrations left behind are (a - x) for both 'A' and 'B'



The rate of reaction at time 't' is directly proportional to the product of concentrations of reactants at that time.

$$\frac{dx}{dt} = k [\text{A}] [\text{B}]$$

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

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

Where 'k' is the rate constant for second order reaction. This is the equation which tells us the speed with which this second order reaction is progressing. Actually, we want such an equation which can tell us the concentrations of the products produced and the concentration of reactants left behind at any time 't'. For this purpose, we have to integrate this equation. Before integration; do the separation of variables. Take the concentration terms on the L.H.S and the time on the R.H.S.

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

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

$$\int (\text{a} - \text{x})^{-2} dx = \frac{(\text{a} - \text{x})^{-2+1} \cdot (-1)}{-2+1} = \frac{(\text{a} - \text{x})^{-1}(-1)}{-1} = \frac{1}{(\text{a} - \text{x})}$$

$$\frac{1}{(\text{a} - \text{x})} = kt + c \quad \dots\dots (2)$$

where 'c' is a constant of integration. In order to determine its value, put the boundary conditions i.e., when 't = 0', x = 0

$$\frac{1}{\text{a}} = c \quad \dots\dots (3)$$

Put this value of 'c' in eq. (2)

$$\frac{1}{(\text{a} - \text{x})} = kt + \frac{1}{\text{a}} \quad \dots\dots (4)$$

Equation (4) is of straight line. When a graph is plotted below 't' on x-axis and $\frac{1}{(\text{a} - \text{x})}$ on y-axis, then a straight line is obtained with the positive slope as shown in the following diagram (4). This line cuts the y-axis above the origin, at a gap of $\frac{1}{\text{a}}$ from the origin.

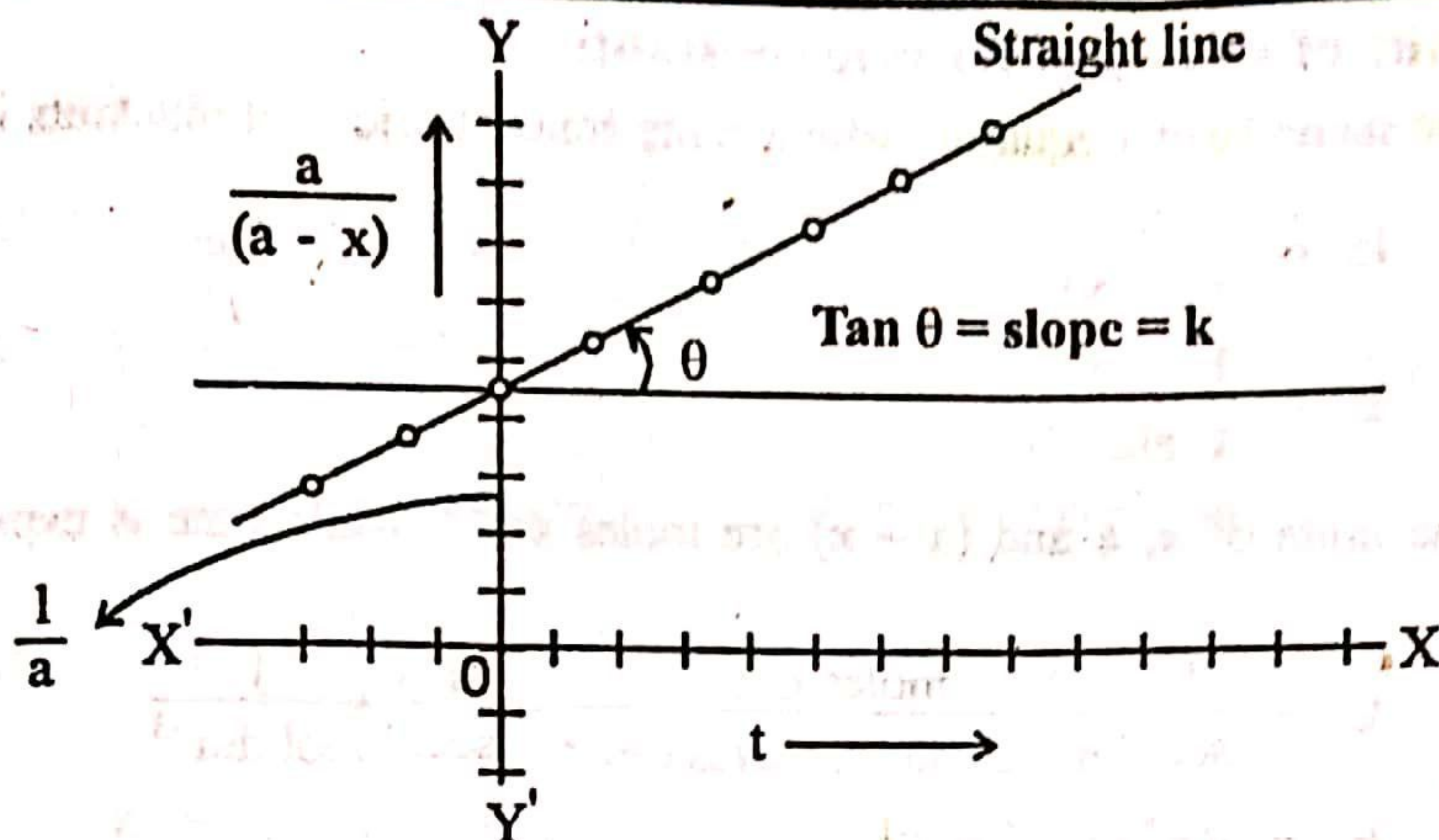


Fig. (4) Graphical representation of a second order reaction with same concentrations of reactants.

See Page 583 Art. No. 11.2.0.

A slope of a straight line which is the value of the $\tan \theta$ gives us the rate constant 'k'.

By rearranging the equation (4)

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

$$\frac{a - a + x}{a(a-x)} = kt$$

$$\frac{x}{a(a-x)} = kt \quad \dots\dots (5)$$

This equation (5) is again the equation of straight line. If a graph is plotted between 't' on x-axis and $\frac{x}{a(a-x)}$ on y-axis, a straight line is obtained passing through the origin as shown in the followed diagram (5). The value of rate constant 'k' is the same as we have derived previously by plotting a graph.

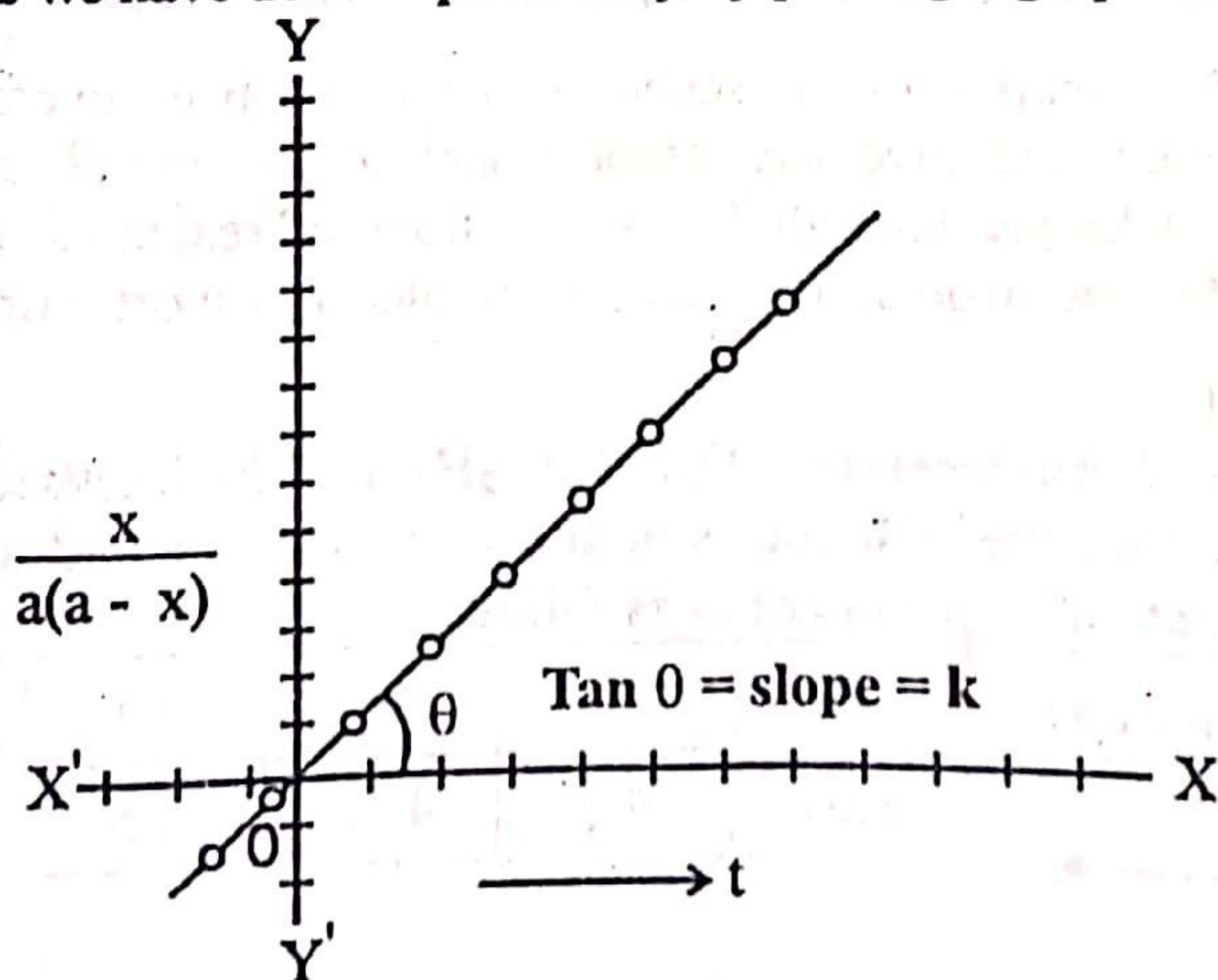


Fig. (5) Graphical representation of a second order reaction with equal concentrations of reactants.

7.4.2 Units of second order rate constant:

The second order equation with a same concentrations of reactants is,

$$kt = \frac{x}{a(a-x)}$$

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

The units of x , a and $(a-x)$ are moles dm^{-3} , while time is expressed in seconds.

$$k = \frac{1}{\text{sec.}} \cdot \frac{\text{moles dm}^3}{\text{moles dm}^{-3} \cdot \text{moles dm}^{-3}} = \frac{1}{\text{sec.}} \cdot \frac{1}{\text{mol dm}^{-3}}$$

$$k = \text{dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}.$$

7.4.3 Half life period of the second order reaction:

The equation for the second order reaction with same concentrations of reactants is

$$kt = \frac{x}{a(a-x)}$$

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

when $x = \frac{a}{2}$ then $t = t_{1/2}$

So,
$$t_{1/2} = \frac{1}{k} \cdot \frac{a/2}{a\left(a - \frac{a}{2}\right)} = \frac{1}{ka}$$

$$[t_{1/2}]_2 = \frac{1}{ka} \quad \dots\dots (6)$$

$[t_{1/2}]_2$ is the symbol for half life period of a second order reaction.

The half life period of the second order reaction is inversely proportional to the rate constant and inversely proportional to the initial concentrations. It means that if we take greater initial concentrations of reactants, then the half life become shorter. In other words, the reaction completes in shorter time.

EXAMPLE (9)

One mole of ethylacetate $\text{CH}_3\text{COOC}_2\text{H}_5$ was hydrolysed with one mole of NaOH . Show that the reaction is of the second order and also calculate the value of k . The data of experiment is as follows:

| | | | | | | |
|----------------|------|-----|------|-----|------|------|
| Time (minutes) | 0 | 4 | 6 | 10 | 15 | 20 |
| $(a-x)$ | 8.04 | 5.3 | 4.58 | 3.5 | 2.74 | 2.22 |

SOLUTION:

Here $a = 8.04$, therefore 5.3, 4.58, 3.5 etc. are the values of $(a-x)$ at different time intervals.

The rate constant k for second order reaction is

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

Substituting the values from the about data:

$$(i) \quad k = \frac{1}{4 \times 8.04} \times \frac{8.04 - 5.3}{5.30} \quad \text{Since } [x = a - (a - x)]$$

$$k = \frac{1}{4 \times 8.04} \times \frac{2.74}{5.30} = 1.615 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$(ii) \quad k = \frac{1}{6 \times 8.04} \times \frac{8.04 - 4.58}{4.58}$$

$$k = \frac{1}{6 \times 8.04} \times \frac{3.46}{4.58} = 1.571 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$(iii) \quad k = \frac{1}{10 \times 8.04} \times \frac{8.04 - 3.5}{3.5}$$

$$k = \frac{1}{80.4} \times \frac{4.54}{3.5} = 1.621 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$(iv) \quad k = \frac{1}{15 \times 8.04} \times \frac{8.04 - 2.74}{2.74}$$

$$k = \frac{1}{15 \times 8.04} \times \frac{5.30}{2.74} = 1.611 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$(v) \quad k = \frac{1}{20 \times 8.04} \times \frac{8.04 - 2.22}{2.22}$$

$$k = \frac{1}{20 \times 8.04} \times \frac{5.82}{2.22} = 1.635 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The value of k in each case is constant, so data represents second order reaction.

EXAMPLE (10)

A second order reaction has equal concentrations of reactants and is 25 % completed in 20 minutes. How much time is required to complete, the reaction by 75 %.

SOLUTION:

For a second order reaction the rate constant is given by

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

(i) When $t = 20$ minutes and $x = 25\%$ then rate constant k is calculated as follows:

$$x = \frac{25}{100} a, \quad x = 0.25 a$$

$$t = 20 \text{ minutes}$$

Putting values

$$k = \frac{1}{20} \frac{0.25a}{a(a - 0.25a)}$$

$$k = \frac{1}{20} \frac{0.25}{0.75a} = \frac{1}{60a} \quad \dots\dots (1)$$

- (ii) When the reaction is 75 % completed, then the rate constant 'k' for time 't' is calculated as follows:

$$x = \frac{75}{100} a = 0.75 a$$

$$t = ?$$

$$\begin{aligned} \therefore k &= \frac{1}{t} \frac{0.75 a}{a(a - 0.75 a)} \\ &= \frac{1}{t} \frac{0.75}{0.25 a} = \frac{3}{at} \quad \dots\dots (2) \end{aligned}$$

Since k is constant for a given reaction, so (1) and (2) are equal

$$\frac{1}{60 a} = \frac{3}{at}$$

$$t = \boxed{180 \text{ minutes}} \quad \text{Ans.}$$

EXAMPLE (11)

The half life period is 60 minutes when the initial concentration of a second order reaction is $0.02 \text{ moles dm}^{-3}$. Calculate the value of rate constant.

SOLUTION:

This problem can be solved in two ways.

- (i) The formula for second order reaction is

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

According to the given data

$$a = 0.02 \text{ mol dm}^{-3}$$

$$t = 60 \text{ min}$$

The value of x at half life is

$$x = \frac{50}{100} \times a = 0.5 a$$

\therefore Substituting the values in the second order rate equation

$$\begin{aligned} k &= \frac{1}{60} \frac{0.5 a}{a(a - 0.5 a)} \\ &= \frac{0.5}{0.5 a} \times \frac{1}{60} = \frac{1}{60 a} \end{aligned}$$

$$k = \frac{1}{60 \times 0.02} = 0.833 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$$

$$\begin{aligned}
 \text{(ii)} \quad t_{1/2} &= \frac{1}{ka} \\
 k &= \frac{1}{t_{1/2} \times a} \\
 &= \frac{1}{60 \text{ min} \times 0.02 \text{ mol dm}^{-3}} \\
 &= \frac{1}{1.2 \text{ mol dm}^{-3} \text{ min}} = \boxed{0.873 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}} \quad \text{Ans.}
 \end{aligned}$$

7.4.4 Examples of second order reaction:

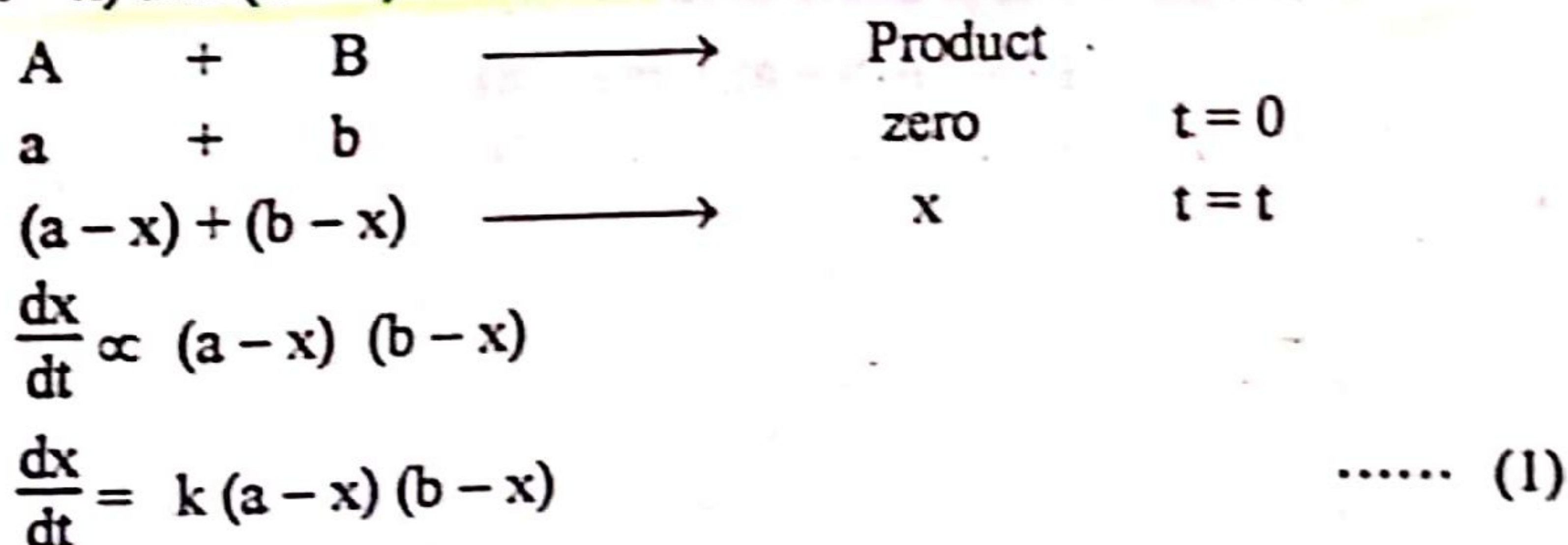
Hydrolysis of an ester by NaOH is a second order reaction



The progress of this reaction is studied volumetrically. The amount of NaOH being consumed is decreasing every moment. It is titrated with standard acids taken in the burette. The graph is plotted between time on x-axis and decreasing concentration on y-axis for NaOH. The rate at any instant can be calculated from the slope of the point.

7.4.5 Second order reactions with different initial concentrations:

Let us consider two substances 'A' and 'B' with initial concentrations 'a' and 'b'. Suppose 'x' moles of each are decomposed into products. According to law of mass action, the rate of a reaction at time 't' will depend upon the concentration (a - x) and (b - x) left behind.



where 'k' is the rate constant for second order reaction.

This equation (1) is telling us the speed with which the reactants are converted into products.

Actually, we want such an equation which tells us the concentration of reactants left behind and those of products formed at any time 't'. For this purpose we have to integrate this equation. First of all separate the variables and take the concentration terms on the L.H.S and the time on the R.H.S.

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

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

The integration of right hand side of this equation is $kt + c$.

In order to integrate the L.H.S., we have to do the partial fractions first of all.

Partial fractions:

Let us proceed to do the partial fractions of L.H.S of above equation.

Split as follows

$$\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)} \quad \dots\dots (3)$$

'A' and 'B' are the constants which have been proposed to be determined.

$$\begin{aligned} \frac{1}{(a-x)(b-x)} &= \frac{A}{(a-x)} + \frac{B}{(b-x)} \\ &= \frac{A(b-x) + B(a-x)}{(a-x)(b-x)} \end{aligned}$$

Since, denominator is common on both sides, so it is cancelled and above equation can be written as

$$1 = A(b-x) + B(a-x)$$

In order to get values of 'A' and 'B' we put (a-x) and (b-x) equal to zero one by one

$$1 = A(b-x) + B(a-x) \quad \dots\dots (4)$$

Put $(a-x) = 0$

So, $x = a \longrightarrow$

Now, put $x = a$ in above equation (4)

$$1 = A(b-a) + B(a-a)$$

$$1 = A(b-a)$$

$$1 = -A(a-b)$$

So, $A = \frac{-1}{(a-b)} \quad \dots\dots (5)$

Let us put

$(b-x) = 0$

or $x = b$

Put value of $x = b$ in equation (4)

$$1 = A(b-b) + B(a-b)$$

$$1 = B(a-b)$$

$$B = \frac{1}{a-b} \quad \dots\dots (6)$$

Now put the value of 'A' and 'B' in equation (3).

Hence,

$$\frac{1}{(a-x)(b-x)} = -\frac{1}{(a-b)(a-x)} + \frac{1}{(a-b)(b-x)} \quad \dots\dots (7)$$

Equation (7) is in the form of partial fractions, so it can be integrated very easily.

$$\begin{aligned}
 &= - \int \frac{dx}{(a-b)(a-x)} + \int \frac{dx}{(a-b)(b-x)} \\
 &= - \frac{1}{(a-b)} \int \frac{dx}{(a-x)} + \frac{1}{a-b} \int \frac{dx}{(b-x)} \\
 &= - \frac{1}{(a-b)} [- \ln(a-x)] + \frac{1}{(a-b)} [- \ln(b-x)] \quad * \\
 &= \frac{1}{(a-b)} \ln(a-x) - \frac{1}{(a-b)} \ln(b-x) \\
 &= \frac{1}{(a-b)} [\ln(a-x) - \ln(b-x)] \\
 &= \frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)}
 \end{aligned}$$

This is the integration of L.H.S.

The complete integration of the equation is

$$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = kt + c \quad \dots\dots (8)$$

'c' is the constant of integration. In order to determine its value, we put the boundary conditions.

When $t = 0$, $x = 0$

$$\frac{1}{(a-b)} \ln \frac{a}{b} = c \quad \dots\dots (9)$$

Putting this value of 'c' from equation (9) into (8)

$$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = kt + \frac{1}{(a-b)} \ln \frac{a}{b} \quad \dots\dots (10)$$

The equation (10) is of straight line and if a graph is plotted between time on x-axis and L.H.S of this equation (10) on y-axis, then a straight line is obtained as shown in the following diagram (6). The line does not pass through the origin.

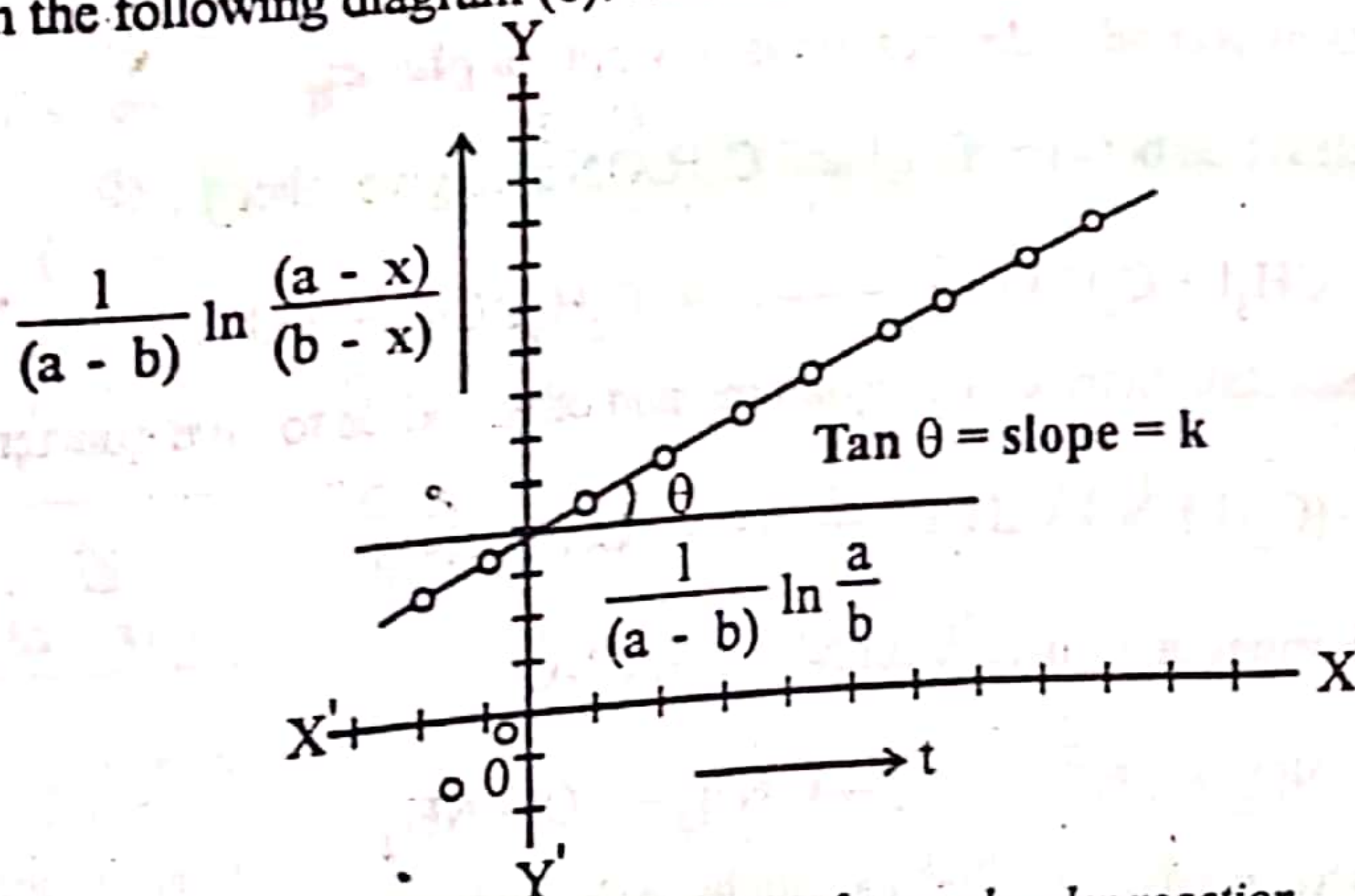


Fig. (6) Graphical representation of second order reaction.

This value of the rate constant 'k' is calculated from the slope of the straight line and that is the value of $\tan \theta$.

This equation can be rearranged by taking the concentration term on the L.H.S.

$$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} - \frac{1}{(a-b)} \ln \frac{a}{b} = kt$$

$$\frac{1}{(a-b)} \left[\ln \frac{(a-x)}{(b-x)} - \ln \frac{a}{b} \right] = kt$$

$$\frac{1}{(a-b)} \left[\ln \frac{b(a-x)}{a(b-x)} \right] = kt \quad \dots\dots (11)$$

This is again the equation of a straight line and if a graph is plotted between time an x-axis and L.H.S of this equation on y-axis, then a straight line is obtained passing through the origin.

The value of the rate constant is same as calculated from the previous equation (10).

7.4.6 Examples of second order reactions in gas phase:

- (i) Thermal decomposition of NO_2 to give N_2 and O_2 .



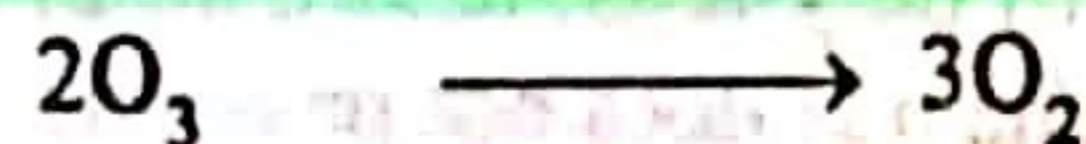
- (ii) Thermal decomposition of HI to give H_2 and I_2 .



- (iii) Thermal decomposition of NOCl to give NO and Cl_2 .

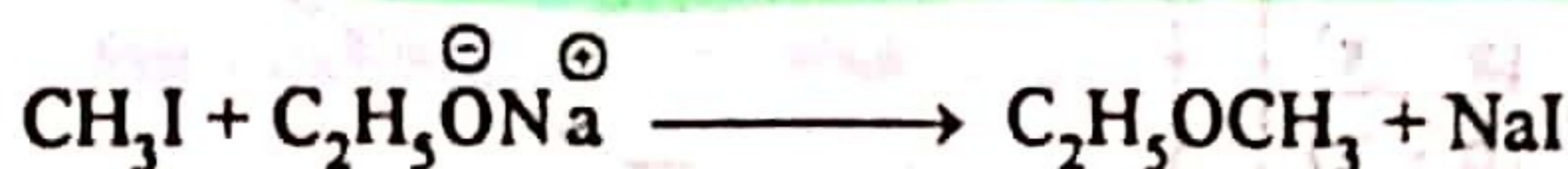


- (iv) Thermal decomposition of ozone to give oxygen.



Examples of second order reactions in solution phase:

- (i) Reaction between CH_3I and $\text{C}_2\text{H}_5\text{ONa}$ to give ether



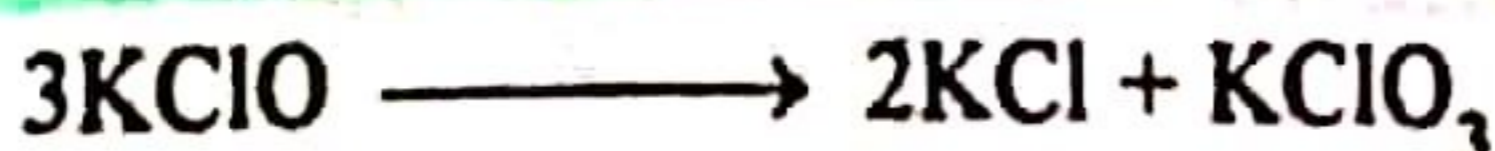
- (ii) Reaction between triethylamine and ethyl iodide to give quaternary salt.



- (iii) Formation of urea from NH_4^+ and CNO^-



- (iv) Decomposition of potassium hypochlorite



7.5.0 THIRD ORDER REACTIONS

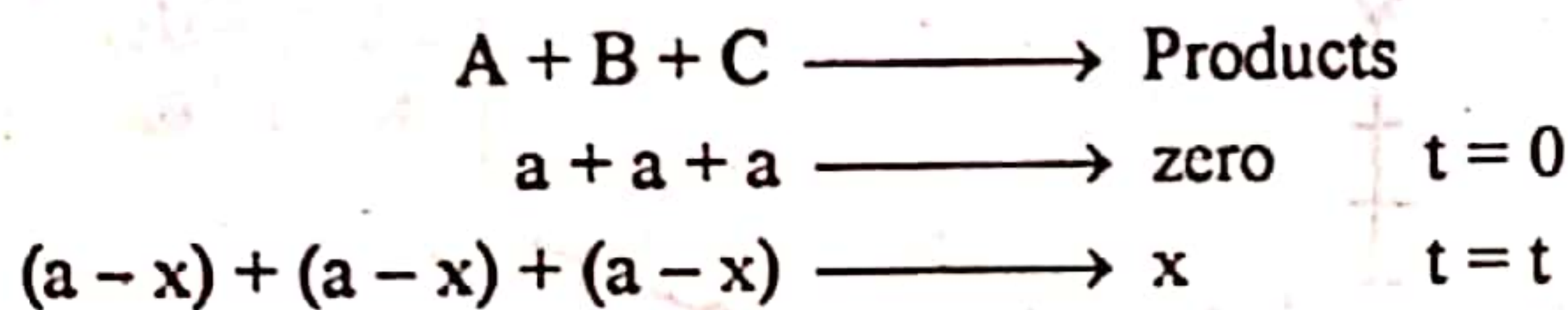
"Those chemical reactions in which the sum of the co-efficients in the rate expression of the reaction is three are called third order reactions." The kinetic equation for the third order reactions can be derived in three ways.

- (i) When the concentrations of all the three reactants are equal.
- (ii) When the concentrations of two of reactants are equal.
- (iii) When the concentrations of all the three reactants are unequal.

7.5.1 Third order reaction with equal concentrations of reactants:

(Page 634)

Suppose our reactants are 'A', 'B' and 'C' and the initial concentrations of each of them is 'a' moles dm^{-3} . If 'x' moles of each of them are transferred to the products, then



The rate of reaction, $\frac{dx}{dt}$ depends upon the remaining concentration of 'A', 'B' and 'C' at time 't'.

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

$$\frac{dx}{dt} = k(a - x)^3 \quad \dots\dots (1)$$

Here, k is the rate constant of third order reaction.

This equation (1) tells us the rate with which the reaction is progressing. Actually we want such an equation which can tell us the concentrations of reactants and products at any time 't'.

For this purpose, we have to integrate this equation (1).

First of all do the separation of variables.

$$\frac{dx}{(a - x)^3} = k dt$$

$$\int \frac{dx}{(a - x)^3} = k \int dt$$

$$\int \frac{dx}{(a - x)^3} = \int (a - x)^{-3} dx = \frac{(a - x)^{-3+1} \cdot (-1)}{-3 + 1} = \frac{(a - x)^2}{2} = \frac{1}{2(a - x)^2}$$

$$\frac{1}{2(a - x)^2} = kt + c \quad \dots\dots (2)$$

'c' is the constant of integration in equation (2). In order to determine the value of 'c' put the boundary conditions in equation (2) that when $t = 0$, $x = 0$

$$\frac{1}{2(a-0)^2} = k \times 0 + c$$

$$\frac{1}{2a^2} = c \quad \dots\dots (3)$$

Putting this value of 'c' from equation (3) into eq. (2)

$$\frac{1}{2(a-x)^2} = kt + \frac{1}{2a^2} \quad \dots\dots (4)$$

Equation (4) is the equation of straight line. If a graph is plotted between time on x-axis and $\frac{1}{2(a-x)^2}$ on y-axis, then a straight line is obtained not passing through the origin Fig (7).

The slope of the straight line gives the value of rate constant 'k'.

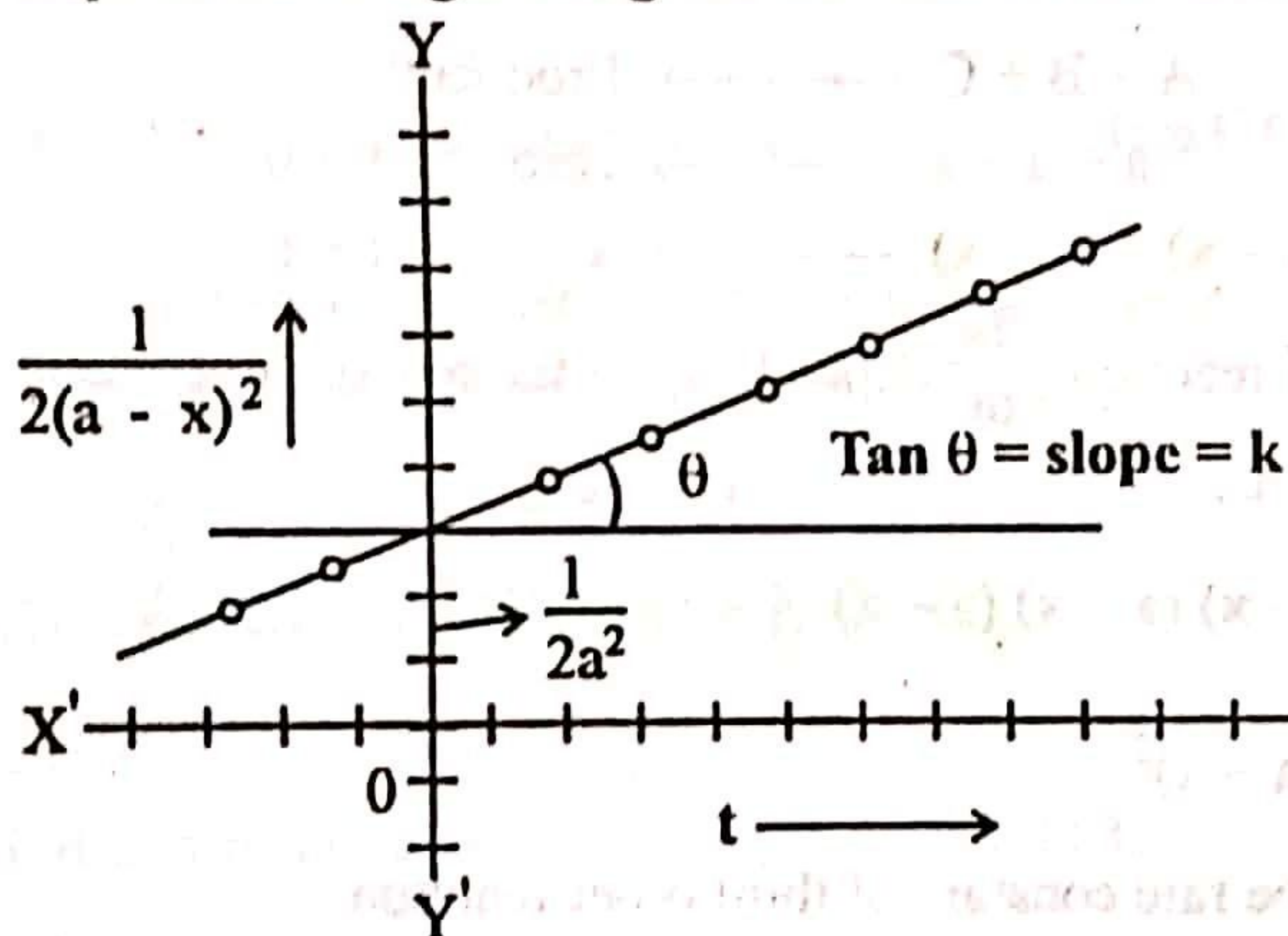


Fig. (7) Graphical representation of a third order reaction with equal concentrations of reactants.

Let us rearrange the equation (4) and join the concentration terms on the R.H.S. and 'kt' on the L.H.S

$$kt = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$$

$$kt = \frac{a^2 - (a-x)^2}{2a^2(a-x)^2}$$

$$kt = \frac{a^2 - a^2 - x^2 + 2ax}{2a^2(a-x)^2}$$

$$kt = \frac{2ax - x^2}{2a^2(a-x)^2}$$

$$kt = \frac{x(2a-x)}{2a^2(a-x)^2}$$

$$k = \frac{1}{t} \frac{x(2a-x)}{2a^2(a-x)^2} \quad \dots\dots (5)$$

By putting the values of 'x' and 't' for a reaction at different time intervals the value of the rate constant 'k' can be calculated. If it comes out to be constant for every reading, then the reaction is third order.

The equation (5) can be written as follows.

$$\frac{x(2a - x)}{2a^2(a - x)^2} = kt \quad \dots\dots (6)$$

The equation (6) is of a straight line and if a graph is plotted between 't' on x-axis and L.H.S of this equation on y-axis then a straight line is obtained passing through the origin, Fig (8).

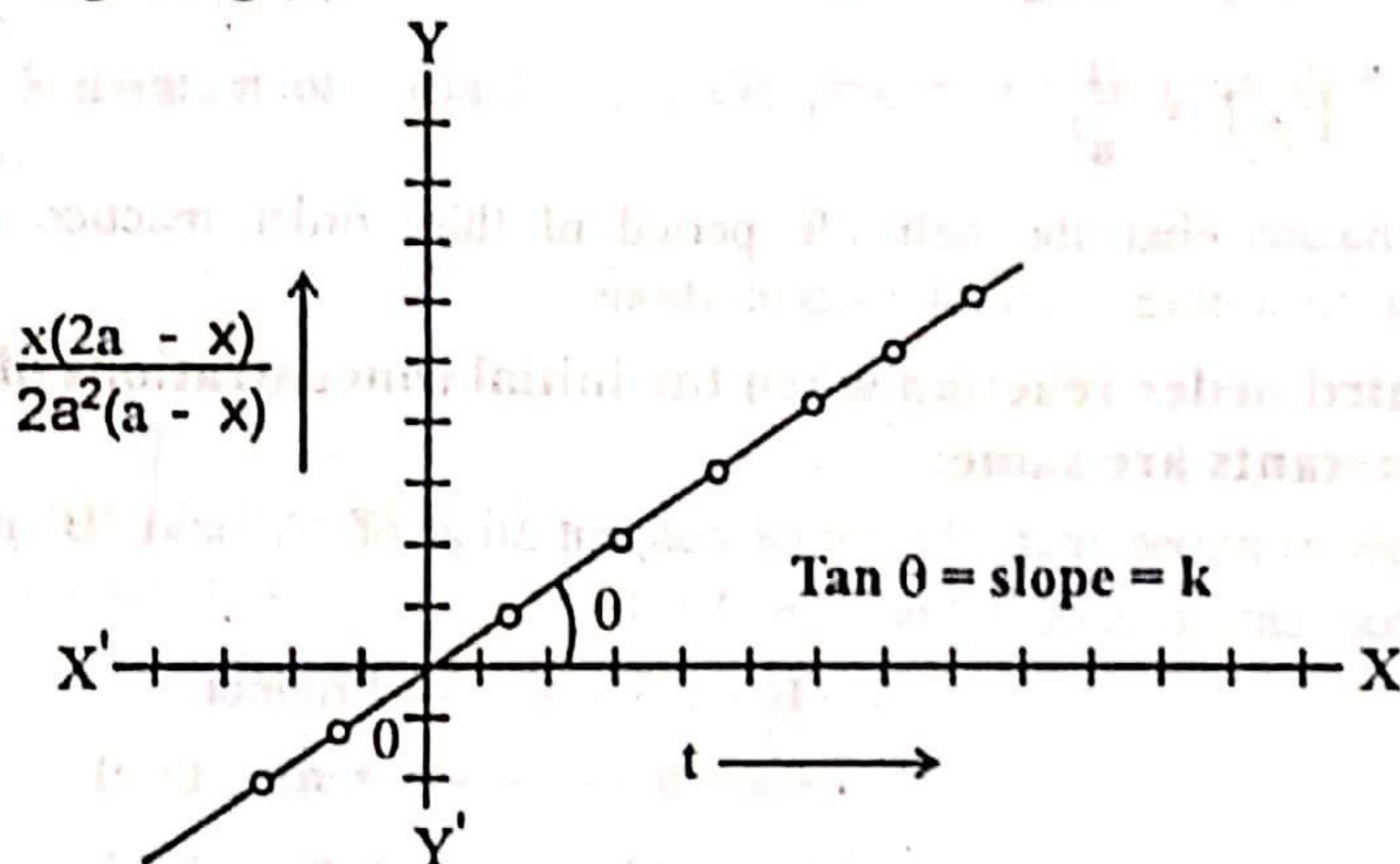


Fig. (8) Graphical representation of third order reaction when concentrations of reactants are equal.

The value of the rate constant 'k' is the same from this graph as we obtained from the previous graphs.

7.5.2 Units of third order rate constant:

In order to derive the units, let us put the units of 'a', (a - x) and 't'.

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

$$k = \frac{1}{\text{sec.}} \cdot \frac{\text{moles dm}^{-3} \cdot \text{moles dm}^{-3}}{(\text{moles dm}^{-3})^2 (\text{moles dm}^{-3})^2}$$

$$k = \frac{1}{\text{sec.}} \cdot \frac{1}{(\text{moles. dm}^{-3})^2}$$

$$k = \frac{1}{\text{sec.}} \cdot \frac{1}{(\text{moles})^2 \cdot \text{dm}^{-6}}$$

$$k = \text{dm}^6 \cdot \text{mol}^{-2} \cdot \text{sec}^{-1}$$

7.5.3 Half life period of third order reaction

0.5a. Third order reaction completes its half life, when the value of the 'x' is

So, when $x = 0.5a$, then $t = t_{1/2}$

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

$$t_{1/2} = \frac{1}{2k} \cdot \frac{0.5a(2a-0.5a)}{a^2(a-0.5a)^2}$$

$$t_{1/2} = \frac{1}{2k} \cdot \frac{1.5a}{a^2 \cdot (0.5a)}$$

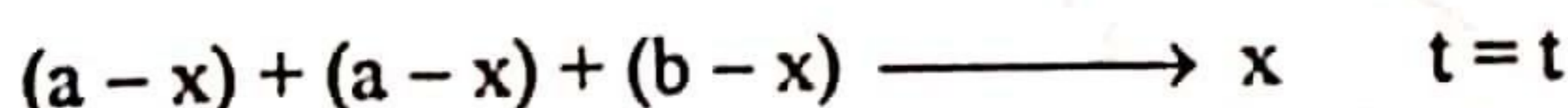
$$t_{1/2} = \frac{3}{2k a^2} = \frac{1.5}{k a^2}$$

$$[t_{1/2}] \propto \frac{1}{a^2}$$

It means that the half life period of third order reaction is inversely proportional to square of initial concentrations.

7.5.4 Third order reaction when the initial concentrations of two reactants are same:

Now suppose that, the initial concentration of 'A' and 'B' is 'a' moles dm^{-3} and concentration of 'C' is 'b' moles dm^{-3} .



According to law of mass action, the rate of chemical reaction is directly proportional to the concentration of reactants at time 't'

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

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

In order to do the integration, variables are to be separated

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

The integration of R.H.S of this equation is 'kt + c'.

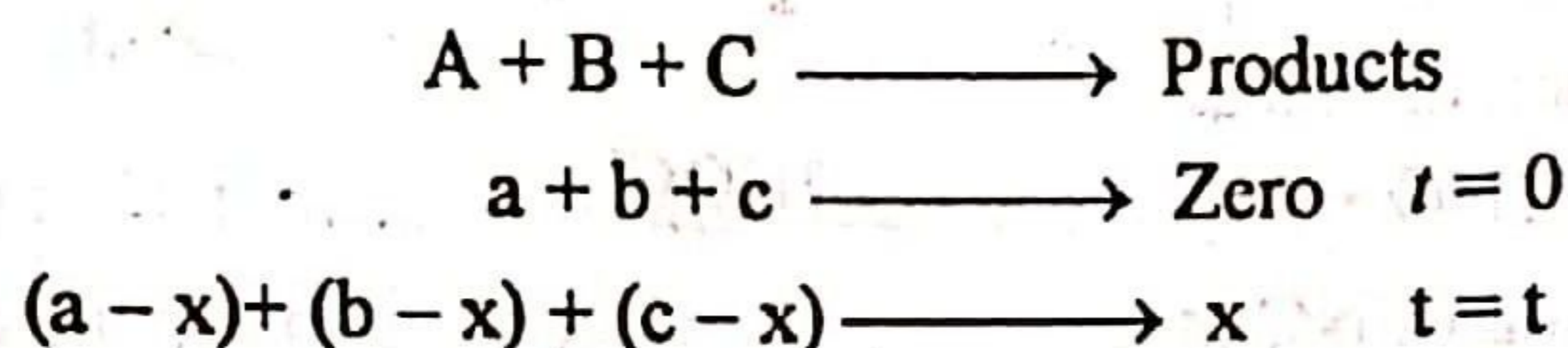
L.H.S of this equation can only be integrated after doing the partial fractions. If we do it and complete the equation by finding the value of integration constant 'c', then the final equation comes out to be,

$$\frac{1}{(a-2b)^2} \left[\frac{2x(2b-a)}{a(a-2x)} + \ln \frac{b(a-2x)}{a(b-x)} \right] = kt \quad \dots\dots (3)$$

This is again the equation of a straight line and a graph can be plotted between 't' on x-axis and all other factors of L.H.S. on the y-axis. The slope of the straight line passing through the origin can be calculated and so the rate constant 'k' can be measured.

7.5.5 Third order reaction when the initial concentrations of all the reactants are different:

The general third order reaction can be written as follows, with initial concentrations 'a', 'b' and 'c'.



So, $\frac{dx}{dt} = k(a - x)(b - x)(c - x)$

Separation of variables and the process of integration needs the partial fractions.

$$\frac{dx}{(a - x)(b - x)(c - x)} = k dt \dots\dots (1)$$

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

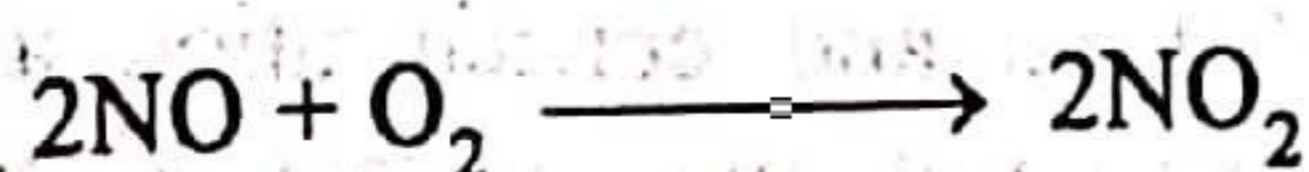
Final expression is as follows

$$\frac{\ln \left[\left(\frac{a - x}{a} \right)^{b - c} \cdot \left(\frac{b - x}{b} \right)^{c - a} \cdot \left(\frac{c - x}{c} \right)^{a - b} \right]}{(a - b)(b - c)(c - a)} = kt \dots\dots (2)$$

This equation (2) is of a straight line and if a graph is plotted between 't' on x-axis and the L.H.S. of this equation (2) on y-axis, then a straight line is obtained passing through the origin.

7.5.6 Examples of third order reactions:

(i) The oxidation of NO into NO₂ is a third order reaction.



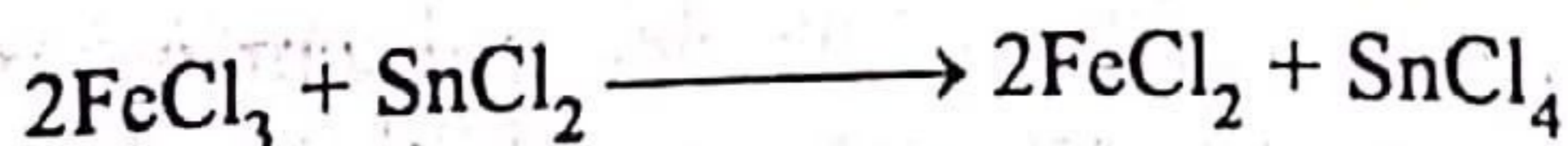
This reaction happens with the decreasing number of molecules. The progress of this reaction can be studied by measuring the decrease in pressure at constant volume. This can be done with the help of manometer.

The initial concentration of NO is 'a' and that of 'O₂' is 'b', so

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

The integrated form of this equation will be the same as mentioned above.

(ii) When FeCl₃ is reacted with SnCl₂, then the reaction is observed as third order.



The progress of reaction is studied by the titration of the reaction mixture with standard solution of K₂Cr₂O₇

Third order reaction in gas phase:

- (i) The reduction of NO with H_2 .



- (ii) Formation of NOCl



- (iii) Formation of NOBr.

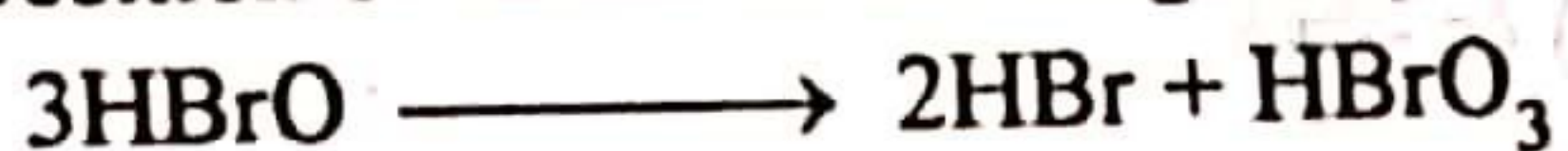


Third order reaction in solution phase:

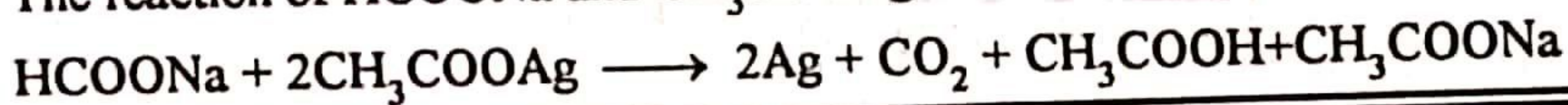
- (i) Reaction between $FeCl_3$ and KI



- (ii) Decomposition of HBrO in the range of pH = 6.4 - 7.8



- (iii) The reaction of HCOONa and CH_3COOAg



7.6.0 METHODS TO DETERMINE THE ORDER OF REACTION

As we have discussed in various examples, that the chemical equations do not give a correct picture of reaction. In order to understand the mechanism of reaction, it is essential to determine its order. Let us discuss some of the methods to determine the order of reactions.

- (1) Method of trial:

In this method, the data of the chemical reaction is collected in the laboratory. The data of the reaction in chemical kinetics means that we measure the concentrations of reactants and products, after definite intervals of time.

- (i) If the values of time and concentration are substituted in first order equation and the value of rate constant 'k' comes out to be constant, then the reaction is first order.

The equation is as follows:

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

- (ii) If the data are substituted in the second order equation, and we get the value of rate constant 'k' same in all the readings, then the reaction is second order. The equation is as follows.

$$k = \frac{1}{t} \ln \frac{b(a-x)}{a(b-x)}$$

- (iii) If the data satisfy the third order equation, then the reaction is third order. It means that the order of reaction is determined with that equation which gives a satisfactory constant value of 'k'. For this reason, this is called the method of trial.

First of all, this method was very popular. Anyhow, it is still extensively used for simple reactions.

(2) Graphical method:

We know that the rate of a chemical reaction decreases with the passage of time. The amount of product 'x' produced in a chemical reaction becomes less and less with the passage of time.

When a graph is plotted between time on x-axis and concentration of products on y-axis, then rising curve is obtained. The slopes of the various points of this curve give us the instantaneous rates of this reaction at various time intervals. It means that the values of $\frac{dx}{dt}$ can be calculated, at different time intervals.

(i) For first order reaction,

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

This is the equation of a straight line, '(a - x)' is independent variable and $\frac{dx}{dt}$ is dependent variable. When a graph is plotted between (a - x) on x-axis and $\frac{dx}{dt}$ on y-axis, and a straight line is obtained, then the reaction is first order. The graph is as follows. Fig. (9)

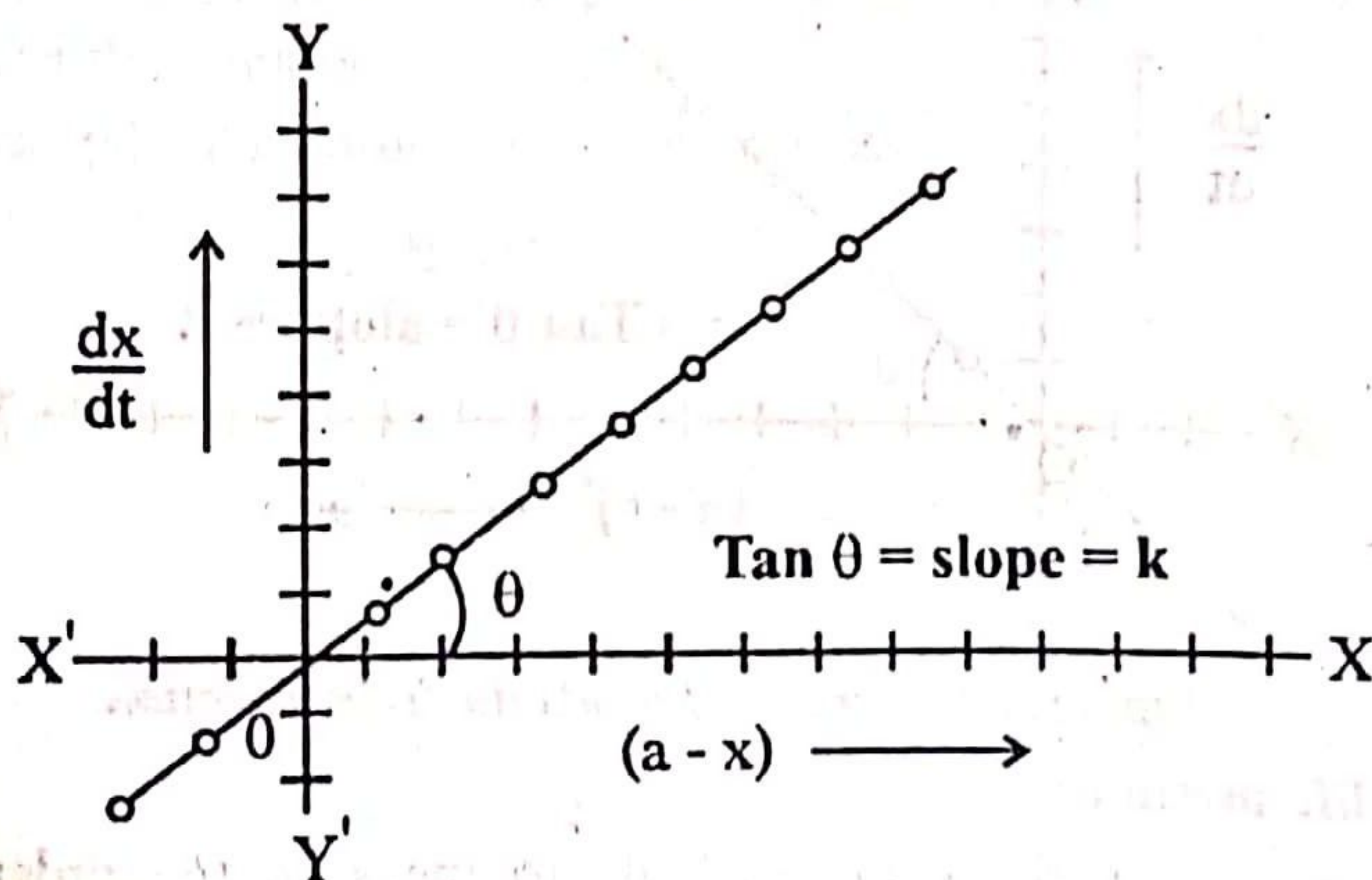


Fig. (9) The graph of first order reaction.

(ii) For the second order reactions,

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

This is an equation of a straight line. When we plot a graph between $(a - x)^2$ on x-axis and $\frac{dx}{dt}$ on y-axis, then the straight line convinces us that the reaction is second order. Fig. (10)

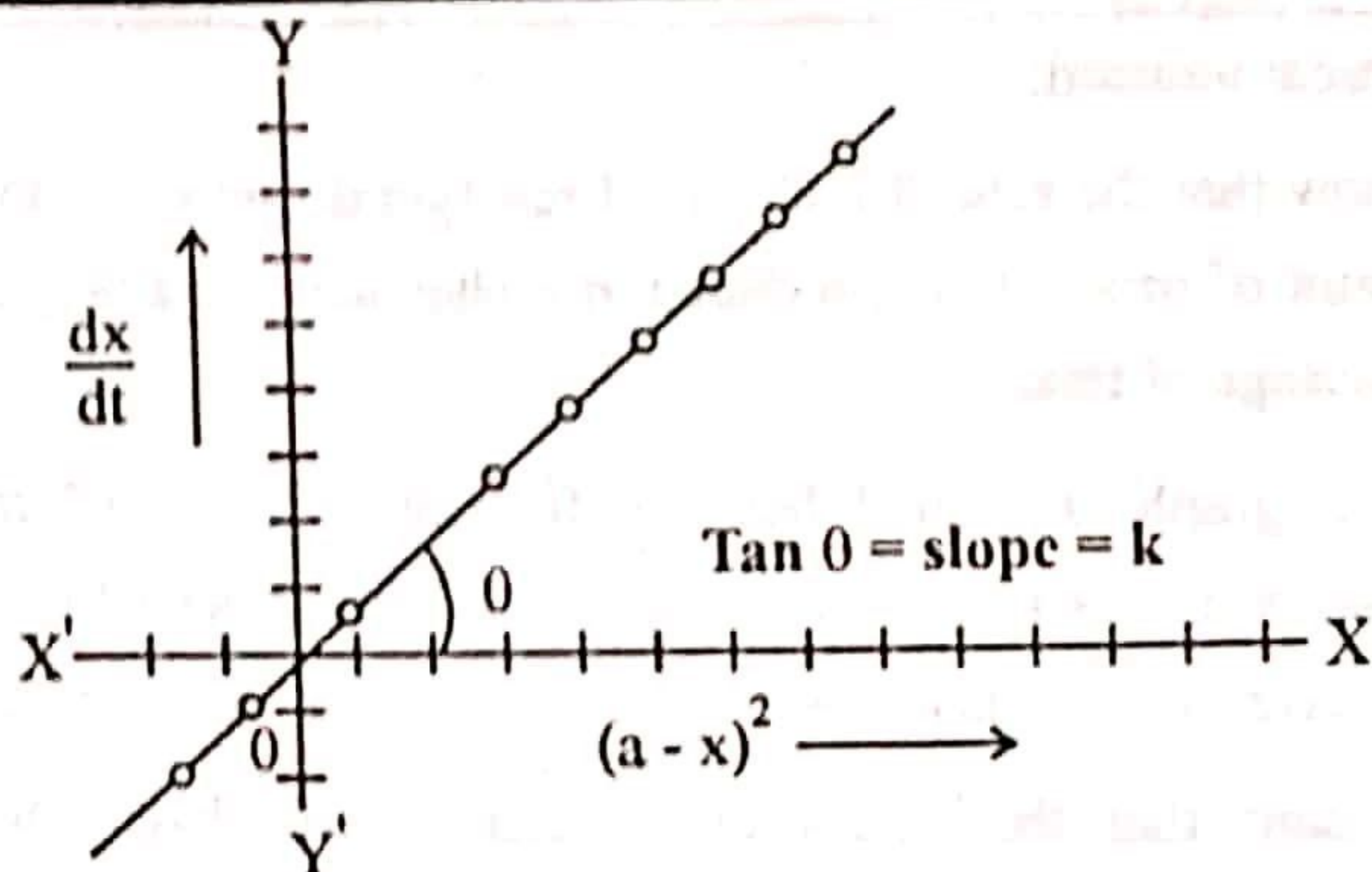


Fig. (10) The graph of a second order reaction.

(iii) For third order reaction

$$\frac{dx}{dt} = k(a-x)^3$$

This is an equation of straight line when a graph is plotted between $(a-x)^3$ an x-axis and $\frac{dx}{dt}$ an y-axis. Under these circumstances, the reaction should be third order. Fig. (11)

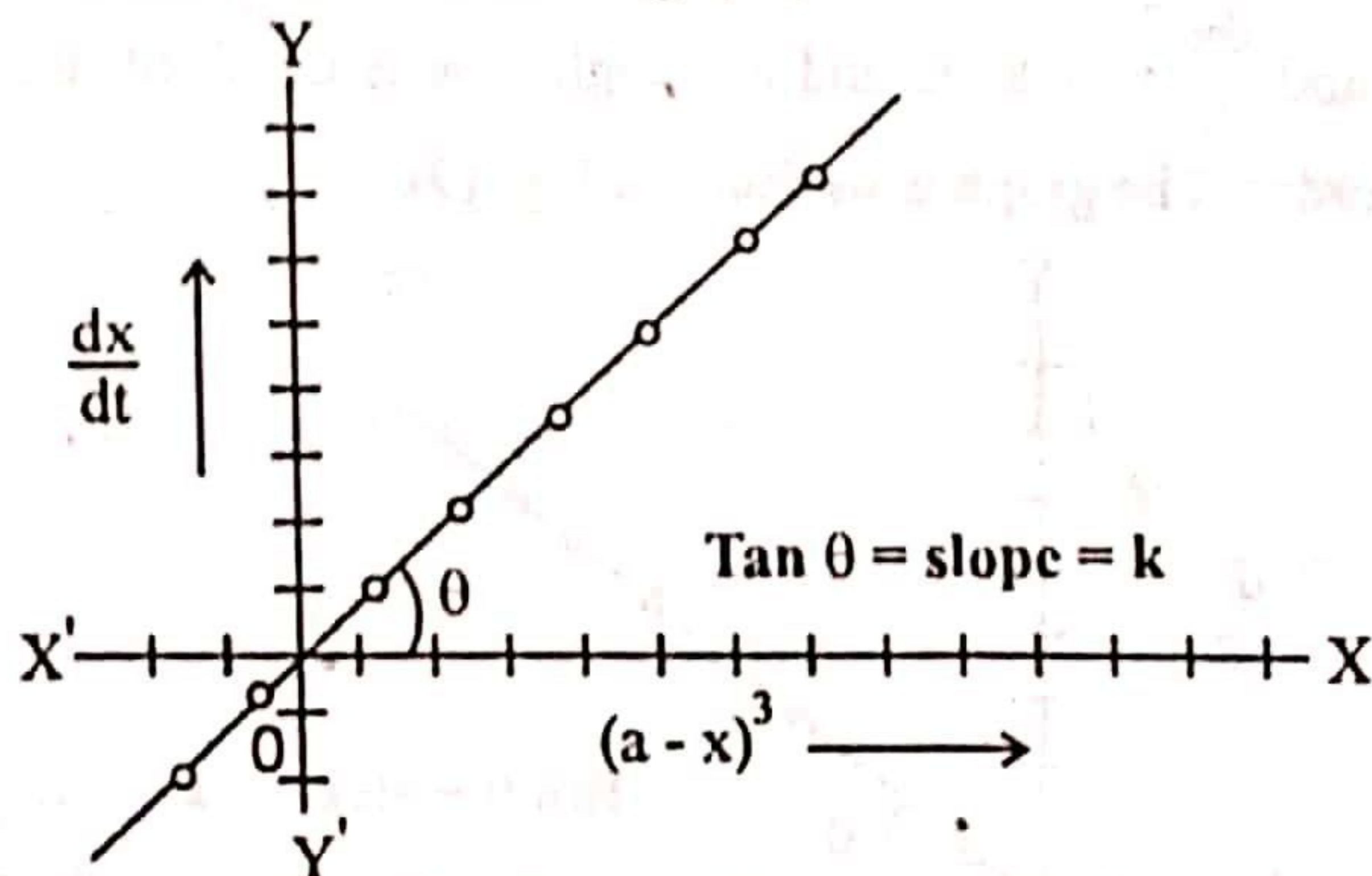


Fig. (11) The graph of a second order reaction.

(3) Half life method:

This is one of the good methods to measure the order of a chemical reaction. In the previous articles we have derived the expressions for half life period of first order, second order and third order reactions. These are as follows.

(i) For first order reaction,

$$(t_{1/2})_1 \propto \frac{1}{a^0}$$

(ii) For second order reaction,

$$(t_{1/2})_2 \propto \frac{1}{a^1}$$

(iii) For third order reaction,

$$(t_{1/2})_3 \propto \frac{1}{a^2}$$

From these three expressions, we conclude that the half life period of n th order reactions is inversely proportional to the initial concentration, one less than the order of reaction. Hence

$$(t_{1/2})_n \propto \frac{1}{a^{n-1}}$$

Let us suppose that, we have reactions whose order is to be measured. At initial concentration ' a_1 ' the half life is ' t_1 '. At initial concentration ' a_2 ' the half life is ' t_2 '. Keeping above explanations in view, we can say that

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \dots\dots (1)$$

$$t_2 \propto \frac{1}{a_2^{n-1}} \quad \dots\dots (2)$$

Let us divide two equations.

$$\frac{t_2}{t_1} = \left(\frac{a_1}{a_2}\right)^{n-1}$$

In order to have the order of reaction ' n ' in the equation in such a way that, it should not remain the exponents of concentrations, we should take the log of this equation.

Now, take the natural log on both sides

$$\ln \frac{t_2}{t_1} = \ln \left(\frac{a_1}{a_2}\right)^{n-1}$$

$$\ln \frac{t_2}{t_1} = (n-1) \ln \frac{a_1}{a_2}$$

$$(n-1) \ln \frac{a_1}{a_2} = \ln \frac{t_2}{t_1}$$

$$(n-1) = \frac{\ln t_2/t_1}{\ln a_1/a_2}$$

$$n = \frac{\ln t_2/t_1}{\ln a_1/a_2} + 1$$

So, if we know two initial concentrations ' a_1 ' and ' a_2 ' and two half life periods, t_1 and t_2 then order can be calculated.

(4) **Differential method:**

This method was given by Van't Hoff. It is also called Van't Hoff differential method.

We know that the rate of a reaction having order 'n' is proportional to the nth power of concentration, so

$$-\frac{dx}{dt} = kc^n$$

Hence 'c' is the concentration of the reactants at any time 't'. The rate of reaction with respect to reactant, c can be written as

$$-\frac{dc}{dt} = kc^n$$

If we do the experiment twice, with two different concentrations 'c₁' and 'c₂' then the rates are as follows.

$$-\frac{dc_1}{dt} = kc_1^n \quad \dots\dots (1)$$

$$-\frac{dc_2}{dt} = kc_2^n \quad \dots\dots (2)$$

Take the common log of equation (1) and (2)

$$\log \left[-\frac{dc_1}{dt} \right] = \log k + n \log c_1 \quad \dots\dots (3)$$

$$\log \left[-\frac{dc_2}{dt} \right] = \log k + n \log c_2 \quad \dots\dots (4)$$

On subtracting equation (4) from equation (3)

$$n = \frac{\log \left[-\frac{dc_1}{dt} \right] - \log \left[-\frac{dc_2}{dt} \right]}{\log c_1 - \log c_2} \quad \dots\dots\dots (5)$$

In order to determine the value of order of reaction 'n' we should know the two concentration 'c₁' and 'c₂' and two rates. The rates of reaction are determined from the slopes of the points on the curves as we have mentioned in second method.

5. Ostwald isolation method or large excess method:

This method is employed for complicated reactions. One of the reactants is isolated by taking two reactants in large excess.

Suppose we have a reaction,



We determine the order of reaction with respect to 'A', 'B' and 'C'. Then the overall order is calculated by adding all the orders.

When we want to determine the order with respect to 'A', then 'B' and 'C' are taken in large excess. In this way 'B' and 'C' do not determine the rate of reaction. Similarly, the reaction is repeated for other two species.

Let the orders with respect to 'A', 'B' and 'C' are 'n_A', 'n_B', 'n_C', then the overall order 'n'

$$n = n_A + n_B + n_C$$

7.6.1 Experimental techniques to follow the reaction rates:

For the study of kinetics of chemical reactions, various techniques are generally employed. Suitable analytical techniques are employed to record the data of the progress of reactions. We note the concentration of reactants and products with the passage of time and this thing is called data.

The suitability of any analytical technique for obtaining the kinetic data depends upon.

- (i) Half life of a reaction.
- (ii) Time scale on which the method operates.

A successful method for measuring the concentrations as a function of time should have the following characteristics.

- (i) The techniques should be instantaneous.
- (ii) We should be able to get a record of rapidly changing concentrations.
- (iii) The techniques should not influence the rate of reaction.

Categories of sampling techniques:

Broadly speaking, there are two categories,

- (a) Direct sampling technique.
- (b) Indirect method.

(i) Direct sampling technique:

The sampling is followed by an actual chemical analysis. At a particular instant, a small aliquot is withdrawn from the reaction vessel and the reaction is arrested. This arresting can be done by suitable procedure. For example, sudden cooling or addition of an acid or a base serves the purpose.

(ii) Indirect sampling techniques:

In these techniques, we study the property of a substance which changes with the change of concentration. We should be able to measure this property with convenience. Some of the physical properties which can be employed are as follows.

- (i) Measurement of volume change.
- (ii) Measurement of density.
- (iii) Measurement of optical rotation for optical active substances.
- (iv) Measurement of electrical conductivity.
- (v) Spectroscopy.
- (vi) Potentiometry.
- (vii) Polarography.
- (viii) Magnetic susceptibility
- (ix) Refractive index

Study of fast reactions:

Some special experimental techniques are employed to study the kinetics of fast reactions. Some of the methods are as follows.

- (i) Flow method
- (ii) Relaxation method
- (iii) Flash photolysis
- (iv) Molecular beam method

7.7.0 ENERGY OF ACTIVATION

We know that the molecules of gases and liquids are colliding among themselves with **certain energies** and **chemical reactions are due to collisions**. Every collision does not lead to the chemical reaction. Chemical reactions take place when the old bonds are broken and new bonds are formed. **In order to break the old bonds, some extra energy is required**. In other words, the reacting molecules attain the **activated state** and become able to convert themselves into products.

It means that the reactants do not pass directly to the products, till they acquire an additional amount of energy more than the average energy of the molecules of reactants in the system. **This energy which is more than the average energy and is just sufficient to convert the reactants into products is called energy of activation.**

Those molecules which possess energy of activation are said to be activated. Take into account the hypothetical reaction



Consider the following diagram (12), in which the reactants are present at higher average energy than the products. According to the diagram, **the average energy of products is less than those of reactants**, so the reaction is exothermic. But reactants have to attain the **activated state** before forming the products.

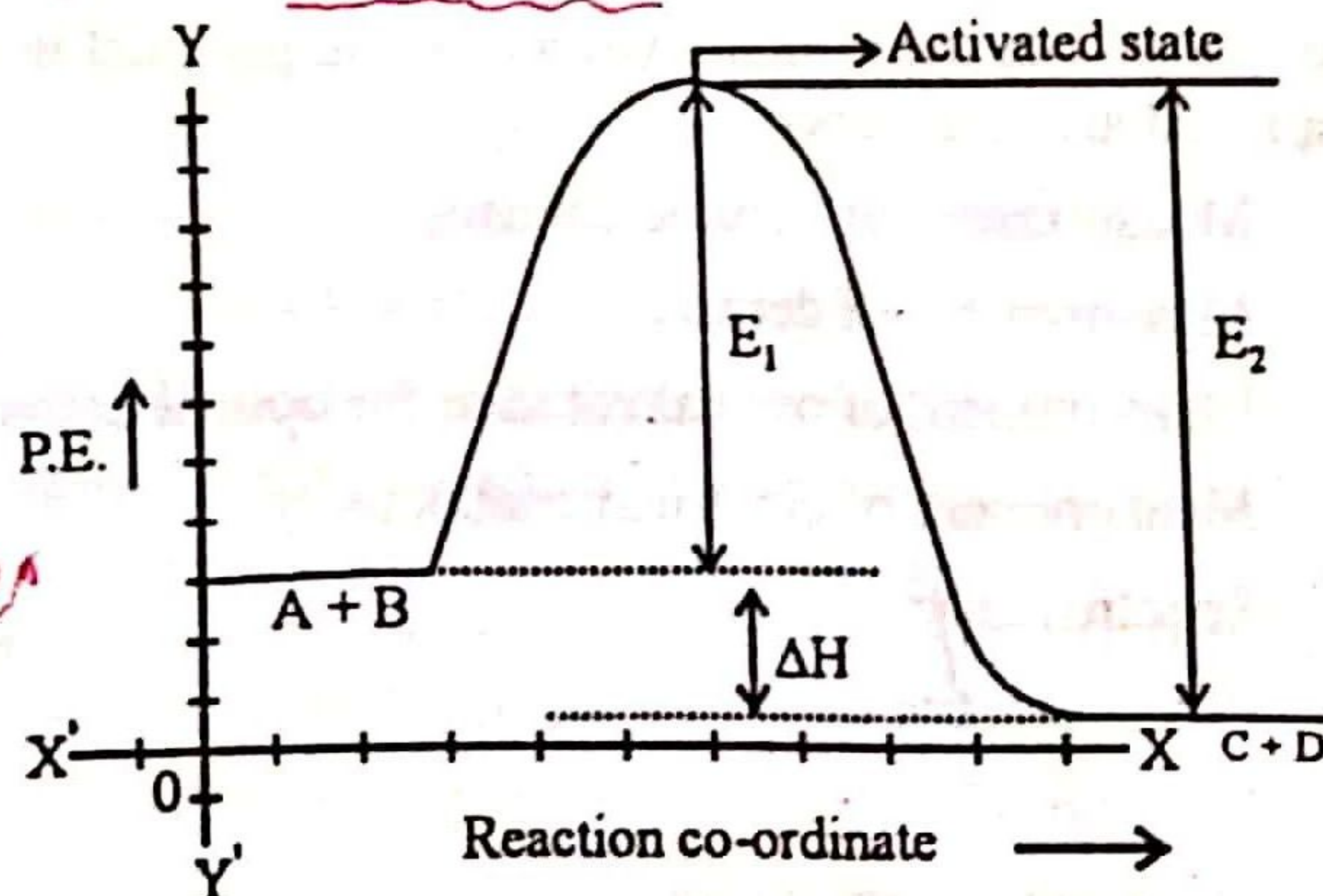


Fig. (12) Idea of energy of activation

Energy
Collision
Old bonds
& New bonds
R → P?
Average Energy?

Average Energy
↳ Reaction
↓
Enol/Endo.
Energy barrier

The molecules of reactants must climb the energy barrier before they can roll down the hill to form the products.

' E_1 ' is the energy of activation for the forward reaction and ' E_2 ' is for the backward reaction. The exothermicity of a reaction is the difference of ' E_1 ' and ' E_2 '.

It is clear from the diagram, that greater the energy barrier smaller the possibility for the conversions of reactants into products. In other words energy of activation is one of the major factors which controls the rate of reaction.

7.7.1 What is the source of energy of activation in a system:

Due to collisions of gas molecules, some of the molecules are activated due to favourable collisions. It depends upon the chance, whether it will get a favourable collision to be activated or unfavourable one to be deactivated. Anyhow, it should be believed beyond doubt that molecules experience millions and millions of collisions per seconds. These are activated and deactivated millions and millions of time per seconds.

In the activated state the molecule may get the chance to be decomposed earlier than to be deactivated and remain as a reactant.

7.7.2 Effect of temperature on the reaction rates:

In the previous discussions of reaction rates in the whole chapter, we have considered that the rate of reaction is influenced by the concentration of reactants. Temperature was thought to be constant. Experiments have told that an increasing temperature increases the reaction rates and do not change the order of reaction. Anyhow, high increase of reaction rates is observed both in gaseous and liquid phase reactions. But be careful that the formation of NO_2 from NO and O_2 , shows the exceptional behaviour. Its rate decreases with the increase of temperature.

Temperature co-efficient: As a rule the increase of temperature by 10°C , doubles the reaction rate. Hence the ratio of rate constants of a reaction at two different temperatures, differing by 10°C , is called temperature co-efficient.

$$\text{Temperature co-efficient} = \frac{k_{35}}{k_{25}} = \frac{k_{308}}{k_{298}} = 2 \text{ to } 3$$

7.7.3 Temperature dependence of reaction rates and Arrhenius equation:

In 1889 Arrhenius experimentally observed the variation of rate constant ' k ' with absolute temperature, ' T '. He gave an empirical relationship between rate constant ' k ' and temperature ' T '.

$$\log k = A' - \frac{B}{T} \quad \dots\dots (1)$$

' A ' and ' B ' are the constants which depend upon the nature of the chemical reactions. According to this equation (1), the increase of temperature ' T ' increases the rate constant ' k '. This equation (1) is equation of a straight line and if graph is plotted between $\frac{1}{T}$ on x-axis and $\log k$ on y-axis, a straight line is obtained with the negative slope Fig. (13).

The value of 'B' is obtained from the slope of the straight line and that of factor 'A' from the intercept of the straight line. Equation (1) is in the form of log, and it can be converted into exponential form.

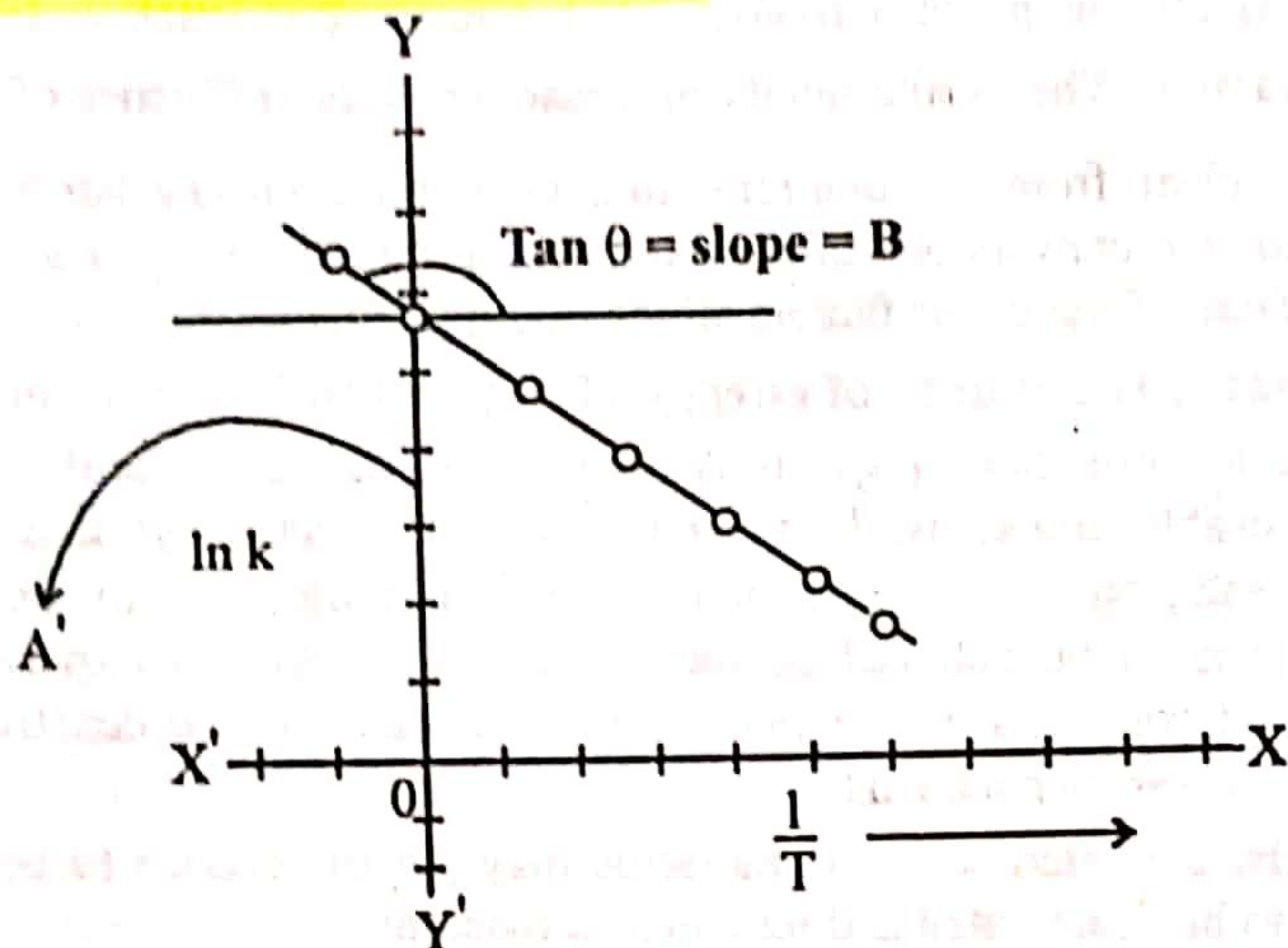


Fig. (13) Plot of $\ln k$ and $\frac{1}{T}$ for Arrhenius equation.

$$\log k = A' - B/T$$

$$k = e^{(A' - B/T)}$$

$$k = e^{A'} \times e^{-B/T} \quad (e^{A'} = A)$$

$$k = Ae^{-B/T} \quad \dots\dots (2)$$

Equation (2) is the exponential form of Arrhenius equation and it serves the same purpose as equation (1). Anyhow, the factor B was replaced by E_a/R and the accepted form of Arrhenius equation is as follows:

$$k = Ae^{-\frac{E_a}{RT}} \quad \dots\dots (3)$$

In equation (3), $e^{-E_a/RT}$ is called Boltzmann factor. Its value is controlled by energy of activation E_a and the temperature, 'T'. This equation (3) is called as Arrhenius equation. Both 'A' and ' E_a ' are independent of temperature and are determined by the properties of reacting molecules. These two factors have a great theoretical significance.

7.7.4 Calculation of energy of activation:

When we take the log of equation (3) and rearrange it, then we get the following expression.

$$\ln k = \ln A e^{-E_a/RT}$$

$$\ln k = \ln A + \ln e^{-E_a/RT}$$

$$\ln k = \ln A - E_a/RT \cdot \ln e \quad \text{Since } (\ln e = 1)$$

So, $\ln k = \ln A - E_a/RT$

or $\ln k = -E_a/RT + \ln A \quad \dots\dots (4)$

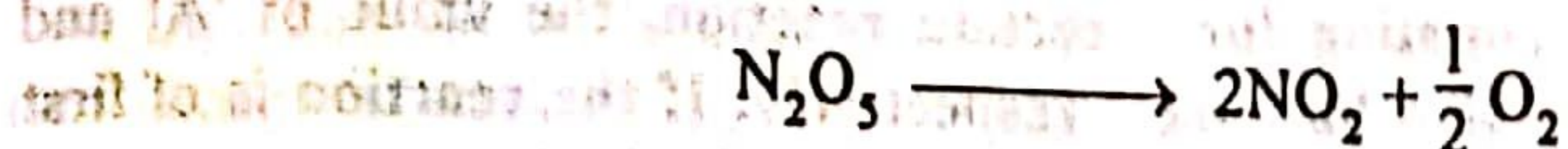
Arrhenius Equation

Theoretical Significance

Equation (4), is of straight line. When a graph is plotted between $1/T$ on x-axis and $\ln k$ on y-axis, then a straight line is obtained with negative slope and positive intercept. From the slope of the straight line, energy of activation ' E_a ' can be calculated. From the value of the intercept, we can have the value of Arrhenius factor ' A '.

Example:

Let us study the decomposition of N_2O_5 which is a first order reaction.



The value of the first order rate constant ' k ' is determined in the laboratory at different temperatures.

A graph is plotted between $1/T$ on x-axis and ' $\ln k$ ' on y-axis as follows. Fig. (14)

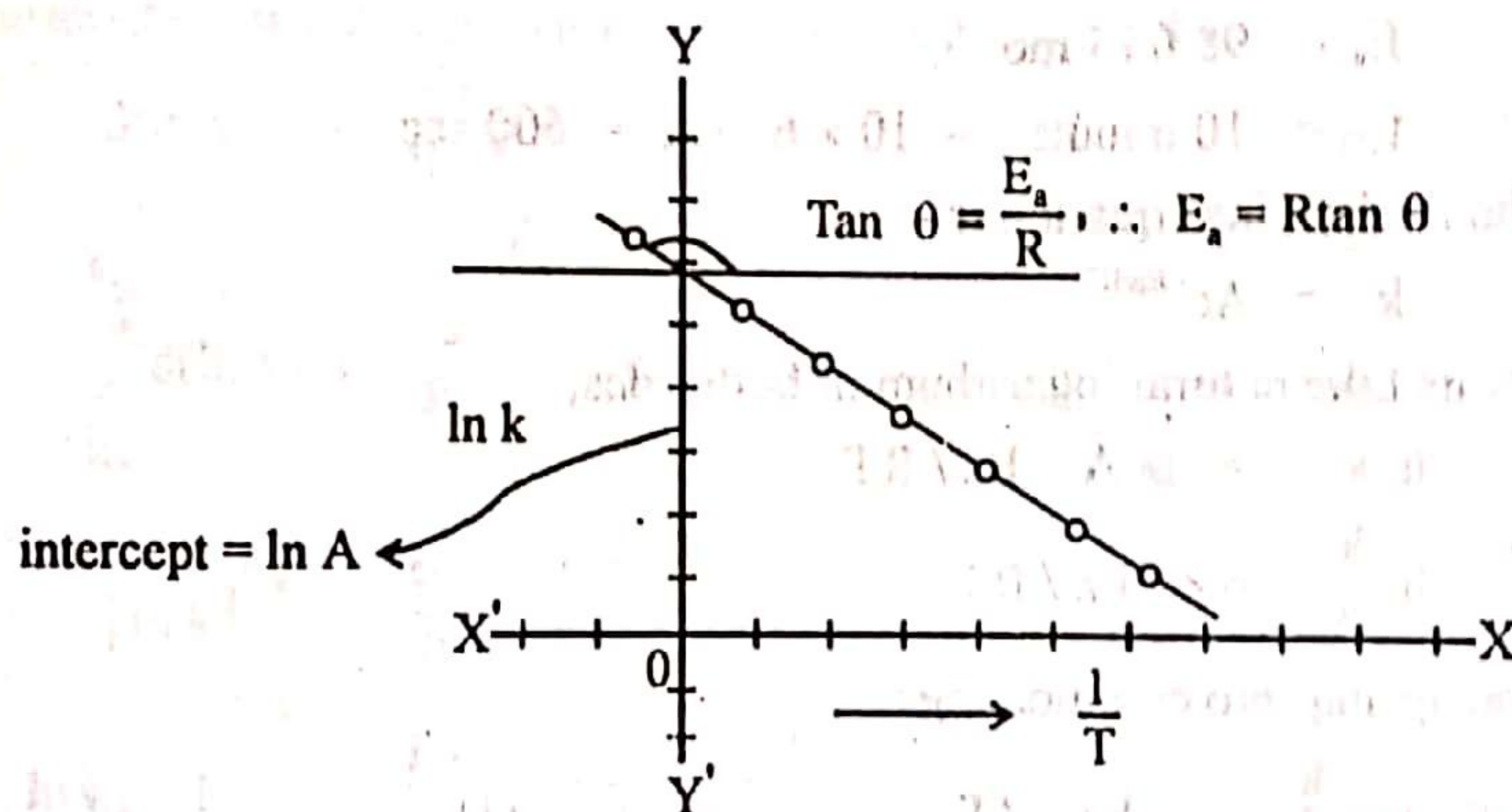


Fig. (16) Measurement of slope of straight line.

The value of the slope of the straight line comes out to be $-5400K$. The energy of action ' E_a ' can be calculated as follows.

$$\text{Slope} = -\frac{E_a}{2.303R}$$

$$E_a = -(-5400K)(2.303)(8.314 \text{ JK}^{-1} \text{ mol}^{-1})$$

$$E_a = 103410 \text{ J mol}^{-1}$$

$$E_a = 103.41 \text{ kJ mol}^{-1}$$

7.7.5 Calculation of Arrhenius factor ' A ':

The value of intercept of the straight line is equal to ' $\ln A$ '.

$$\ln A = \text{intercept}$$

Taking the antilog on both sides.

$$A = \text{Antilog}(\text{intercept})$$

$$A = 4.3 \times 10^{13}$$

Its units are same as for the specific rate constant. The Arrhenius equation for decomposition of N_2O_5 becomes.

$$k = 4.3 \times 10^{13} \cdot e^{-103410/RT} \dots\dots (5)$$

When we substitute the value of temperature in equation (5), then we can get the rate constant for thermal decomposition of N_2O_5 at that temperature.

EXAMPLE (12)

In the Arrhenius equation for a certain reaction, the value of 'A' and 'Ea' are $4 \times 10^{13} \text{ s}^{-1}$ and $98.6 \text{ kJ mole}^{-1}$ respectively. If the reaction is of first order at what temperature will its half life period be 10 minutes.

SOLUTION:

Data:

$$A = 4 \times 10^{13} \text{ sec}^{-1}$$

$$E_a = 98.6 \text{ kJ mol}^{-1}$$

$$t_{1/2} = 10 \text{ minutes} = 10 \times 60 \text{ sec} = 600 \text{ sec}$$

The Arrhenius equation is

$$k = Ae^{-E_a/RT}$$

Let us take natural logarithm of both sides,

$$\ln k = \ln A - E_a / RT$$

$$\ln \frac{k}{A} = - E_a / RT$$

Converting into common log

$$2.303 \log \frac{k}{A} = - E_a / RT \dots\dots (1)$$

First of all get the k from half life period

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{600 \text{ sec}} = 1.155 \times 10^{-3} \text{ sec}^{-1}$$

Putting the values in equation (1)

$$2.303 \log \frac{1.155 \times 10^{-3} \text{ sec}^{-1}}{4 \times 10^{13} \text{ sec}^{-1}} = \frac{-98.6 \times 10^3 \text{ J mole}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times T}$$

$$-16.54 = \frac{-98600}{19.147 T \text{ K}^{-1}}$$

$$T = \frac{98600 \text{ K}}{19.147 \times 16.54} = \boxed{311.34 \text{ K}}$$

7.7.6 Evaluation of energy of activation from two temperatures:

In the above mentioned example, we are able to calculate the energy of activation 'Ea' when the reaction is performed at various temperatures, and a graph is obtained. It is also possible to change the shape of the Arrhenius equation from which 'Ea' can be calculated, if we know two rate constants at two temperatures.

We know that,

$$\ln k = \ln A - \frac{E_a}{RT}$$

Differentiate this equation with respect to temperature.

$$\frac{d(\ln k)}{dT} = 0 + E_a/RT^2$$

$$\frac{d(\ln k)}{dT} = E_a/RT^2 \quad \dots\dots (6)$$

Equation (6) is differentiated form of Arrhenius equation. It tells us the rate of change of natural log of rate constant with respect to temperature. If we integrate this equation (6) then we will get original equation (4). But now, we want to integrate this equation (6) within limits.

We suppose that at temperature ' T_1 ' the rate constant is ' k_1 ' and at temperature ' T_2 ' the rate constant is ' k_2 '.

Separate the variables by bringing temperature on R.H.S.

$$d(\ln k) = \frac{E_a}{RT^2} \cdot dT$$

$$\int_{k_1}^{k_2} d(\ln k) = \frac{E_a}{R} \int_{T_1}^{T_2} \left(\frac{dT}{T^2}\right)$$

$$[\ln k]_{k_1}^{k_2} = \frac{E_a}{R} \left[-\frac{1}{T}\right]_{T_1}^{T_2}$$

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

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

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

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots\dots (7)$$

According to the equation (7), we can calculate the value of E_a if we know two temperatures ' T_1 ' and ' T_2 ' and two rate constants ' k_1 ' and ' k_2 '.

EXAMPLE (13)

The rate of particular reaction becomes four times when the temperature changes from 20°C to 40°C . Calculate the energy of activation for such a reaction.

SOLUTION:

Let two rate constants are k_1 and k_2 so, $\frac{k_2}{k_1} = \frac{4}{1} = 4$.

$$T_1 = 20^\circ\text{C} + 273 = 293\text{ K} \quad \text{and} \quad T_2 = 40^\circ\text{C} + 273 = 313\text{ K}$$

Applying the relation of rate constant and temperature

$$\log \frac{k_2}{k_1} = \frac{E_a (T_2 - T_1)}{2.303 RT_1 T_2}$$

Substituting the values in the above equation,

$$\log 4 = \frac{E_a (313 - 293)}{2.303 \times 8.314 \times 293 \times 313}$$

$$0.6020 = \frac{20 E_a}{2.303 \times 8.314 \times 293 \times 313}$$

Rearranging the equation

$$E_a = \frac{0.6020 \times 2.303 \times 8.314 \times 293 \times 313}{20}$$

$$= 52854.55 \text{ J mol}^{-1}$$

Hence activation energy = $52.85 \text{ kJ mol}^{-1}$ Ans.

7.7.7 The Arrhenius parameter for some important reactions:

Some of the following reactions which are unimolecular and bimolecular are mentioned along with their energies of activation and Arrhenius factor 'A'. The units for energy of activation is kJ mol^{-1} . For first order reaction, the units of Arrhenius factor 'A' is sec^{-1} , and for second order reaction it is $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$.

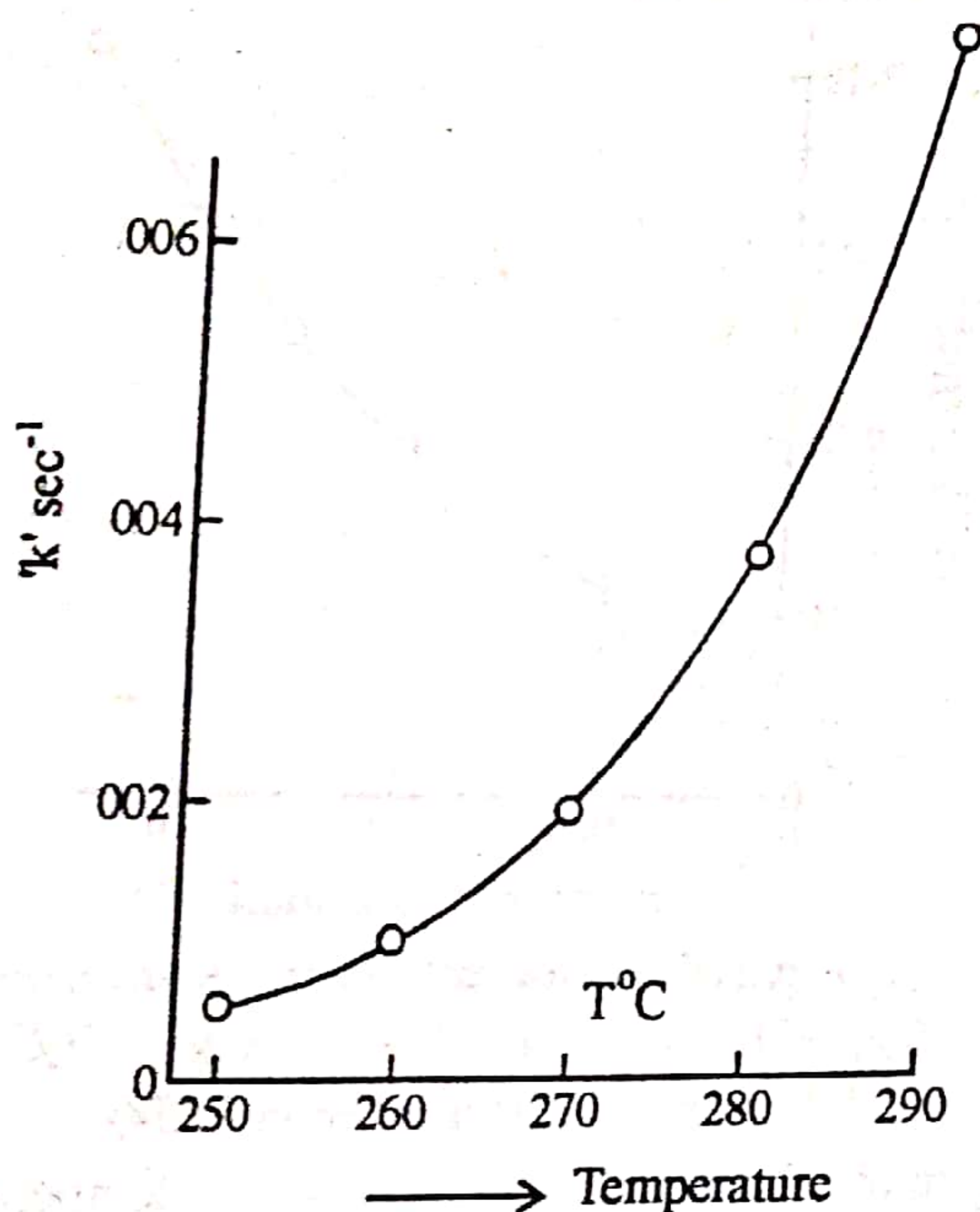
| (1) | Unimolecular reactions | E_a kJ mol^{-1} | A sec^{-1} |
|-------|--|-------------------------------|------------------------|
| (i) | $\text{C}_2\text{H}_5\text{Cl} \longrightarrow \text{C}_2\text{H}_4 + \text{HCl}$ | 254.4 | 4×10^{14} |
| (ii) | $\text{C}_2\text{H}_5\text{Br} \longrightarrow \text{C}_2\text{H}_4 + \text{HBr}$ | 218.8 | 7×10^{12} |
| (iii) | $\text{CH}_3\text{COOC}_2\text{H}_5 \longrightarrow \text{C}_2\text{H}_4 + \text{CH}_3\text{COOH}$ | 200.0 | 3×10^{12} |
| (iv) | $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{COOH} \longrightarrow \text{C}_6\text{H}_3(\text{NO}_2)_3 + \text{CO}_2$ | 96.2 | 1×10^{14} |

| (2) | Bimolecular reactions | E_a kJ mol^{-1} | A $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ |
|-------|---|-------------------------------|--|
| (i) | $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$ | 186.2 | 1.6×10^{11} |
| (ii) | $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$ | 112.5 | 9.4×10^9 |
| (iii) | $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{C}_2\text{H}_5\text{OH}$ | 61.5 | 7.9×10^5 |
| (iv) | $\text{CH}_3\text{I} + (\text{C}_2\text{H}_5)_3\text{N} \longrightarrow [\text{CH}_3\text{N}^+(\text{C}_2\text{H}_5)_3] \text{I}^-$ | 40.6 | 2.1×10^4 |

7.7.8 Variation of rate constants with temperature:

It is known fact that the rate constant of a reaction increases with the increase of temperature. In order to illustrate it, we can study the values of rate constants at various temperatures, and can plot a graph between temperature on x-axis and rate constant 'k' on y-axis. Some of the example are as follows.

- (i) The decomposition of diazo compounds was studied by Ramsperger in 1928. The data shows the following graph Fig. (15). It is a first order reaction.



Fig(15) First-order gas reaction $C_3H_7N_2C_3H_7 = C_6H_{14} + N_2$
(Ramsperger, 1928).

- (ii) The reaction of CH_3I with C_2H_5ONa was studied by Heacht and Conrad in 1889. The graphs is as shown in Fig. (16). It is a second order reaction.

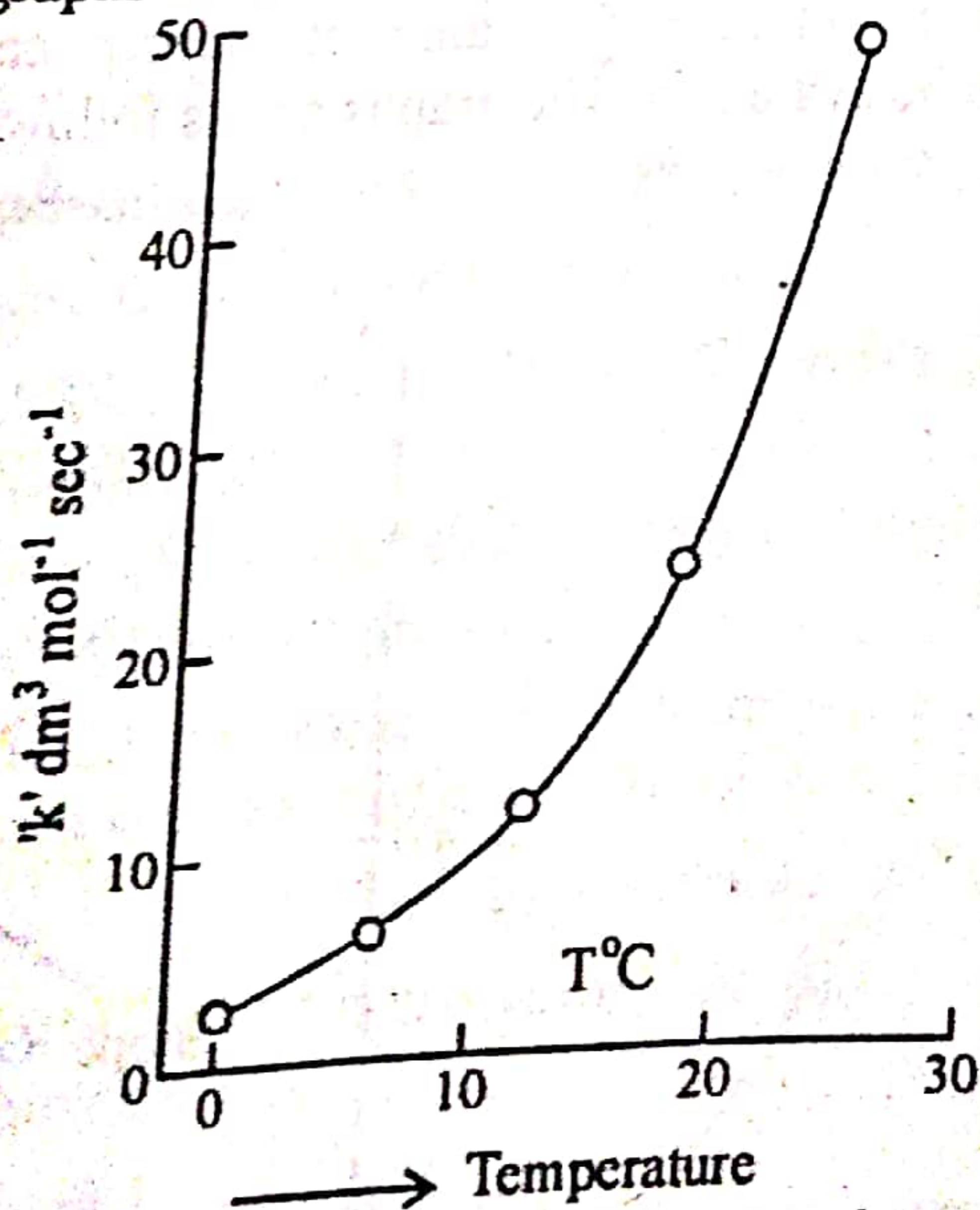


Fig. (16) Second-order reaction in solution
 $C_2H_5ONa + CH_3I = C_2H_5OCH_3 + NaI$

- (iii) The reaction of acetic acid with CH_3OH in the presence of an acid was studied by Williamson and Hinshelwood in 1934. The graph is shown in the Fig. (15). It is a second order reaction.

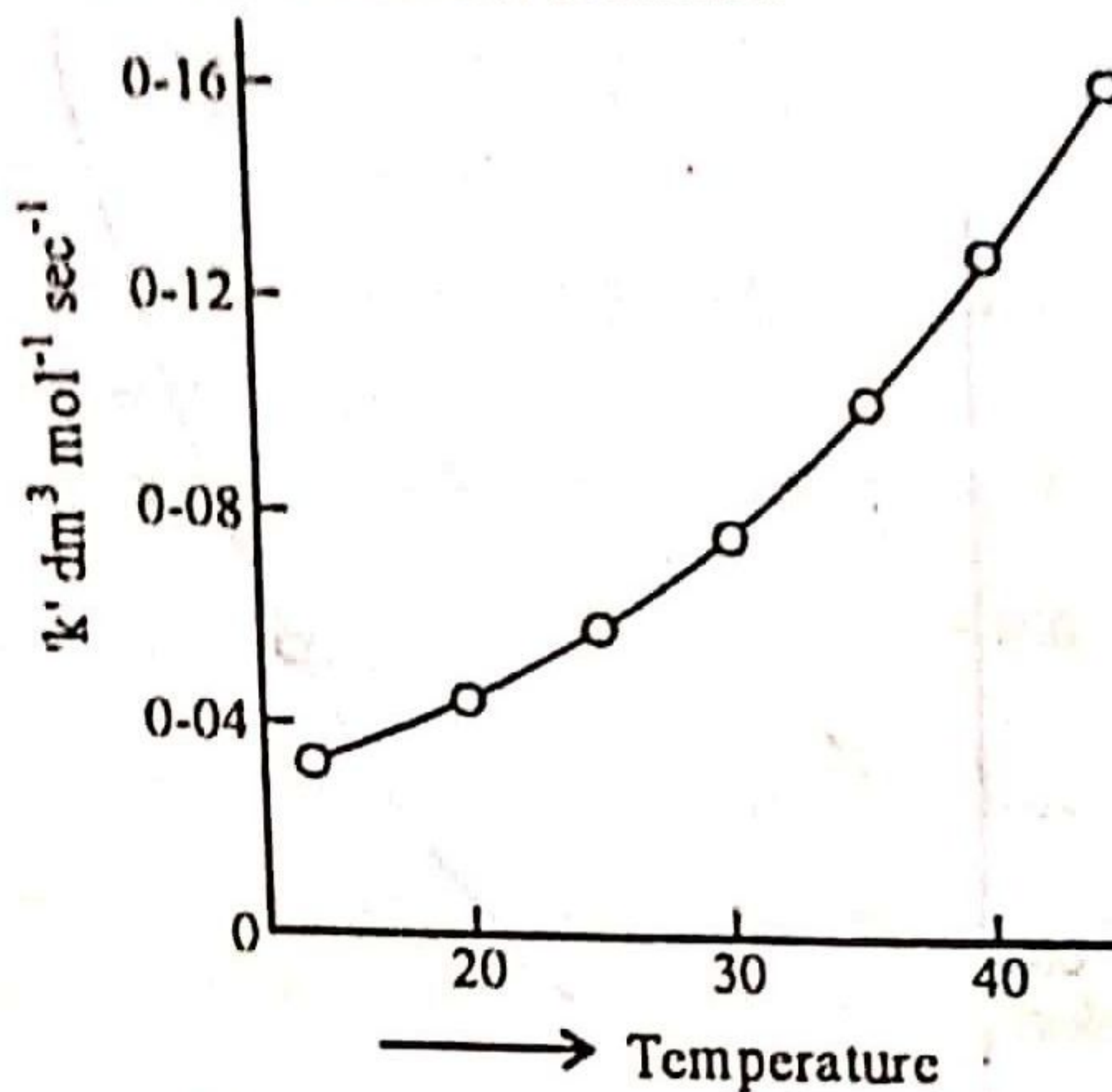


Fig. (17) Acid-catalyzed reaction
 $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH} = \text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$
 (Williamson and Hinshelwood, 1934).

All these graphs show that the increase of temperatures make the 'k' values to increase.

7.7.9 Arrhenius Plots:

For the above mentioned reactions, we can plot $\frac{1}{T}$ on x-axis and 'log k' on y-axis. The straight lines are obtained. The values of intercept can be calculated and energies of activation can be evaluated. The graphs are as follows Fig.(18a, b, c)

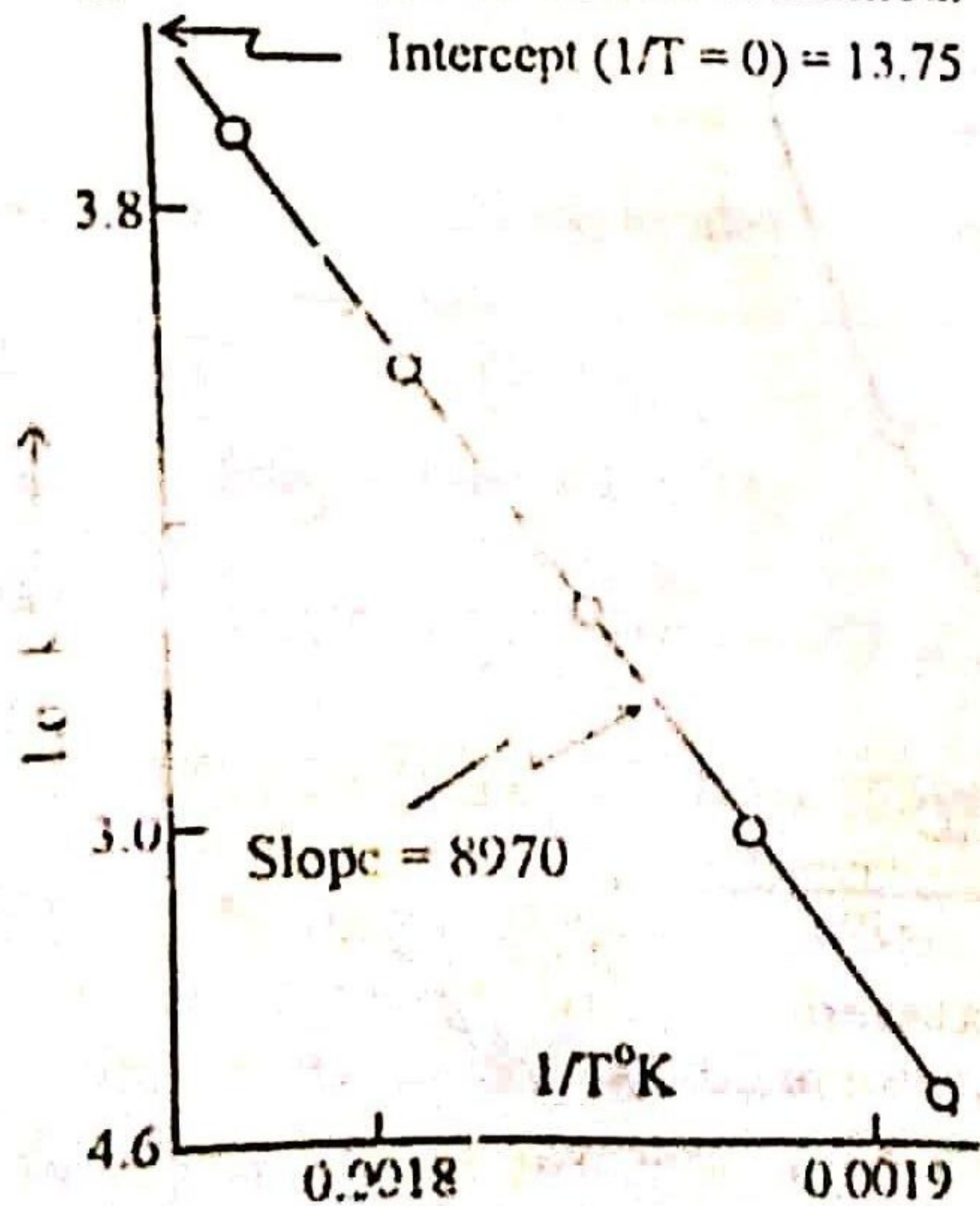


Fig. (18)
 Decomposition of diazo compounds

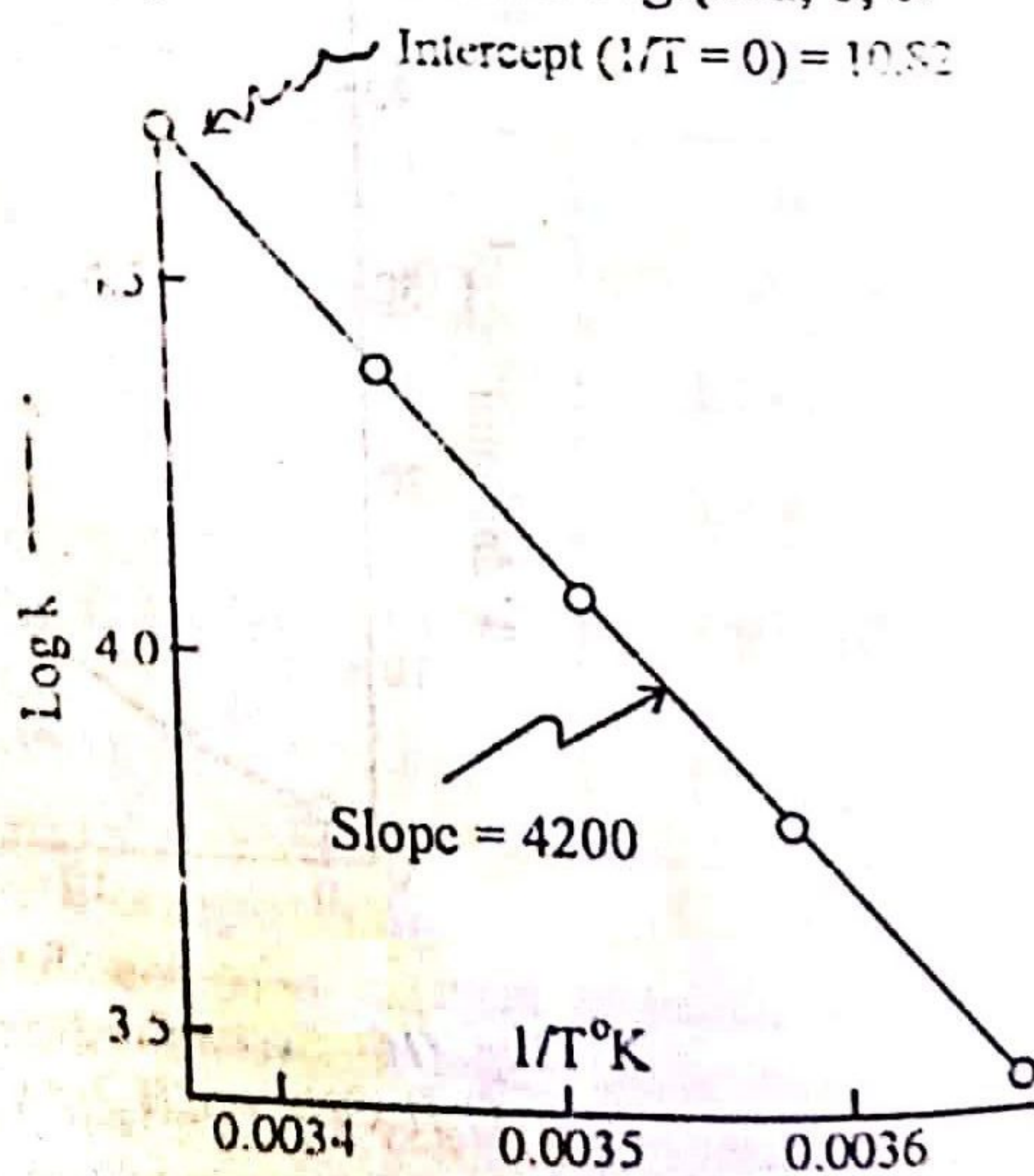


Fig. (19)
 Reaction of CH_3I with $\text{C}_2\text{H}_5\text{ONa}$

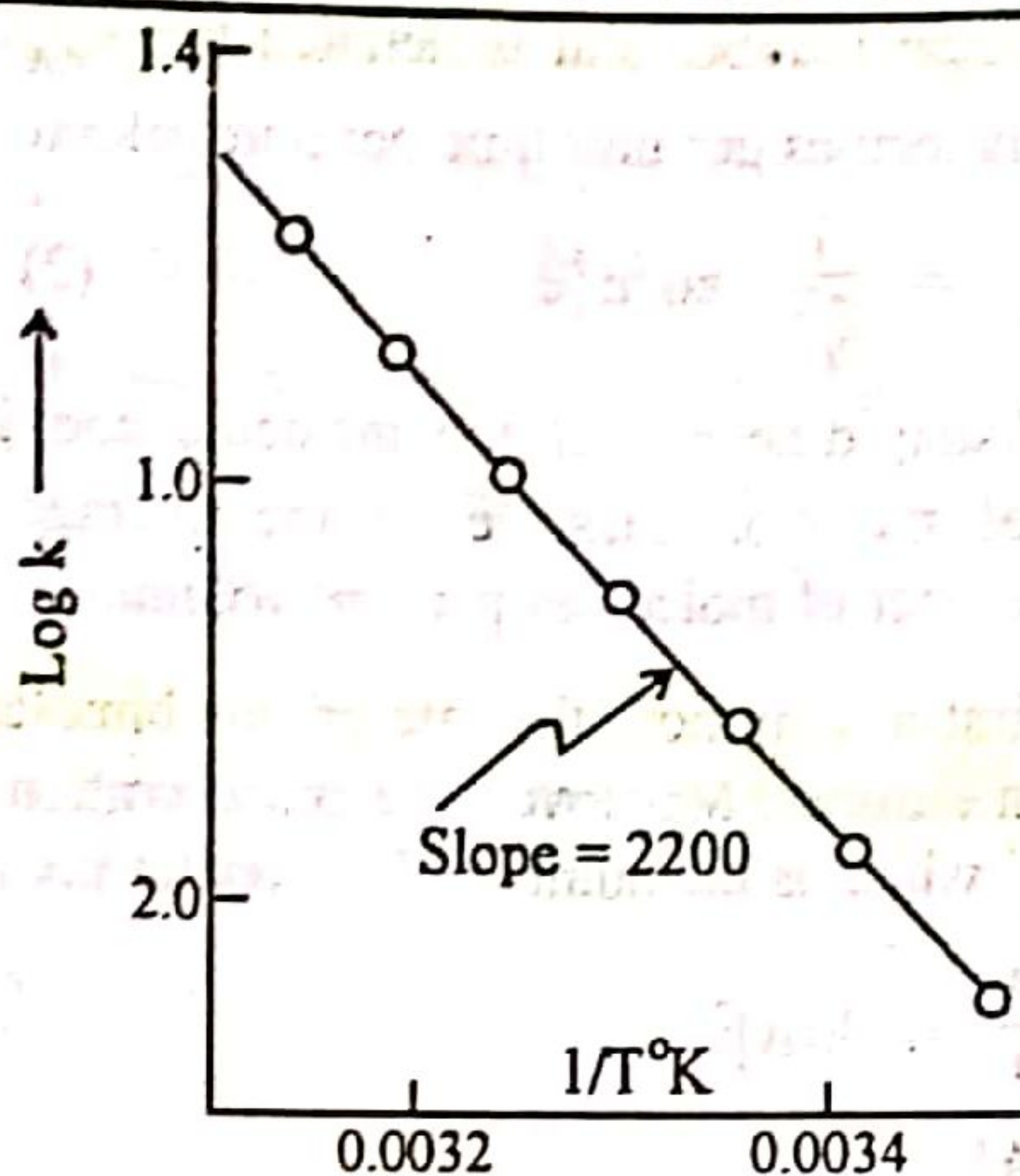


Fig. (20) Acid-catalyzed reaction
 $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH} = \text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$

7.8.0 THEORIES OF REACTION RATES

Theories of reaction rates have been put forward to understand the basic factors which control the rates of reaction.

Two theories are important:

- (1) The collision theory
- (2) Transition state theory

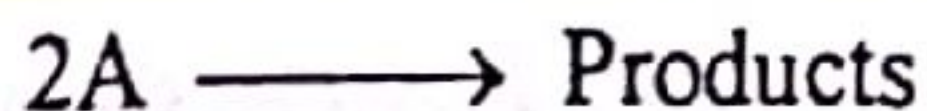
We discuss these two theories one by one.

7.8.1 The Collision Theory

This theory is based upon two postulates.

- (i) Molecules must collide among themselves to do a chemical reaction.
- (ii) The energies of the colliding molecules must be at least equal to the activation energy ' E_a '.

In order to do the mathematical explanation of this theory, let us consider a bimolecular reaction with same type of molecules *i.e.*, 'A'.



According to law of mass action, the rate of reaction depends upon the concentration of substance 'A'.

$$\frac{-d[\text{A}]}{dt} = k[\text{A}]^2 \quad \dots\dots (1)$$

Since, collisions are must for doing a chemical reaction, so we should take into account the number of collisions happening among the molecules of substance

'A'. This is called collision number and is denoted by ' Z_{AA} '. It is the number of collisions between like molecules per unit time per unit volume.

$$Z_{AA} = \frac{1}{\sqrt{2}} \cdot \pi \sigma^2 n_A^2 \bar{c} \quad \dots\dots (2)$$

' σ ' is the collision diameter of the molecule and it is the quantitative measurement of size of the molecules. ' \bar{c} ' is the average velocity of the gas molecules. ' n_A ' is the number of molecules per unit volume.

According to first assumption, the rate of this bimolecular reaction should be equal to the collision number. Moreover, the concentration of the substance 'A' may be replaced by ' n_A ' which is the number of molecules per unit volume.

$$\text{As} \quad -\frac{d[A]}{dt} = k[A]^2$$

$$\text{Hence} \quad \frac{-d[A]}{dt} = kn_A^2$$

$$\frac{-d[A]}{dt} = Z_{AA}$$

In other words,

$$kn_A^2 = Z_{AA}$$

$$k = \frac{Z_{AA}}{n_A^2} \quad \dots\dots (3)$$

According to the equation (3), the rate constant of the reaction is expressed in terms of collision number ' Z_{AA} ' and number of molecules per unit volume.

The units of the rate constant of bimolecular reaction are $\text{dm}^3 \text{mol}^{-1} \text{sec}^{-1}$. The units of R.H.S of equation (3) should be changed accordingly. Hence equation (3) is converted into

$$k = \left[\frac{N_A}{10^3} \right] \times \frac{Z_{AA}}{n_A^2} \cdot \text{dm}^3 \text{mol}^{-1} \text{sec}^{-1} \quad \dots\dots (4)$$

Let us substitute the value of Z_{AA} in equation (4) and simplify it.

$$k = \left[\frac{N_A}{10^3} \right] \times \frac{1}{\sqrt{2}} \cdot \pi \sigma^2 \bar{c} \text{ dm}^3 \text{mol}^{-1} \text{sec}^{-1} \quad \dots\dots (5)$$

' \bar{c} ' is the average velocity and has the expression.

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

Let us put this expression of ' \bar{c} ' in equation (5)

$$k = 2 \left(\frac{N_A}{10^3} \right) \sigma^2 \sqrt{\frac{\pi RT}{M}} \text{ dm}^3 \text{mol}^{-1} \text{sec}^{-1} \quad \dots\dots (6)$$

If we join equation (4) and (6) then,

$$\left(\frac{N_A}{10^3}\right) \cdot \frac{Z_{AA}}{n_A^2} = 2\left(\frac{N}{10^3}\right) \sigma^2 \sqrt{\frac{\pi RT}{M}} \quad \dots\dots (7)$$

Let us now consider that the reaction is taking place at unit concentration. Under these circumstances,

$$\left[\frac{N_A}{10^3}\right] \frac{Z_{AA}}{n_A^2} = Z^0$$

' Z^0 ' is the collision number at unit concentration. When we give the units of second order reactions to ' Z^0 ' then

$$Z^0 = \left(\frac{N_A}{1000}\right) \times \frac{Z_{AA}}{n_A^2}$$

Under these circumstances, we can say that

$$k = Z^0 = 2\left(\frac{N_A}{10^3}\right) \sigma^2 \sqrt{\frac{\pi RT}{M}} \quad \dots\dots (8)$$

Simply, we can say that

$$k = Z^0 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}. \quad \dots\dots (9)$$

According to equation (8) and (9), we can calculate the rate constant for this bimolecular reaction, if we know the collision diameter ' σ ' temperature ' T ' and molar mass ' M ' of the reacting substance.

Verification of equation:

This equation can be verified by two ways.

- (i) By calculating the effect of temperature on rate constant.
- (ii) By comparing the experimental and theoretical rate constants.

Effect of temperature: Equation (8), tells us that if we increase the temperature by 10°C , then there happens an increase in the rate constant by 1%. Actually, 10°C rise of temperature increases the rate 200%. It means that this equation can not explain the effect of temperature change on the rate constant.

Comparison of theoretical and experimental rate constants:

If we calculate the value of ' k ' or ' Z^0 ' from equation (8) by substituting the values of parameters like ' σ ', ' T ' and ' M ', then the value of ' k ' comes out to be very high, as compared to the experimental value of ' k ' for the same reaction.

It means that the number of collision ' Z^0 ' calculated by equation (8), can not help us to give the actual value of ' k '.

The reason is that all the collisions are not fruitful to bring about a chemical reaction.

Concept of energy of activation:

We have not been able to get the correct equation, because we did not introduce the idea of energy of activation which is our second assumption in the

theory. The reality is that only those collisions are fruitful which have energy equal to energy of activation. Such collisions will be fruitful and will lead to the chemical reaction.

How to determine the activated molecules:

In order to calculate the molecules having energy equal to the energy of activation, we should take the help of Boltzmann's factor. Actually Boltzmann has given a law which is called energy distribution law. According to this law,

$$n^* = nc^{-\frac{E_a}{RT}}$$

n^* = number of activated molecules

n = total number of molecules

E_a = energy of activation

T = temperature

$e^{-\frac{E_a}{RT}}$ = Boltzmann's factor

The value of ' n^* ' gives us the concentration of activated molecules which enables us to know the number of effective collisions. In our case, ' Z^o ' corresponds to ' n ' which is the total number of collisions and out of which some are fruitful corresponding to ' n^* '.

Hence, number of effective collisions = $Z^o e^{-E/RT}$

If these collisions lead to the chemical reaction then the rate constant ' k ' which depends upon the effective collision is written as follows.

$$k = Z^o e^{-\frac{E_a}{RT}} \dots\dots (10)$$

This equation (10) is applicable for many reactions which are simple. For these reactions, the experimental and theoretical rate constants agree with each other.

7.8.2 Failures of equation $k = Z^o e^{-\frac{E_a}{RT}}$ based on collision theory:

As we have pointed out above, that the equation of the collision theory is not adequate for determining the rate constant. It is applicable to simple reactions in solution and the gaseous phase reactions.

However, this theory fails in the following situations.

- (i) When ethyl alcohol and acetic anhydride are reacted at 79°C, then the experimental rate constant is 10^5 times lower than theoretical rate constant.
- (ii) When ethyl iodide is reacted with triethylamine at 140°C, then the experimental rate constant is 10^8 times lower than theoretical rate constant.
- (iii) When COS reacts with water vapours at 300°C, then the experimental rate constant is 10^6 times less.

7.8.3 Modification of the equation:

The low values of experimental rate constants is due to the orientation effect. Only those collisions will prove to be fruitful which happen when the collisions are taking place between those atoms which have to make the bonds. For this purpose the R.H.S of this equation should be multiplied with a factor less than unity. This is called probability factor. Greater the complexity of structures of reacting substances, smaller the P-factor.

$$k = PZ^{\circ}e^{-E_a/RT} \quad \dots\dots (11)$$

When the reacting molecules are of very small sized, then 'P' approaches unity. If we compare this equation with Arrhenius equation, $k = Ae^{-E_a/RT}$


$$\text{Then } A = PZ^{\circ}$$

$$P = \frac{A}{Z^{\circ}}$$

Arrhenius factor 'A' is calculated from Arrhenius plots and 'Z^o' is calculated theoretically. So the probability factor 'P' can be calculated.

Following table (1) shows the value of 'A', 'Z^o' and 'P' for some of the reactions.

Table (1) Values of A, Z^o and P for some reactions

| Reactions | A | Z ^o | $P = \frac{A}{Z^{\circ}}$ |
|---|----------------------|----------------------|---------------------------|
| (1) $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$ | 4.6×10^{10} | 4.6×10^{10} | 1.00 |
| (2) $2\text{NOCl} \longrightarrow 2\text{NO} + \text{Cl}_2$ | 7.3×10^{10} | 7.7×10^{10} | 1.00 |
| (3) $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$ | 1.5×10^{10} | 5×10^{11} | 0.3 |
| (4) $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$ | 9.4×10^9 | 1.6×10^{11} | 6.0×10^{-2} |
| (5) $\text{C}_2\text{H}_4 + \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ \longrightarrow  | 3.00×10^7 | 7.5×10^{11} | 4×10^{-3} |

Shortcomings of collision theory:

The collision theory in the form of equation (11) is also not applicable to following cases.

- When the complex molecules are involved in the chemical reactions.
- When the chain mechanism is to be obeyed by the chemical reactions.
- When the reaction is surface catalyzed.

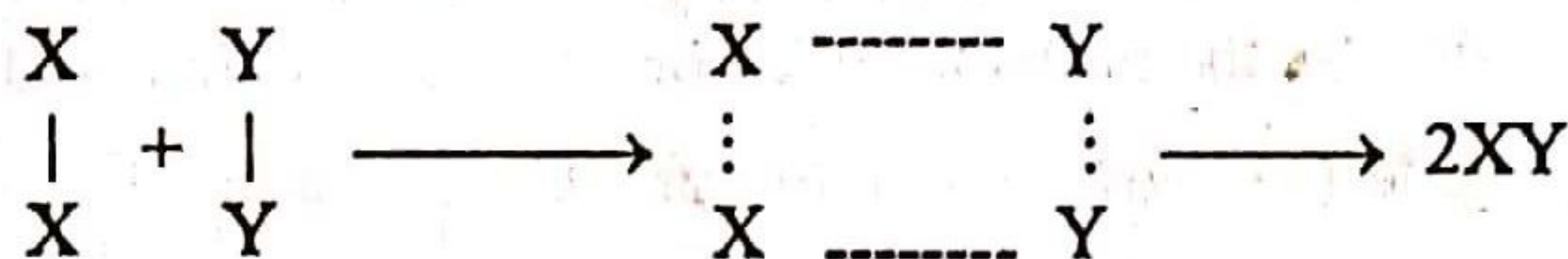
7.9.0 TRANSITION STATE THEORY

7.9.1 Introduction:

Transition state theory tells us the continuous series of changes in bond distances when the reacting molecules approach each other. During these changes in configuration of molecules, energy changes also take place. The molecules which are reacting form a specific configuration before getting transformed into products. Such a configuration is called as transition state or activated complex.

The transition state which is formed does not represent an observable substance. It cannot be isolated. It is assumed to possess properties such as bond length, molecular weight, enthalpy alongwith the rotational and vibrational degrees of freedom. These properties are possessed by real molecules.

The transition state of the reaction corresponds to the highest point on the potential energy diagram. The two reacting molecules 'X₂' and 'Y₂' can be visualized to form the product XY through the transition state as shown in the diagram.



reactant molecules

transition state

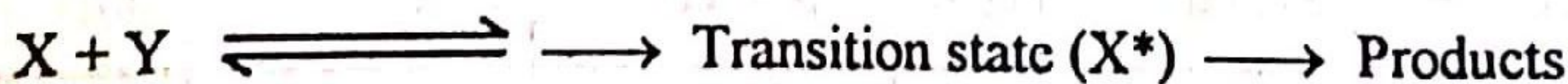
product

7.9.2 Many step reactions:

Some of the reactions take place in a single step but many reactions occur through several steps. Each step passes through a transition state and a intermediate is formed. The overall rate of the reaction is governed by the slowest step. This step is called rate determining step.

7.9.3 Mathematical equation:

Let us consider the reaction



By using some fundamental properties of reacting molecules it was shown by Eyring that the rate constant 'k' for any reaction of this type is given by:

$$k = \frac{RT}{N_A h} K^* \quad \dots \dots (1)$$

In equation (1), 'N_A' is Avogadro's number and 'K*' is an equilibrium constant for the formation of activated complex from the reacting molecules.

$$K^* = \frac{X^*}{[X][Y]}$$

The equilibrium constant 'K*' is related with free energy change 'ΔG*' by well known equation from thermodynamics.

$$\Delta G^* = -RT \ln K^*$$

$$\ln K^* = -\Delta G^* / RT$$

Transition state
highest point
of P.E.

Eyring
1935
Rate &
Temperature

Gas-phase
kinetics
only.

Taking antilog on both sides

$$K^* = e^{-\Delta G^*/RT} \dots\dots (2)$$

ΔG^* is the free energy for activation. Putting equation (2) in equation (1)

$$k = \frac{RT}{N_A h} e^{-\Delta G^*/RT} \dots\dots (3)$$

7.9.4 Significance of equation of transition state theory:

Equation (3) gives us the information about the effect of temperature and free energy change on the rate constant of chemical reaction. This equation has two factors i.e. $RT / N_A h$ and $e^{-\Delta G^*/RT}$. If the temperature is constant then the first factor is constant and so the rate constant depends upon the second factor which involves the free energy change. If ' ΔG^* ' has a negative value then the second factor is greater than unity and the rate constant k is favourable for the chemical reaction. Greater the negative value of ' ΔG^* ', greater the rate constant of the chemical reaction.

p = probability factor
steric factor

7.9.5 Advantages of transition state theory over collision theory:

- (i) In collision theory of reaction rates, we have a probability factor 'P' which is introduced arbitrarily. But in transition state theory the introduction of the entropy of activation ΔS^* has been justified.
- (iii) In collision theory of reaction rates, we simply assume that the molecules of the reactants collide together and change into products, but in transition state theory, we introduce the concept of formation of activated complex which is more appropriate.

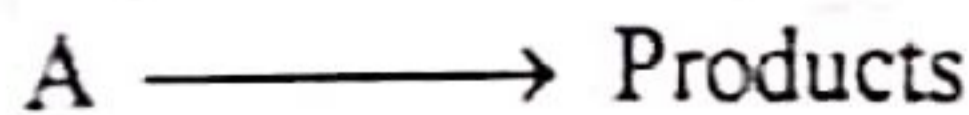
7.10.0 COLLISION THEORY OF UNIMOLECULAR REACTIONS

Concept of collision
Concept of transition state

7.10.1 Lindmann's mechanism:

It is a known fact, that collisions between molecules must occur to attain energy for reaction. It is believed that all the reactions must be at least bimolecular. Therefore in a unimolecular reaction, only one molecule takes part in the chemical reaction. In order to understand the progress of such reactions, Lindmann (1922) proposed that such reactions also proceed to the forward direction by collisions and attain energy equal to the energy of activation.

Let us suppose that the molecules of reactant is A and is forming the products.



The rate of disappearance of A

$$-\frac{d[A]}{dt} \propto [A]$$

$$-\frac{d[A]}{dt} = k[A]$$

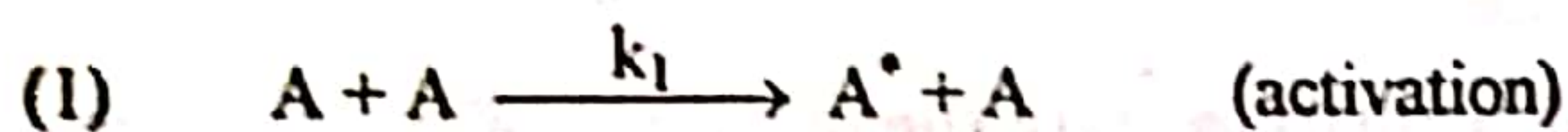
Where, k = rate constant of this reaction.

According to the Lindemann, the molecules of substance 'A' are colliding among themselves. During these collisions some of the molecules attain the energy equal to the energy of activation. The activated molecules of 'A' are denoted by 'A*'.
 The added energy increases the vibrational amplitude and may lead to dissociation. Further, Lindemann proposed that, the activated molecules do not decompose immediately, but remain in activated state for a fruitful period. It may be deactivated through collisions with less energetic molecules.

In other words, there are two ways to disappear 'A*'

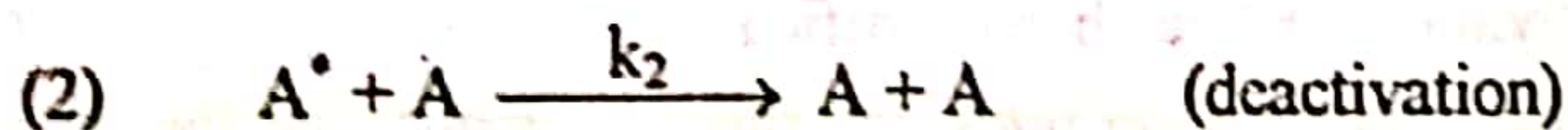
- (i) They may collide with deactivated molecules of 'A' and undergo deactivation.
- (ii) The activated molecules are decomposed into products before collisions.

Hence, the three steps are given as below.

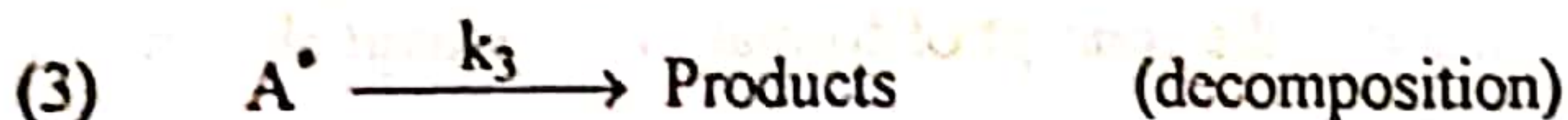


$$\text{Rate} = k_1[A][A]$$

$$\text{Rate} = k_1[A]^2 \quad \dots\dots (1)$$



$$\text{Rate} = k_2[A^*][A] \quad \dots\dots (2)$$



$$\text{Rate} = k_3[A^*] \quad \dots\dots (3)$$

Where 'k₁', 'k₂' and 'k₃', are the rate constants of three steps.

The overall rate of this reaction is evaluated from step (3). If we want to determine the rate of reaction from step (3), then we need the concentration of 'A*', which is an intermediate.

Steady state approximation:

In order to determine the concentration of 'A*', we apply the steady state approximation. According to this approximation the rate of formation of short lived intermediate 'A*' in low concentration is equal to the rate of disappearance of 'A*'.
 Rate of appearance of 'A*' = k₁[A]²
 Rate of disappearance of 'A*' = k₂[A*][A] + k₃[A*]

During the progress of this reaction, these two rates are equal

$$k_1[A]^2 = k_2[A^*][A] + k_3[A^*]$$

$$k_1[A]^2 = [A^*] \{k_2[A] + k_3\}$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3} \quad \dots\dots (4)$$

The overall progress of reaction is noted from step (3), which gives the products.

$$-\frac{d[A]}{dt} = k_3 [A^*]$$

Putting the value of "A*" from equation (4) into equation (3)

$$\text{so, } -\frac{d[A]}{dt} = \frac{k_3 k_1 [A]^2}{k_2 [A] + k_3} \quad \dots\dots (5)$$

Conditions of pressure and order of reaction:

There are two situations under which such reactions can be studied.

(1) At high pressure:

When the pressure of this reaction is higher, then the molecules of gaseous substance 'A' come very close to each other. The possibility for the collisions increase. In other words, the comparison of equations (2) and (3), shows that

$$k_2 \gg k_3$$

$$k_2 [A^*] [A] \gg k_3 [A^*]$$

$$k_2 [A] \gg k_3$$

So, we neglect 'k₃' in the denominator of equation (5)

$$-\frac{d[A]}{dt} = \frac{k_1 \cdot k_3 [A]^2}{k_2 \cdot [A]}$$

$$-\frac{d[A]}{dt} = \frac{k_1 \cdot k_3 [A]}{k_2} \quad \dots\dots (6)$$

$$-\frac{d[A]}{dt} = \text{constant } [A]^1 \quad \dots\dots (7)$$

So, at high pressure the reaction is first order.

(2) At low pressure:

When the pressure of gaseous substance is low, then molecules of type 'A*' get sufficient time to be deactivated. Step '3', is more prominent than step '2'. Hence.

$$k_3 \gg k_2 [A]$$

and $k_2 [A]$ is neglected in the denominator

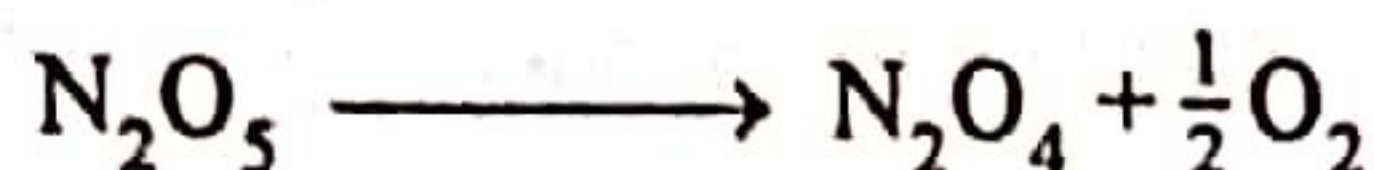
$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_3}$$

$$-\frac{d[A]}{dt} = k_1 [A]^2 \quad \dots\dots (8)$$

At low pressure reaction is second order. The change of first order to second order reaction at low pressure has been observed with unimolecular reactions.

Examples:

(i) Thermal decomposition of azomethane

(ii) Thermal decomposition of N_2O_5 

These two reactions confirm the Lindmann's mechanism. When the reactions are happening in solutions their collisions are very frequent with solvent molecules. The unimolecular change is rate controlling and mechanism is first order i.e., the conditions of high pressure are prevailing.

7.11.0 REACTION MECHANISM

We know that the chemical reactions involve the breakage and the formation of certain chemical bonds. It means that the geometrical configuration of atoms in the molecules of the products will be entirely different from those of reactants. Actually, we have to find out that how these changes occur at molecular level.

The sequence of the steps, through which a reaction is supposed to take place is called reaction mechanism. The reaction mechanism is only a tentative proposal. It should be consistent with the available evidence.

Anyhow, it can be modified with some new experimental facts. All those steps which are to be written to complete a mechanism of a reaction are called elementary steps.

An elementary step should have the following characteristics.

- (i) It may be real or imaginary.
- (ii) It should involve three or less than three reactant molecules or ions.
- (iii) It should be in the form of a balanced chemical equation.

The experiments involving the knowledge of reaction mechanisms may involve the radioactive tracers. Spectroscopic identifications of short-lived intermediates also help to propose a mechanism. The dependence of the reaction rates on the concentrations also help us to know the mechanisms.

Keep it in mind that, a complicated chemical reaction may proceed through a sequence of elementary reactions and simply looking overall reaction might have a complicated mechanism. Whenever, we accept the mechanism of a reaction, then the postulated mechanism should be consistent with the experimental rate law. This can be done by subjecting the elementary steps of the postulated mechanism to some rules of chemical kinetics.

7.11.1 How to assign the mechanism to a reaction:

We know that the slowest step of a complex reaction determine its rate and order. This slowest step may not be essentially last. Once the slowest step is obtained from the rate law, then all other steps are mere predictions. That is why, more than one mechanisms can be advanced for the same reaction. Briefly, we can say that for assigning a mechanisms we should proceed as follows:

- (i) Find out the rate law of the reaction experimentally.
- (ii) The rate law tells us the molecularly and order of the slowest step.
- (iii) Predict the other steps in such a way that when we add all the steps, then original equation may be obtained for the complex reaction.

Bond
breakage
formation

Seq. of steps
reaction mechanism

Elementary
step

Complicated
reaction
Seq. of elementary
reactions