7.2.0 ZERO ORDER REACTION

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

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

A	→	Product	
'a' moles		zero moles	t = 0
(a − x) moles		'x' moles	t = t (at any time t)

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 concentrations of the products is a constant quantity. In order to integrate this equation, separate 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 $t = 0, \quad x = 0$

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

$$c = 0$$

Hence the final equation is

$$\boxed{x = kt} \qquad \ldots\ldots (1)$$

This "k" is called **the rate constant for zero under 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 (اکائیاں) of Zero Order Rate Constant:

Since, $x = kt$

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

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."***

(ریٹ آف ری ایکشن کی اکائی اور زیرو آرڈر کے ریٹ کانسٹنٹ کی اکائی ایک ہی ہوتی ہے۔)

7.2.2 Examples of Zero Order Reaction:

(i) The decomposition of NH_3 on tungston, of pH_3 on MO and of HI on gold surface are zero order reactions.

$2NH_3 \xrightarrow{Tungston} N_2 + 3H_2$ Rate of reaction = $k[NH_3]^0$

$2PH_3 \xrightarrow{Mo} 2P + 3H_2$ Rate of reaction = $k[PH_3]^0$

$2HI \xrightarrow{gold\ surface} H_2 + I_2$ Rate of reaction = $k[HI]^0$

(ii) 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.

(iii) Reactions which are catalyzed by enzymes are also zero order.

7.3.0 FIRST ORDER REACTIONS

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}.

A	$\longrightarrow$ Product	
'a' moles	zero moles	t = 0
(a – x) moles	'x' moles	t = t

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

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

$$\frac{dx}{dt} = k(a-x) \qquad \ldots\ldots (1)$$

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.

The terms regarding conc. as dX and (a – x) are taken on L.H.S and of time i.e., dt is taken on R.H.S.

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

Putting signs of integration.

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

$$-\ln(a-x) = kt + c \qquad \ldots\ldots (2)$$

$$\int \frac{dx}{(a-x)} = \ln(a-x)(-1) = -\ln(a-x)$$

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

(کیونکہ جس وقت ری ایکشن شروع ہوتا ہے اس وقت پراڈکٹس نہیں ہوتے۔)

Put these values in equation (2)

$$-\ln(a-0) = k \times 0 + c$$

$$-\ln a = c \qquad \ldots\ldots (3)$$

Now put this value of 'c' in equation (2)

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

Multiply with negative

$$\ln(a-x) = -kt + \ln a \qquad \ldots\ldots (4)$$

(y = ± mx ± c ایک ایسے گراف کی مساوات ہے جو x اور y کے درمیان پلاٹ کرنے سے سیدھی لائن دیتا ہے۔ اس میں m سلوپ ہے
...یپٹ ہے۔)

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

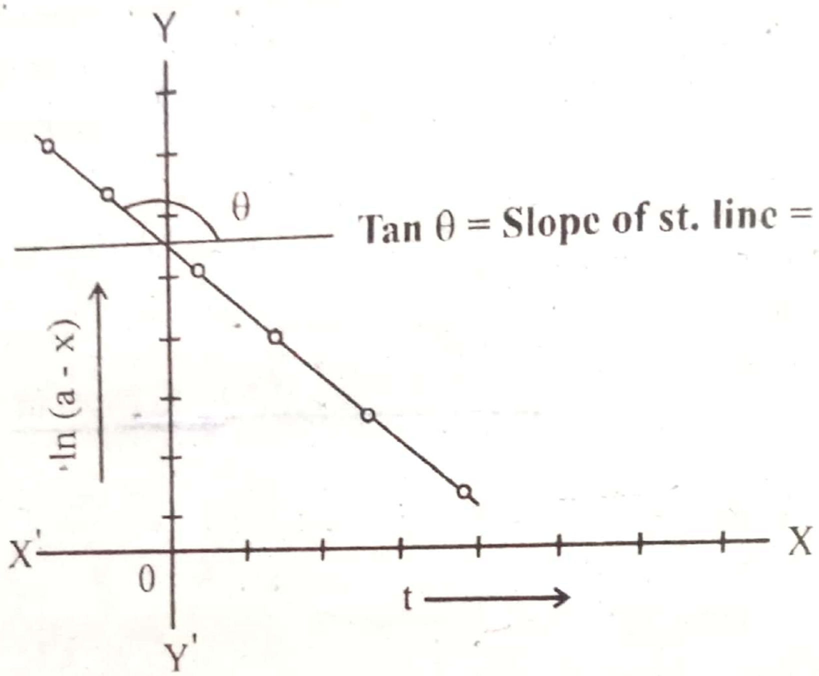

Fig. (7.1) Straight line graph for first order reaction.

The slope of the straight line is obtained by taking the tangent of the angle which this l... 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

$$\ln(a-x) = -kt + \ln a \qquad \ldots\ldots (4)$$

Take ln a on L.H.S

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

Rearrange it

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

Apply the formula of ln

$$\boxed{\ln\frac{a}{(a-x)} = kt} \qquad \ldots\ldots (5)$$

The equation (5) is the equation of a straight line *i.e.,* y = m × +0. When a graph is plotte... between time on x-axis and ln $\frac{a}{(a-x)}$ on y-axis, then a straight line with positive slope is obtaine... passing through the origin. The tangent of the angle gives the value of rate constant 'k'. The line passe... through the origin because there is no intercept in the equation (5) Fig. (7.2).

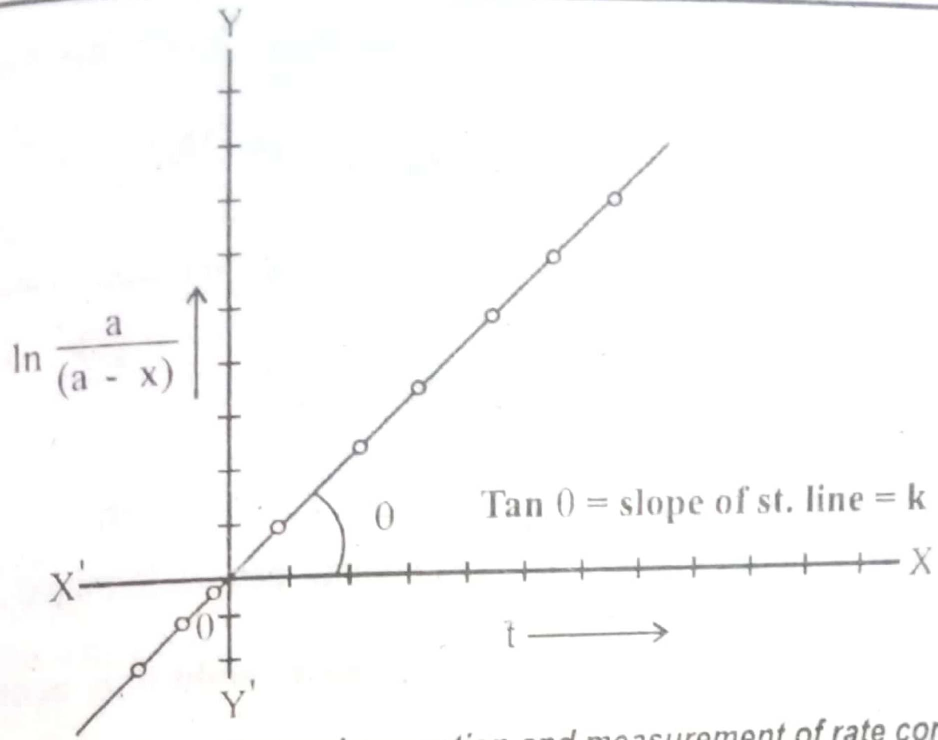

Fig. (7.2) Graph for a first order reaction and measurement of rate constant k.

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.

∴ ln = 2.303 log

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

Rearranging

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

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 $\frac{k}{2.303}$ $(y = m \times +0)$

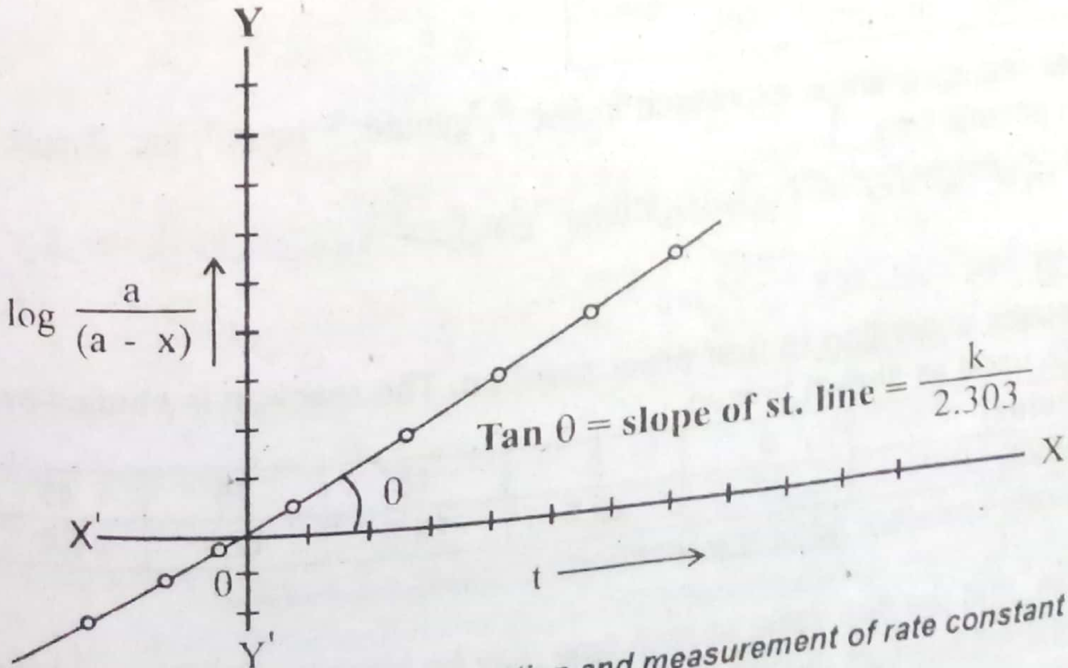

Fig. (7.3) Graph for a first order reaction and measurement of rate constant k.

7.3.1 Exponential form of First order equations:

The equ... exponential form by taking the antilog on both sides.

be used, with the passage of time.

(4) **Inversion of cane sugar:**

This reaction is catalyzed by dilute HCl.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{dil. HCl}} C_6H_{12}O_6 + C_6H_{12}O_6$$

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'

$$A + B \longrightarrow \text{Product}$$

$$a + a \longrightarrow \text{zero} \qquad t = 0$$

$$(a - x) + (a - x) \longrightarrow x \qquad t = t$$

The rate of reaction at time 't' is directly proportional to the product of concentrations of reactants at that time. This is first according to law of mass action.

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

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

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

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.

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

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

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

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

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

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

Put this value of 'c' in equation (2)

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

Equation (4) is of straight line (y = mx + c). When a graph is plotted below 't' on x-axis and $\frac{1}{(a-x)}$ on y-axis, then a straight line is obtained with the positive slope as shown in the following diagram (7.4). This line cuts the y-axis above the origin, at a gap of $\frac{1}{a}$ from the origin.

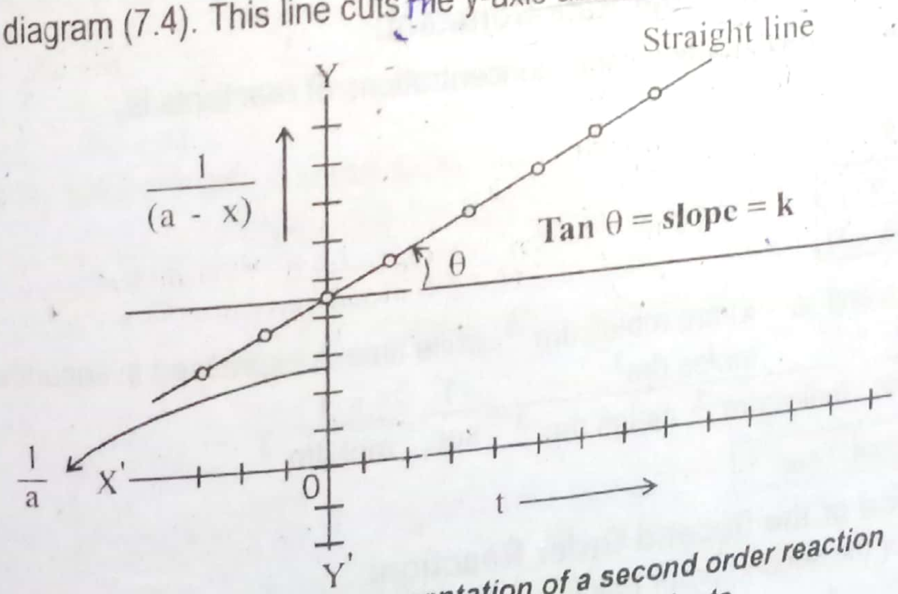

Fig. (7.4) Graphical representation of a second order reaction with same concentrations of reactants.

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

By rearranging the equation (4)

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

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

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

This equation (5) is again the equation of straight line ($y = mx + 0$). 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 (7.5). The value of rate constant 'k' is the same as we have derived previously by plotting a graph.

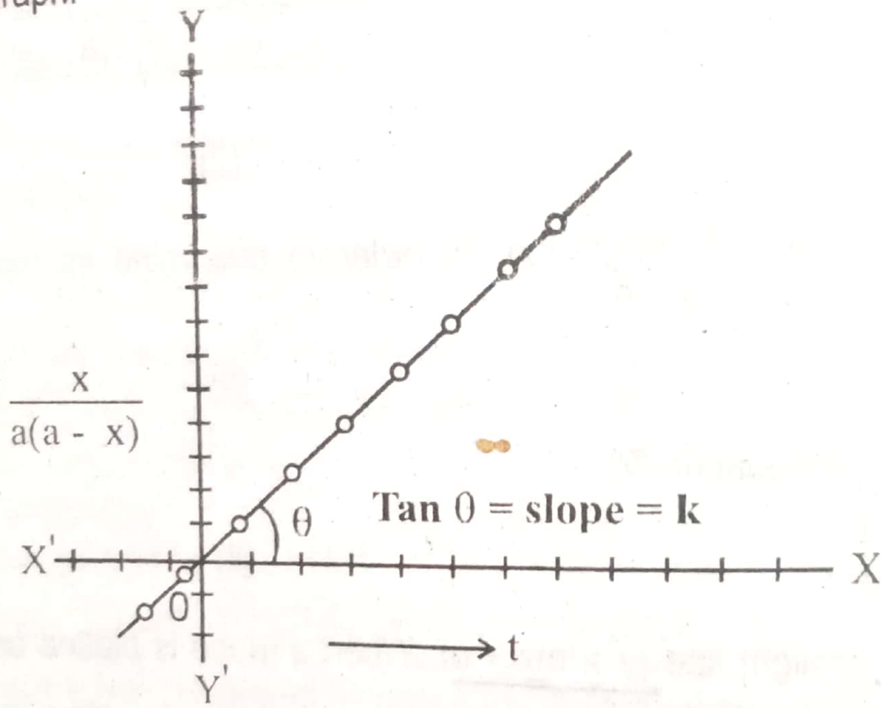

Fig. (7.5) Graphical representation of a second order reaction with equal concentrations of reactants.

7.4.2 Units (اکائیاں) 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.

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

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

7.4.3 Half Life Period of the Second Order Reaction:

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

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

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

$$\int \frac{d}{(a-x)^2}$$

$$\int (a-x)^{-2} \cdot dx$$

$$- \frac{(a-x)^{-2+1}}{-2+1} \quad \frac{d}{dx}(\not{a}-x) \rightarrow -1$$

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

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

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

$$\int \frac{dx}{(a-x)} \qquad \frac{d}{dx} \not{a}-x$$

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

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

→ value of derivative.

$$\therefore \frac{f'(x)}{f(x)} = \ln f(x)$$

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(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 (آپس میں تصادم کر رہے ہیں) with certain energies and chemical reactions are due to collisions. Every collision does not lead to the chemical reaction (مالیکیولز کے درمیان ہر تصادم ری ایکشن کا سبب نہیں بنتا). 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 (زیادہ توانائی والی حالت) and become able to convert themselves into products.

It means that the reactants do not pass directly to the products, till they acquire on additional amount of energy (توانائی کی ایک فالتو مقدار) 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 posses energy of activation are said to be activated. Take into account the hypothetical reaction

$$A + B \rightleftharpoons C + D$$

Consider the following diagram (7.12), in which the reactants are present at higher average energy (زیادہ اوسط انرجی والے) than the products. According to the diagram, the average energy of products is less than those of reactants, so the reaction is exothermic (گرمی باہر نکالنے والا). But reactants have to attain (حاصل کرنا پڑتا ہے) the activated state before forming the products.

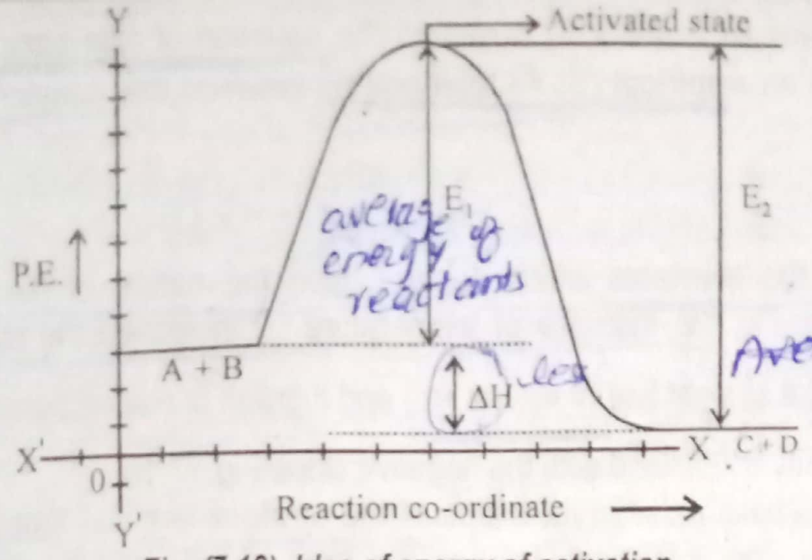

Fig. (7.12) Idea of energy of activation

The molecules of reactants must climb (اوپر چڑھنا) the energy barrier (رکاوٹ) before they can role down the hill (پہاڑی سے نیچے آنا) to form the products.

'E_1' is the energy of activation for the forward reaction (آگے جانے والا ری ایکشن) 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 (توانائی کے لئے رکاوٹ) smaller the possibility (ممکن ہونا) 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 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 (مناسب تصادم). It depends upon the chance, whether it will get a favourable collision to be activated or unfavourable (نامناسب) one to be deactivated. Anyhow, it should be believed beyond doubt (بغیر شک و شبہ کے) 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 (ٹوٹ جانا) 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 abso... temperature, 'T'. He gave an **empirical** (تجرباتی) **relationship** between rate constant 'k' and tempera... 'T'.

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

'A' and 'B' are the constants which depend upon the nature of the chemical reactio... According to this equation (1), the increase of temperature 'T' increases the rate constant 'k'. T... equation (1) is equation of a straight line (y = –mx + c) and if graph is plotted between $\frac{1}{T}$ on x-axis a... **log k on y-axis,** a straight line is **obtained with the negative slope** Fig. (7.13).

The value of 'B' is obtained from the **slope of the straight line** and that of factor 'A' from t... **intercept of the straight line.** Equation (1) is in the form of log, and it can be converted in... exponential form.

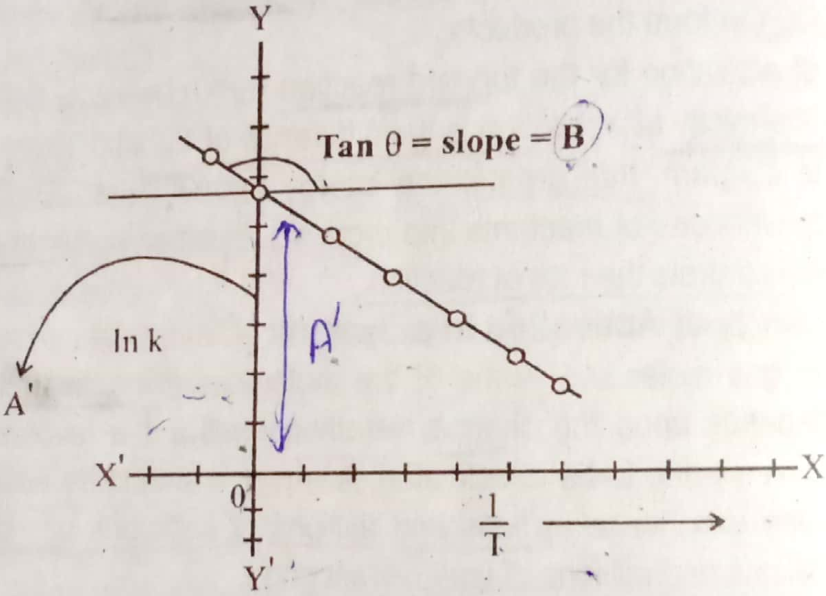

Fig. (7.13) Plot of ln k and $\frac{1}{T}$ for Arrenius equation.

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

Taking anti ln (دائیں جانب والی چیزیں 'e' کی پاور بن گئی ہیں)

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

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

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

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 Ea/R and the accepted form of Arrhenius equation is as follows:

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

In equation (3), $e^{-Ea/RT}$ **is called Baltzmann factor**. Its value is controlled by energy of activation Ea and the temperature, 'T'. This equation (3) is called as Arrhenius equation. Both 'A' and 'Ea' 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 natural log *i.e.*, ln of equation (3) and rearrange it, then we get the following expression.

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

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

$\ln k = \ln A - Ea/RT \, . \ln e$ Since $(\ln e = 1)$

(ln کا بیس بھی 'e' ہے۔ کسی مقدار کا log لیں اور اس کا بیس بھی وہی ہو تو جواب ایک آتا ہے۔)

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

or $\boxed{\ln k = -Ea/RT + \ln A}$ ...... (4)

Equation (4), is of straight line (y = mx + c). When a graph is plotted between 1/T which corresponds x, on x-axis and ln k which corresponds to y 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 'Ea' 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.

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

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

A graph is plotted between 1/T an x-axis and 'ln k' an y-axis as follows. Fig. (7.14)

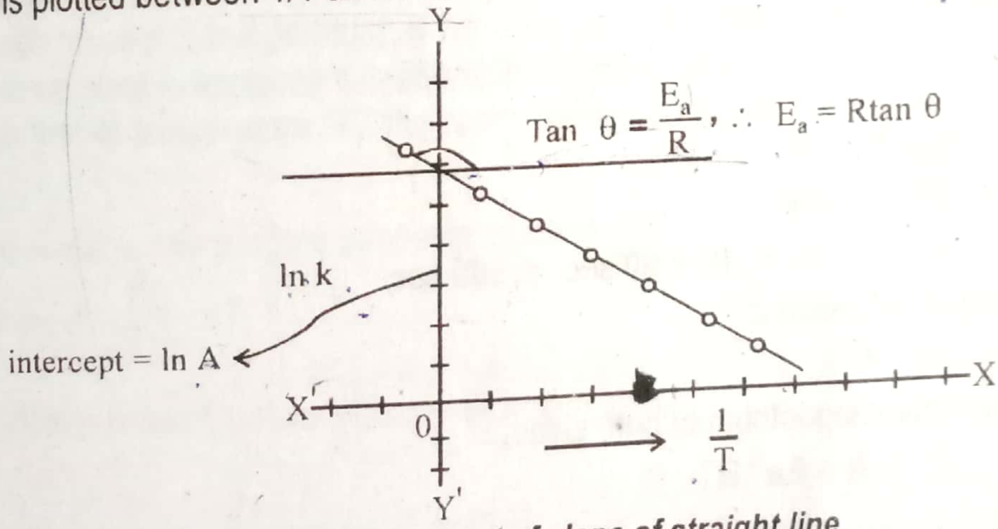

Fig. (7.14) Measurement of slope of straight line.

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

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

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

$$Ea = 103410\ J\ mol^{-1}$$

$$Ea = 103.41\ kJ\ mol^{-1}.$$

7.7.5 Calculation of Arrhenius Factor 'A':

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

ln A = intercept

Taking the antiln on both sides.

A = Antiln (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.