

CHEMICAL KINETICS

Part I-Experimental Aspect

Introduction:

The chapter deals with the answer to the question 'how fast a chemical reaction can go.' Obviously, the term that relates the question is to study 'the rate of reaction' and its dependence with conc. of the reactants and experimental temperature. If we get sufficient information of this dependence, we can conduct the reaction with our desirable rate.

Very fast reactions (such as ionic reactions) and very slow reactions (such as $\text{H}_2 + \text{Cl}_2$ in dark) are not discussed in this chapter. We shall study the reactions that occur with moderate rate, for example, decomposition of H_2O_2 , hydrolysis of ester, mutarotation of glucose, decomposition of N_2O_5 , etc.

Rate of a chemical reaction:

Since rate of a chemical reaction depends on time from the start of the reaction, it is defined as the rate of change of conc. of reactant or product at a particular instant of time.

Let us take a simple reaction, $\text{A} \rightarrow \text{P}$. The reaction rate, $r = -\frac{d[\text{A}]}{dt}$ or, $r = \frac{d[\text{P}]}{dt}$.

[Since with time, [A] decreases and [P] increases so the rate is always positive quantity.]

If we consider the chemical reaction, $\nu_1\text{A}_1 + \nu_2\text{A}_2 = \nu_3\text{A}_3 + \nu_4\text{A}_4$

or, $0 = -\nu_1\text{A}_1 - \nu_2\text{A}_2 + \nu_3\text{A}_3 + \nu_4\text{A}_4$ or, $0 = \sum \nu_i\text{A}_i$,

where ν_i 's are the stoichiometric coefficients, $\nu_i = (-ve)$ for the reactants and $\nu_i = (+ve)$ for the products. A_i 's are the reacting components.

The number of moles of the reacting components changes with the extent of reaction (ξ) as,

$$n_i = n_i^0 + \nu_i \xi,$$

where n_i = number of moles of i th component at the advancement of ξ and n_i^0 at the initial time when $\xi = 0$.

So, $\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt}$ or, $\frac{1}{V} \frac{dn_i}{dt} = \nu_i \frac{1}{V} \frac{d\xi}{dt}$ or, $\frac{1}{\nu_i} \left[\frac{dn_i}{dt} \right] = \frac{1}{V} \frac{d\xi}{dt}$ or, $\frac{1}{\nu_i} \frac{d[A_i]}{dt} = \frac{1}{V} \frac{d\xi}{dt}$

This $\frac{d\xi}{dt}$ is called rate of conversion of the reaction and $\frac{1}{\nu_i} \frac{d[A_i]}{dt}$ is called rate of the reaction.

Thus the rate of the reaction, $r = -\frac{1}{\nu_1} \frac{d[A_1]}{dt} = -\frac{1}{\nu_2} \frac{d[A_2]}{dt} = \frac{1}{\nu_3} \frac{d[A_3]}{dt} = \frac{1}{\nu_4} \frac{d[A_4]}{dt}$. This type of expression of

the rate of reaction is independent on the reacting component with which it is expressed.

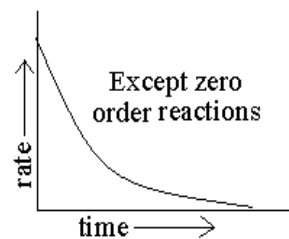
For the reaction, $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$,

the rate of the reaction is $r = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$.

Question: The rate of a reaction is $1.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$. Calculate the rate in molecules $\text{cm}^{-3} \text{ s}^{-1}$ unit.

[Burdwan Univ. 2002]

Answer: Rate = $1.0 \times 10^{-5} (6.023 \times 10^{23} \text{ molecule}) \times (10 \text{ cm})^{-3} \text{ s}^{-1} = 6.023 \times 10^{15} \text{ molecule cm}^{-3} \text{ s}^{-1}$.



Question: Consider the reaction: $A + 2B \rightarrow 3C$. If at time t , degree of advancement of the reaction is ξ ,

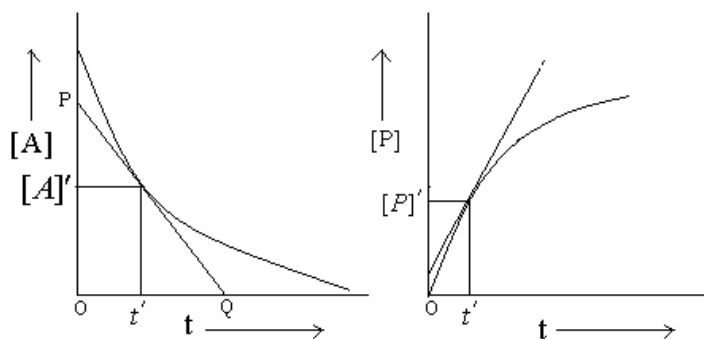
write down the relation among $-\frac{d[A]}{dt}$, $-\frac{d[B]}{dt}$ and $\frac{d[C]}{dt}$.

Answer: See the Text above, $-\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{1}{V} \frac{d\xi}{dt}$

Determination of reaction rate:

For determination of rate of a reaction, $A \rightarrow P$, we need data of the conc. of either reactants or products at different time intervals. For this, aliquot amount of the reaction mixture is separated by pipette and is immediately added to sufficient ice-cold water (inert solvent). The reaction rate is suddenly arrested due to dilution and lowering of temperature of the reaction mixture. With dilution, conc. of reactants is decreased and thus rate is also decreased. At low temperature, reaction rate is also slowed down. These two factors simultaneously act to quench the reaction rate.

The conc. of the reactants or products is now estimated either by chemical methods or by physical methods. The conc. is now put in a table at different time intervals and conc. vs. time plot is made. Rate is now determined by the slope of the tangent drawn at t' (say).



temperature is fixed

time	conc. of reactant	conc. of product
0	$[A]_0$	0
t_1	$[A]_1$	$[P]_1$
t_2	$[A]_2$	$[P]_2$
t_3	$[A]_3$	$[P]_3$
t_4	$[A]_4$	$[P]_4$
t_5	$[A]_5$	$[P]_5$

So the rate at t' or at $[A]'$ is given by $r = -\frac{d[A]}{dt} = \frac{OP}{OQ}$ from the reactant conc. vs. time plot or from product conc. vs. time plot as shown above.

The initial rate of the reaction (r_0) is determined from the slope of the tangent drawn at zero time or at initial conc. of reactant $[A]_0$.

The chemical methods of estimation of conc. involve the titration with suitable reagent using proper indicator. The physical methods involve the change of any physical properties of a reacting component of the system. These properties may be pressure, conductivity, optical rotation, optical density, etc.

Factors on which the reaction rate depends:

There are several factors that can influence the rate of a reaction.

- (1) The nature of the reactants.
- (2) The conc. or effective mass of the reactants (mass action law)
- (3) The temperature at which the reaction is occurring (Arrhenius equation)
- (4) Presence of some foreign substance (catalyst)
- (5) Degree of fineness of the catalyst (heterogeneous catalysis)
- (6) Absorption of radiation of suitable frequency (photochemistry).

The reaction rate is enhanced by the increase of factors (2) to (6).

Question: In a kinetic study of a reaction in an aqueous medium, it is customary to stop the reaction by adding large excess of cold water. Explain the underlined words. **[Burdwan Univ. 1994]**

Answer: See above Text.

Rate equation (rate law) and order of reaction:

Dependence of reaction rate with the conc. of reacting components at a given temperature is expressed by the rate equation. Mass action law guides the basis of formulation of rate equation. This rate equation can only be formulated on the basis of experimental data.

For example, decomposition of hydrogen peroxide, $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ follows the rate equation, $-\frac{d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2]$. That is, the rate of decomposition of H_2O_2 depends on single power of H_2O_2 conc. Thus, if conc. of H_2O_2 is doubled, the rate is also doubled. This type of reactions is called first order reactions. Rate equation can not be deduced from the stoichiometric equation of the reaction.

Again, for the reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$, the rate law is $-\frac{d[\text{H}_2]}{dt} = k[\text{H}_2][\text{I}_2]$. This reaction is second order as the rate equation contains two conc. terms.

The reaction $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$, the rate equation is $-\frac{d[\text{Cl}_2]}{dt} = k[\text{NO}]^2[\text{Cl}_2]$. Thus the reaction is 2nd order with respect to NO and 1st order with respect to Cl_2 ; the total order is 3. Reactions higher than third order are not possible since in that case more than three molecules have to collide simultaneously.

If the reaction $\text{A} + \text{B} \rightarrow \text{P}$ follows α th order with respect to A and β order with respect to B, then the rate equation is $\frac{d[\text{P}]}{dt} = k[\text{A}]^\alpha [\text{B}]^\beta$. The total order of this reaction, $n = \alpha + \beta$.

The order may be fraction and even zero. Decomposition of acetaldehyde, $\text{CH}_3\text{CHO} \xrightarrow{500^\circ\text{C}} \text{CH}_4 + \text{CO}$ follows the rate equation, $-\frac{d[\text{CH}_3\text{CHO}]}{dt} = k[\text{CH}_3\text{CHO}]^{3/2}$, so the order of the reaction is $3/2$.

Decomposition of HI on gold surface, $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ is zero order so the rate of the decomposition of HI does not depend on the conc. of HI.

For some reactions such as formation of HBr, $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$, the rate equation as formulated by Bodenstein is $\frac{1}{2} \frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k'[\text{HBr}]/[\text{Br}_2]}$ and thus the order of the reaction can not be assigned to. Only at the initial stages of the reaction when $[\text{HBr}]/[\text{Br}_2] \ll 1$, the reaction is 1st order with respect to H_2 and $1/2$ order with respect to Br_2 ; the total order becomes $3/2$. Rate equation is thus an experimental format.

Rate constant (k):

k in the above rate equation is called rate constant and it is constant for a reaction at a given temperature unless the experimental condition is changed to a large extent. It may be defined as the rate of the reaction when the conc. of the reactants is unity i.e., each reactant at conc. of one mol/lit. This is why it is also called specific reaction rate.

For n th order reaction $\text{A} \rightarrow \text{P}$, the rate equation is $-\frac{d[\text{A}]}{dt} = k[\text{A}]^n$, the unit of rate is conc./time so it is

$\text{mol lit}^{-1}\text{sec}^{-1}$. The unit of rate constant, k for n th order reaction is $\text{conc.}^{1-n} \text{time}^{-1} = \text{mol}^{1-n} \text{lit}^{n-1} \text{sec}^{-1}$.

From the unit of rate constant, it is possible to identify the order of the reaction. For example, k of decomposition of HI is $3.5 \times 10^{-7} \text{mol}^{-1} \text{lit sec}^{-1}$ at 556 K, so the order of the reaction is $1 - n = -1$ or, $n = 2$. Thus the order of a reaction is the sum the conc. terms on which the rate of the reaction depends. Since the order is based on the experiment, hence it depends on the experimental conditions also.

Thus decomposition of azomethane $[(\text{CH}_3)_2\text{N}_2]$ is 1st order at moderate to high P but 2nd order at very low P.

In many elementary reaction (in which the products are formed from the reactants in a single step), the rate law happens to reflect the stoichiometric equation. Thus the stoichiometric equation for the dissociation of HI is $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ and the reaction is 2nd order.

For multistep reactions, the order of the slowest step becomes the order of the whole reaction.

Purpose of the rate equation:

The study of rate law has two purposes. One is of practical importance to know how the reaction rate depends on the conc. of the reacting components. Thus it permits to predict the reaction rate at a given conc. of the reacting components. Further, we classify the various reactions on the basis of order and so some reactions are 1st order, some are 2nd order and so on.

Reactions of a particular order have some common features.

The second one is of theoretical importance. It helps to build up possible mechanism of the reaction. By mechanism of a reaction we mean the detailed description of the paths by which the reactants move to the products. The accepted mechanism must conform to the observed rate equation.

Molecularity of a reaction:

Most of the reactions proceed through a series of elementary (simple) reactions. These elementary reactions are classified according to the number of molecules they participate. The reactions involving one molecule are called unimolecular reactions; the reactions involving two molecules are called bimolecular reactions, etc. For elementary reactions, order and molecularity are same.

For multistep reactions, there is no overall molecularity though they may have definite order. Order can be predicted from molecularity for elementary reactions only.

Molecularity must be integral but order may be fraction even zero.

The order of a reaction is obtained only from experimental results but molecularity is given on the basis of some proposed mechanism of the reaction. Since order is an experimental property so it depends on experimental condition while molecularity is a theoretical supposition.

However, overall reactions are neither characterized by molecularity nor each and every reaction is characterized by definite order.

Question: For the elementary reaction $A + B \xrightarrow{k} 2C$, express $d[A]/dt$ and $d[C]/dt$ in terms of:

(i) the reaction rate (r)

(ii) rate constant (k) and the molar conc. of A and B.

Answer: (i) The reaction rate (r) = $-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[C]}{dt}$. (ii) $-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[C]}{dt} = k[A][B]$.

Question: Distinguish between the 'molecularity' and 'order' of a chemical reaction. Give examples. (3)

Answer:

[Burdwan Univ. 1992]

Order: It is sum of the conc. terms on which the rate of reaction actually depends in the rate equation.

It is determined by experiments only and it has no relation with stoichiometric coefficients of the balanced equation of the reaction. It need not be a whole number, it may have fraction even zero. It is for only overall reaction and no separate steps are written to obtain it.

Molecularity: It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction. It is always a whole number. It can be calculated by simply adding the molecules of the slowest step. Each step has its own molecularity in a multi-step reaction and so overall molecularity of this type of reaction has no significance. Only in elementary (one-step) reactions, order and molecularity are same.

INTEGRATED RATE EQUATIONS

Introduction:

The differential rate equation shows the dependence of reaction rate with the conc. of the reacting species. But the integrated form of the rate equation provides easy method of determination of rate constant and hence calculation of conc. of these reacting species at any time from the start of the reaction.

We shall discuss the kinetics of zero, first, second and nth order reactions in detail.

ZEROth ORDER REACTIONS

Differential rate equation:

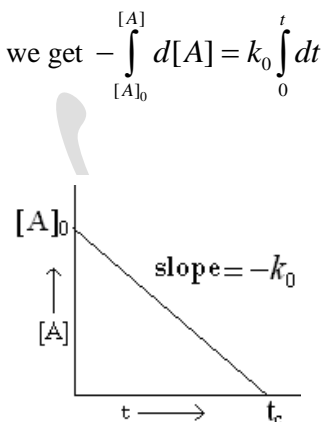
Rate of this type of reactions does not depend on the conc. of the reactants. Let the reaction is represented by $A \rightarrow P$, the differential rate law is $-\frac{d[A]}{dt} = k_0[A]^0$ or, $-\frac{d[A]}{dt} = k_0$, where k_0 is the rate constant of the zeroth order reaction.

Integrated rate equation: The above equation when integrated within limits, we get $-\int_{[A]_0}^{[A]} d[A] = k_0 \int_0^t dt$

or, $[A] = -k_0 t + [A]_0$, where $[A]$ is the conc. of A at time t and $[A]_0$ is at zero time.

Determination of rate constant (k_0):

$[A]$ is determined at different time intervals by suitable physical or chemical method and $[A]$ is plotted against t . From the slope, the rate constant (k_0) can be obtained for the reaction at a given temperature. Unit of rate constant = conc./time mol L⁻¹ sec⁻¹.

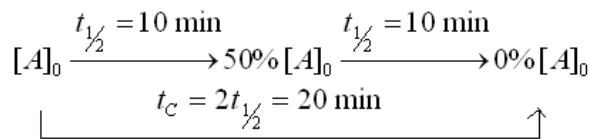


Half-life period ($t_{1/2}$):

It is the time required for the conc. of the reactant to be cut in half. Thus when $t = t_{1/2}$, $[A] = [A]_0/2$ in the rate equation, so $[A]_0/2 = -k_0 t_{1/2} + [A]_0$ or, $t_{1/2} = [A]_0/2k_0$. That is, half life period is proportional to the initial conc. of the reactant.

Completion time (t_c): It is the time required to complete the reaction, so in the rate equation,

when $t = t_c$, $[A] = 0$. Putting in the rate equation, we get $0 = -k_0 t_c + [A]_0$ or, $t_c = [A]_0/k_0$. At this time whole of the reactant is converted into product. Thus 1st order reactions undergo completion. So, t_c is twice of $t_{1/2}$ for the zero order reaction and thus this type of reaction goes to completion.



Some examples of the zero order reaction:

- (A) Photochemical reactions like $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \xrightarrow{\text{sunlight}} 2\text{HCl}(\text{g})$ is a zero order reaction.
 (B) Zero order reactions generally takes place in a heterogeneous system.

Gaseous reactants are adsorbed on the surface of the catalyst where it is converted into product. The rate of the reaction is proportional to the fraction of the surface of the catalyst covered by the reactant and the fraction is proportional to the conc. of the unadsorbed gaseous reactant in the lower range and follows 1st order kinetics. When the surface of the catalyst is fully covered, any further increase in the conc. of gaseous reactant is not adsorbed and fraction of the surface of the catalyst remains unity. The rate of the reaction becomes independent of the conc. of the reactant and the reaction becomes zero order.

- (1) $\text{CH}_2 = \text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \xrightarrow{\text{Ni}} \text{CH}_3 - \text{CH}_3(\text{g})$.
 (2) $2\text{NH}_3(\text{g}) \xrightarrow{\text{W}} \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ (3) $2\text{HI}(\text{g}) \xrightarrow{\text{Au}} \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
 (4) $2\text{N}_2\text{O}(\text{g}) \xrightarrow{\text{Au}} 2\text{N}_2(\text{g}) + \text{O}_2(\text{g})$

(C) Enzyme catalyzed reaction is zero order with respect to substrate when the substrate conc. is high.



Order and molecularity of zero order reaction:

Since for elementary reactions, order and molecularity are same so zero order reactions can not be elementary reactions. Heterogeneous catalyzed reactions are found to be zero order reactions under certain experimental condition.

Some solved problems:

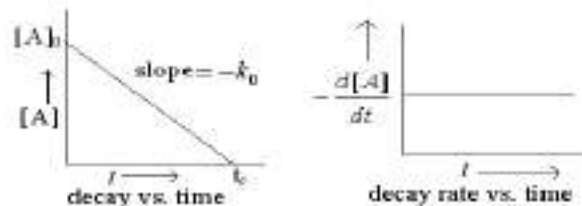
(1) What is zero order reaction? Cite some examples. What is the molecularity of this type of reactions? Plot the decay and decay rate vs. time for this kind of reactions. **[Burdwan Univ. 1991]**

Hints: For 1st, 2nd and 3rd questions see the Text above.

4th part: For zero order reactions, decay of reactant is given by $[A] = -k_0t + [A]_0$ and

decay rate $-\frac{d[A]}{dt} = k_0$, constant. So the

plots are given as:



(2) A chemical reaction is known to be zero order with $k = 5 \times 10^{-8} \text{ mol L}^{-1} \text{ sec}^{-1}$. How long does it take to change conc. from $4 \times 10^{-4} \text{ mol L}^{-1}$ to $2 \times 10^{-2} \text{ mol L}^{-1}$? **[Burdwan Univ. 1995]**

Hints: $[A]_0 - [A] = [P] = k t$. With increase of time, the conc. of the product, [P] is increased,

$$\text{so } t_2 - t_1 = \frac{[P]_2 - [P]_1}{k} = \frac{(2 \times 10^{-2} - 4 \times 10^{-4}) \text{ mol L}^{-1}}{5 \times 10^{-8} \text{ mol L}^{-1} \text{ sec}^{-1}} = 3.92 \times 10^5 \text{ sec}.$$

(3) A zero order reaction cannot be a single-step reaction. – justify. **[Calcutta Univ. 2012]**

Hints: See the Text above.

(4) At certain temperature, half life periods of decomposition of NH_3 in contact with tungsten are as follows:

Pressure (mm of Hg) \rightarrow	200	100	50
$t_{1/2}$ periods (relative) \rightarrow	3.52	1.92	1.00.

Find the overall order of the reaction. **[West Bengal Civil Service Exam. 1995]**

Hints: Half life period of the reaction is directly proportional to the initial pressure of NH_3 .

Hence the reaction is zero order.

Question: The half life of any zero order reaction is

- (a) independent of conc. (b) proportional to inverse of conc. (c) proportional to conc.
(d) proportional to square of the conc. **[IIT – JAM, 2012]**

FIRST ORDER REACTIONS

Differential rate equation:

Rate of these reactions depends on the single power of conc. term of the reactant in the rate equation. Thus for the reaction, $A \rightarrow P$, the differential rate equation is $-\frac{d[A]}{dt} = k_1[A]$, ----- (1)

where k_1 is the rate constant of the first order reaction.

Integrated rate equation: Separating the variables and integrating within proper limits, we get

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = k_1 \int_0^t dt \quad \text{or,} \quad \ln[A] = -k_1 t + \ln[A]_0 \quad \text{-----}(2)$$

Reshuffling the equation, we have $\ln \frac{[A]_0}{[A]} = k_1 t$, ----- (3)

where [A] and $[A]_0$ are the conc. of A at time t and at the start of the reaction. Again, $[A] = [A]_0 e^{-k_1 t}$ -----(4)

Problem: For a reaction, the rate constant is $k = 1.5 \times 10^{-3} \text{ sec}^{-1}$. If the initial conc. of the reactant is 0.5(M), find the rate after half an hour.

Solution: The rate after half an hour is given as $-\frac{d[A]}{dt} = k_1[A] = k_1[A]_0 e^{-k_1 t}$. Putting the data given, we have

$$\text{the rate} = 1.5 \times 10^{-3} \text{ sec}^{-1} \times 0.5 \text{ mol lit}^{-1} \times e^{-1.5 \times 10^{-3} \text{ sec}^{-1} \times 30 \times 60 \text{ sec}} = 5.04 \times 10^{-5} \text{ mol lit}^{-1} \text{ sec}^{-1}.$$

Experimental determination of rate constant (k_1):

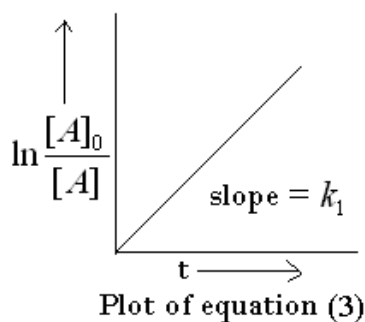
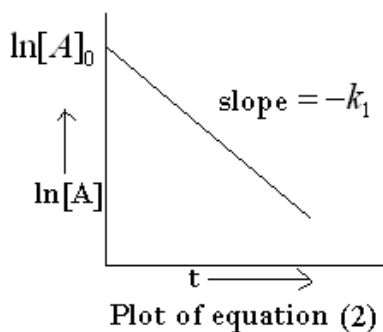
Collection of kinetic data of conc. of A at different time intervals helps to find the rate constant (k_1) of the first order reaction.

These data are shown in the adjoining table.

When equation (2) is used to plot $\ln [A]$ vs. t , it gives straight line and the slope gives $-k_1$. However, the equation (3) may be used and $\ln \frac{[A]_0}{[A]}$ vs. t plot gives slope = k_1 .

temperature is fixed

time	conc. of reactant	conc. of product
0	$[A]_0$	0
t_1	$[A]_1$	$[P]_1$
t_2	$[A]_2$	$[P]_2$
t_3	$[A]_3$	$[P]_3$
t_4	$[A]_4$	$[P]_4$
t_5	$[A]_5$	$[P]_5$



Characteristic features of first order reactions:

(1) **Significance of rate constant (k_1):** The first order rate law is given in equation (1). Rearranging the equation, we get $k_1 = \frac{(-d[A]/[A])}{dt}$, where $(-d[A]/[A])$ is the fraction of the reactant A decomposing in

dt time and thus $\frac{(-d[A]/[A])}{dt}$ is the fraction decomposing in unit time provided $[A]$ is kept constant within the time period dt . Thus for first order reaction, k_1 is the fraction that is decomposed in unit time.

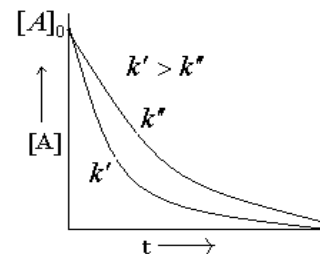
For example, let k_1 of decomposition of H_2O_2 at $25^\circ\text{C} = 0.04 \text{ min}^{-1} = 4\% \text{ per min}$.

It means that 4% H_2O_2 is decomposed per minute provided $[\text{H}_2\text{O}_2]$ is kept constant during this one minute period by adding H_2O_2 from outside at 25°C .

Question: What is the significance of k , the specific rate constant for a 1st order reaction? Show diagrammatically the effect of increasing k value on the conc. vs. time graph for a first order process at constant temperature. (4) [Burdwan Univ. 1994]

Answer: See above for significance. Higher the value of k of a reaction, greater is the fraction decomposed and so greater fall of conc. of A with time t . The graph is given here;

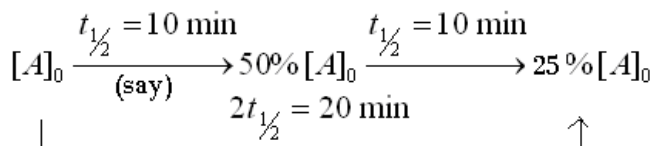
(2) **Incompleteness of the reaction:** Equation (4), $[A] = [A]_0 e^{-k_1 t}$ shows that when the reaction is complete, $[A] = 0$ and this is possible only at $t \rightarrow \infty$ i.e. $[A]_0$ can be zero only at infinite time. So the reaction is never complete in finite time.



(3) **Half life period ($t_{1/2}$):** In equation (2),

when $t = t_{1/2}$, $[A] = [A]_0/2$.

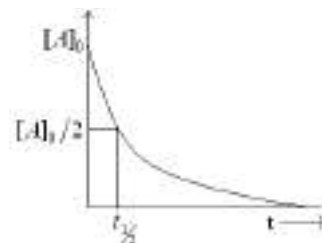
Putting, we get $t_{1/2} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1}$.



This expression shows that $t_{1/2}$ is independent of initial conc. of the reactant and so like k_1 , $t_{1/2}$ is also constant for a reaction at a particular temperature

(4) **Unit of k_1 :** $k_1 = \frac{-d[A]/[A]}{dt}$,

so unit of $k_1 = (\text{conc.}/\text{conc.})/\text{time} = \text{time}^{-1}$. Thus unit of $k_1 = \text{sec}^{-1}$. The unit of k_1 does not contain conc. term so this rate constant is independent of choice of conc. It means that mode of choice of conc. does not affect the value of k_1 . So for determination of k_1 by the use of equation (2) or (3) instead of conc. of A, any property (P), which is directly proportional to $[A]$, may be used.



(5) **Fraction decomposing in time t:** The equation (4) is $\frac{[A]}{[A]_0} = e^{-k_1 t}$ or, $\frac{[A]_0 - [A]}{[A]_0} = (1 - e^{-k_1 t})$.

So the fraction decomposed in time $t = (1 - e^{-k_1 t})$ and it is independent of initial conc. of the reactant.

Question: Show that the conc. of the product for a first order irreversible reaction during initial period (time t is very small) is given by the equation $[P] = [A]_0 \left(kt - \frac{1}{2} k^2 t^2 \right)$. [Union Public service Commission, 1995]

Answer: From the above relation, we get $[P] = [A]_0 - [A] = [A]_0 (1 - e^{-kt}) = [A]_0 \left\{ 1 - \left(1 - kt + \frac{1}{2} k^2 t^2 \right) \right\}$,

neglecting the higher powers (kt) and when t is very small for initial period. Thus, $[P] = [A]_0 \left(kt - \frac{1}{2} k^2 t^2 \right)$.

Problem: Calculate the half life period for the decomposition of N_2O_5 at 25 °C and fraction decomposed after 8 hours, given $k = 3.38 \times 10^{-5} \text{ sec}^{-1}$. (4) [Burdwan Univ. 1992]

Answer: Half life period = 20,500 sec and fraction decomposed = 0.622.

(6) **Average life (t_{av}):** It can simply be obtained from the significance of the rate constant.

k_1 = fraction of the reactant decomposing in unit time, hence complete fraction of the reactant decomposes $1/k_1$ time. Thus the completion time (t_c) for 1st order reaction = $1/k_1$.

However, 1st order reaction will never be complete, so the completion time is only the average life (t_{av}) and this can be calculated by statistical method.

Time limit for survival of the molecules ranges from 0 to ∞ . So, $t_{av} = \int_0^{\infty} t \times \left(\frac{-d[A]}{[A]_0} \right)$, where $\left(\frac{-d[A]}{[A]_0} \right)$

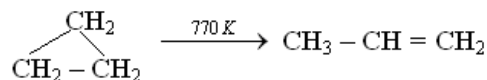
is the fraction of initial conc. of the reactant that survives up to time t and it means that this conc. of the reactant decomposes after time t .

$$t_{av} = \frac{1}{[A]_0} \int_0^{\infty} t \times (-d[A]) = \frac{1}{[A]_0} \int_0^{\infty} t \times k_1 [A] dt = \frac{1}{[A]_0} \int_0^{\infty} t \times k_1 [A]_0 e^{-k_1 t} dt = k_1 \int_0^{\infty} t \times e^{-k_1 t} dt = k_1 \times \frac{\Gamma(2)}{k_1^2} = \frac{1}{k_1}$$

[Since $-\frac{d[A]}{dt} = k_1 [A]$ and so $-d[A] = k_1 [A] dt$ and again, $[A] = [A]_0 e^{-k_1 t}$].

Examples of 1st order reaction:

First order elementary reactions are unimolecular reactions. These are either isomerisations or decompositions. Isomerisation reaction: cyclopropane to propene,



Decomposition of azomethane: $(\text{CH}_3)_2\text{N}_2 \xrightarrow{400\text{K}} \text{C}_2\text{H}_6 + \text{N}_2$.

Other multistep 1st order reactions are

decomposition of H_2O_2 , decomposition of N_2O_5 , hydrolysis of ester catalyzed by acid, etc.

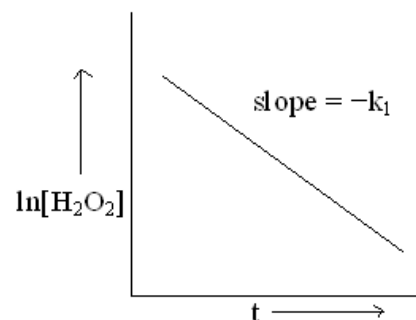
Decomposition of H_2O_2 catalyzed by Fe^{3+} ion: (An example of chemical method for kinetic study)

The reaction is represented by equation as $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$.

100 ml of 0.03 % H_2O_2 and 2 ml of 5 % FeCl_3 solution are kept separated in a thermostat at constant temperature and then both are mixed. The reaction starts. Aliquot amount of reaction mixture is pipetted out

and then added to a large excess ice cold water. The reaction is arrested (quenched). The amount of undecomposed H_2O_2 is estimated by titrating with KMnO_4 solution. The volume of KMnO_4 is a measure of undecomposed H_2O_2 . This is done at other time intervals and a table is prepared. These data are plotted to obtain k_1 of the reaction.

time in min.	$[\text{H}_2\text{O}_2]$ in terms of V_{KMnO_4} in ml
0	46.1
5	37.1
10	29.8
20	19.6
30	12.2
50	5.0



Decomposition of N_2O_5 in CCl_4 solution: (An example of physical method for kinetic study)

The reaction is represented as $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$. The kinetic data are given in the form a problem. A solution of N_2O_5 in CCl_4 at 45 °C produces 5.02 cc of O_2 in 1198 sec, 7.33 cc of O_2 in 2315 sec and a maximum of 9.58 cc of O_2 after a long time. Show that these results conform to a first order rate law for decomposition of N_2O_5 , and find first order rate constant. [Civil Service Commission, 1995]

Illustration: N_2O_5 and NO_2 remain dissolved in CCl_4 solution but O_2 gas is evolved as the reaction proceeds.

The volumes of O_2 gas are collected at different time intervals and are used to determine rate constant of the reaction. The integrated rate equation for 1st order reaction is $k = \frac{1}{t} \ln \frac{[A]_0}{[A]}$.

In the problem, $[A]_0 = [\text{N}_2\text{O}_5] \propto 9.58$ cc of O_2 . At 1198 sec, $[A] = [\text{N}_2\text{O}_5] \propto (9.58 - 5.02)$ cc of O_2 and at 2315 sec, $[A] = [\text{N}_2\text{O}_5] \propto 9.95$ cc of O_2 . Putting the values in the rate equation, we get

$$\text{At 1198 sec, } k = \frac{1}{1198\text{sec}} \ln \frac{9.58\text{cc}}{(9.58 - 5.02)\text{cc}} = 6.2 \times 10^{-4} \text{ sec}^{-1}$$

$$\text{and at 2315 sec, } k = \frac{1}{2315\text{sec}} \ln \frac{9.58\text{cc}}{(9.58 - 7.83)\text{cc}} = 7.34 \times 10^{-4} \text{ sec}^{-1}. \text{ So the results conform}$$

the reaction is first order and the rate constant is equal to $\frac{1}{2} (6.2 + 7.34) \times 10^{-4} = 6.77 \times 10^{-4} \text{ sec}^{-1}$.

Question: The kinetics of the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ in liquid bromine medium was measured independently for three different initial conc. of N_2O_5 : 0.11, 0.07 and 0.05 mol L^{-1} . The half life of the reaction was found to be 4.5 hours for all these concentrations. The order of the reaction is

(A) 0 (B) 1 (C) 2 (D) 0.5 **Answer:** (B) 1.

[IIT – JAM, 2015]

Problem: The composition of gas phase reaction, $2A \rightarrow B$ was monitored by measuring the total pressure as a function of time. The following results were recorded.

Time/sec \rightarrow	0	100	200	300	400
Pressure/mm of Hg \rightarrow	400	322	288	268	256.

What is the order of the reaction and what is the value of rate constant. [Civil service Exam. 1997]

Solution: The reaction is given by the equation as $2A \rightarrow B$, Let the initial conc. of the reactant is $[A]_0$ and after time t , the conc. is $[A]$, then conc. of product, B is $\frac{1}{2}([A]_0 - [A])$.

The total conc. = $[A] + \frac{1}{2}([A]_0 - [A]) = \frac{1}{2}([A]_0 + [A])$. Let the reaction follows 1st order kinetics, then the rate equation is $k_1 = \frac{1}{t} \ln \frac{[A]_0}{[A]}$, in which $[A]_0 \propto P_0 = KP_0$ and $\frac{1}{2}([A]_0 + [A]) \propto P = KP$.

Thus, $[A] = 2KP - [A]_0 = K(2P - P_0)$. Now the rate equation is $k_1 = \frac{1}{t} \ln \frac{P_0}{(2P - P_0)}$. Putting the data

at different times, we get $k_1 = \frac{1}{100 \text{ sec}} \ln \frac{400}{(2 \times 322 - 400)} = 4.94 \times 10^{-3} \text{ sec}^{-1}$ after 100 sec,

$k_1 = 4.62 \times 10^{-3} \text{ sec}^{-1}$ after 200 sec, $k_1 = 3.59 \times 10^{-3} \text{ sec}^{-1}$ after 300 sec and $k_1 = 3.18 \times 10^{-3} \text{ sec}^{-1}$ after 400 sec. The result shows that the rate constant k_1 is same in the different runs following 1st order kinetics. Thus the order of the reaction is one. The average rate constant of the reaction is $k_1 = \frac{1}{4}(4.94 + 4.62 + 3.59 + 3.18) \times 10^{-3} \text{ sec}^{-1}$ or, $k_1 = 4.01 \times 10^{-3} \text{ sec}^{-1}$.

Problem: For the reaction $R \rightarrow P$, the plot of $\ln[R]$ versus time (t) gives a straight line with a (-ve) slope. The half life for the reaction is 3 min [$\ln 2 = 0.693$, $\ln 0.1 = -2.303$].

(i) Derive the expression of $t_{1/2}$ (ii) Calculate the slope of the straight line (iii) calculate the time required for the conc. of R to decrease to 10 % of the initial value. [IIT – JAM 2011]

Solution: Hints. (i) According to the problem, $\ln[R] = -kt + Z$. Differentiating with respect to t , we get

$\frac{1}{[R]} \frac{d[R]}{dt} = -k$ or, $-\frac{d[R]}{dt} = k[R]$, so the reaction is 1st order. Now when $t = 0$, $Z = \ln[R]_0$.

So the integrated rate equation is $\ln[R] = -kt + \ln[R]_0$. When $t = t_{1/2}$, $[R] = \frac{1}{2}[R]_0$, thus the expression of the half life of the reaction is $t_{1/2} = \ln 2/k$ or, $t_{1/2} = 0.693/k$.

(ii) The slope of the rate constant is $-k_1 = -0.693/t_{1/2} = -0.693/3 \text{ min} = -0.231 \text{ min}^{-1}$.

(iii) Time required for the conc. R to decrease to 10 % of the initial conc.

$$t = \frac{1}{k_1} \ln \frac{[R]_0}{[R]} = \frac{1}{0.231 \text{ min}^{-1}} \ln \frac{[R]_0}{0.1[R]_0} = \frac{1}{0.231 \text{ min}^{-1}} \ln 10 = 9.97 \text{ min}.$$

Question: For the reaction $a + B \rightarrow Z$, the conc. of Z at time t is given by $[Z] = [A]_0(1 - e^{-kt}) + [Z]_0$,

where k is the rate constant. The rate law is

(A) $-\frac{d[Z]}{dt} = k[A]$ (B) $\frac{d[Z]}{dt} = k[A]$ (C) $\frac{d[Z]}{dt} = k[Z]$ (D) $\frac{d[Z]}{dt} = k[A][B]$.

Answer: (B). $\frac{d[Z]}{dt} = k[A] = k([A]_0 - [Z])$ or, $\int_0^{[Z]} \frac{d[Z]}{([A]_0 - [Z])} = k \int_0^t dt$ or, $-\ln([A]_0 - [Z]) = kt - \ln[A]_0$.

But $[A]_0 - [Z] = [A] = [A]_0 e^{-kt}$ or, $[Z] = [A]_0(1 - e^{-kt})$

Question: A first-order chemical reaction is 10 % complete in 10 minutes. Its half-life is (given $\log 3 = 0.48$)

(1) 50.50 minutes (2) 7.5 minutes (3) 95.6 minutes (4) 75.2 minutes.

Answer: (4).

[Adm to M Sc, BHU 2013]

Problem: An elementary gaseous reaction $A_2(g) \rightarrow B(g) + \frac{1}{2} C(g)$ shows an increase in pressure from 100 torr to 120 torr in 5 minutes. Find the rate of disappearance of A_2 in torr per minutes.

Solution: Let the initial mol of A_2 is a and after time t , x mol of A_2 has reacted.

$$\text{Thus } a \propto 100 \text{ torr or, } a - x + x + \frac{1}{2}x = \left(a + \frac{1}{2}x\right) \propto 120 \text{ torr or, } x \propto 2(120 - 100) = 40 \text{ torr.}$$

$$\text{The rate constant, } k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{1}{5 \text{ min}} \ln \frac{100 \text{ torr}}{(100 - 40) \text{ torr}} = 0.102 \text{ min}^{-1}.$$

$$\text{Rate of disappearance of } A_2, -\frac{d[A_2]}{dt} = k(a-x) = 0.102 \text{ min}^{-1} \times (100 - 40) \text{ torr} = 6.1 \text{ torr min}^{-1}.$$

Question: Inversion of sugar follows first order rate law which can be followed by noting the change in angle of rotation of plane polarized light in the polarimeter. If θ_∞ , θ_t and θ_0 are the angle of rotation at times $t = \infty$, $t = t$ and $t = 0$, then find the expression of rate constant of the above reaction.

Answer: The angle of rotation changes from (+ve) to (-ve) direction i.e. dextro-rotatory to laevo-rotatory.

$$\text{Thus, } [A]_0 \propto (\theta_0 - \theta_\infty) \text{ and } [A] \propto (\theta_0 - \theta_\infty) - (\theta_0 - \theta_t) \propto (\theta_t - \theta_\infty).$$

$$\text{The expression of first order rate constant is given by } k = \frac{1}{t} \ln \frac{[A]_0}{[A]} \text{ or, } k = \frac{1}{t} \ln \frac{(\theta_0 - \theta_\infty)}{(\theta_t - \theta_\infty)}.$$

Example: Let after time t 18 mins, $\theta_t = 17.73$ while $\theta_0 = +24.09$ and $\theta_\infty = -10.74$. Putting these values, we get

$$\text{the rate constant } k_1 = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{t} \ln \frac{(\theta_0 - \theta_\infty)}{(\theta_t - \theta_\infty)} = \frac{1}{18 \text{ min}} \ln \frac{(24 + 10.74)}{(17.73 + 10.74)} = 1.117 \times 10^{-2} \text{ min}^{-1}.$$

Question: The half-life of a first order reaction varies with temperature according to

$$(A) \ln t_{1/2} \propto 1/T \quad (B) \ln t_{1/2} \propto T \quad (C) t_{1/2} \propto 1/T^2 \quad (D) t_{1/2} \propto T^2 \quad [\text{GATE, 2002}]$$

Answer: Correct option is (A). **Hints:** $k = Ae^{-E_a/RT}$ or, $\frac{\ln 2}{t_{1/2}} = Ae^{-E_a/RT}$ (Since the reaction is first order).

$$\text{So, } t_{1/2} = \ln 2 \times A^{-1} e^{E_a/RT} \text{ or, } t_{1/2} \propto e^{1/T} \text{ or, } \ln t_{1/2} \propto 1/T.$$

Question: An irreversible, homogeneous reaction $A \rightarrow$ products, has the rate expression:

$$\text{Rate} = \frac{2[A]^2 + 0.5[A]}{1 + 50[A]}, \text{ where } [A] \text{ in the range } 0.5 - 50 \text{ mol/m}^3. \text{ For very high conc. of } A,$$

the reaction order tends to (A) 0 (B) 1 (C) 1.5 (D) 2. [GATE, 2015]

Answer: (B). Hints: $\text{Rate} = \frac{2[A]^2 + 0.5[A]}{1 + 50[A]}$; $0.5 < [A] < 50 \text{ (mol/m}^3)$

$$\text{For very high of } [A] \text{ (say } 50 \text{ mol/m}^3), 0.1 [A] \ll 2[A]^2 \text{ and } 50 [A] \gg 1, \text{ so rate} = \frac{2[A]^2}{50[A]} = \frac{1}{25} [A].$$

So the reaction is first order.

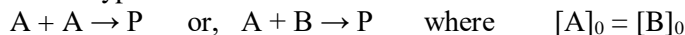
SECOND ORDER REACTIONS

Differential rate law:

Rate of this type of reactions depends on two conc. terms. This may occur in two different ways.

(i) When the two conc. terms are of same magnitude and (ii) when they are of different magnitude.

(1) Let us consider the first type when the conc. of the two reactants are of same magnitude:



The differential rate equation is then $-\frac{d[A]}{dt} = k_2[A][B] = k_2[A]^2$ ----- (1),

where k_2 is the rate constant of the second order reaction. It depends on temperature and catalyst used if any for the reaction.

Integrated rate law:

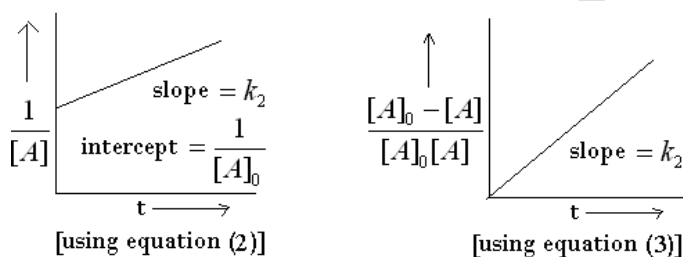
Separating the variables and Integrating the above differential rate law within proper limits, we get

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k_2 \int_0^t dt \quad \text{or, } \frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t \text{-----(2) or, } \frac{[A]_0 - [A]}{[A]_0[A]} = k_2 t \text{----- (3).}$$

These two are the integrated forms of rate equation of the second order reaction when $[A]_0 = [B]_0$.

Evaluation of rate constant (k_2):

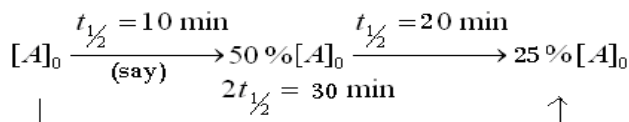
The conc. of reactant remaining undecomposed are determined either by chemical methods or by physical methods at different time intervals. Now $1/[A]$ is plotted against t . The rate constant (k_2) is obtained from the slope by using equation (2). Equation (3) may also be used and the left hand side is plotted against t .



Characteristics of second order reactions:

(1) **Half-life period ($t_{1/2}$):** In equation (2), putting $t = t_{1/2}$ and $[A] = \frac{[A]_0}{2}$, we get

$$\frac{2}{[A]_0} = \frac{1}{[A]_0} + k_2 t_{1/2} \quad \text{or, } t_{1/2} = \frac{1}{k_2[A]_0}. \text{ Thus the half-life period of second order reaction is inversely proportional to the initial conc. of the reactant, } [A]_0. \text{ That is, } t_{1/2} \text{ doubles when } [A]_0 \text{ is cut to half.}$$



(2) **Unit of rate constant (k_2):**

Unit of $k_2 = \text{conc.}^{-1} \text{ time}^{-1} = \text{mol}^{-1} \text{ L sec}^{-1}$, if conc. is used as mol/L and time is in sec. Thus, the value of k_2 depends on the choice of unit of conc. If the unit of conc. is changed, magnitude of k_2 is also changed. For example, given $k_2 = 3.5 \times 10^{-7} \text{ mol}^{-1} \text{ L sec}^{-1}$. The value of k_2 in $\text{molecule}^{-1} \text{ cc sec}^{-1}$ is $k_2 = 3.5 \times 10^{-7} \times (6.023 \times 10^{23} \text{ molecule})^{-1} \times (10^3 \text{ cc}) \times \text{sec}^{-1} = 5.8 \times 10^{-28} \text{ molecule}^{-1} \text{ cc sec}^{-1}$.

(3) **Incompleteness of the reaction:** The integrated rate equation is $\frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t$ and this shows that

when the reaction would be complete, $[A]$ would be zero and that would be possible only when $t \rightarrow \infty$. This means that the reaction will never be complete.

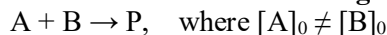
(4) **Fraction of reactant decomposing in time t :**

From the rate equation (3), we have the fraction of A decomposing in time t is

$$\frac{[A]_0 - [A]}{[A]_0} = [A]k_2 t. \text{ Again from equation (1), } \frac{1}{[A]} = \frac{1 + [A]_0 k_2 t}{[A]_0} \text{ or, } [A] = \frac{[A]_0}{1 + [A]_0 k_2 t}.$$

Putting this value, we get $\frac{[A]_0 - [A]}{[A]_0} = \frac{[A]_0 k_2 t}{1 + [A]_0 k_2 t} = 1 - \frac{1}{1 + [A]_0 k_2 t}$. So, the fraction of A decomposed in time t is $1 - \frac{1}{1 + [A]_0 k_2 t}$ and undecomposed is $\frac{1}{1 + [A]_0 k_2 t}$. Thus time for 50% completion is obtained from $1 - \frac{1}{1 + [A]_0 k_2 t_{0.5}} = 0.5$ or, $t_{0.5} = 1/(k_2[A]_0)$. Similarly for 75 % completion, time required is obtained from $1 - \frac{1}{1 + [A]_0 k_2 t_{0.75}} = 0.75$ or $t_{0.75} = \frac{3}{k_2[A]_0}$. Thus, $\frac{t_{0.5}}{t_{0.75}} = \frac{1}{3}$.

(1) When conc. of the two reactants are of different magnitude



The rate equation of this second order reaction is $-\frac{d[A]}{dt} = k_2[A][B]$, ----- (4) but $[A]_0 - [A] = [B]_0 - [B]$

or, $[B] = [B]_0 - [A]_0 + [A]$, putting this in the rate equation, we get $-\frac{d[A]}{dt} = k_2[A]([B]_0 - [A]_0 + [A])$

$$\text{or, } -\frac{d[A]}{[A]([B]_0 - [A]_0 + [A])} = k_2 dt \quad \text{or, } \frac{1}{[A]_0 - [B]_0} \left(\frac{d[A]}{[A]} - \frac{d[A]}{[B]_0 - [A]_0 + [A]} \right) = k_2 dt.$$

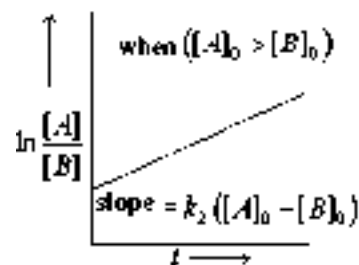
Integrating within limits, we get $\frac{1}{([A]_0 - [B]_0)} \left(\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} - \int_{[A]_0}^{[A]} \frac{d[A]}{[B]_0 - [A]_0 + [A]} \right) = k_2 \int_0^t dt$

$$\text{or, } \frac{1}{([A]_0 - [B]_0)} \left(\ln \frac{[A]}{[A]_0} - \ln \frac{[B]_0 - [A]_0 + [A]}{[B]_0 - [A]_0 + [A]_0} \right) = k_2 t \quad \text{or, } \frac{1}{([A]_0 - [B]_0)} \ln \frac{[A][B]_0}{[A]_0([B]_0 - [A]_0 + [A])} = k_2 t \quad \text{----- (5)}$$

$$\text{but, } [B] = [B]_0 - [A]_0 + [A], \text{ so the integrated rate equation is } \frac{1}{([A]_0 - [B]_0)} \ln \frac{[A][B]_0}{[A]_0[B]} = k_2 t \quad \text{----- (6)}$$

$$\text{or, } \ln \frac{[A]}{[B]} = k_2 ([A]_0 - [B]_0)t + \ln \frac{[A]_0}{[B]_0} \quad \text{----- (7)}$$

Thus the plot of $\ln \frac{[A]}{[B]}$ vs. t gives a straight line from the slope of which k_2 can be determined.



Case 1: Pseudo unimolecular reaction: (When one of the reactants is taken in large excess)

Let $[B]_0 \gg [A]_0$ then $[A]_0 - [B]_0 \approx -[B]_0$ and there is small difference between $[B]$ and $[B]_0$

as B is present in large amount, so the rate equation under this condition becomes $-\frac{1}{[B]_0} \ln \frac{[A][B]_0}{[A]_0[B]_0} = k_2 t$

or, $\ln \frac{[A]_0}{[A]} = (k_2[B]_0) t$ or, $\ln \frac{[A]_0}{[A]} = k_1 t$, (where $k_1 = k_2[B]_0$). This is a first order reaction. This type of

reaction is called pseudo unimolecular reaction. Two molecules participate in the elementary reaction still it obeys first order kinetics. So depending on the condition, bimolecular elementary reaction obeys first order kinetics like unimolecular elementary reaction.

Though elementary bimolecular reactions are 2nd order but when one reactant is present in excess, elementary bimolecular reactions behaves like elementary unimolecular reactions and so the name is pseudo unimolecular reactions.

Case 2: Integrated rate equation (5), $\frac{1}{([A]_0 - [B]_0)} \ln \frac{[A][B]_0}{[A]_0([B]_0 - [A]_0 + [A])} = k_2 t$ can be reduced to equation (2) when $[B]_0 \rightarrow [A]_0$.

The above equation (5) can be rearranged as $\frac{1}{([A]_0 - [B]_0)} \ln \left[1 + \frac{([A]_0 - [B]_0)([A]_0 - [A])}{[A]_0 \{ [B]_0 - ([A]_0 - [A]) \}} \right] = k_2 t$.

But when $[B]_0 \rightarrow [A]_0$, $\frac{([A]_0 - [B]_0)([A]_0 - [A])}{[A]_0([B]_0 - [A]_0 + [A])} \ll 1$. Expanding $\ln(1+x) = x$ when $x \ll 1$. The

rate equation is $\frac{1}{([A]_0 - [B]_0)} \times \frac{([A]_0 - [B]_0)([A]_0 - [A])}{[A]_0([B]_0 - [A]_0 + [A])} = k_2 t$ or, $\frac{([A]_0 - [A])}{[A]_0([B]_0 - [A]_0 + [A])} = k_2 t$.

Again, as $[B]_0 \rightarrow [A]_0$, so, $\frac{([A]_0 - [A])}{[A]_0[A]} = k_2 t$ or, $\frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t$.

Thus, when $[B]_0 \rightarrow [A]_0$, the equation (5) reduces to the equation (2)

Problem: Let the stoichiometric equation of a reaction is $A + 2B \rightarrow P$

but the reaction is nevertheless 1st order reaction with respect to both A and B. If a and b are initial amount of A and B (per unit volume), and x is the amount of A that has disappeared in time t . Find is the equation for the rate of disappearance of A.

Answer: The rate of disappearance of A is $\frac{dx}{dt} = k_2(a-x)(b-2x)$ and

the integrated rate equation is $\frac{1}{(2a-b)} \ln \frac{b(a-x)}{a(b-2x)} = k_2 t$

Some examples of 2nd order reactions:

- (i) Alkaline hydrolysis of ester (saponification reaction): $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
- (ii) Gas phase decomposition of HI: $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$.

Experimental determination of rate constant of saponification reaction:

The reaction is $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$.

A reaction mixture is prepared by mixing known quantity of ester with known volume of alkali (NaOH) solution.

Let $[A]_0$ and $[B]_0$ are the initial conc. of ester and alkali respectively. At frequent intervals of time, a portion of reaction mixture is removed, quenched and titrated with standard oxalic acid solution using phenolphthalein indicator. The unreacted amount of OH^- in reaction mixture is obtained from the oxalic acid used in the titration and this value is $[B]$. The value of $[A]$ is obtained from the relation $[A]_0 - [A] = [B]_0 - [B]$ from known

values of $[A]_0$ and $[B]_0$. Now using equation (7) $\ln \frac{[A]}{[B]} = k_2([A]_0 - [B]_0)t + \ln \frac{[A]_0}{[B]_0}$, plot of $\ln \frac{[A]}{[B]}$ vs. t

gives a straight line with slope $k_2([A]_0 - [B]_0)$, from which the value of k_2 is obtained.

Question: Ethyl acetate and sodium hydroxide in an ethanol-water mixture at 303 K exhibit a hydrolysis reaction. In an experiment in which 0.05 mol dm^{-3} each reactant were present at time $t = 0$, the time for half change was 1800 s and the time for three-quarters change was 5400 s. Deduce the order of the reaction and calculate the rate constant. At what time 10 % reaction complete. [WBCS, 1999]

Answer: $t_{1/2}/t_{3/4} = \frac{1}{2^{n-1} + 1}$, where n is the order of the reaction. Putting the values, $\frac{1}{3} = \frac{1}{2^{n-1} + 1}$ or, $n = 2$.

Now for 2nd order reaction, rate constant $k = \frac{1}{t_{1/2} \times [A]_0} = \frac{1}{1800 \text{ s} \times 0.05 \text{ mol dm}^{-3}} = \frac{1}{90} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

Again, time required $t = \frac{1}{k} \times \frac{[A]_0 - [A]}{[A]_0[A]} = 90 \text{ mol dm}^{-3} \text{ s} \times \left(\frac{0.1[A]_0}{[A]_0 \times 0.9 \times 0.05} \right) \text{ mol}^{-1} \text{ dm}^3 = 200 \text{ s}$.

Question: For the reaction $aA \rightarrow \text{products}$, the plot of $1/[A]$ vs. time (t) gives a straight line. The order of the reaction is (A) 0 (B) 1 (C) 2 (D) 3. **Answer: (C)** [IIT – JAM, 2005]

Question: For a reaction with rate equation $-\frac{dc}{dt} = kc^2$. c_0 and c are the conc. of the reactant at time 0 and t respectively. If 10 min were required for c_0 to become $c_0/2$, the time required for c_0 to become $c_0/4$ is (A) 10 min (B) 20 min (C) 30 min (D) 40 min [IIT – JAM, 2007]

Answer: (C)

Question: The decomposition of gaseous acetaldehyde at T (K) follows second order kinetics. The half life of this reaction is 400 s when the initial pressure is 250 Torr. What will be the rate constant (in $\text{Torr}^{-1} \text{ s}^{-1}$) and half life (in s) respectively, if the initial pressure of acetaldehyde is 200 Torr at the same temperature.

(1) 10^5 and 500 (2) 10^{-5} and 400 (3) 10^{-5} and 500 (4) 10^{-4} and 400.

Answer: (3)

[NET (CSIR – UGC) 2011(I)]

Question: For a reaction $A \rightarrow \text{products}$, the plot of $1/[A]$ vs. time (t) is a straight line with (+ve) intercept. What is the order of the reaction?

[Calcutta Univ. 2011]

Answer: As given, $\frac{1}{[A]} = kt + Z$ or $\frac{d}{dt} \left(\frac{1}{[A]} \right) = k$ or, $-\frac{1}{[A]^2} \frac{d[A]}{dt} = k$ or, $-\frac{d[A]}{dt} = k[A]^2$.

Order of the reaction is 2.

Question: For a particular reaction at constant temperature, a plot of inverse of reactant conc. $\left(\frac{1}{[A]} \right)$ vs. time is a straight line with a slope of $4.0 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$. The time required (in seconds) for 1.0 M of reactant to decrease to 0.25 M is

(A) 18.8 (B) 34.7 (C) 75.0 (D) 187.5

[IIT – JAM, 2013]

Answer: Slope = rate constant (k) = $4.0 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$. The time required for 2nd order reaction is

$t = \frac{1}{k_2} \frac{[A]_0 - [A]}{[A]_0[A]}$ or, $t = \frac{1}{4.0 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}} \frac{(1.0 - 0.25) \text{ mol L}^{-1}}{1.0 \times 0.25 (\text{mol L}^{-1})^2} = 75 \text{ s}$. Correct option is (C).

Question: The half-life of a second order reaction $2A \rightarrow \text{products}$ whose initial conc. was 0.01 mol L^{-1} , was found to be 300 minutes. Its rate constant is

(1) $0.36 \text{ mol L}^{-1} \text{ min}^{-1}$ (2) $3.6 \text{ mol L}^{-1} \text{ min}^{-1}$ (3) $0.63 \text{ mol L}^{-1} \text{ min}^{-1}$ (4) $0.036 \text{ mol L}^{-1} \text{ min}^{-1}$

Answer: (1)

[Adm to M Sc, BHU 2013]

Question: A reaction follows second order rate law, $-d[A]/dt = k[A]^2$, if

(a) a plot of $[A]$ versus t is a straight line (b) a plot of $1/[A]$ versus t is a straight line

(c) a plot of $\ln[A]$ versus t is a straight line (d) a plot of $e^{[A]}$ versus t is a straight line [GATE, 2005]

Answer: The correct option is (b).

n th ORDER REACTIONS

Let the reaction is represented as $A \rightarrow P$ which follows n th order kinetics.

The differential rate equation is $-\frac{d[A]}{dt} = k_n[A]^n$. Separating the variables and integrating within limits,

we have integrated rate equation, $\frac{1}{[A]^{n-1}} = \frac{1}{[A]_0^{n-1}} + (n-1)k_n t$.

The unit of the rate constant, $k_n = \text{conc}^{1-n} \text{time}^{-1} = \text{mol}^{1-n} \text{L}^{n-1} \text{sec}^{-1}$.

Half life period ($t_{1/2}$): When $t = t_{1/2}$, $[A] = [A]_0/2$, putting, we get $t_{1/2} = \frac{1}{(n-1)k_n} \left[\frac{2^{n-1}-1}{[A]_0^{n-1}} \right]$.

Thus half life period of n th order reaction is inversely proportional to $[A]_0^{n-1}$ i.e. $t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$.

Similarly, $t_{3/4} = \frac{1}{(n-1)k_n} \left[\frac{4^{n-1}-1}{[A]_0^{n-1}} \right]$ and $\frac{t_{1/2}}{t_{3/4}} = \frac{2^{n-1}-1}{4^{n-1}-1} = \frac{2^{n-1}-1}{(2^{n-1})^2-(1)^2} = \frac{1}{2^{n-1}+1}$. Thus, $\frac{t_{1/2}}{t_{3/4}} = \frac{1}{2^{n-1}+1}$.

The ratio is thus a function of n only. This relation can be used to determine order of a reaction. $t_{1/2}$ and $t_{3/4}$ are determined from the plot of $[A]$ vs. t for the reaction $A \rightarrow P$.

Question: Show that the ratio $t_{1/2} : t_{3/4}$ of the n th order reaction can be written as a function of n only. What is the utility of the ratio? Calculate its value for 2nd order reaction. (5) [Burdwan Univ. 1992]

Answer: See above. The value is $1/2$.

Problem: The decomposition of a gas at an initial pressure of 600 mm Hg was studied in a closed vessel at a certain temperature. The gas is found to be 50 % decomposed in 30 min and 75 % decomposed in 90 min. Show that the reaction is 2nd order and calculate the rate constant (clearly stating unit). [Calcutta Univ. 1985]

Solution: $\frac{t_{0.5}}{t_{0.75}} = \frac{1}{2^{n-1}+1} = \frac{30 \text{ min}}{90 \text{ min}} = \frac{1}{3}$ or, $n = 2$. Thus the reaction is second order.

Again, for 2nd order reaction, $k_2 = \frac{1}{[A]_0 \times t_{0.5}} = \frac{1}{600 \text{ mm Hg} \times 30 \text{ min}}$ or, $k_2 = 5.5 \times 10^{-5} (\text{mm Hg})^{-1} \text{min}^{-1}$.

1st order reaction is a special case of n th order reaction.

By putting $n = 0, 2, 3$ etc. we get the corresponding integrated rate equation except $n = 1$. The reaction of n th order rate equation can be transformed into the reaction of 1st order rate equation as follows:

The n th rate equation is $\frac{1}{[A]^{n-1}} = \frac{1}{[A]_0^{n-1}} + (n-1)k_n t$. Multiplying the equation with $[A]_0^{n-1}$, we get

$\frac{[A]_0^{n-1}}{[A]^{n-1}} = 1 + (n-1)[A]_0^{n-1}k_n t$ or, $\ln \left\{ \frac{[A]_0}{[A]} \right\}^{n-1} = \ln \{ 1 + (n-1)[A]_0^{n-1}k_n t \}$, but when $n \rightarrow 1$, $(n-1) \rightarrow 0$.

Thus, expanding $\ln(1+x) \approx x$, when $x \rightarrow 0$, we have $(n-1) \ln \left\{ \frac{[A]_0}{[A]} \right\} = (n-1)[A]_0^{n-1}k_n t$.

Again, when $(n-1) \rightarrow 0$, $[A]_0^{n-1} \approx 1$. The equation is transformed into 1st order rate equation, $\ln \left\{ \frac{[A]_0}{[A]} \right\} = k_1 t$.

Problem: What will be the initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and the conc. of the reactant is 0.2 mol dm^{-3} ? How much of the reactant will be converted into products in 200 min?

[Adm Test to B Tech, Roorkee]

Answer: Initial reaction rate = $k_1[A]_0$ { The reaction is 1st order as the unit of k is only time⁻¹ }
 $= 10^{-3} \text{ min}^{-1} \times 0.2 \text{ mol dm}^{-3} = 2 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$.

Integrated equation of 1st order reaction is $\ln \frac{[A]_0}{[A]} = k_1 t$ or, $[A]_0 - [A] = [A]_0 (1 - e^{-k_1 t})$.

Now putting the data, we get the reactant converted into product, $[A]_0 - [A]$

$$= 0.2 \text{ mol dm}^{-3} (1 - e^{-10^{-3} \text{ min}^{-1} \times 200 \text{ min}}) = 0.0364 \text{ mol dm}^{-3}.$$

Problem: In a gaseous reaction, when the inverse of the pressure of the reactant is plotted against time, a straight line is obtained with intercept equal to 150 bar^{-1} and slope equal to $2 \times 10^{-3} \text{ bar}^{-1} \text{ s}^{-1}$. Calculate the half life for the reaction. [Civil Service Exam.1994]

Answer: For n th order reaction $A \rightarrow P$, the rate equation is $\frac{1}{[A]^{n-1}} = \frac{1}{[A]_0^{n-1}} + (n-1)k_n t$. Since inverse of P of the reactant vs. t is a straight line, hence $n = 2$ i.e. reaction is 2nd order and rate equation is $\frac{1}{P} = \frac{1}{P_0} + k_2 t$. The intercept $\frac{1}{P_0} = 150 \text{ bar}^{-1}$ or, $P_0 = \frac{1}{150} \text{ bar}$ and slope $k_2 = 2 \times 10^{-3} \text{ bar}^{-1} \text{ s}^{-1}$.

$$\text{Half life of the 2}^{\text{nd}} \text{ order reaction, } t_{1/2} = \frac{1}{P_0 \times k_2} = 150 \text{ bar} \times \frac{1}{2 \times 10^{-3} \text{ bar}^{-1} \text{ s}^{-1}} = 7.5 \times 10^4 \text{ s}.$$

Determination of order of a reaction

Order of a reaction is an experimental quantity and it is obtained from the experimental kinetic data of conc. of reactants or products at different time intervals during the progress of the reaction. However, it is always advisable to study the order of the reaction at the initial stages. Otherwise it may lead to erroneous results due to complications developed in the later stages.

Though various methods are used, we shall restrict only to few methods which are more popular.

(1) Method of half-life period:

Half-life or any fractional life (t_ϕ) is the time to decompose the reactant to half or any fraction of its initial conc. It could be shown that for n th order reaction, $t_\phi \propto \frac{1}{[A]_0^{n-1}}$ for the reaction, $A \rightarrow \text{Products}$.

So, for two sets of experiments of the

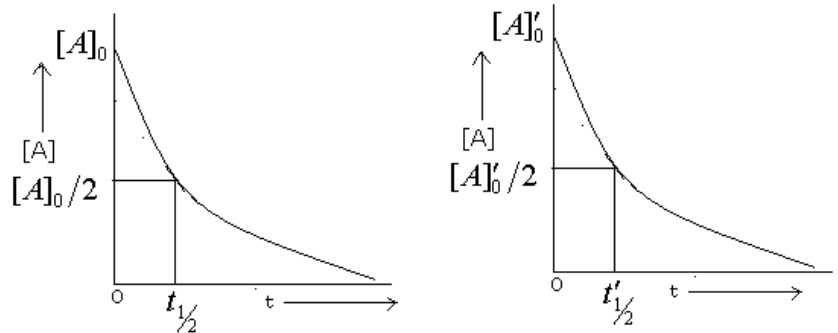
reaction with different initial conc. of reactant, $t_\phi / t'_\phi = ([A]_0' / [A]_0)^{n-1}$

Taking log, we have $\log \left(\frac{t_\phi}{t'_\phi} \right) = (n-1) \log \left(\frac{[A]_0'}{[A]_0} \right)$ or, $n = 1 + \frac{\log t_\phi - \log t'_\phi}{\log [A]_0' - \log [A]_0}$. If $t_\phi = t_{1/2}$, then it could

be obtained from the plot of $[A]$ vs. t. Reactant conc. $[A]$ are determined at different time intervals for the plot.

Ratio-variation method:

This method is widely used to evaluate the order of the reaction when more than one reactant are participating. For example, the reaction is $A + B \rightarrow \text{Products}$. The rate equation is $R = k[A]^\alpha[B]^\beta$, where α and β are the orders of the reaction with respect to A and B respectively. The overall order of the reaction is $\alpha + \beta$.



Let us consider one set of the reaction where [B] is kept constant while [A]₀ is doubled. If initial rates of the reaction in the two sets are considered, then $\frac{R_1^0}{R_2^0} = \frac{k([A]_0)^\alpha ([B]_0)^\beta}{k\{2[A]_0\}^\alpha ([B]_0)^\beta}$ or, $\frac{R_1^0}{R_2^0} = \frac{1}{2^\alpha}$, α can be determined.

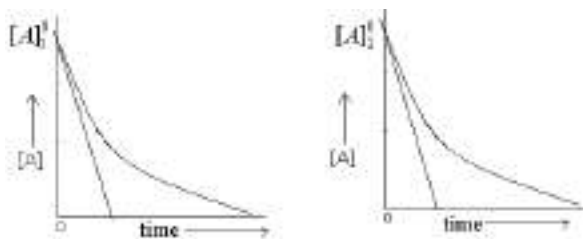
In another set, [A]₀ is kept same but [B]₀ is doubled so, $\frac{R_1^0}{R_3^0} = \frac{k([A]_0)^\alpha ([B]_0)^\beta}{k([A]_0)^\alpha \{2[B]_0\}^\beta}$ or, $\frac{R_1^0}{R_3^0} = \frac{1}{2^\beta}$,

thus β is obtained from R_1^0/R_3^0 . The overall order of the reaction is thus, $n = \alpha + \beta$.

(3) Differential method:

This method was suggested by Van't Hoff. The differential rate equation for two sets of n th order reaction is given as $R_1 = k_n[A]_1^n$ and $R_2 = k_n[A]_2^n$. The ratio of the initial rates is $\frac{R_1^0}{R_2^0} = \left\{ \frac{([A]_0)_1}{([A]_0)_2} \right\}^n$.

R_1^0 and R_2^0 are the initial rate of the two sets at initial conc. of the reactant, $([A]_0)_1$ and $([A]_0)_2$. These rates are determined from the slope of the tangent drawn at the initial conc. of the plot [A] vs. t.



Problem (1): The decomposition of acetaldehyde in gas phase was studied at 791K. The results of the study are:
 Initial conc. in mol L⁻¹ → 9.72 × 10⁻³ 4.56 × 10⁻³
 Half-life in sec → 328 572

(a) What is the order of the reaction? (b) Calculate the rate constant of the reaction.

Solution: We have the relation, $\frac{t_{1/2}}{t'_{1/2}} = \left(\frac{[A]_1}{[A]_2} \right)^{n-1}$. Putting the values, we get

$$\frac{572 \text{ sec}}{328 \text{ sec}} = \left(\frac{9.72 \times 10^{-3} \text{ mol L}^{-1}}{4.56 \times 10^{-3} \text{ mol L}^{-1}} \right)^{n-1}. \text{ Solving we get } n = 1.735. \text{ Again, } k = \frac{1}{(n-1)t_{1/2}} \left\{ \frac{2^{n-1} - 1}{[A]_0^{n-1}} \right\}.$$

Putting the 1st set values, we get

$$k = \frac{1}{(1.735-1)328 \text{ sec}} \left\{ \frac{2^{1.735-1} - 1}{(9.72 \times 10^{-3} \text{ mol L}^{-1})^{1.735-1}} \right\} = 0.083 \text{ (L/mol)}^{0.735} \text{ sec}^{-1}.$$

Problem (2): For the reaction, 2NO + Cl₂ → 2NOCl, it was found that on doubling the conc. of both reactants, the rate increases by eight-fold. But on doubling the conc. of Cl₂ alone, the rate only doubles. What is the order of the reaction with respect to NO and Cl₂?

[West Bengal Civil Service, 1995]

Solution: Let the rate equation, $R = k[NO]^\alpha [Cl_2]^\beta$ and the overall order of the reaction is $\alpha + \beta$.

Using the condition given, $8R = k\{2[NO]\}^\alpha \{2[Cl_2]\}^\beta$. Taking the ratio, $8 = 2^\alpha \times 2^\beta = 2^{\alpha+\beta} = 2^3$.

Thus $\alpha + \beta = 3$. Again, using the 3rd condition, we get $2 = 2^\beta$, so $\beta = 1$, hence $\alpha = 2$.

The reaction is 2nd order with respect to NO and 1st order with respect to Cl₂.

Problem (4): The rate of the reaction $2A + B \rightarrow C$ becomes doubled when the conc. of B is only doubled and the rate becomes eight fold when conc. of both A and B doubled. Find out the order of the reaction with respect to A and B.

Answer: 1st order with respect to A and 2nd order with respect to B. [Calcutta Univ. 2011]

Problem (3): For a reaction, $A \rightarrow B + C$, it is found that the rate increases by a factor 2.25 when the conc. of A is increased by a factor of 1.5 at the same temperature. What is the order with respect to A.

[Burdwan Univ. 1989]

Solution: We have $R_1/R_2 = ([A]_1/[A]_2)^n$ or, $2.25 = (1.5)^n$ or, $(1.5)^2 = (1.5)^n$ or, $n = 2$.

The reaction is 2nd order with respect to A.

Question: While it is expected that a larger amount of substance would take a longer time to decompose, the dependence of half life on the initial conc. does not indicate so, in general. Explain.

[Burdwan Univ. 1996]

Answer: Decomposition rate is not generally constant except zero order reaction. The rate equation shows that larger the initial amount of reacting substance, greater is its decomposition rate and smaller time is required to for its half decomposition. Only for zero order reaction, reaction rate is constant and so larger amount of the substance requires larger time and half decomposition time is proportional to initial conc. For other type of reactions, greater amount substance requires lesser time to decompose.

Question: The conc. of a reactant undergoing decomposition was 0.1, 0.08 and 0.067 mol L⁻¹ after 1.0, 2.0 and 3.0 hr respectively. The order of the reaction is

1. 0 2. 1 3. 2 4. 3 [NET (CSIR – UGC), 2011 (II)]

Answer: 3. 2 (2nd order). Hints: $-\frac{\Delta[A]}{\Delta t} \propto [A]^n$. Thus $-\frac{0.08-0.1}{2.0-1.0} \propto (0.1)^n$ and $-\frac{0.067-0.08}{3.0-2.0} \propto (0.08)^n$.

Solving we get $n = 2$.

Question: For the reaction $2NO + 2H_2 \xrightarrow{700^\circ C} N_2 + 2H_2O$

(i) Write the expression for the rate of the reaction in terms of the change in conc. of NO and H₂O.

(ii) Given the following data for the above reaction, find the order of the reaction with respect to

(a) NO and (b) H₂ and the rate constant for the reaction along with the proper unit.

	$[NO]_{t=0} (\text{mol dm}^{-3})$	$[H_2]_{t=0} (\text{mol dm}^{-3})$	Initial rate ($\text{mol dm}^{-3} \text{s}^{-1}$)
Experiment 1	0.025	0.01	2.4×10^{-6}
Experiment 2	0.025	0.005	1.2×10^{-6}
Experiment 3	0.0125	0.01	0.6×10^{-6}

[IIT-JAM, 20014]

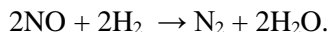
Answer: (i) $Rate = -\frac{1}{2} \frac{d[NO]}{dt} = \frac{1}{2} \frac{d[H_2O]}{dt}$. (ii) The order with respect to NO is 2 and with respect to H₂ is 1.

So the rate equation is $Rate = -\frac{1}{2} \frac{d[NO]}{dt} = k[NO]^2[H_2]$, putting the data in the experiment,

we get $2.4 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1} = k(0.025 \text{ mol dm}^{-3})^2 (0.01 \text{ mol dm}^{-3})$

or, $k = 0.384 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$. (See the Text for full answer.)

Question: The method of initial rates is used to determine the rate law for the reaction given below:



The following initial rates were determined.

P_{NO} (torr)	P_{H_2} (torr)	Initial Rate (torr/s)
200	400	0.46
400	200	0.92
400	400	1.85

These data imply which of the following rate law

(A) $Rate = k P_{NO}$ (B) $Rate = k P_{NO} P_{H_2}$ (C) $Rate = k P_{NO} P_{H_2}^2$ (D) $Rate = k P_{NO}^2 P_{H_2}$

(E) $Rate = k P_{NO}^2 P_{H_2}^2$

[GRE Sample Question]

Answer: (D)

COMPLEX OR SIMULTANEOUS REACTIONS:

Many reactions occur in multisteps instead of single step. These multistep reactions are complicated and rate equation does not correspond to the stoichiometric equation. The complex reactions are of three types:

(A) Reversible or opposing reactions (B) consecutive reactions and (C) side or parallel reactions.

We shall consider only the simplest most type of these reactions.

(A) Reversible or opposing reactions:

(Not to be confused with word "reversible" used in a thermodynamic process)

Simplest type is that both are 1st order reactions. The products formed react to give the reactants back. $A \xrightleftharpoons[k_{-1}]{k_1} B$. The differential rate equation is $-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$ -----(1)

But the conc. of A is $[A] = [A]_0 - [B]$, Inserting this, the rate equation becomes

$$\frac{d[B]}{dt} = k_1([A]_0 - [B]) - k_{-1}[B] \quad \text{or,} \quad \frac{d[B]}{dt} = k_1[A]_0 - (k_1 + k_{-1})[B]. \quad \text{----- (2)}$$

Separating the variables and integrating within limits, we get $\int_0^{[B]} \frac{d[B]}{k_1[A]_0 - (k_1 + k_{-1})[B]} = \int_0^t dt$.

$$\text{or,} \quad \frac{1}{(k_1 + k_{-1})} \ln \frac{k_1[A]_0}{k_1[A]_0 - (k_1 + k_{-1})[B]} = t \quad \text{or,} \quad \ln \frac{k_1[A]_0}{k_1[A]_0 - (k_1 + k_{-1})[B]} = (k_1 + k_{-1})t. \quad \text{----- (3)}$$

Special case: When the reverse rate is very slow, k_{-1} is very small and then $k_1 \gg k_{-1}$, the equation turns into

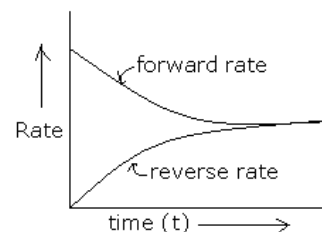
$$\ln \frac{[A]_0}{[A]_0 - [B]} = k_1 t \quad \text{or,} \quad \ln \frac{[A]_0}{[A]} = k_1 t \quad \text{-- a simple 1st order reaction.}$$

In the above reaction, both forward and backward steps occur simultaneously. At the start, rate of the forward step is maximum and it decreases as the reactant conc. is decreased. On the other hand, the rate of the backward step starts from zero and then increases as the product conc. increases. After some time, both the rates are equal and the reaction attains equilibrium. No further change occurs and overall rate of the reaction is zero.

So, in equation (2) at equilibrium $\frac{d[B]}{dt} = 0$ or, $k_1[A]_0 - (k_1 + k_{-1})[B]_e = 0$

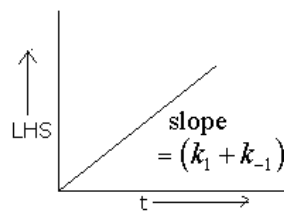
$$\text{or,} \quad k_1[A]_0 = (k_1 + k_{-1})[B]_e. \quad \text{----- (4)}$$

Putting this in the equation (3), $\ln \frac{[B]_e}{[B]_e - [B]} = (k_1 + k_{-1})t$. ----- (5)



Evaluation of k_1 and k_{-1} :

The values of $[B]$ at different time intervals, and at equilibrium, $[B]_e$ are determined. A plot of $\ln \frac{[B]_e}{[B]_e - [B]}$ vs. t could be made and from



the slope of the straight line, $(k_1 + k_{-1})$ can be known.

Again at equilibrium, $k_1[A]_0 = (k_1 + k_{-1})[B]_e$ or, $k_1([A]_0 - [B]_e) = k_{-1}[B]_e$ or, $k_1[A]_e = k_{-1}[B]_e$ so the equilibrium constant of the reaction, $K_e = \frac{k_1}{k_{-1}} = \frac{[B]_e}{[A]_e}$. Determination of equilibrium conc. of the product and

reactant gives the value of $\frac{k_1}{k_{-1}}$ and the individual value of k_1 and k_{-1} of the reaction are determined.

Otherwise, k_1 can be evaluated directly as given here. From equation (4), we have $k_1 + k_{-1} = \frac{k_1[A]_0}{[B]_e}$ -----(6)

Putting in equation (5), it becomes $\ln \frac{[B]_e}{[B]_e - [B]} = \frac{k_1[A]_0}{[B]_e} t$. The plot of LHS vs. t gives straight line with slope equal to $\frac{k_1[A]_0}{[B]_e}$ from which k_1 can be determined. Now from equation (6), k_{-1} of the reaction can be calculated.

Time required for $[B]$ to attain half of $[B]_e$:

Putting $[B] = \frac{1}{2} [B]_e$ in the equation (5), we get $\ln \frac{[B]_e}{[B]_e - (1/2)[B]_e} = (k_1 + k_{-1})t$ or, $t = \frac{\ln 2}{(k_1 + k_{-1})} = \frac{0.693}{(k_1 + k_{-1})}$.

It is the time when conc. of B produced half its equilibrium value.

Problem (a): In a first order reaction, $A \rightleftharpoons B$, the initial conc. of A and B are $[A]_0$ and zero respectively. At equilibrium, the conc. of A and B becomes $[A]_e$ and $[B]_e$ respectively. Derive an expression for the time taken by B to attain a conc. equal to $\frac{1}{2} [B]_e$.
[Union Public Service commission, 1992]

Solution: Shown above.

Problem (b): In the above problem, let $k_1 = 1.2 \times 10^{-3} \text{ sec}^{-1}$ and $k_{-1} = 3.3 \times 10^{-2} \text{ min}^{-1}$, find the time required to produce B to half of its equilibrium conc.

Solution: Given, $k_1 = (1.2 \times 10^{-3} \times 60) \text{ min}^{-1} = 7.2 \times 10^{-2} \text{ min}^{-1}$ and $k_{-1} = 3.3 \times 10^{-2} \text{ min}^{-1}$.

Thus, time required to produce B half of its equilibrium conc. is $t = \frac{0.693}{(7.2 + 3.3) \times 10^{-2} \text{ min}^{-1}} = 6.6 \text{ min}$.

Evaluation of conc. of A and B at equilibrium and at any time, t :

If the rate constants k_1 and k_{-1} , and the initial conc. of A, $[A]_0$ are known, we can find the conc. of A and B at equilibrium ($t \rightarrow \infty$), and at any time, t .

Evaluation of B at equilibrium: The equation (4) is $k_1[A]_0 = (k_1 + k_{-1})[B]_e$, so $[B]_e = \frac{k_1}{k_1 + k_{-1}} [A]_0$.

Evaluation of A at equilibrium: $[A]_e = [A]_0 - [B]_e = [A]_0 - \frac{k_1}{k_1 + k_{-1}} [A]_0$ or, $[A]_e = \frac{k_{-1}}{k_1 + k_{-1}} [A]_0$

Evaluation of B at any time t: The equation (5) is $\ln \frac{[B]_e}{[B]_e - [B]} = (k_1 + k_{-1})t$ or, $[B] = [B]_e \left[1 - e^{-(k_1 + k_{-1})t} \right]$.

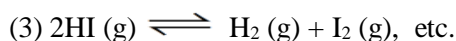
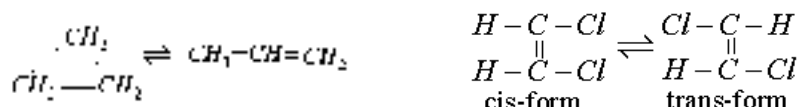
Putting the value of $[B]_e$, we have $[B] = \frac{k_1}{k_1 + k_{-1}} [A]_0 \left[1 - e^{-(k_1 + k_{-1})t} \right]$.

Evaluation of A at any time t: $[A] = [A]_0 - [B] = [A]_0 - \frac{k_1}{k_1 + k_{-1}} [A]_0 \left[1 - e^{-(k_1 + k_{-1})t} \right]$

$$= [A]_0 \left[1 - \frac{k_1}{k_1 + k_{-1}} \left\{ 1 - e^{-(k_1 + k_{-1})t} \right\} \right] = [A]_0 \left[\frac{k_{-1}}{k_1 + k_{-1}} + \frac{k_1}{k_1 + k_{-1}} e^{-(k_1 + k_{-1})t} \right] = \frac{k_1}{k_1 + k_{-1}} [A]_0 \left[\frac{k_{-1}}{k_1} + e^{-(k_1 + k_{-1})t} \right]$$

or,
$$[A] = \frac{k_1}{k_1 + k_{-1}} [A]_0 \left[\frac{k_{-1}}{k_1} + e^{-(k_1 + k_{-1})t} \right]$$

Examples: (1) Isomerisation of cyclopropane into propene (2) cis-trans Isomerisation of 1,2 dichloroethylene



Question: Consider the opposing reaction, $A \xrightleftharpoons[k_{-1}]{k_1} B$. Both the forward and backward processes are 1s order.

At t = 0, conc. a 0

At t = t, conc. (a - x) x. Write the rate equation and integrate. Show that the

expression may be written as $\ln \frac{x_e}{x_e - x} = (k_1 + k_{-1})t$, where x_e is the equilibrium value of x.

Discuss the case where $k_1 \gg k_{-1}$.

[Burdwan Univ. 1995]

Answer: See the Text as above in which $[B]_e = x_e$, $[B] = x$, $[A]_0 = a$ and $[A] = a - x$.

Problem: For the reaction, $A \xrightleftharpoons[k_{-1}]{k_1} B$, $k_1 = 5.65 \times 10^{-3} \text{ sec}^{-1}$, $k_{-1} = 7.6 \times 10^{-3} \text{ sec}^{-1}$ and initial conc.

of A is 0.15M. Find the $[A]_e$ and $[A]$ after 10 sec. [Answer: $[A]_e = 0.086 \text{ M}$ and $[A]_{10} = 0.142 \text{ M}$]

Question: For a reversible reaction $A \xrightleftharpoons[k_{-1}]{k_1} X$ in which both the forward and reverse reactions are first order and the initial conc. of A is a_0 and the equilibrium conc. of X is x_e , the value of k_{-1} in terms of k_1 is given by

(1) $k_1(a_0 - x_e)$ (2) $k_1 a_0 / x_e$ (3) $k_1(a_0 - x_e) / x_e$ (4) $k_1 x_e / (a_0 - x_e)$

Answer: (3)

[Adm to M Sc, BHU 2013]

Question: For the reaction $2\text{AB}_2 \rightleftharpoons \text{A}_2\text{B}_4$, the reaction rate for A_2B_4 formation is

(1) $2k_1[AB_2] - k_{-1}[A_2B_4]$ (2) $(2k_1 - k_{-1})[AB_2]$ (3) $\frac{2k_1}{k_{-1}}[AB_2]$ (4) $2k_1[AB_2]^2 - k_{-1}[A_2B_4]$

Answer: (4).

[Adm to M Sc, BHU 2015]

Question: For a reaction of the type $X \xrightleftharpoons[k_2]{k_1} Y$, the correct rate expression is ($[Z]_0$ and $[X]$ correspond to the conc. of X at time t = 0 and t = t, respectively)

(A) $-\frac{d[X]}{dt} = k_1[X]_0 - (k_1 + k_2)[X]$ (B) $-\frac{d[X]}{dt} = (k_1 + k_2)[X] - k_2[X]_0$

(C) $-\frac{d[X]}{dt} = (k_1 + k_2)[X]_0 - k_1[X]$ (D) $-\frac{d[X]}{dt} = (k_1 - k_2)[X] - k_1[X]_0$ [GATE, 2013]

Answer: (B). Hints: $-\frac{d[X]}{dt} = k_1[X] - k_2[Y] = k_1[X] - k_2([X]_0 - [X]) = (k_1 + k_2)[X] - k_2[X]_0$.

Question: For reaction involving two steps given below:

First step $G \rightleftharpoons 2H$ and second step: $G + H \rightarrow P$, assume that the first step attains equilibrium very rapidly. The rate of formation of P is proportional to

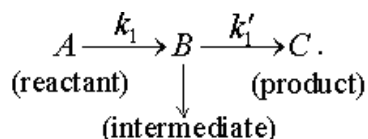
(A) $[G]^{1/2}$ (B) $[G]$ (C) $[G]^2$ (D) $[G]^{3/2}$. [GATE, 2012]

Answer: (D). Hints: $K_{eq} = [H]^2/[G]$ or, $[H] = \sqrt{K_{eq}} [G]^{1/2}$. Thus the rate of formation of P is

$$\frac{d[P]}{dt} = k[G][H] = (k\sqrt{K_{eq}})[G]^{3/2}.$$

(B) Consecutive reactions:

In this type of reaction, the product formed in one step acts as reactant in another step. The simplest type consists of two steps with one intermediate. Both steps are irreversible 1st order.



Let the initial conc. of A is $[A]_0$ and after any time t, conc. of A, B and C are $[A]$, $[B]$ and $[C]$ such that

$$[A]_0 = [A] + [B] + [C]. \text{----- (1)}$$

The rate equation for disappearance of A is $-\frac{d[A]}{dt} = k_1[A]$.

Separating and integrating the above, we get $[A] = [A]_0 e^{-k_1 t}$. ----- (2)

Rate equation for accumulation of B is $\frac{d[B]}{dt} = k_1[A] - k'_1[B]$ or, $\frac{d[B]}{dt} + k'_1[B] = k_1[A]_0 e^{-k_1 t}$.

Multiplying by integration factor $e^{k'_1 t}$, we get $\frac{d[B]}{dt} e^{k'_1 t} + k'_1[B] e^{k'_1 t} = k_1[A]_0 e^{-k_1 t} \times e^{k'_1 t}$

or, $\frac{d}{dt}([B] e^{k'_1 t}) = k_1[A]_0 e^{(k'_1 - k_1)t}$. Separating the variables and integrating, $[B] e^{k'_1 t} = \frac{k_1}{k'_1 - k_1} [A]_0 e^{(k'_1 - k_1)t} + Ic$.

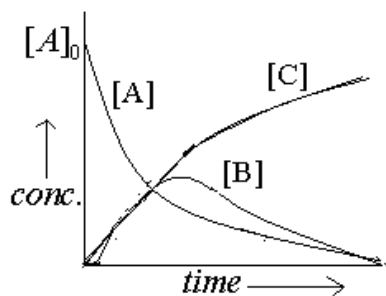
But when t = 0, $[B] = 0$ so, $Ic = -\frac{k_1}{k'_1 - k_1} [A]_0$. Now putting the value of Ic, we get

$$[B] e^{k'_1 t} = \frac{k_1}{k'_1 - k_1} [A]_0 (e^{(k'_1 - k_1)t} - 1) \text{ or, } [B] = \frac{k_1}{k'_1 - k_1} [A]_0 (e^{-k_1 t} - e^{-k'_1 t}). \text{----- (3)}$$

Now, $[C] = [A]_0 - [A] - [B]$ or, $[C] = [A]_0 - [A]_0 e^{-k_1 t} - \frac{k_1}{k'_1 - k_1} [A]_0 (e^{-k_1 t} - e^{-k'_1 t})$

$$\text{or, } [C] = [A]_0 \left\{ 1 - e^{-k_1 t} - \frac{k_1}{k'_1 - k_1} (e^{-k_1 t} - e^{-k'_1 t}) \right\} \text{ or, } [C] = [A]_0 \left\{ 1 - \frac{k'_1}{k'_1 - k_1} e^{-k_1 t} - \frac{k_1}{k_1 - k'_1} e^{-k'_1 t} \right\}. \text{----- (4)}$$

These (2), (3) and (4) are the expressions of $[A]$, $[B]$ and $[C]$ at time t after the start of the reaction. $[A]$, $[B]$ and $[C]$ change with time and it can be shown by plotting these conc. vs. time.



[A] starts from $[A]_0$ and decays exponentially with time. $[A] \rightarrow 0$ when $t \rightarrow \infty$.

[B] starts from 0 and attains maximum and then falls exponentially with increase of time. $[B] \rightarrow 0$ as $t \rightarrow \infty$.

[C] does not appear as B is not formed initially because B has to be formed first. This is induction period. However it becomes less important for the reaction when k'_1 is high.

Typical curve of variation of conc. vs. time during the progress of the reaction $A \xrightarrow{k_1} B \xrightarrow{k'_1} C$ in which k_1 is comparable to k'_1 .

Calculation of time at which [B] attains maximum:

Differentiating [B] with respect to t in equation (3) we get $\frac{d[B]}{dt} = \frac{k_1[A]_0}{k'_1 - k_1} (-k_1 e^{-k_1 t} + k'_1 e^{-k'_1 t})$.

But when $t = t_{\max}$, $\frac{d[B]}{dt} = 0$, so $0 = \frac{k_1[A]_0}{k'_1 - k_1} (-k_1 e^{-k_1 t_{\max}} + k'_1 e^{-k'_1 t_{\max}})$ or, $k_1 e^{-k_1 t_{\max}} = k'_1 e^{-k'_1 t_{\max}}$ ----- (5)

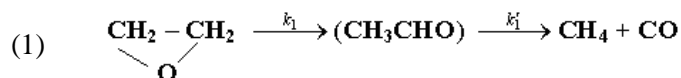
$$\text{or, } \frac{k_1}{k'_1} = e^{(k_1 - k'_1)t_{\max}} \quad \text{or, } t_{\max} = \frac{\ln k_1 - \ln k'_1}{k_1 - k'_1} \text{ ----- (6)}$$

Putting $t = t_{\max}$, we can get $[B]_{\max}$. Thus, $[B]_{\max} = \frac{[A]_0}{k'_1 - k_1} (k_1 e^{-k_1 t_{\max}} - k'_1 e^{-k'_1 t_{\max}}) = \frac{[A]_0}{k'_1 - k_1} (k'_1 e^{-k'_1 t_{\max}} - k_1 e^{-k_1 t_{\max}})$

or, $[B]_{\max} = [A]_0 e^{-k'_1 t_{\max}}$. Putting t_{\max} from equation (6), we get $[B]_{\max} = [A]_0 \left(\frac{k'_1}{k_1}\right)^{\frac{k_1}{k_1 - k'_1}}$.

[Mathematics: $k_1 t_{\max} = \frac{k'_1}{k_1 - k'_1} \ln \frac{k_1}{k'_1}$ or, $-k'_1 t_{\max} = \frac{k'_1}{k_1 - k'_1} \ln \frac{k'_1}{k_1} = \ln \left(\frac{k'_1}{k_1}\right)^{\frac{k'_1}{k_1 - k'_1}}$ or, $e^{-k'_1 t_{\max}} = \left(\frac{k'_1}{k_1}\right)^{\frac{k'_1}{k_1 - k'_1}}$.]

Examples of simple consecutive reactions:



Two important conclusions:

From the equations of this type of reaction, it is possible to draw two useful concepts which are very much helpful to derive the differential rate law of multistep complex reactions.

(1) Slowest step is rate determining step in multistep reactions:

Let the reaction is $A \xrightarrow{k_1} B \xrightarrow{k'_1} C$ i.e. $k_1 \gg k'_1$.

Then, $[C] = [A]_0 \left\{ 1 - \frac{k'_1}{k'_1 - k_1} e^{-k_1 t} - \frac{k_1}{k_1 - k'_1} e^{-k'_1 t} \right\}$, but $k_1 - k'_1 \approx k_1$, $k'_1 - k_1 \approx -k_1$

$[C] = [A]_0 \left\{ 1 + \frac{k'_1}{k_1} e^{-k_1 t} - e^{-k'_1 t} \right\}$, again $\frac{k'_1}{k_1}$ is also small, and $e^{-k_1 t}$ is very small so $\frac{k'_1}{k_1} e^{-k_1 t} \rightarrow 0$.

The conc. of C under this condition is $[C] = [A]_0 (1 - e^{-k'_1 t})$.

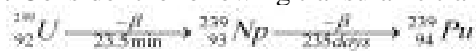
The formation of product C is controlled by the slowest step and it appears as the reaction $A \xrightarrow{k_1'} C$ and its rate equation is $\frac{d[C]}{dt} = k_1'[A] = k_1'([A]_0 - [C])$, separating and integrating within limits, we get

$$[C] = [A]_0(1 - e^{-k_1't})$$

This concludes that slowest step decides the formation of product and it is the elementary step that becomes the rate determining step.

Similarly, if $A \xrightarrow[\text{slow}]{k_1} B \xrightarrow[\text{fast}]{k_1'} C$, $[C] = [A]_0(1 - e^{-k_1't})$, the reaction appears as $A \xrightarrow{k_1} C$.

Problem: Consider the following transuranic transformation with half life as indicated



If one starts with 10^{16} number of uranium atoms initially, approximately how many plutonium atoms will be created after 400 days. **[Burdwan Univ. 1991]**

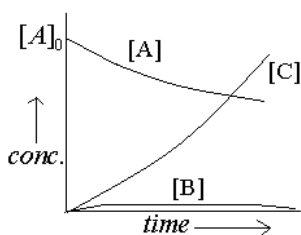
Solution: $N_{Pu} = N_U^0 \left(1 - \frac{k_1'}{k_1' - k_1} e^{-k_1 t} - \frac{k_1}{k_1 - k_1'} e^{-k_1' t} \right)$, but $t_{1/2} \ll t_{1/2}'$ so $k_1 \gg k_1'$ thus $N_{Pu} = N_U^0 (1 - e^{-k_1' t})$.

Now putting the values, we get $N_{Pu} = 10^{16} \left(1 - e^{-\frac{0.693}{235\text{days}} \times 400\text{days}} \right) = 6.9 \times 10^{15}$.

Thus, number of Pu atoms will be created approximately after 400 days = 6.9×10^{15} .

(2) Steady-state approximation of the reactive intermediate:

When the intermediate is highly reactive, situation becomes such that as soon as B forms, it immediately breaks into product, C. The conc. vs. time curve under this situation is shown as under:



[A] decreases slowly as k_1 is small. [B] remains practically low and constant during the progress of the reaction except at the beginning (when [B] has to build from zero) and at the end (when it must drop to zero). [C] also increases at the rate of [A] decomposes to the intermediate B. The conc. of B from the equation (3)

$$[B] = \frac{k_1}{k_1' - k_1} [A]_0 (e^{-k_1 t} - e^{-k_1' t})$$

but for the reaction $A \xrightarrow[\text{slow}]{k_1} B \xrightarrow[\text{fast}]{k_1'} C$, $k_1' \gg k_1$ as B is highly reactive and so short-lived.

So, $[B] = \frac{k_1}{k_1'} [A]_0 e^{-k_1 t} = \frac{k_1}{k_1'} [A]$ or, $k_1 [A] = k_1' [B]$

i.e. rate of formation of B ($k_1 [A]$) is equal to the rate of decomposition of B ($k_1' [B]$), thus [B] remains steady and $\frac{d[B]}{dt} = 0$. It means that rate of accumulation of B is zero. This is known as steady-state approximation.

This principle states that when the intermediate is highly reactive, its conc. remains low and steady during the reaction and $\frac{d[\text{intermediate}]}{dt} = 0$. This concept helps to solve the kinetics of multistep reactions.

The above consecutive reaction can be taken for illustration to show how the kinetics becomes simple when the intermediate, B is highly reactive and the above concept is applied.

$\frac{d[B]}{dt} = k_1 [A] - k_1' [B]$, but $\frac{d[B]}{dt} = 0$, if B is highly reactive. Thus, $[B] = \frac{k_1}{k_1'} [A]$ or, $[B] = \frac{k_1}{k_1'} [A]_0 e^{-k_1 t}$.

Thus by using the steady-state concept, it is possible to know the conc. of the intermediate.

Now the rate of formation of the product, C is $\frac{d[C]}{dt} = k_1' [B] = k_1' \times \frac{k_1}{k_1'} [A]_0 e^{-k_1 t} = k_1 [A]_0 e^{-k_1 t}$.

Separating the variables and integrating within limits, we can get $[C] = [A]_0 (1 - e^{-kt})$.

Thus, it is easy to formulate the kinetics of the reaction by using this steady-state principle.

Example: [Burdwan Univ. 2003] The reaction, $2NO + O_2 \xrightarrow{k} 2NO_2$ follows the reaction mechanism, $2NO \xrightleftharpoons{K_e} N_2O_2$ (rapid)----- (1) and $N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ (slow). Formulate the rate equation and show that observed rate constant (k) decreases with increase of temperature.

Answer: $\frac{1}{2} \frac{d[NO_2]}{dt} = k_2 [N_2O_2][O_2]$. But the intermediate conc. is obtained by first rapid equilibrium step,

$K_e = \frac{[N_2O_2]}{[NO]^2}$ or, $[N_2O_2] = K_e [NO]^2$. The rate equation of the reaction according to the mechanism is

$\frac{1}{2} \frac{d[NO_2]}{dt} = (k_2 K_e) [NO]^2 [O_2] = k [NO]^2 [O_2]$, where the observed rate constant $k = k_2 K_e$

The reaction is 2nd order with respect to NO and 1st order with respect to O₂. Further, the rate constant (k₂) behaves normally and increases with temperature. The equilibrium constant (K_e) decreases with increase of temperature as the dimerisation process, $2NO \xrightleftharpoons{K_e} N_2O_2$ (rapid) is exothermic in nature. The decrease of K_e is sufficiently large to make the term (k₂K_e) to decrease with increase of temperature.

Statement: For the reaction $2NO + O_2 \xrightarrow{k} 2NO_2$, the rate constant is observed to decrease with temperature.

Reason: As per the proposed mechanism, first step is the dimerisation of nitric oxide which is exothermic.

Assertion: Rate law = k₂ K [NO]²[O₂]. **[GATE, 2005]**

Question: Consider the following reaction scheme involving equilibrium followed by a rate determining step.

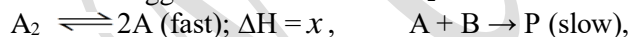
The apparent rate constant for the formation of the product is given by



(A) K (B) k/K (C) kK (D) k + K **[Adm to Hyderabad Central Univ. 2014]**

Answer: (C).

Question: The reaction mechanism suggested for a reaction $A_2 + 2B \rightarrow 2P$ is as follows:



where A is a reaction intermediate and K is the equilibrium constant of the first step. Deduce the rate law for the reaction. What can you say about the sign of x if the overall rate constant is found to decrease as temperature increases. **[Calcutta Univ. 2012], [Adm to M Sc, BHU, 2015]**

Answer: The of the reaction, $\frac{d[P]}{dt} = k_2 [A][B]$, where k₂ is rate constant of the 2nd step. Using $K = \frac{[A]^2}{[A_2]}$ for

the fast step, we have $[A] = K[A_2]$. Putting in the rate equation, we get the rate law as

$\frac{d[P]}{dt} = k_2 \sqrt{K[A_2]} [B]$ or, $\frac{d[P]}{dt} = (k_2 \sqrt{K}) [A_2]^{1/2} [B]$. But the overall rate law is

$\frac{d[P]}{dt} = k [A_2]^{1/2} [B]$, where $k = k_2 \sqrt{K}$. This overall rate constant, k is found to decrease with

increase of temperature. Since, k₂ increase with rise of T, Hence K is decreased with rise of T and this is possible only when the first reaction is exothermic and so the sign of x = (-ve).

Question: A consecutive chemical reaction, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ is first at both the stages with rate constant as k₁ and k₂. The time required to attain the maximum conc. B is given by

$$(1) \frac{0.693}{k_1 + k_2} \quad (2) \frac{(\ln k_1 - \ln k_2)}{(k_1 - k_2)} \quad (3) \frac{(\ln k_1 + \ln k_2)}{(k_1 + k_2)} \quad (4) \frac{(k_1 + k_2)}{(k_1 - k_2)}$$

Answer: (2)

[Adm to M Sc, BHU 2013]

Question: The energy of activation for the decomposition of NO_2 into NO and O_2 is negative which may be due to one of the following:

- (1) Increase of entropy on decomposition of NO (2) Formation of stable intermediate
 (3) Formation of free radicals (4) Decrease of enthalpy on formation of NO and O_2 .

Answer: (4).

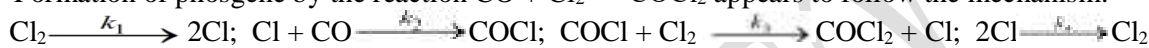
[Adm to M Sc, BHU 2013]

Question: For the reaction of the type, $\text{P} \xrightarrow{k_1} \text{Q} \xrightarrow{k_2} \text{R}$, given that $[\text{P}]_0 = 1.0 \text{ M}$; $k_1 = 1 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 1 \times 10^{-4} \text{ s}^{-1}$, the time at which the conc. of Q and R are 0.5966 M and 0.0355 M , respectively, is
 (a) 500 s (b) 750 s (c) 1000 s (d) 1500 s. [GATE, 2004]

Answer: Correct option (c). Hints: $[\text{P}] = [\text{P}]_0 - [\text{Q}] - [\text{R}] = (1.0 - 0.5966 - 0.0355) \text{ M} = 0.3679 \text{ M}$.

Using the 1st step, we get the time, $t = \frac{1}{k_1} \ln \frac{[\text{P}]_0}{[\text{P}]} = \frac{1}{1 \times 10^{-3} \text{ s}^{-1}} \ln \frac{1.0 \text{ M}}{0.3679 \text{ M}} = 1000 \text{ s}$.

Question: Formation of phosgene by the reaction $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ appears to follow the mechanism:



Assuming that the intermediates COCl and Cl are in a steady state, find the rate law for the formation of COCl_2 . [GATE, 2000]

Answer: $\frac{d[\text{COCl}_2]}{dt} = k_3[\text{COCl}][\text{Cl}_2]$ and $\frac{d[\text{COCl}]}{dt} = k_2[\text{CO}][\text{Cl}] - k_3[\text{COCl}][\text{Cl}_2] - k_4[\text{COCl}] = 0$ ----- (1) and

$\frac{d[\text{Cl}]}{dt} = 2k_1[\text{Cl}_2] - k_2[\text{CO}][\text{Cl}] + k_3[\text{COCl}][\text{Cl}_2] + k_4[\text{COCl}] - 2k_5[\text{Cl}]^2 = 0$ ----- (3). Adding (2) and (4),

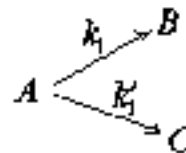
$[\text{Cl}] = \sqrt{k_1/k_5} [\text{Cl}_2]^{1/2}$. So, $[\text{COCl}] = \frac{k_2[\text{CO}][\text{Cl}]}{k_3[\text{Cl}_2] + k_4} = \frac{k_2(\sqrt{k_1/k_5})[\text{CO}][\text{Cl}_2]^{1/2}}{k_3[\text{Cl}_2] + k_4}$. From it, rate law is derived

(C) Parallel or side reactions:

The reactants decompose in more than one way yielding different sets of products with different rate constants. The reaction producing maximum amount product is called main or major reaction and other is side reaction.

The simplest type is that both the reactions are of first order and irreversible (so that products are not inter-convertible).

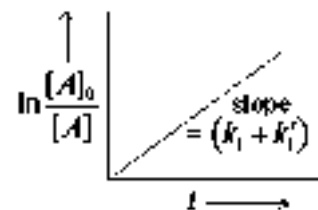
The rate equation is, $-\frac{d[\text{A}]}{dt} = \frac{d[\text{B}]}{dt} + \frac{d[\text{C}]}{dt} = k_1[\text{A}] + k'_1[\text{A}]$



or, $-\frac{d[\text{A}]}{dt} = (k_1 + k'_1)[\text{A}]$. Separating the variables and integrating within limits, the integrated rate law is

$\ln \frac{[\text{A}]_0}{[\text{A}]} = (k_1 + k'_1)t$ ----- (1). So the plot of $\ln \frac{[\text{A}]_0}{[\text{A}]}$ vs. t gives

a straight line and its slope gives the value of $(k_1 + k'_1)$. Again, since both the



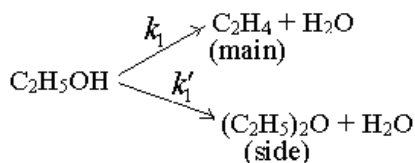
steps are of same order, hence $\frac{\text{rate formation of B}}{\text{rate formation of C}} = \frac{k_1[\text{A}]}{k'_1[\text{A}]} = \frac{k_1}{k'_1}$

or, $\frac{\text{formation of B at the end}}{\text{formation of C at the end}} = \frac{k_1}{k'_1}$ ----- (2).

So from the equations (1) and (2) individual values of k_1 and k'_1 can be evaluated.

Equation (2) refers to **Wegscheider's test** which states that the ratio of conc. of B and C at any time becomes constant if both the parallel reactions are of same order. This test is used to differentiate parallel reaction from opposing and consecutive reactions.

Examples: (1) Dehydration of ethanol (2) Formation of α - D glucose and β - D glucose in solution from aldehydic forms of D - glucose.
 (3) Nitration of phenol gives o-nitro phenol (main product) and p-nitro phenol (side product).



Calculation of [A], [B] and [C] at time t:

From equation (1) we have $\ln \frac{[A]_0}{[A]} = (k_1 + k'_1)t$ so, $[A] = [A]_0 e^{-(k_1+k'_1)t}$.

Again, $\frac{d[B]}{dt} = k_1[A] = k_1[A]_0 e^{-(k_1+k'_1)t}$ or, $d[B] = k_1[A]_0 e^{-(k_1+k'_1)t} dt$. Integrating within limits, we get

$$\int_0^{[B]} d[B] = k_1[A]_0 \int_0^t e^{-(k_1+k'_1)t} dt \quad \text{or,} \quad [B] = \left(\frac{k_1}{k_1 + k'_1} \right) [A]_0 \left\{ 1 - e^{-(k_1+k'_1)t} \right\}.$$

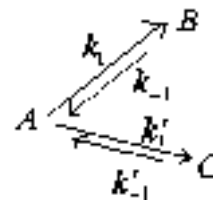
Similarly, since $\frac{[B]}{[C]} = \frac{k_1}{k'_1}$, so the conc. of C, $[C] = \left(\frac{k'_1}{k_1 + k'_1} \right) [A]_0 \left\{ 1 - e^{-(k_1+k'_1)t} \right\}$.

In this type, the products are not inter-convertible as the reactions are irreversible. So under this condition, the product formed rapidly will be the one that dominates in the products. Such reactions are called kinetically controlled reactions and the most rapidly formed product is known as the **kinetically controlled product**.

When the products are inter-convertible:

This case is possible when both the reactions are reversible with appreciable rate constants, B may react to give the product, C and vice-versa. $B \rightleftharpoons C$

(1) If we wait an infinite time so that the system reaches equilibrium, the thermodynamically stable product dominates in the final products and the relative amount of B and C is determined by the ratio of their equilibrium constants.



$$\frac{[B]_e/[A]_e}{[C]_e/[A]_e} = \frac{K_1}{K'_1} \quad \text{or,} \quad \frac{[B]_e}{[C]_e} = \frac{K_1}{K'_1} \quad \text{at } t \rightarrow \infty \text{ i.e. the reaction at equilibrium.}$$

This reaction is equilibrium controlled reaction. The most stable product (having lowest G^0 value) dominates in the final products. Thus it is also called **thermodynamically controlled product**.

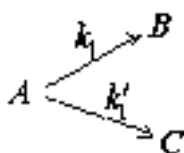
(2) On the otherhand, during the early stages of the reaction when any reverse or inter-conversion of B and C are negligible,

$\frac{[B]}{[C]} = \frac{k_1}{k'_1}$. Higher value of rate constant dominates in the products and we have **kinetically controlled product**.

If the rate constants k_{-1} and k'_{-1} are much less than those for the forward reactions k_1 and k'_1 , the product will be kinetically controlled even when A has been nearly all consumed.

(3) It frequently happens that $k_1 \gg k'_1$ but $K_1 \ll K'_1$, then B is favoured kinetically and C is favoured thermodynamically. At the early stages, B will be kinetically controlled main product but at infinite time (at equilibrium), C will be thermodynamically controlled product.

Problem:



For a parallel reaction with k_1 and k'_1 equal to $3.42 \times 10^{-2} \text{ min}^{-1}$ and $1.14 \times 10^{-2} \text{ min}^{-1}$ respectively. Calculate the % of A converted into B and C and also find the ratio of [B] and [C] after 20 min.

Solution: The equation (1) gives $\ln \frac{[A]_0}{[A]} = (k_1 + k_1')t$ or, $\frac{[A]}{[A]_0} = e^{-(k_1+k_1')t}$. Putting the values given, we get

$$\frac{[A]}{[A]_0} = e^{-(3.42+1.14) \times 10^{-2} \text{ min} \times 20 \text{ min}} = e^{-0.912} = 0.40 = 40\% .$$

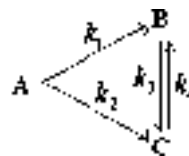
So the % of A converted into B and C after 20 min = 100 – 40 = 60.

Again, from equation (2), we get $\frac{[B]}{[C]} = \frac{k_1}{k_1'} = \frac{3.42 \times 10^{-2} \text{ min}^{-1}}{1.14 \times 10^{-2} \text{ min}^{-1}} = 3$. This is the ratio of B and C after 20 min.

Question: For the following chemical reactions $A \xrightarrow{k_1} B$, $A \xrightarrow{k_2} C$, $B \xrightarrow{k_3} C$, $C \xrightarrow{k_4} B$,
The rate constants k_1 and k_2 are at least 1000 times slower than either k_3 and k_4 . During the course of the above reactions the ratio of the products B and C will be

A) $[B]/[C] = k_3/k_4$ B) $[B]/[C] = k_4/k_3$ C) $[B]/[C] = k_2 k_3/k_1 k_4$ D) $[B]/[C] = k_1/k_2$.

Answer: B). The above four reactions show that the products B and C are interconvertible with high speeds



[Adm to M Sc TIFR, 2014]

Question: The overall rate law of the following complex reaction,

$2A \xrightleftharpoons{K_1} A_2$ (fast equilibrium); $A + B \xrightleftharpoons{K_2} C$ (fast equilibrium); $A_2 + C \xrightarrow{k_3} P + 2A$ (slow)
by steady state approximation would be

(1) $K_1 K_2 k_3 [A]^3 [B]$ (2) $K_2 K_1 k_3 [A] [B]^3$ (3) $K_1 K_2 k_3 [A] [B]^2$ (4) $K_1 K_2 k_3 [A] [B]$

[NET (CSIR – UGC), 2011(II)]

Answer: The correct option is (1). Hints: Overall rate $\frac{d[P]}{dt} = k_3 [A_2][C]$. But using the steady state

approximation, we have $[A_2] = K_1 [A]^2$, and $[C] = k_2 [A][B]$. Inserting these conc. in the rate law,

we get $\frac{d[P]}{dt} = K_1 K_2 k_3 [A]^3 [B]$.

Effect of temperature on rate constant – Arrhenius equation:

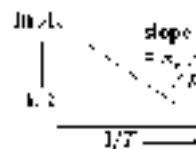
Rate constant (k) of a reaction strongly depends on temperature. For many reactions in solution near at room temperature, k becomes doubles to triples for 10^0 rises in temperature.

The temperature coefficient of rate constant, $\frac{k_{T+10}}{k_T} \approx 2$ to 3. or, $\frac{k_T}{k_{T+10}} \approx \frac{1}{2}$ to $\frac{1}{3}$.

In 1889, Svante Arrhenius noted that for many reactions, the relation $k = A e^{-E_a/RT}$ holds good. A and E_a are constants for a reaction. A is called pre-exponential term, sometimes called Arrhenius factor and E_a is activation energy.

Evaluation of the constants A and E_a : Taking logarithm of the above relation, we get $\ln k = \ln A - \left(\frac{E_a}{R}\right) \frac{1}{T}$.

When rate constant (k) of a reaction is determined at different temperatures and $\ln k$ is plotted against $(1/T)$, a straight line is obtained. The slope of the curve gives the value $-(E_a/R)$ from which E_a is determined experimentally.



This is the only method to determine activation energy (E_a). The reactions that give such straight line curve are called Arrhenius-type of reactions. Activation energy of a reaction is the excess energy that reactants must have to acquire to undergo chemical reaction. Pre exponential term may be determined from the intercept of the curve.

Activation energy (E_a) can also be determined approximately by knowing the rate constant of the reaction at two different temperatures, $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$, where k_1 and k_2 are the determined rate constants at the two temperatures, T_1 and T_2 .

Once E_a of a reaction is known, it becomes easy to calculate the rate constant and thus the rate of the reaction at any other temperature. Differentiation form of the Arrhenius equation is given as $\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$.

Formulation of Arrhenius equation:

Let us consider a reversible reaction, $A \xrightleftharpoons[k_{-1}]{k_1} B$ and the equilibrium constant, $K = k_1/k_{-1}$.

The variation of K with T is given by van't Hoff equation, $\frac{d \ln K}{dT} = \frac{\Delta E}{RT^2}$,

where $\Delta E = \text{heat of reaction} = E_B - E_A = (E_X - E_A) - (E_X - E_B) = E_{a,1} - E_{a,-1}$. When the reactant A attains the energy, E_X , it breaks down into products, B and $E_X - E_A = E_{a,1}$, activation of the forward reaction and $E_X - E_B = E_{a,-1}$, the activation energy of the backward reaction.

Putting in the van't Hoff equation, we get $\frac{d \ln(k_1/k_{-1})}{dT} = \frac{E_{a,1} - E_{a,-1}}{RT^2}$. Separating the equation for forward and

backward reactions, $\frac{d \ln k_1}{dT} = \frac{E_{a,1}}{RT^2} + C$ (constant) and $\frac{d \ln k_{-1}}{dT} = \frac{E_{a,-1}}{RT^2} + C$ (constant). C is any value

including zero. Arrhenius took the value of $C = 0$.

So the Arrhenius equation in general is written as $\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$ or, $E_a = RT^2 \frac{d \ln k}{dT}$.

Again, $\int d \ln k = \frac{E_a}{R} \int \frac{dT}{T^2}$ or, $\ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$ or, $\ln\left(\frac{k}{A}\right) = -\frac{E_a}{R} \cdot \frac{1}{T}$ or, $k = Ae^{-E_a/RT}$.

E_a is assumed constant and independent of temperature.

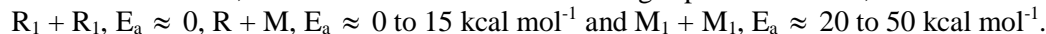
Characteristics of Arrhenius equation: The equation, $k = Ae^{-E_a/RT}$ implies the following characteristics:

- The rate constant (k) increases exponentially with increase of temperature (T).
- Reactions having higher value of activation energy (E_a) will have smaller value of k and the reaction will proceed at slower rate.
- For reactions having zero activation energy ($E_a = 0$), $k = A$, independent of temperature. The reaction proceeds with optimum rate. Free radical recombination reactions are of this type (such as, $\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$).

(d) Temperature co-efficient of rate constant, $\frac{k_{T+10}}{k_T} = \frac{Ae^{-E_a/R(T+10)}}{Ae^{-E_a/RT}} = e^{\frac{E_a}{RT} - \frac{E_a}{R(T+10)}} = e^{\frac{10E_a}{RT(T+10)}}$.

- Temperature co-efficient is large for the reactions having large value of E_a and it means that reactions of high activation energy are more sensitive to temperature change.
- Temperature co-efficient is also larger at lower temperature than at higher temperature.

With zero activation energy, the rate constant is essentially temperature-independent. If R denotes a free radical and M is closed-shell molecule, then for exothermic bimolecular gas phase reactions,



Apparent exception of the Arrhenius equation:

Many complex (multi-step) reactions are found to proceed slowly at higher temperature. In these reactions, the activation energy is (-ve). One example is the reaction between NO and O₂, 2NO + O₂ → 2NO₂. The observed rate constant is found to decrease with increase of rise of temperature and according to Arrhenius equation, the activation energy becomes (-ve).

In some reactions, the Arrhenius plot is found to be curved. This indicates that the activation energy is a function of T. Advanced theoretical formulation of rate constant is $k = aT^m e^{-E_a/RT}$ or $\frac{k}{T^m} = a e^{-E_a/RT}$.

In that case, $\ln\left(\frac{k}{T^m}\right)$ vs. $\frac{1}{T}$ will give straight line and from the slope $-\left(\frac{E_a}{R}\right)$, E_a can be obtained.

For explanation, see the text.

Problem (1): The rate constant of a reaction is $1.5 \times 10^7 \text{ sec}^{-1}$ at 50 °C and $4.5 \times 10^7 \text{ sec}^{-1}$ at 100 °C.

Evaluate the Arrhenius parameters A and E_a .

[IIT, KGP 1995, Adm to B. Tech.]

Solution: Using the Arrhenius equations $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$ and $k = A e^{-E_a/RT}$

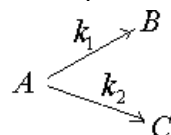
and putting the data, we get the answer, $E_a = 5294 \text{ cal/mol}$ and $A = 5.4 \times 10^{10} \text{ sec}^{-1}$.

Problem (2): A bottle of milk stored at 30 °C sours in 36 hrs. When the same milk is stored at 5 °C sours after one week. Assuming that the rate constant to be inversely related to the souring time, estimate the activation energy of a chemical reaction associated with the souring process.

Solution: According to the condition, $k \propto \frac{1}{t}$ (where t is souring time). Thus the Arrhenius equation when

applied for the process, we get $\ln \frac{t_1}{t_2} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$. Putting the data, we get $E_a = 43.15 \text{ kJ mol}^{-1}$.

Problem (3): For two parallel reactions, show that the activation energy, E for the disappearance of A is given in terms of activation energy E_1 and E_2 for the two paths by



$$E = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}. \quad [\text{Burdwan Univ. 2002, 2005, 2007, IIT, KGP, 2001}]$$

Solution: Arrhenius equation is $\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2}$ or, $\frac{1}{k_1} \left(\frac{dk_1}{dT} \right) = \frac{E_1}{RT^2}$ or, $\frac{dk_1}{dT} = \frac{k_1 E_1}{RT^2}$ and $\frac{dk_2}{dT} = \frac{k_2 E_2}{RT^2}$ is for

2nd parallel reaction. Now, $\frac{dk_1}{dT} + \frac{dk_2}{dT} = \frac{k_1 E_1 + k_2 E_2}{RT^2}$ or, $\frac{d(k_1 + k_2)}{dT} = \frac{k_1 E_1 + k_2 E_2}{RT^2}$. Again for disappearance

of A, the equation is $\frac{dk}{dT} = \frac{k E}{RT^2}$ or $\frac{d(k_1 + k_2)}{dT} = \frac{k E}{RT^2}$ as $k_1 + k_2 = k$. Equating, we get $E = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$.

Problem (4): State Arrhenius equation showing the variation of k with T. The specific rate constant (k) for a reaction depends on T as $k = B\sqrt{T} 10^{-C/T}$. Express the energy of activation in terms of C.

[Burdwan Univ. 2000]

Answer: 1st part: Arrhenius equation that shows the variation of k with T is $k = A e^{-E_a/RT}$ or $\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$.

2nd part: Given, $k = B\sqrt{T} 10^{-C/T}$ or, $\log k = \log B + \frac{1}{2} \log T - \frac{C}{T}$ or, $\ln k = \ln B + \frac{1}{2} \ln T - \frac{2.303 C}{T}$.

$$\text{Differentiating, } \frac{d \ln k}{dT} = 0 + \frac{1}{2T} + \frac{2.303 C}{T^2} = \frac{d \ln k}{dT} = \frac{2.303 C + (1/2)T}{T^2}.$$

$$\text{Equating with Arrhenius equation, } \frac{d \ln k}{dT} = \frac{E_a}{RT^2}, \text{ we get } E_a = 2.303RC + \frac{1}{2}RT.$$

Question (5): The rate law of one the mechanisms of pyrolysis of acetaldehyde at 520 °C and 0.2 bar is

$$\text{Rate} = - \left[k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} \right] [\text{CH}_3\text{CHO}]^{3/2}.$$

The overall activation energy (E_a) in terms of the rate law is

$$(1) E_a(2) + E_a(1) + 2E_a(4) \quad (2) E_a(2) + \frac{1}{2}E_a(1) - E_a(4) \quad (3) E_a(2) + \frac{1}{2}E_a(1) - \frac{1}{2}E_a(4)$$

$$(4) E_a(2) - \frac{1}{2}E_a(1) + \frac{1}{2}E_a(4).$$

[NET (CSIR – UGC), 2010]

Answer: Overall rate constant, $k = k_2 \left(\frac{k_1}{2k_4} \right)^{1/2}$. Using Arrhenius equation of T-dependence of rate constant,

$$\text{we have } Ae^{-E_a/RT} = A_2 e^{-E_a(2)/RT} \left[\frac{A_1 e^{-E_a(1)/RT}}{2A_4 e^{-E_a(4)/RT}} \right]^{1/2} = \left[A_2 \left(\frac{A_1}{2A_4} \right)^{1/2} \right] e^{- \left[\frac{E_a(2) + \frac{1}{2}E_a(1) - \frac{1}{2}E_a(4)}{RT} \right]}.$$

Equating we get the overall activation energy, $E_a = E_a(2) + \frac{1}{2}E_a(1) - \frac{1}{2}E_a(4)$. Correct option is (3).

Question(6): For a reaction, the rate constant at 25 °C is doubled when the temperature is raised to 45 °C.

The activation energy (in kJ mol⁻¹) of the reaction is ----- (Given ln 2 = 0.69)

Answer: 27.29

[IIT – JAM, 2015]



Question(7): For the opposing reaction

The forward reaction has values $E_a = 100 \text{ kJ mol}^{-1}$ and $A = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

The equilibrium conc. of A, B, C and D are 1.0 M, 2.0 M, 5.0 M and 4.0 M respectively at 700 K.

(1) The values of k_1 and k_{-1} , respectively, at this temperature are

- (a) $20 \text{ M}^{-1} \text{ s}^{-1}$ and $2.0 \text{ M}^{-1} \text{ s}^{-1}$ (b) $345 \text{ M}^{-1} \text{ s}^{-1}$ and $34.5 \text{ M}^{-1} \text{ s}^{-1}$ (c) $34.5 \text{ M}^{-1} \text{ s}^{-1}$ and $3.45 \text{ M}^{-1} \text{ s}^{-1}$
 (d) $200 \text{ M}^{-1} \text{ s}^{-1}$ and $20 \text{ M}^{-1} \text{ s}^{-1}$.

(2) The rate constant (k_1) for the forward reaction at 1000 K is

- (a) $5.98 \times 10^4 \text{ M}^{-1} \text{ min}^{-1}$ (b) $5.98 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ (c) $1.00 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (d) $5.98 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$

Answer: In (1), the correct option is (b) and in (2) the correct option is (d).

[GATE, 2003]

$$\text{Hints: } k_1 = Ae^{-E_a/RT} = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \times e^{-100 \text{ kJ mol}^{-1} / (8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \times 300 \text{ K})} = 342 \text{ M}^{-1} \text{ s}^{-1}.$$

$$\text{Equilibrium constant } K_e = k_1/k_{-1} = ([C][D])/([A][B]) = (5.0 \text{ M} \times 4.0 \text{ M})/(1.0 \text{ M} \times 2.0 \text{ M}) = 10.$$

Thus, $k_{-1} = k_1/K_e = 342/10 = 34.2 \text{ M}^{-1} \text{ s}^{-1}$. Arrhenius equation gives k_1 at 1000K = $5.96 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

CHAIN REACTIONS:

Introduction:

Reactions with molecules having closed-shell electrons generally involve high activation energy, and the reactions are slow; though free energy for the overall reaction is favourable.

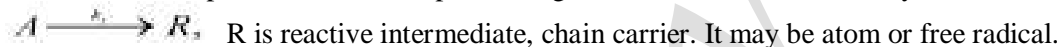
Faster reaction paths frequently involve reactions between free radicals and molecules. Radicals have unpaired electrons and so its reaction with a molecule having paired electrons gives rise to another free radical. In this way, radical-centre is maintained and gives rise to chain reaction.

Thus in this type of reactions, a long series of more easy self-repeating steps continue in which final product is formed along with active intermediate free radicals called chain carriers.

Steps in the chain reactions:

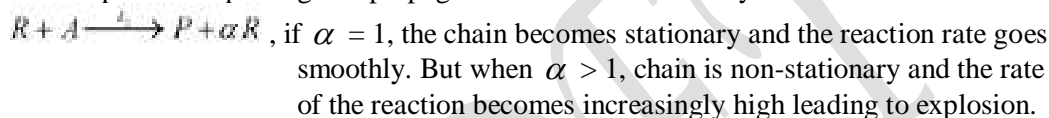
The chain reaction, $A \rightarrow P$ involves generally following three steps:

- (1) Chain initiation: Chain carrier is produced in this step. Some agent, called chain initiator may be used.

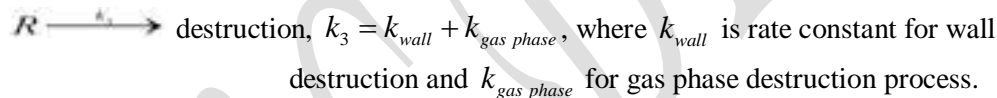


- (2) Chain propagation: Chain carrier attacks the reactant to give product and another chain carrier back.

This step is self-repeating and propagates the chain more easily.



- (3) Chain termination: This reaction should never stop until all the reactant material is consumed. At the other or chain break-up hand, if the chain carriers collide at the wall of the container and stick at the wall or combine with the other radicals to form a spin pair molecules, they are destroyed and the chain is broken.



Using the steady-state concept for the free radical, R, we have $k_1[A] + k_2\alpha[A][R] - k_2[A][R] - k_3[R] = 0$

$$\text{or, } k_1[A] + k_2(\alpha - 1)[A][R] - k_3[R] = 0 \quad \text{and } [R] = \frac{k_1[A]}{k_3 - k_2[A](\alpha - 1)} \quad \text{or, } [R] = \frac{k_1[A]}{(k_w + k_g) - k_2[A](\alpha - 1)}$$

Chain length: It is the number of chain propagation steps in between chain initiation and chain termination

steps. Mathematically, chain length = $\frac{(d[P]/dt)}{(-d[A]/dt)_{\text{initiation step}}}$. So, chain length is defined as number of product

molecules formed per chain carrier produced in the initiation step.

Test of chain mechanism:

This type of reaction may be tested as follows:

- (a) If the reaction rate decreases by increasing the area / volume ratio of the reaction vessel, the reaction follows chain mechanism as chain carriers are destroyed by wall destruction.
- (b) The reaction rate is also reduced by introducing some species like NO, propylene which destroy the chain carrier by chemical combination. If this happens, then the reaction follows chain mechanism. These added substances are called scavenger as they remove the active chain carriers from the reaction vessel.

Some typical examples of Chain reaction:

- (1) **Formation of HBr from H₂ and Br₂ (An example of stationary chain reaction, $\alpha = 1$)**

It is an example of thermal chain reaction. The typical gas phase reaction is $H_2 + Br_2 \rightarrow 2HBr$.

In 1906, Bodenstein formulated the rate equation from the experimental data and it is

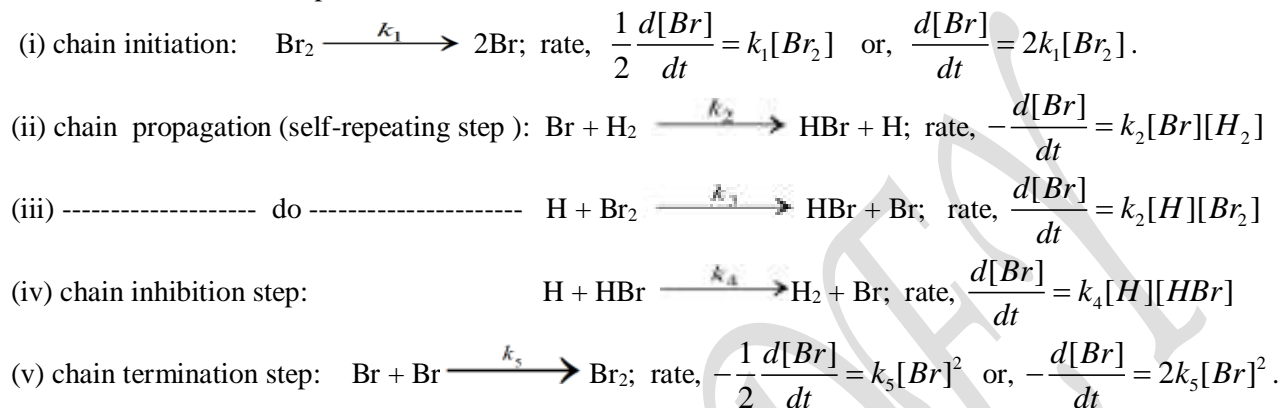
$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'[HBr]/[Br_2]}. \quad \text{Temperature range of the reaction is 500 K to 1500 K.}$$

[HBr] is present in the rate equation as denominator and so HBr appears to act as reactant in some step of the reaction i.e. inhibition step is there in the process.

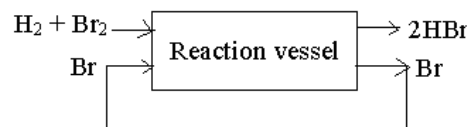
If no HBr is present initially, the initial rate is directly proportional to $[H_2][Br_2]^{1/2}$. If sufficient HBr is added initially, so that $k'[HBr]/[Br_2] \gg 1$, the initial rate is directly proportional to $[H_2][Br_2]^{3/2}/[HBr]$ and it is seen that doubling the initial [HBr] cuts the initial rate in half. These are experimental data that led to Bodenstein to formulate the rate equation of the reaction.

Proposed scheme of the reaction:

In 1919, Christiansen, Herzfeld and Polanyi proposed a scheme of self-propagating steps of chain mechanism. The steps are as:



The chain carrier Br attacks H_2 molecule with the formation of HBr and another chain carrier H. But rate of this step is slow due to high activation energy (≈ 18 kcal/mol) involved in the step. This H-atom then attacks Br_2 molecule with the formation of the product HBr, and Br-atom is regenerated.



These steps take place repeatedly to continue the cycle.

The chain carriers H and Br atoms remain steady in their conc.

during the reaction and the rate proceeds smoothly.

H-atom by chance attacks HBr, especially when HBr accumulates in large amount in the reaction vessel. This step inhibits the formation of product HBr.

Finally Br-atoms combine to produce Br_2 and the chain is terminated. Using the above steps, rate equation is formulated which is same as Bodenstein had derived.

Formulation of rate equation of the reaction:

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \text{ ----- (1)}$$

Taking steady state concept for H-atom and Br-atom as these chain carriers are reactive and its conc. is steady,

$$\frac{d[Br]}{dt} = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 = 0 \text{ -----(2)}$$

$$\text{and } \frac{d[H]}{dt} = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] = 0 \text{ ----- (3)}$$

$$\text{Adding equation (2) and (3), we get } 2k_1[Br_2] = 2k_5[Br]^2 \text{ or, } [Br] = \sqrt{(k_1/k_5)} [Br_2]^{1/2} \text{ ----- (4)}$$

$$\text{Again from equation (3), we get } [H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} = \frac{k_2\sqrt{(k_1/k_5)} [H_2][Br_2]^{1/2}}{k_3[Br_2] + k_4[HBr]}, \text{ using (4) for [Br].}$$

Putting equation (3) in equation (1), $\frac{d[HBr]}{dt} = 2k_3[H][Br_2]$. Replacing [H] and dividing by 2, we get the

$$\text{rate equation, } \frac{1}{2} \frac{d[HBr]}{dt} = \frac{k_3 k_2 \sqrt{(k_1/k_5)} [H_2][Br_2]^{3/2}}{k_3[Br_2] + k_4[HBr]} = \frac{k_2 \sqrt{(k_1/k_5)} [H_2][Br_2]^{1/2}}{1 + (k_4/k_3)([HBr]/[Br_2])} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'([HBr]/[Br_2])}$$

Comments on the rate equation:

(1) Order of the reaction: At the initial stages, $[Br_2] \gg [HBr]$ so, $1 + k'([HBr]/[Br_2]) \approx 1$.

or, rate equation at the initial stages is $\frac{1}{2} \frac{d[HBr]}{dt} = k[H_2][Br_2]^{1/2}$ and the order of the reaction is $1 + \frac{1}{2} = \frac{3}{2}$.

$$(2) \text{ Chain length of the reaction} = \frac{\frac{1}{2} \frac{d[HBr]}{dt}}{\frac{1}{2} \frac{d[Br_2]}{dt}} = \frac{k[H_2][Br_2]^{1/2} / \{1 + k'([HBr]/[Br_2])\}}{k_1[Br_2]}$$

$$= \frac{k[H_2][Br_2]^{1/2}}{k_1[Br_2] + k_1k'[HBr]}, \text{ where } k = k_2\sqrt{(k_1/k_5)} \text{ and } k' = \frac{k_4}{k_3}.$$

(3) Calculation of overall activation energy of the reaction:

At the initial stages, the rate equation is $\frac{1}{2} \frac{d[HBr]}{dt} = k_2\sqrt{(k_1/k_5)}[H_2][Br_2]^{1/2}$. But plotting $[HBr]$ vs. t , we obtain the initial rate ($t = 0$) from the limiting slope. Using several different values of initial conc. of $[H_2]_0$ and $[Br_2]_0$, we can obtain the overall rate constant, $k = k_2\sqrt{k_1/k_5}$.

Problem: Using Arrhenius equation, find the expression of the overall activation energy of the reaction $H_2 + Br_2 \rightarrow 2HBr$ at the initial stages in terms of the activation energies of the steps involved.

Given, $k = k_2\sqrt{(k_1/k_5)}$, where k is the overall rate constant of the formation of HBr at the initial stages.

Solution: Arrhenius equation is $Ae^{-E/RT} = A_2e^{-E_2/RT} \left(A_1e^{-E_1/RT} / A_5e^{-E_5/RT} \right)^{1/2} = A_2(A_1/A_5)^{1/2} e^{-(2E_2+E_1-E_5)/2RT}$.

Comparing, $A = A_2(A_1/A_5)^{1/2}$ and $E = (2E_2 + E_1 - E_5)/2$.

Let the activation energies of the steps are given as, $E_1 = 192$ kJ/mol, $E_2 = 74$ kJ/mol and $E_5 = 0$. Find the overall activation energy of the formation of HBr and calculate the initial rate at 300°C relative to that at 250°C . [Answer: $E = 170$ kJ/mol and rates is 30 times larger].

(4) Comment on the inhibition step of the reaction:

We have $\frac{\text{rate (iv)}}{\text{rate (iii)}} = \frac{k_4[HBr][H]}{k_3[Br_2][H]} = \frac{k_4[HBr]}{k_3[Br_2]}$. It appears that Br_2 and HBr are competing for H-atom.

The success of HBr in the competition is determined by the relative rates of the steps (iv) and (iii).

If the inhibition step would be $Br + HBr \rightarrow Br_2 + H$, then H_2 and HBr would compete for reaction with

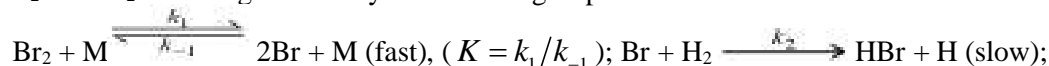
Br-atom and then the denominator in the rate equation would be $\frac{k_4[HBr]}{k_2[H_2]}$.

(5) Reaction speed: The reaction is slow due to high activation energy involved in the step (ii),

$Br + H_2 \xrightarrow{k_2} HBr + H$ and the rate = $k_2[Br][H_2]$, where $k_2 = A_2e^{-E_2/RT}$. However, the rate is increased

when temperature of the reaction is increased and this is due to enhanced value of k_2 .

Question: H_2 and Br_2 react to give HBr by the following steps:



$H + Br_2 \xrightarrow{k_3} HBr + Br$ (fast). The probable rate law for the above sequence is

(a) rate = $k_2(K)^{1/2}[H_2][Br_2]^{1/2}$ (b) rate = $k_2[H_2][Br_2]$ (c) rate = $k_2(k_1)^{1/2}[H_2][Br_2]^{1/2}$

(d) rate = $k_2(K)^{1/2}[H_2][Br]^{1/2}$.

[GATE, 2003]

Answer: The correct option is (a). Hints: In multi step reactions, slowest step determines the rate of the reaction.

Thus the rate of the reaction = $k_2[Br][H_2]$. But rapid equilibrium process determines $[Br]$, so

$$K = \frac{[Br]^2[M]}{[Br_2][M]} \text{ or, } [Br] = \sqrt{K} [Br_2]^{1/2}. \text{ Putting } [Br], \text{ the rate} = k_2 \sqrt{K} [H_2][Br_2]^{1/2}.$$

Explosive or non-stationary chain reaction ($\alpha > 1$):

For the reaction $A \rightarrow P$, following the chain mechanism as outlined earlier, the conc. of chain carrier (R) is given by the expression,

$$[R] = \frac{k_1[A]}{(k_w + k_g) - k_2(\alpha - 1)[A]} \quad \text{----- (1)}$$

For this type of non-stationary chain reaction, $\alpha > 1$.

Thus, as the reaction proceeds, more and more the free radicals are generated. The reaction rate is also more and more increased. A stage is reached when

$$k_2(\alpha - 1)[A] = (k_w + k_g).$$

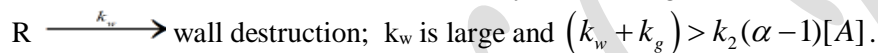
Denominator is zero and $[R]$ becomes infinity. This leads to very high reaction rate and the system explodes.

Effect of pressure on the reaction rate:

The rate of this type of reaction is largely dependent on pressure aside the temperature. Some striking features of this chain reaction are shown below by the plot of reaction rate vs. pressure.

1st pressure limit:

At low pressure, $[A]$ is also small, diffusion of the free radicals to the wall of the reaction vessel is rapid as the reactant molecules are widely dispersed. The radicals stick to the wall and are destroyed according to



The denominator in the equation (1) is (+ve). Rate of destruction of free radicals dominate over the rate of branching and the reaction proceeds smoothly without suffering any explosion.

This condition continues with increase of pressure (P) up to the limit $P < P_1$. When the pressure exceeds P_1 , explosion starts. This pressure (P_1) is called first explosion limit.

2nd pressure limit:

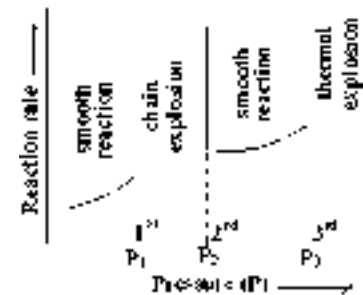
As the pressure is increased and becomes $P \geq P_1$, $[A]$ is increased and the rate of branching of free radicals $k_2(\alpha - 1)[A][R]$ is increased but the rate of termination of free radicals $(k_w + k_g)[R]$ is decreased due to less rate of diffusion of the radicals to the wall of the vessel and $(k_w + k_g) = k_2[A](\alpha - 1)$. The denominator becomes zero, $[R]$ reaches infinity, rate of the reaction attains very high value and the reaction explodes. With increase of pressure, $k_2[A](\alpha - 1) = (k_w + k_g)$ is maintained up to $P < P_2$, 2nd pressure limit.

As the pressure is further increased, free radicals suffer three-body collision and are destroyed with the reactant molecules which are thickly populated in the reaction vessel at this pressure.

$R \xrightarrow{k_g} \text{gas phase destruction dominates and again } (k_w + k_g) > k_2[A](\alpha - 1)$, and the reaction proceeds steadily as the denominator of the equation (1) is (+ve) and finite. This occurs when $P > P_2$, the 2nd pressure limit (P_2) after which the reaction goes on smoothly and this continues up to $P \geq P_3$, 3rd pressure limit.

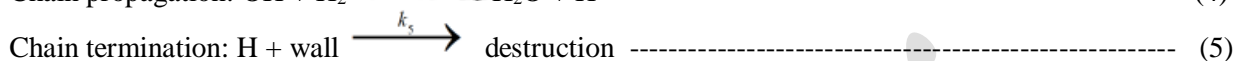
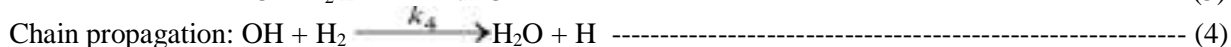
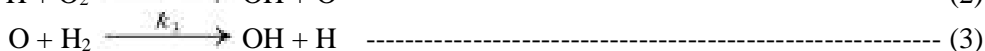
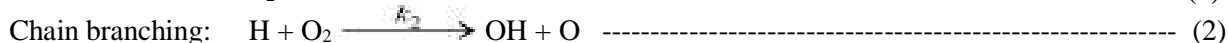
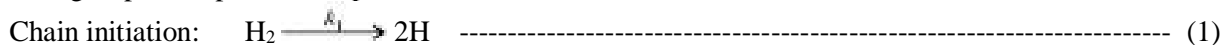
3rd explosion limit:

These reactions are usually exothermic and heat of reaction accumulates within this gas phase. The temperature is increased leading to increase the rate of the reaction which ultimately reaches the explosion. This is the thermal explosion. The pressure at which the thermal explosion starts is the 3rd pressure limit (P_3).



An example of non-stationary (explosion) chain reaction: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$.

The mechanism of the reaction is not very clear but Hinshelood and his co-workers proposed the following steps to explain the experimental observations.



The reaction is usually conducted at 550°C in a closed vessel. The first explosion limit can be explained by the help of the above mechanism.

At low pressure (below 10^{-3} bar), the reaction rate is slow and proceed smoothly. With the increase of pressure, the free radicals increase exponentially than the rate of termination and explosion occurs. The magnitude of the 1st pressure limit (P_1) at which explosion begins, depends on the relative rates for branching $2k_2[\text{H}][\text{O}_2]$ and termination $k_5[\text{H}]$. So long termination rate dominates over the branching rate, reaction goes smoothly. However the exact value of P_1 depends also on nature the vessel surface and the size and shape of the vessel. This supports the concept of wall destruction of the chain carriers. This explosion is called chain explosion.

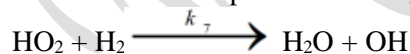
To explain the 2nd limit (P_2), above which there is no explosion, another termination step is to be considered and it is the gas phase destruction.



In a mixture of oxygen and hydrogen, M may be hydrogen or oxygen.

This termination step prevents the exponentially increase in the number of free radicals and this step is more important as the pressure is increased especially the conc. of O_2 . Again the gas phase termination step dominates over the branching step and the reaction proceeds smoothly.

The propagation step (4) is exothermic and fast. The heat of reaction is getting accumulated in the vessel and temperature is increased. This result an increase of rate of the reaction and at very high pressure P_3 , rate becomes tremendously high. The reaction again explodes. This is thermal explosion and P_3 is the 3rd explosion limit at which this explosion starts. At this high pressure, another propagation step begins to occur and more heat is generated that results more rise of temperature of the gas mixture.



Thus, at $P < P_1$, smooth reaction occurs. When $P_1 \leq P \leq P_2$, chain explosion continues.

Again at $P_2 \leq P \leq P_3$ smooth reaction goes. At $P \geq P_3$, thermal explosion occurs.

Question: Observe the following statements:

I. In the $\text{H}_2 - \text{O}_2$ reaction, explosion occurs when the rate of chain branching exceeds that of chain termination.

II. The order of the reaction, $nA \rightarrow \text{products}$ is 2.5. For the reaction, $t_{1/2} \propto [A]_0^{-3/2}$.

III. Unimolecular gas phase reactions are second order at low pressure but become first order at high pressure.

Which of the following is correct?

1. I, II, III are correct 2. only II is correct 3. only III is correct 4. I and II are correct.

Answer: Correct option is 1 (I, II and III are correct).

[NET (CSIR – UGC), 2013 (I)]

Question: The rate constant of a reaction changes by 2 % when its temperature is raised by 0.1°C at 25°C .

The standard enthalpy of the reaction at this temperature is $121.6 \text{ kJ mol}^{-1}$. Find the energy of activation for the reverse reaction.

[Civil Service Examination, 1996]

Answer: We have the relation $E_1 = RT^2 \left(\frac{d \ln k}{dT} \right) = RT^2 \left(\frac{dk/k}{dT} \right)$

$$= 8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} (298 \text{ K})^2 \left(\frac{0.02}{0.1 \text{ K}} \right) = 147.6 \text{ kJ mol}^{-1}.$$

But, $\Delta H = E_1 - E_{-1}$ or activation of reverse reaction, $E_{-1} = E_1 - \Delta H = 147.6 - 121.6 = 26 \text{ kJ mol}^{-1}$.

Question: A certain 1st order reaction is 20 % complete in 15 min. at 20 °C. How long will it take to complete 40 % of the reaction at 40 °C? (The average value of the energy of activation for the reaction is 23.03 kcal mol⁻¹ within this temperature range). (Burdwan Univ. 1992)

Answer: $k_{293\text{K}} = \frac{1}{15 \text{ min}} \ln \frac{[A]_0}{[A]_0 - 0.20[A]_0} = 0.015 \text{ min}^{-1}$ and $k_{313\text{K}} = \frac{1}{t \text{ min}} \ln \frac{[A]_0}{[A]_0 - 0.40[A]_0} = \frac{0.51}{t \text{ min}}$.

Now, $\ln \frac{k_{313\text{K}}}{k_{293\text{K}}} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$ or, $\ln \frac{0.51/t \text{ min}}{0.015 \text{ min}^{-1}} = \frac{23.03 \text{ kcal mol}^{-1}}{2 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1}} \left(\frac{20 \text{ K}}{293 \text{ K} \times 313 \text{ K}} \right)$ or, $t = 2.8 \text{ min}$.

Part II - Theoretical Aspect

Introduction:

This part of chemical kinetics deals with the theoretical aspect of elementary reactions at the molecular level. The calculation of rate constant (k) of a chemical reaction from the properties of individual atoms, ions and molecules of reactants is highly challenging.

Collision Theory of Elementary Bimolecular Gas Phase reactions:

The collision theory attempts to explain the mechanism of chemical reactions and to formulate the expression of rate constant (k) in terms of the molecular properties of reactants.

Let us first try to explain the elementary bimolecular gas phase reactions and the following postulates are used to formulate the theory.

Postulates:

- (1) The reactant molecules must come closer through either by collisions (in gas) or by encounter (in liquid). [Transport property]
- (2) Only those collisions or encounters are effective for reaction in which the reactants can acquire activation energy (E_a) of the reaction. [Energy criterion]
- (3) At the time of effective collisions, the reactant molecules should have proper orientation or alignment. [Steric criterion]

Evidence in support of postulate (2):

As all the collisions are not effective for chemical reaction, that can be justified by the following logistic arguments:

(a) For the reaction $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$, at 700 K and 1 atmosphere pressure, the frequency of binary collisions (Z) i.e. number of collisions between two HI molecules per cc per sec is about 10^{28} , but kinetic data show that the number of HI molecules decomposing per cc per sec is only about 10^{18} at the above temperature and pressure.

This justifies that all the collisions are not effective for reaction. In the above example, $(10^{28}/10^{18}) = 10^{10}$ collisions lead to decompose one pair of HI molecules.

(b) Again the frequency of collisions between two like molecules and between two unlike molecules are given

as

$$Z_{BB} = \frac{1}{\sqrt{2}} \pi \sigma_B^2 \sqrt{\frac{8RT}{\pi M_B}} (N'_B)^2, \quad Z_{BC} = \pi \sigma_{BC}^2 \sqrt{\frac{8RT}{\pi} \left(\frac{1}{M_B} + \frac{1}{M_C} \right)} N'_B N'_C,$$

where N'_B and N'_C are the number of molecules of B and C per cc of the gas.

Thus the frequency of collision, $Z \propto \sqrt{T}$, when volume of the gas (V) is kept constant and so N'_B and N'_C are

not affected by T. [Rate = $-\frac{1}{\nu_i} \frac{d[A_i]}{dt} = -\frac{1}{V} \left(\frac{1}{\nu_i} \frac{dn_i}{dt} \right)$ shows that rate of the reaction is dependent on the rate of

change of number of moles of the reacting component (i) only when V is kept constant].

Thus, $\frac{Z_{710K}}{Z_{700K}} = \sqrt{\frac{710}{700}} = 1.01$, this means that if every collision were effective, then per 10 K rise in

temperature, the reaction rate would increase by 1 % only. But kinetic measurements show that rate often increases by 100 % to 200 % per 10 K increase of temperature.

Activation Energy of the reaction (E_a):

The KE of the molecules obeys Boltzmann-Maxwell distribution law. Some molecules have very high KE (fast moving molecules) and some have small KE (slow moving molecules). But the molecules in gas are in random chaotic motion and so they undergo incessant molecular collisions with constant reshuffle of translational kinetic energy among themselves. When these pair of reactant molecules in their binary collisions acquires additional energy equal to the activation energy (E_a), they undergo chemical reaction. If E_a is the activation energy per mole of the reaction, then $\epsilon_a = E_a/N_A$ is equal to difference of the average total energy

(translational and internal) of those pairs of reactant molecules that are undergoing chemical reaction and the average total energy of all pairs of reactant molecules. That is, ε_a of pair of molecules

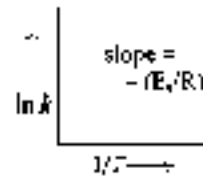
$= \varepsilon_{av}$ total energy of pair of reactant molecules undergoing reaction – ε_{av} total energy of all pairs of reactant molecules existing. This energy is essential for the pair of molecules to initiate the breaking of the relevant bond(s) to cause reaction.

According to Boltzmann distribution of energy, the number of collisions undergoing reaction

(effective collisions) is given as $Z_{effective} = Z \times e^{E_a/RT}$.

This activation energy of the reaction can be determined from Arrhenius plot of

$\ln k$ vs. $1/T$ in the relation, $\ln k = \ln A - \left(\frac{E_a}{R}\right) \frac{1}{T}$,



where A is pre-exponential factor, k is rate constant and E_a is the activation energy of the reaction. E_a is determined from the slope and A from the extrapolated intercept.

Now for the elementary bimolecular gas phase reaction $B + C \rightarrow \text{Product(s)}$,

the number of molecules of B reacting per cc per sec

$$-\frac{dN'_B}{dt} = Z_{effective} = Z_{BC} e^{E_a/RT} = \left[\pi \sigma_{BC}^2 \sqrt{\frac{8RT}{\pi} \left(\frac{1}{M_B} + \frac{1}{M_C} \right)} N'_B N'_C \right] e^{E_a/RT}$$

Converting the rate of the reaction in terms of number of moles of B reacting per litre per sec, we get

$$-\frac{dN'_B}{dt} = -\frac{d[B]}{dt} \times \left(\frac{N_A}{10^3} \right), \quad N'_B = [B] \times \left(\frac{N_A}{10^3} \right) \quad \text{and} \quad N'_C = [C] \times \left(\frac{N_A}{10^3} \right)$$

Thus according to the collision theory reaction rate (R)

$$-\frac{d[B]}{dt} = \left[\left(\frac{10^3}{N_A} \right) \pi \sigma_{BC}^2 \sqrt{\frac{8RT}{\pi} \left(\frac{1}{M_B} + \frac{1}{M_C} \right)} [B][C] \right] e^{E_a/RT}$$

[B] and [C] are the respective molar conc. of the reactants B and C. But the experimental rate equation of the elementary bimolecular (subsequently 2nd order) reaction Rte (R) $-\frac{d[B]}{dt} = k[B][C]$, where k is the

experimental rate constant of the reaction. Equating with the collision theory rate equation, we get

$$k = \left(\frac{N_A}{10^3} \right) \pi \left(\frac{\sigma_B + \sigma_C}{2} \right)^2 \sqrt{\frac{8RT}{\pi} \left(\frac{1}{M_B} + \frac{1}{M_C} \right)} e^{E_a/RT}$$

For the gas phase elementary bimolecular reaction, $2B \rightarrow \text{Product(s)}$,

putting $M_B = M_C$, $\sigma_B = \sigma_C$ and multiplying by $\left(\frac{1}{2}\right)$ in order to avoid double counting, we get the rate

$$\text{constant for the reaction} \quad k = \left(\frac{N_A}{10^3} \right) \frac{1}{\sqrt{2}} \pi \sigma_B^2 \sqrt{\frac{8RT}{\pi M_B}} e^{E_a/RT}$$

So expressions of the two rate constants (k) are given here: For the reaction $B + C \rightarrow \text{Products}$,

$$\text{rate } r = -\frac{d[B]}{dt} \quad \text{and the rate constant } k = \left(\frac{N_A}{10^3} \right) \pi \left(\frac{\sigma_B + \sigma_C}{2} \right)^2 \sqrt{\frac{8RT}{\pi} \left(\frac{1}{M_B} + \frac{1}{M_C} \right)} e^{E_a/RT}$$

$$\text{and for the reaction } 2B \rightarrow \text{Products, rate } r = \frac{1}{2} \left(-\frac{d[B]}{dt} \right) \quad \text{and rate constant } k = \left(\frac{N_A}{10^3} \right) \frac{1}{\sqrt{2}} \pi \sigma_B^2 \sqrt{\frac{8RT}{\pi M_B}} e^{E_a/RT}$$

or,

$$k = 2 \left(\frac{N_A}{10^3} \right) \sigma_B^2 \sqrt{\frac{\pi RT}{M_B}} e^{E_a/RT}$$

Example to show calculation of rate constant for a reaction:

For the reaction $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ at 556 K and 1 atm pressure, the rate constant is calculated by taking the values $\sigma_{\text{HI}} = 3.5 \text{ \AA}$, $E_a = 44 \text{ kcal mol}^{-1}$, $M_{\text{HI}} = 128 \text{ gm mol}^{-1}$, we have the rate constant,

$$k_{\text{cal}} = 2 \left(\frac{6.023 \times 10^{23} \text{ mol}^{-1}}{10^3 \text{ cm}^3 \text{ lit}^{-1}} \right) \times (3.5 \times 10^{-8} \text{ cm})^2 \sqrt{\frac{3.14 \times 8.31 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1} \times 556 \text{ K}}{128 \text{ gm mol}^{-1}}} \times e^{44 \text{ kcal mol}^{-1} / 2 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1} \times 556 \text{ K}}$$

$$= 2 \times 6.023 \times 10^{20} \times 12.25 \times 10^{-16} \times 3.37 \times 10^4 \times 6.54 \times 10^{-18} \text{ lit mol}^{-1} \text{ sec}^{-1} = 3.25 \times 10^{-7} \text{ lit mol}^{-1} \text{ sec}^{-1}.$$

Experimental value of rate constant for the reaction at the above temperature is $k_{\text{exp}} = 3.5 \times 10^{-7} \text{ lit mol}^{-1} \text{ sec}^{-1}$.

The agreement is good considering the crude assumptions involved in the theory.

For many reactions, $k_{\text{cal}} > k_{\text{exp}}$. So in the 1920s, hard-sphere-collision theory is modified by adding a factor P to the right sides of k_{cal} expression. This factor is called steric factor or probability factor in accordance of the postulate 3 of the theory. Thus the expression of the rate constant for the reaction, $\text{B} + \text{C} \rightarrow \text{Product}(\text{s})$,

$$k = P \times \left(\frac{N_A}{10^3} \right) \pi \left(\frac{\sigma_B + \sigma_C}{2} \right)^2 \sqrt{\frac{8RT}{\pi} \left(\frac{1}{M_B} + \frac{1}{M_C} \right)} e^{E_a/RT}.$$

The agreement for the inclusion of P is that the colliding molecules must be properly oriented in their effective collision at the point of impact to produce reaction. Thus the steric factor may be defined as the fraction of the effective collisions in which the molecules have right orientation at the time of collision.

That is,

$$P = \frac{\text{reactive collisions}}{\text{effective collisions}} = \frac{k_{\text{exp}}}{k_{\text{cal}}}.$$

P lies within 0 to 1. For example, in the reaction $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$, we should expect the reaction to occur if the carbon-end of CO hits the O_2 but not if oxygen end hits O_2 i.e. when O_2 hits the C-end of CO, reaction is possible but not if O_2 hits the O-end of CO.



The hard sphere collision theory provides no way to calculate P theoretically. Instead, P is found from the ratio of $k_{\text{exp}}/k_{\text{cal}}$ i.e. from the ratio of experimental k and collision theory k . Thus for $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$,

$P = 1/230 = 0.0043$. It means that 230 effective collisions produce one reactive collision which leads to reaction. Thus P is a factor that brings the theory into agreement with experiment. The value of P ranges from 1 to 10^{-6} , the smaller values are for reactions involving larger molecules, as expected due to lack of proper alignment.

T-dependence of Arrhenius pre-exponential term (A):

The collision theory predicts that pre-exponential term (A) in Arrhenius equation $k = Ae^{E_a/RT}$ is temperature dependent. The relation is $k = A'\sqrt{T} e^{E_a/RT}$, where $A = A'\sqrt{T}$.

The linear plot of $\ln k$ vs. $1/T$ in Arrhenius equation is explained by the fact that $\frac{1}{2} \ln T$ does not change much with change of T in comparison to (E_a/RT) term. Thus in the equation $\ln k = \ln A' + \frac{1}{2} \ln T - \left(\frac{E_a}{R} \right) \frac{1}{T}$,

$$\frac{1}{2} \ln T \text{ almost remains constant with change of temperature and the equation becomes } \frac{d \ln k}{dT} = \frac{E_a + (1/2)RT}{RT^2}.$$

Question: The elementary bimolecular gas phase reaction $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$ has activation energy 214.2 kJ/mol at 2700 K. Estimate the rate constant for the reaction by applying the collision theory of reaction rate at 2700 K. The molecular diameters of O_2 and CO are 3.6×10^{-10} m and 3.7×10^{-10} m, respectively. Also estimate the probability factor (steric) for the reaction if the observed rate constant is $3.45 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. **[Calcutta Univ. 2009]**

Answer: $k_{cal} = \left(\frac{N_A}{10^3}\right) \pi \left(\frac{\sigma_B + \sigma_C}{2}\right)^2 \sqrt{\frac{8RT}{\pi} \left(\frac{1}{M_B} + \frac{1}{M_C}\right)} e^{E_a/RT}$. Now putting the data in the equation, we get

$$k_{cal} = 3.14 \left(\frac{6.023 \times 10^{23} \text{ mol}^{-1}}{10^3 \text{ cm}^3 \text{ L}^{-1}}\right) \left(\frac{3.6 + 3.7}{2} \times 10^{-8} \text{ cm}\right)^2 \sqrt{\frac{8 \times 8.31 \times 10^7 \times 2700 \text{ K}}{3.14} \left(\frac{1}{28} + \frac{1}{32}\right)} \text{ cm s}^{-1} \times e^{-214.2 \text{ kJ mol}^{-1} / 8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \times 2700 \text{ K}}$$

$$= 3.52 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}. \text{ The steric factor, } P = \frac{k_{obs}}{k_{cal}} = \frac{3.45 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}}{3.52 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}} = 98.$$

Question: State the assumptions incorporated in the kinetic theory of collision. In the light of the theory, arrive at the expression of rate constant for a bimolecular reaction assuming frequency of collision, $Z_{AB} = C\sqrt{T}\bar{N}_A\bar{N}_B$ (\bar{N}_A and \bar{N}_B are the number of molecules of the reactant A and B per unit volume of the reaction mixture).

Answer: $Z_{effective} = Z_{AB} \times e^{-E_a/RT}$ and $Z_{AB} = C\sqrt{T}\bar{N}_A\bar{N}_B$. Let \bar{N}_A and \bar{N}_B are the number of molecules per litre, then the number of molecules decomposing per litre

$$-\frac{dN_A}{dt} = Z_{effective} = Z_{AB} \times e^{-E_a/RT} = C\sqrt{T}\bar{N}_A\bar{N}_B \times e^{-E_a/RT}.$$

But the rate of the reaction in terms of number of moles of A reacting per litre per sec

$$= -\frac{d[A]}{dt} \times N_{Avo} = C\sqrt{T}[A][B] \times (N_{Avo})^2 e^{-E_a/RT} \text{ or, } -\frac{d[A]}{dt} = C\sqrt{T}[A][B]N_{Avo} \times e^{-E_a/RT}.$$

The experimental rate law of the reaction between $A + B \rightarrow \text{Products}$, rate $-\frac{d[A]}{dt} = k[A][B]$.

Comparing the two, we get the expression of rate constant of the reaction, $k = N_{Avo} C\sqrt{T} \times e^{-E_a/RT}$

Collision theory of elementary unimolecular gas phase reactions

Introduction: Unimolecular reactions are either Isomerisation (viz cyclopropane to propene) or decomposition (viz azomethane to ethane and nitrogen). In this type of reactions, only one molecule participates and elementary unimolecular reactions are kinetically 1st order reactions. It appears difficult to explain unimolecular reactions by collision theory due to the following reasons:

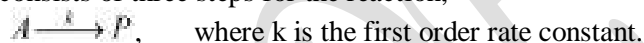
Dilemma to explain:

- (1) As per requirement in the collision theory, at least one bimolecular collision is required for activation and subsequent decomposition and rearrangement of bonds in the reactant molecule. So the collisional activation becomes bimolecular and hence 2nd order reaction. Thus how can a unimolecular or 1st order reactions be explained by collision theory?
- (2) Again 1st order or elementary unimolecular reactions such Isomerisation or dissociation in gas phase are 1st order at high pressure (1 atm or higher) and 2nd order at low pressure (at 10 to 100mm of Hg).
- (3) Unimolecular reactions generally have large activation energy. This raises another interesting point ; how is this large activation energy supplied?

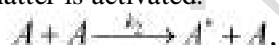
Therefore, a scheme must have to be chalked out that can explain all the above salient features of the unimolecular reactions.

Lindemann scheme for the reaction:

In 1922, Lindemann (Trans Faraday Soc.) proposed a scheme that explains the mechanism of the unimolecular reactions. The Scheme consists of three steps for the reaction,



- (a) Activation step: A molecule of A collides with another molecule A and one is activated to acquire enough additional energy (E_a) so that it can decompose or isomerize. KE of one molecule A is transferred to another A molecule and the latter is activated.



where k_2 is rate constant of bimolecular activation step and A^* is activated molecule.

$$\text{Rate of activation step} = k_2[A]^2$$

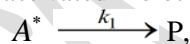
- (b) Deactivation step: There is some time-lag between activation and of A and decomposition of A^* . Within this times-lag, the activated molecule may have chance to be de-activated by collision with other normal molecule (A).



where k_{-2} is the rate constant of bimolecular deactivation step. The rate of deactivation step = $k_{-2}[A^*][A]$.

The above two steps are not elementary chemical steps (since no new compounds are formed in these steps) but are elementary physical steps in which only the energy is transferred. This type of energy-transfer is common in many other processes.

- (c) Decomposition step: The activated molecules that can survive the time-lag are decomposed to product (P).



where k_1 is the rate constant in the decomposition step and the rate of decomposition = $k_1[A^*]$.

P may be several species but it is supposed that they do not take part in activation or de-activation collisions (it may be possible that P is solid). If it does so, the discussion will be substantially modified. Thus the total scheme of Lindemann is given as:



Applying steady-state approximation to the reactive species A^* , we have $\frac{d[A^*]}{dt} = 0$

$$\text{or, } k_2[A]^2 - k_{-2}[A^*][A] - k_1[A^*] = 0 \quad \text{or, } [A^*] = \frac{k_2[A]^2}{k_{-2}[A] + k_1}. \quad \text{Overall rate of the reaction, } r = \frac{d[P]}{dt} = k_1[A^*].$$

Putting the $[A^*]$, we get the overall rate of the rate of the reaction, $r = \frac{k_1 k_2 [A]^2}{k_{-2} [A] + k_1}$. ----- (1)

The expression does not seem to give the 1st order kinetics. However, till now we do not say anything about the relative rates of the different processes involved in the reaction.

Two limiting cases for equation (1) can be considered.

(a) When $k_{-2} [A] \gg k_1$ i.e., the rate of deactivation step is much greater than the rate of decomposition step,

$k_{-2} [A^*] [A] \gg k_1 [A^*]$. This may happen when $[A]$ is large or $k_{-2} \gg k_1$.

The rate equation (1) becomes $r = \left(\frac{k_1 k_2}{k_{-2}} \right) [A]$. the reaction follows 1st order kinetics (time-lag is high).

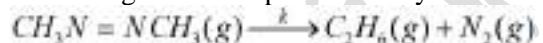
(b) When $k_1 \gg k_{-2} [A]$, i.e. the rate of decomposition step is much greater than the rate of deactivation step,

$k_1 [A^*] \gg k_{-2} [A^*] [A]$. This may happen when $[A]$ is very small or $k_1 \gg k_{-2}$.

The rate equation (1) becomes $r = k_2 [A]^2$, the reaction follows 2nd order kinetics (time-lag is small).

Depending on reaction and temperature, the transition from 1st to 2nd order generally starts at pressure between 10 to 100 mm of Hg.

Lindemann hypothesis has the advantage that it can be tested experimentally. Ramsperger in 1927 (Am. Chemical Soc.) verified by conducting the decomposition study of azomethane,



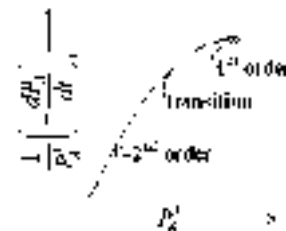
The rate equation (1) can be rearranged as: $\frac{1}{[A]} \left(-\frac{d[A]}{dt} \right) = \frac{k_1 k_2 [A]}{k_{-2} [A] + k_1}$.

Thus at low conc. of A, $\frac{1}{[A]} \left(-\frac{d[A]}{dt} \right) = k_2 [A]$ and at high conc. of A, $\frac{1}{[A]} \left(-\frac{d[A]}{dt} \right) = \left(\frac{k_1 k_2}{k_{-2}} \right) = \text{constant}$.

Ramsperger used initial rate and measured the pressure of the azomethane gas at the initial point of the reaction.

He plotted $\frac{1}{P_A^0} \left(-\frac{dP_A}{dt} \right)_0$ vs. P_A^0 , where $\left(-\frac{dP_A}{dt} \right)_0$ is the initial rate of the

reaction. The following curve is obtained which can only be explained by Lindemann mechanism. At low pressure of azomethane, the curve is straight line passing through origin and at high pressure, LHS is constant.



However rigorous treatment of Lindemann mechanism shows some limitations.

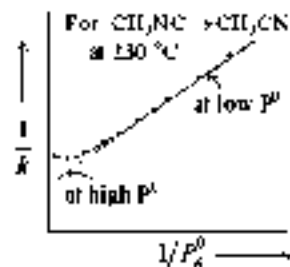
For the reaction $A \xrightarrow{k} P$, the experimental rate equation is $r = k[A]$ as the reaction is unimolecular elementary reaction and so it follows 1st order kinetics. k is experimentally determined 1st order rate constant. Equating this rate equation with that obtained from Lindemann scheme, we get

$$k[A] = \frac{k_1 k_2 [A]^2}{k_{-2} [A] + k_1} \text{ or, } k = \frac{k_1 k_2 [A]}{k_{-2} [A] + k_1} \text{ or, } \frac{1}{k} = \frac{k_{-2}}{k_1 k_2} + \frac{1}{k_2} \frac{1}{[A]}. \text{ In terms of pressure, } \frac{1}{k} = \frac{k_{-2}}{k_1 k_2} + \frac{1}{k_2} \frac{1}{P_A^0}.$$

Thus Lindemann expression predicts a linear plot of $\frac{1}{k}$ vs. $\frac{1}{P_A^0}$.

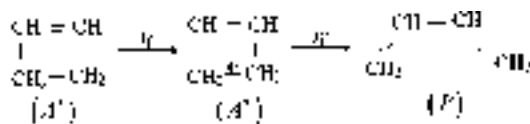
But the plot obtained for the isomerisation of $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ at 230 °C shows substantial non-linearity. Deviation is prominent at high pressure where the experimental value of k is lower than predicted by Lindemann mechanism.

This due to the oversimplification of the mechanism adopted. k_1 is assumed constant for the decomposition step. This implies that all the activated molecules (A^*) are not decomposed so the decomposition step was modified by Hinshelwood as follows.





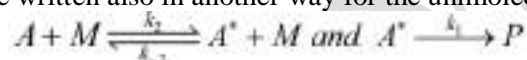
The molecule A acquires activation energy and the energy is dispersed over number of bonds [non-specific excitation]. This is energized molecule (A^*). But when the excitation energy is concentrated to the particular bond(s), it is called activated state of the molecule (A^\ddagger) [specific excitation]. One reaction is cited as an example: conversion of cyclobutene to butadiene.



In A^* , the excitation energy is distributed among the four bonds but in A^\ddagger , the energy is concentrated (by intra-molecular energy transfer) to CH_2-CH_2 bond only and the energy exceeds the vibrational stability level so the bond breaks. Thus energized (A^*) turns into activated state of the molecule (A^\ddagger), then it is isomerised to the product (P). This explains that experimental value of rate constant is less than the calculated value from Lindemann scheme.

Alternative Approach:

Lindemann scheme can be written also in another way for the unimolecular reaction $A \xrightarrow{k} P$ as:



where M is either A or any other inert species. When $M = A$, the formulation is same as given above.

The rate equation (1) of formation of P is then $r = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_1}$.

(a) When $k_{-1}[M] \gg k_1$, the rate equation becomes $r = \left(\frac{k_1 k_2}{k_{-1}}\right)[A]$ and the reaction follows 1st order kinetics.

(b) When $k_1 \gg k_{-1}[M]$, the rate equation is $r = k_2[A][M]$. If $M = A$, it is 2nd order but if $M \neq A$, it is pseudo 1st order reaction.

It is noted that when an inert gas (M) is present in the reaction vessel and is capable to activate the reactant molecule (A), the reaction becomes always first order with respect to A both at high pressure and at low pressure.

Question: Outline briefly Lindemann scheme for determining rate constant of a gas phase isomerisation reaction $A \rightarrow B$. Show that the expression obeys a first order kinetics at high pressure. What will happen at low pressure? (4 + 1 + 2) [Burdwan Univ. 1996]

Answer: Shown above the alternate formulation of Lindemann scheme.

Question: The mechanism of isomerisation of cyclobutene (CB) to 1,3 butadiene (BD) is as follows:



(a) Show that the rate law is $\frac{d[\text{BD}]}{dt} = \frac{k_2 k_1 [\text{CB}]^2}{k_{-1}[\text{CB}] + k_2}$.

(b) The apparent 1st order rate constant $k_{app} = \frac{k_2 k_1 [\text{CB}]}{k_{-1}[\text{CB}] + k_2}$. At the CB conc. of $1 \times 10^{-5} \text{ mol dm}^{-3}$, the value of

k_{app} reaches 50 % of its limiting value obtained at very high conc. [CB]. Evaluate the ratio k_2/k_{-1} .

[IIT-JAM, 2012]

Answer: 1st part: See the text as above.

2nd part: The limiting value of k_{app} for the reaction occurs at high conc. of [CB] and $k_{-1}[\text{CB}] \gg k_2$.

The limiting value of apparent 1st order rate constant, $k_{app} = \frac{k_2 k_1}{k_{-1}}$.

But at $[CB] = 1 \times 10^{-5} \text{ mol/dm}^{-3}$, $k_{app} = \frac{1}{2} \frac{k_2 k_1}{k_{-1}}$. Putting in the expression of k_{app} , we get

$$\frac{1}{2} \frac{k_2 k_1}{k_{-1}} = \frac{k_2 k_1 [CB]}{k_{-1} [CB] + k_2} \quad \text{or,} \quad \frac{1}{2 k_{-1}} = \frac{[CB]}{k_{-1} [CB] + k_2} \quad \text{or,} \quad \frac{k_2}{k_{-1}} = [CB] = 1 \times 10^{-5} \text{ mol/dm}^{-3}.$$

Question: Cite one example of unimolecular reaction. In the Lindemann mechanism, 'apparent' first order rate constant $k_{app} = \frac{k_2 k_1 c}{k_{-1} c + k_2}$. At low conc., the value of k_{app} decreases.

If, when the conc. is $10^{-5} \text{ mol L}^{-1}$ the value of k_{app} reaches 90 % of its limiting value at $c = \infty$, what is the ratio of k_2/k_{-1} ?

[Burdwan Univ. 2009, 2015]

Answer: 1st part: One example of the unimolecular reaction is decomposition of azomethane.

2nd part: See the answer of Question, IIT – JAM, 2012. Answer is $1.11 \times 10^{-6} \text{ mol/dm}^{-3}$.

Question: Species A undergoes a unimolecular reaction as



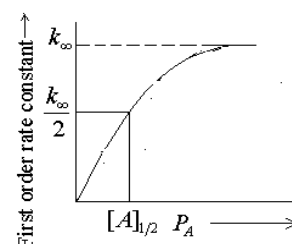
For this reaction, the first order rate constant at high pressure is k_∞ .

The first order rate constant becomes $k_\infty/2$ when pressure of A

is $[A]_{1/2}$. The value of k_1 will be

1. $k_\infty/[A]_{1/2}$ 2. $k_\infty [A]_{1/2}$ 3. $k_\infty - [A]_{1/2}$ 4. $[A]_{1/2}/k_\infty$.

[IIT – JAM, 2014(II)]



Answer: Correct option (1). Hints: First order rate constant is

$$k = \frac{k_1 k_2 [A]}{k_{-1} [A] + k_2} \quad \text{but } k \text{ is } k_\infty \text{ when } [A] \text{ is high so that } k_{-1} [A] \gg k_2 \text{ and } k_\infty = \frac{k_1 k_2}{k_{-1}}.$$

The rate equation is arranged as $\frac{1}{k} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1} \frac{1}{[A]}$ Putting the condition $[A] = [A]_{1/2}$ when $k = \frac{k_\infty}{2}$

$$\text{we get } \frac{2}{k_\infty} = \frac{1}{k_\infty} + \frac{1}{k_1} \frac{1}{[A]_{1/2}} \quad \text{or } k_1 = k_\infty/[A]_{1/2}.$$

Question: For a unimolecular reaction $A \xrightarrow{k} P$, the rate R is given by the relation $R = k [A]$.

The mechanism of the reaction is $A + M \xrightleftharpoons[k_{-1}]{k_1} A^* + M$ and $A^* \xrightarrow{k_2} P$

$$\text{Show that } k = \frac{k_1 k_2}{(k_{-1} + k_2) [M]}.$$

[Calcutta Univ. 2010]

Answer: Hint: Following the mechanism, we have $R = \frac{k_1 k_2 [A] [M]}{k_{-1} [M] + k_2}$. Comparing with the experimental rate

$$\text{equation } R = k [A], \text{ we get } k [A] = \frac{k_1 k_2 [A] [M]}{k_{-1} [M] + k_2} \quad \text{or, } k = \frac{k_1 k_2 [M]}{k_{-1} [M] + k_2} \quad \text{or, } k = \frac{k_1 k_2}{(k_{-1} + k_2) [M]}.$$

Question: The isomerisation of cyclopropane follows the Lindemann mechanism. It is found that the rate constant at high pressure is $1.5 \times 10^{-4} \text{ sec}^{-1}$ and that at low pressure is $6 \times 10^{-6} \text{ torr}^{-1} \text{ sec}^{-1}$.

Find the pressure of cyclopropane at which the reaction changes its order. [NET(CSIR-UGC), 2008]

Answer: For the Lindemann scheme of unimolecular reaction, $A + A \xrightleftharpoons[k_{-2}]{k_2} A^* + A; A^* \xrightarrow{k_1} P$, the rate of the reaction, $R = \frac{k_1 k_2 P^2}{k_{-2} P + k_1}$. At high pressure, $R = \frac{k_1 k_2}{k_{-2}} P = R = k P$ and at low pressure, $R = k_2 P^2$.

At the transition from 1st order to 2nd order, the rates are equal so $k_2 P^2 = k P$ or, $P = k/k_2$.

Putting the value, we get $P = 1.5 \times 10^{-4} \text{ sec}^{-1} / 6 \times 10^{-6} \text{ torr}^{-1} \text{ sec}^{-1} = 25 \text{ torr}$.

Question: "Unimolecular reactions are not always first order." – Justify the statement using Lindemann mechanism. **[Calcutta Univ, 2013]**

Answer: At high pressure, unimolecular reaction is 1st order but at low pressure it becomes 2nd pressure See the Text as above.

Hinshelwood modification of Unimolecular mechanism:

For elementary unimolecular reaction $A \xrightarrow{k} P$, Hinshelwood modified the steps as follows
 $A + A \xrightarrow{k_1} A^* + A$ (energization); $A + A^* \xrightarrow{k_{-1}} A + A$ (de-energization);
 $A^* \xrightarrow{k'} A^*$ (activation by intramolecular energy transfer) and $A^* \xrightarrow{k''} P$ (decomposition).

Rate equation can be formulated from the above mechanism. $\frac{d[P]}{dt} = R = k'' [A^*]$ but $[A^*] = \frac{k_1'}{k_{-1}''} [A^*]$ and

Putting, $[A^*] = \frac{k_2 [A]^2}{k_{-2} [A] + k_1'}$ $[A^*] = \frac{k_1'}{k_{-1}''} \times \frac{k_2 [A]^2}{k_{-2} [A] + k_1'}$ so the rate $R = k_1'' \times \frac{k_1'}{k_{-1}''} \times \frac{k_2 [A]^2}{k_{-2} [A] + k_1'}$ or, $R = \frac{k_1' k_2 [A]^2}{k_{-2} [A] + k_1'}$.

Thus first order rate constant, $k = \frac{k_1' k_2 [A]}{k_{-2} [A] + k_1'}$. But k_1' is the rate constant of the intramolecular energy-transfer

step which is slow and so k_1' is smaller than k_1 of Lindemann decomposition step. This explains the smaller value of 1st order rate constant k .

Problem: The effective rate constant (experimental rate constant) of a first order reaction following Lindemann mechanism has the following values:

$k = 2.5 \times 10^{-3} \text{ sec}^{-1}$ when $[A] = 5 \times 10^{-2} \text{ (M)}$ and $k = 4.2 \times 10^{-3} \text{ sec}^{-1}$ when $[A] = 9.8 \times 10^{-2} \text{ (M)}$.

Find the rate constant for the activation step (k_2) and the ratio of k_{-2}/k_1 .

Solution: According to Lindemann mechanism, we have $\frac{1}{k} = \frac{k_{-2}}{k_1 k_2} + \frac{1}{k_2 [A]}$. Putting the values in the equation,

$$\frac{1}{2.5 \times 10^{-3} \text{ sec}^{-1}} = \frac{k_{-2}}{k_1 k_2} + \frac{1}{k_2 \cdot 5 \times 10^{-2} \text{ (M)}} \quad \text{and} \quad \frac{1}{4.2 \times 10^{-3} \text{ sec}^{-1}} = \frac{k_{-2}}{k_1 k_2} + \frac{1}{k_2 \cdot 9.8 \times 10^{-2} \text{ (M)}}$$

Subtracting the two equations, we get rate constant of activation step, $k_2 = 6.04 \times 10^{-2} \text{ mol}^{-1} \text{ L sec}^{-1}$.

Let the 2nd equation on rearrangement is $\frac{k_2}{4.2 \times 10^{-3} \text{ sec}^{-1}} = \frac{k_{-2}}{k_1} + \frac{1}{9.8 \times 10^{-2} \text{ (M)}}$.

Now inserting the value of k_2 , we get $k_{-2}/k_1 = 4.18 \text{ (M)}$.

Problem: The effective rate constant for a first order reaction which has a Lindemann mechanism has the values at 127 °C: $1.88 \times 10^{-4} \text{ sec}^{-1}$ at $P = 1.25 \text{ kPa}$ and $k = 1.14 \times 10^{-5} \text{ sec}^{-1}$ at $P = 10.9 \text{ Pa}$. Find out the rate constant for the activation step in the mechanism. **[Answer: $1.104 \times 10^{-6} \text{ Pa}^{-1} \text{ sec}^{-1}$]**

Transition State Theory (TST) or Theory of Absolute Reaction Rate

Limitation of Collision Theory

- (1) The collision theory fails to explain and interpret the steric factor (P) in the rate equation

$$\text{Rate} = PZ e^{-E_a/RT}$$

- (2) The collision theory is more or less satisfactory to explain the gas phase reactions. But it fails to explain the reactions in the condensed phase.

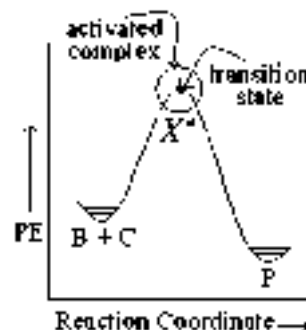
This theory was proposed by Polanyi and Eyrine in 1935. TST can explain the unimolecular and bimolecular reactions both in gas phase and condensed phase. This theory consists of the following postulates:

Postulates of TST

- (1) Let the reaction is represented by $B + C \rightarrow \text{Product(s)}$. The reactant molecules which have an additional energy (E_a) and come close to each other, will form activated

complex (X^\ddagger). The energy of the activated complex is sufficient to reach the peak of the PE diagram. Activated complex is the region near the potential maximum, and transition state corresponds to the maximum itself.

- (2) The activated complex sometimes also approximately refers to the transition state (X^\ddagger) which is formed by some loose association or bonding of reactant molecules with necessary rearrangement of valence bonds and energy. The activated complex (super molecule) is unstable and so has transient existence but it is treated formally as a definite molecule with independent entity. It remains in equilibrium with the reactant molecules.



$B + C \rightleftharpoons X^\ddagger$ and the equilibrium constant is $K_x = \frac{[X^\ddagger]}{[B][C]}$, where $[X^\ddagger]$ is the conc. (molecules/cc)

of the activated complex. Suffix ' \ddagger ' (dagger) refers to the activated complex. So, $[X^\ddagger] = K_x[B][C]$

- (3) When the reactant molecules B and C form activated complex X^\ddagger , some of the translational and rotational degrees of freedom of B and C are converted into vibrational degrees of freedom in X^\ddagger . The complex has vibrational degree of freedom = $3(N_B + N_C) - 6$, where N_B and N_C are the number of atoms of the reactants B and C molecules, respectively. Out of these vibrational degrees of freedom, one mode is of different character from the rest. This mode corresponds to a very large vibrational amplitude which allows the complex to dissociate into products. The frequency of this decomposition vibration is low and its energy is given as

$$\epsilon_{vib} = h\nu_\ddagger \text{ (from Plank's quantum theory), and } \epsilon_{vib} = k_B T \text{ (from the law of equipartition of energy).}$$

Thus equating the two, we have $h\nu_\ddagger = k_B T$ and the decomposition frequency $\nu_\ddagger = k_B T/h$.

Formulation of the theory

The activated complex is a transient species during the pass-over from the initial state to the final state and unable to turn back. $X^\ddagger \rightarrow \text{Products (P)}$.

Only those activated complex molecules that can acquire this frequency (ν_\ddagger) will undergo decomposition.

So the rate of the reaction (R), $\frac{d[P]}{dt} = \nu_\ddagger [X^\ddagger]$, but $\nu_\ddagger = k_B T/h$ and $[X^\ddagger] = K_x[B][C]$.

Inserting the two terms in the rate equation, we have the rate, $\frac{d[P]}{dt} = \left(\frac{k_B T}{h}\right) K_x[B][C]$.

But the experimental rate equation for the reaction $B + C \rightarrow P$ is $\frac{d[P]}{dt} = k[B][C]$.

Equating these two rate equations, we get expression of experimentally determined rate constant of the reaction,

$$k = \left(\frac{k_B T}{h} \right) K_{\ddagger} (c_0^{1-m}) \text{ ----- (1)}$$

c_0 is the standard conc. and m is the number of molecules participating in the elementary reaction or order of the reaction. This term c_0^{1-m} is used in the expression to give proper unit of k .

This expression is retained not only for two reactants but for any reaction at any conc. unit chosen.

To express k in terms of experimentally determinable quantities, it is dealt with either from thermodynamics or from partition function. We shall use here the thermodynamics for further treatment.

From van't Hoff reaction isotherm, we have $-RT \ln K_{\ddagger} = \Delta G_{\ddagger}^0$ or, $K_{\ddagger} = e^{-\Delta G_{\ddagger}^0/RT} = e^{-(\Delta H_{\ddagger}^0 - T\Delta S_{\ddagger}^0)/RT}$

$$K_{\ddagger} = e^{\Delta S_{\ddagger}^0/R} e^{-\Delta H_{\ddagger}^0/RT}, \text{ ----- (2)}$$

where ΔG_{\ddagger}^0 = the standard Gibbs free energy of activation = standard Gibbs free energy of the activated complex and the reactants. That is, $\Delta G_{\ddagger}^0 = G_{\ddagger}^0 - (G_B^0 + G_C^0)$. Similarly, ΔH_{\ddagger}^0 and ΔS_{\ddagger}^0 are the standard enthalpy of activation and standard entropy of activation, respectively.

Therefore the rate constant of the reaction is $k = \left(\frac{k_B T}{h} e^{\Delta S_{\ddagger}^0/R} c_0^{1-m} \right) e^{-\Delta H_{\ddagger}^0/RT}$ ----- (3)

Now, using equation (1), standard enthalpy of activation ΔH_{\ddagger}^0 can be replaced by Arrhenius activation energy E_a which is experimentally determinable.

$$k = \left(\frac{k_B T}{h} \right) K_{\ddagger} (c_0^{1-m}) \text{ or, } \ln k = \ln(k_B/h) + \ln T + \ln(c_0^{1-m}) + \ln K_{\ddagger} \text{ or, } \frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K_{\ddagger}}{dT}.$$

Utilizing the Arrhenius equation and van't Hoff reaction isochore, we get $\frac{E_a}{RT^2} = \frac{1}{T} + \frac{\Delta U_{\ddagger}^0}{RT^2} = \frac{RT + \Delta U_{\ddagger}^0}{RT^2}$.

Equating, we get $E_a = RT + \Delta U_{\ddagger}^0$, where ΔU_{\ddagger}^0 is the standard internal energy of activation of the reaction.

But, $\Delta U_{\ddagger}^0 = \Delta H_{\ddagger}^0 - \Delta n_g RT$. Inserting this expression, it is possible to connect ΔH_{\ddagger}^0 with E_a .

Using above equations, we get $E_a = RT + \Delta U_{\ddagger}^0 = RT + \Delta H_{\ddagger}^0 - \Delta n_g RT$ or, $\Delta H_{\ddagger}^0 = E_a + (\Delta n_g - 1)E_a$ ----- (4)

Now, replacing ΔH_{\ddagger}^0 , in the expression of rate constant, we have $k = \left(\frac{k_B T}{h} e^{\Delta S_{\ddagger}^0/R} c_0^{1-m} e^{-(\Delta n_g - 1)E_a/RT} \right) e^{-E_a/RT}$.

Δn_g is the change in the number of moles of activated complex and the reactants. However, for condensed phase reaction, $\Delta n_g = 0$. For 1st order gas phase reaction, $\Delta n_g = 0$ and $-(\Delta n_g - 1) = 1$; for 2nd order reaction, $\Delta n_g = -1$ and $-(\Delta n_g - 1) = 2$. Let $-(\Delta n_g - 1) = m$, identified with the order of the reaction.

Thus, the rate constant of the reaction is given as

$$k = \left(\frac{k_B T}{h} e^{\Delta S_{\ddagger}^0/R} c_0^{1-m} e^m \right) e^{-E_a/RT} \text{ ----- (5)}$$

Equating with Arrhenius equation, $k = A e^{-E_a/RT}$, we have the expression of pre-exponential term

$$A = \frac{k_B T}{h} e^{\Delta S_{\ddagger}^0/R} c_0^{1-m} e^m \text{ ----- (6)}$$

This relation is used to calculate ΔS_{\ddagger}^0 of the reaction from the value of A which is determined experimentally.

But, $\Delta S_{\ddagger}^0 = S_{\ddagger}^0 - (S_B^0 + S_C^0)$ and for bimolecular reaction, the sign of ΔS_{\ddagger}^0 is generally negative. All gas phase reactions lead to the conversion of translational and rotational degrees of freedom of the reactants to vibrational

degrees of freedom of TS. The widely spaced energy levels of the latter type of molecular motion implies a smaller entropy and this gives a negative value of ΔS_{\ddagger}^0 .

Only for unimolecular reaction, when the activated state is more disordered than the reactant (which is the usual case), the sign of ΔS_{\ddagger}^0 is positive.

The steric factor (P) is related with the term $e^{\Delta S_{\ddagger}^0/R}$, for more complex reaction, ΔS_{\ddagger}^0 is more negative and steric factor (P) becomes more less than one.

Problem: The rate constant of reaction in transition state theory is given by $k = \left(\frac{k_B T}{h} \right) K_{\ddagger}$. Use the theory to find the expression of ΔG_{\ddagger}^0 , ΔH_{\ddagger}^0 and ΔS_{\ddagger}^0 of the reaction.

Solution: We have $k = \frac{k_B T}{h} (c_0)^{1-m} K_{\ddagger}$, or, $\ln k = \ln(k_B/h) + \ln T + \ln(c_0^{1-m}) + \ln K_{\ddagger}$

$$\text{or, } \frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K_{\ddagger}}{dT} \quad \text{or, } \frac{E_a}{RT^2} = \frac{1}{T} + \frac{\Delta U_{\ddagger}^0}{RT^2} = \frac{RT + \Delta U_{\ddagger}^0}{RT^2} \quad \text{or, } \Delta U_{\ddagger}^0 = E_a - RT.$$

Again, $\Delta H_{\ddagger}^0 = \Delta U_{\ddagger}^0 + \Delta n_g^{\ddagger} RT$ or, $\Delta H_{\ddagger}^0 = E_a + (\Delta n_g^{\ddagger} - 1)RT$. But $\Delta n_g^{\ddagger} - 1 = -m$, where m = order of the reaction. Thus, $\Delta H_{\ddagger}^0 = E_a - mRT$.

Again, from van't Hoff reaction isotherm, $K_{\ddagger} = e^{-\Delta G_{\ddagger}^0/RT}$.

$$\text{Thus, } k = \frac{k_B T}{h} (c_0)^{1-m} e^{-\Delta G_{\ddagger}^0/RT} = \frac{k_B T}{h} (c_0)^{1-m} e^{-(\Delta H_{\ddagger}^0 - T\Delta S_{\ddagger}^0)/RT}$$

or, $k = \left(\frac{k_B T}{h} e^m c_0^{1-m} e^{\Delta S_{\ddagger}^0/R} \right) e^{-E_a/RT}$. Comparing with Arrhenius equation, we get

$$A = \frac{k_B T}{h} e^m c_0^{1-m} e^{\Delta S_{\ddagger}^0/R} \quad \text{or, } \Delta S_{\ddagger}^0 = R \left[\ln \left(\frac{Ah}{k_B T c_0^{1-m}} \right) - m \right]$$

Now, $\Delta G_{\ddagger}^0 = \Delta H_{\ddagger}^0 - T\Delta S_{\ddagger}^0$, Inserting the expression, we have $\Delta G_{\ddagger}^0 = E_a - RT \ln \left(\frac{Ah}{k_B T c_0^{1-m}} \right)$.

Problem: For a bimolecular decomposition of HI, the rate constant is $2.8 \times 10^{-7} \text{ mol}^{-1} \text{ lit sec}^{-1}$ at 556 K.

The activation energy is $44,300 \text{ cal mol}^{-1}$. Calculate the entropy of activation. [Calcutta Univ. 1987]

Solution: $\Delta S_{\ddagger}^0 = 22.48 \text{ cal mol}^{-1} \text{ K}^{-1}$.

Problem: The rate constant of a second order gas phase reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ is $0.0234 \text{ lit mol}^{-1} \text{ sec}^{-1}$ at 400°C , and activation energy is 150 kJ mol^{-1} . Calculate ΔH_{\ddagger}^0 , ΔG_{\ddagger}^0 and ΔS_{\ddagger}^0 for the reaction.

Solution: $\Delta H_{\ddagger}^0 = 138.8 \text{ kJ mol}^{-1}$, $\Delta G_{\ddagger}^0 = 190.3 \text{ kJ mol}^{-1}$ and $\Delta S_{\ddagger}^0 = -76.5 \text{ J K}^{-1} \text{ mol}^{-1}$.

Problem: For the reaction $A + B \rightleftharpoons X_{\ddagger} \rightarrow P$, $E_a = 20.0 \text{ kJ mol}^{-1}$ at 300 K. The enthalpy change for the formation of the activated complex from the reactants in kJ mol^{-1} is

(a) 12 (b) 15 (c) 23 (d) 25 [GATE, 2004]

Solution: The correct option is (b). Hints: $\Delta H_{\ddagger}^0 = E_a + (\Delta n_g - 1)E_a$, here $\Delta n_g = -1$, so $\Delta H_{\ddagger}^0 = E_a - 2RT$

or, $\Delta H_{\ddagger}^0 = 20 \text{ kJ mol}^{-1} - 2 \times 8.31 \times 10^{-3} \text{ kJ mol}^{-1} \times 300 \text{ K} = 20.0 - 4.986 = 15 \text{ kJ mol}^{-1}$.

Question: The activation energy and entropy of a bimolecular gas phase reaction at 600 K are 200 kJ mol^{-1} and $-200 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The free energy of activation is
(1) 70 kJ mol^{-1} (2) 80 kJ mol^{-1} (3) 310 kJ mol^{-1} (4) 320 kJ mol^{-1} [Adm to M Sc, BHU 2011]

Answer: The correct option is (3). Hints: $\Delta G_{\ddagger}^{\circ} = \Delta H_{\ddagger}^{\circ} - T\Delta S_{\ddagger}^{\circ} = E_a - mRT - T\Delta S_{\ddagger}^{\circ}$
 $= 200 \text{ kJ mol}^{-1} - 2 \times 8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \times 600 \text{ K} - 600 \text{ K} \times (-200 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) = 310 \text{ kJ mol}^{-1}$.

Question: The activation energy of a gas phase association between F_2 and IF_5 ; a first order reaction, is 58.6 kJ mol^{-1} . The activation enthalpy at 340 K is
(1) 53 kJ mol^{-1} (2) 55.8 kJ mol^{-1} (3) 58.6 kJ mol^{-1} (4) 61.4 kJ mol^{-1} [Adm to M Sc, BHU 2011]

Answer: The correct option is (1). Hints: $\Delta H_{\ddagger}^{\circ} = E_a - mRT = 58.6 \text{ kJ mol}^{-1} - 2 \times 8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$
 $= 53 \text{ kJ mol}^{-1}$.

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Effect of Ionic Strength on Ionic Reactions – Primary Kinetic Salt Effect

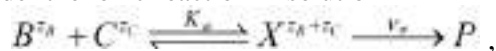
Introduction:

Due to electrostatic interactions, kinetics of reaction between ions substantially deviates from those observed in reactions between non-electrolytes. The rate constant of ionic reactions depends upon the charge of the reacting ions and also on the ionic strength (i) of the solution. It also depends on the dielectric constant (D) of the solution.

The effect of ionic strength on rate constant is called the primary kinetic salt effect.

Formulation of the effect:

Bronsted (1922) and later Bjerrum made a satisfactory treatment on the effect using the concept of transition state theory. Let us consider the ionic reaction in solution



where z_B and z_C are the valences of the reacting species and $z_B + z_C$ is the valence of the activated complex. The equilibrium constant of the rapid equilibrium process is given as

$$K_{\ddagger} = \frac{a_{X_{\ddagger}}}{a_B \times a_C} = \frac{[X_{\ddagger}] f_{X_{\ddagger}}}{[B] f_B \times [C] f_C} \quad \text{or, } [X_{\ddagger}] = K_{\ddagger} [B][C] \times \frac{f_B \times f_C}{f_{X_{\ddagger}}}.$$

The rate equation for the formation of the product, $\frac{d[P]}{dt} = \nu_{\ddagger} [X_{\ddagger}] = (\nu_{\ddagger} K_{\ddagger}) [B][C] \times \frac{f_B \times f_C}{f_{X_{\ddagger}}}$

or, $\frac{d[P]}{dt} = k_0 [B][C] \times \frac{f_B \times f_C}{f_{X_{\ddagger}}}$, where $k_0 = (\nu_{\ddagger} K_{\ddagger})$ is the rate constant of the ionic reaction when $f \rightarrow 1$.

$[X_{\ddagger}]$ and $f_{X_{\ddagger}}$ are the molar conc. and molar scale activity coefficient of the activated complex. ν_{\ddagger} is the decomposition frequency with which the activated complex breaks into the product (P). $\nu_{\ddagger} = \frac{k_B T}{h}$ and

$$k_0 = \nu_{\ddagger} K_{\ddagger} = \left(\frac{k_B T}{h} e^2 c_0^{-1} e^{\Delta S_{\ddagger}^0 / R} \right) e^{E_a / RT}.$$

The activity coefficient of an ion is related with ionic strength (i) of the solution by Debye-Huckel limiting law, $\log f_j = -A z_j^2 \sqrt{i}$, where $A = \text{Debye-Huckel constant} \propto \frac{1}{(DT)^{3/2}}$ and 25 °C in aqueous solution, $A = 0.51$.

But, for this elementary bimolecular reaction (which is 2nd order reaction also), the experimental rate equation is

$$\frac{d[P]}{dt} = k [B][C],$$

where k is experimentally determined rate constant of the reaction. Equating with the formulated rate equation,

we get $k = k_0 \frac{f_B \times f_C}{f_{X_{\ddagger}}}$.

Taking logarithm, we have $\log k = \log k_0 + \log f_B + \log f_C - \log f_{X_{\ddagger}}$. Now using Debye-Huckel limiting law,

$$\log k = \log k_0 - A z_B^2 \sqrt{i} - A z_C^2 \sqrt{i} + A (z_B + z_C)^2 \sqrt{i} = \log k_0 + A [(z_B + z_C)^2 - z_B^2 - z_C^2] \sqrt{i} - A \sqrt{i} + A \sqrt{i}$$

$$\text{or, } \log k = \log k_0 + 2A z_B z_C \sqrt{i} \text{ ----- (1)}$$

This is Bronsted- Bjerrum equation relating the effect of ionic strength (i) on the rate constant (k) of ionic reaction. At 25 °C in aqueous solution, $A = 0.51$ and the equation is $\log k_0 + 1.02 z_B z_C \sqrt{i}$.

This equation shows that $k = k_0$ when $i \rightarrow 0$ i.e. at the zero ionic strength of the solution

If the products have different charges than the reactants, the ionic strength is change significantly during the reaction, k will also change as the reaction proceeds. To avoid this, a large amount of inert salt is often added to keep i essentially fixed during the reaction.

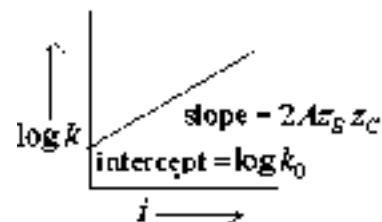
The equation (1) is written as $\log\left(\frac{k}{k_0}\right) = 2Az_B z_C \sqrt{i} = \log\left(\frac{k}{k_0}\right) = 1.02z_B z_C \sqrt{i}$ (at 25 °C in aqueous solution). The ionic strength is calculated from Lewis-Randall relation, $i = \frac{1}{2} \sum c_j z_j^2$.

Three possibilities may arise depending on the charge of the reacting ions.

(A) When z_B and z_C are the same sign, $z_B z_C = (+ve)$ and rate constant (k) increases with the increase of ionic strength (i) of the solution.

Examples: (I) $[Co(NH_3)_5 Br]^{+2} + Hg^{+2}$, $z_B z_C = 4$

(II) $S_2O_8^{-2} + 2I^{-1} \rightarrow I_2 + 2SO_4^{-2}$, $z_B z_C = 2$. [Calcutta Univ. 2013]



(B) When z_B and z_C are of opposite sign, $z_B z_C = (-ve)$ and

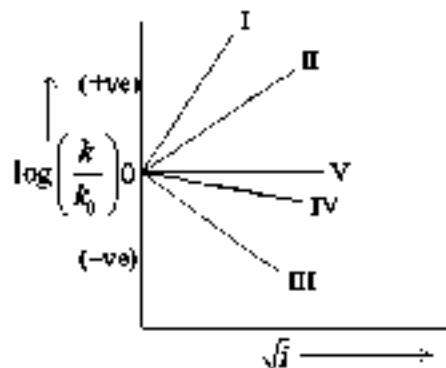
the rate constant (k) decreases with the increase of ionic strength (i) of the solution.

Examples: (III) $[Co(NH_3)_5 Br]^{+2} + OH^{-1}$, $z_B z_C = -2$ [Calcutta Univ. 2014]

(IV) $NH_4^{+1} + CNO^{-1} \rightarrow CO(NH_2)_2$, $z_B z_C = -1$

(C) When one of the reactants is uncharged, $z_B z_C = 0$ and the rate constant (k) remains unchanged with the change of ionic strength (i) of the solution.

Example: (V) $C_{12}H_{22}O_{11} + OH^{-1}$, $z_B z_C = 0$.



Nature of ionic reactions:

Ionic reactions are very fast but the reactions where bond-breaking and bond-making processes are involved, its rate is moderate. The well-known example is the isomerisation of $NH_4 CNO$ to urea. the reaction rate is measured by titrating the cyanate with $AgNO_3$ solution or by measuring the conductance of the reaction mixture. It is 2nd order reaction.

Stability of activated complex in ionic solution:

For the ions of like sign, the increasing ionic strength (by addition of inert ions) increases the rate constant. This can be understood in terms of the formation of a single, highly charged activated complex from two ions of like charges. The process is favoured by high ionic strength because of the favourable interaction of the new ion with its denser ionic atmosphere.

Some other examples of ionic reactions:

(1) $2CH_2BrCOO^{-} + S_2O_3^{-2} \rightarrow 2CH_2(S_2O_3)COO^{-} + Br^{-}$, $z_B z_C = 2$

(2) $[Cr(NH_2CONH_2)_6]^{+3} + 6H_2O \rightarrow [Cr(H_2O)_6]^{+3} + 6NH_2CONH_2$, $z_B z_C = 0$

(3) $CH_2ICOOH + CNS^{-} \rightarrow 2CH_2(CNS)COOH + I^{-}$, $z_B z_C = 0$.

Example of the effect: Primary kinetic salt effect is large, even at modest ionic strength. For $z_B z_C = +2$,

the values of k/k_0 at $i = 10^{-3}, 10^{-2}, 10^{-1}$ are 1.15, 1.51 and 2.7, respectively.

Problem: The rate constant of a reaction $A^{+1} + B^{-2} \rightarrow \text{Product}$, is measured at 0.001 ionic strength and at 0.01 ionic strength at 25 °C in water. What is the expected ratio of the rate constants?

Solution: Hints: $\log \frac{k_{0.001}}{k_{0.01}} = 2 \times (+1)(-2) \times 0.51 (\sqrt{0.001} - \sqrt{0.01}) = 0.1395$ or, $\frac{k_{0.001}}{k_{0.01}} = 1.379$.

Question: The rate constant for a reaction $A^{+1} + B^{n+} \rightarrow P$ is measured in two different aqueous solution of ionic strengths 0.01 M and 0.04 M. If $\log \frac{k_{0.04}}{k_{0.01}} = 0.3$, the charge n on B is closest to

- (a) 1 (b) 2 (c) 3 (d) 6

[NET(CSIR - UGC), 2014 (II)]

Answer: The correct option is (c).

$\log \frac{k_{0.04}}{k_{0.01}} = 2 \times (+1)(+n) \times 0.51 (\sqrt{0.04} - \sqrt{0.01})$ or, $0.3 = 1.01 \times n (0.2 - 0.1)$ or, $n \approx 3$.

CATALYSIS

Introduction:

We observed that there are many reactions which, while having large equilibrium constant, proceed at extremely low rate. So to take advantage of these reactions, especially for industrial processes, it is important to find ways to increase their rate. A suitable catalyst can help to increase their rates.

Definition:

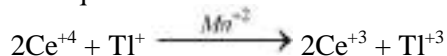
A catalyst is a substance that accelerates the rate of a chemical reaction without itself being consumed. It provides an alternative route of lower activation energy and so the rate of the reaction is increased. The substance remains unchanged both in mass and composition at the end of the reaction. This effect is called catalysis.

An example of the catalyzed reaction is the decomposition of KClO_3 by the catalyst MnO_2 .

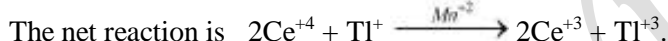
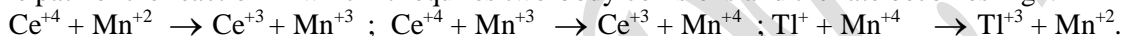


The product O_2 gas gets out of phase and so the reaction tends to complete (large value of equilibrium constant).

Another example in aqueous solution is



In absence of catalyst Mn^{+2} , the reaction requires three-body collisions and hence rate is slow. But the catalyst changes the path of the reaction in which it requires two-body collisions and the rate becomes high.



This shows that catalyst provides an alternative path of the reaction that leads to easy formation of the product.

Some reactions slow down the rate of chemical reaction and are often called negative catalyst. But such behaviour does not suit the function of the catalyst as it would provide an alternative path of higher activation energy. In that case, the reaction would follow the unanalyzed path of lower activation energy. As for example, H_2SO_4 acts an inhibitor in the decomposition of H_2O_2 . Inhibitors may destroy a catalyst present in the system or may react with reaction intermediate in the chain reaction.

Characteristics of Catalysts:

(1) the catalyst remains unchanged in mass and composition at the end of the reaction. However, the physical state such as particle size or colour of the catalyst may change.

For example, coarse grains of MnO_2 used in the decomposition of KClO_3 becomes finely divided powder after the reaction.

This suggests that the catalyst participates during the course of the reaction.

(2) A very minute quantity of a catalyst can produce large effect on the reaction rate.

For example, 1.7×10^{-4} gm Pt in colloidal state can produce 1.8 cc of O_2 gas per minute from the decomposition of H_2O_2 . The catalyst remains equally effective even after the production of 10 litre of O_2 .

This suggests that the catalyst though participates in the reaction; it is regenerated at the end of the reaction.

(3) A catalyst can not start a reaction but only increases the speed of a spontaneous reaction.

The criteria of spontaneity of a chemical reaction is given by $\Delta G_{T,P} < 0$. Since the catalyst is reproduced at the end and it provides an alternative route of the reaction without changing the composition at equilibrium, it does not contribute to the $\Delta G_{T,P}$ value of the reaction. But G is a state function and so $\Delta G_{T,P}$ of the reaction remains same as it does not depend on the path of a process.

This argument explains that a catalyst can not initiate a reaction, it only can change the reaction rate which is already occurring in its absence.

(4) The catalyst can not affect the final state of equilibrium.

This can be explained from the van't Hoff reaction isotherm, $\Delta G_{T,P}^0 = -RT \ln K_p$. Since catalyst does not contribute any free energy to the system, hence $\Delta G_{T,P}^0$ remains same as it is in absence of the catalyst. Thus K_p , the equilibrium constant of the reaction remains unaffected.

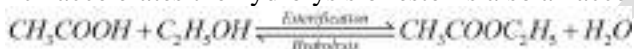
However, if we consider it more rigorously, then in homogeneous catalysed reactions (reactants and catalyst are in same phase), a catalyst can change the equilibrium composition slightly. The activity equilibrium constant of

a reaction, $K_a = \prod (a_i)_{eq}^{V_i}$, where $a_i = x_i \gamma_i$. The catalyst remains in the same phase as the reactants and products so it will change the activity coefficients (γ_i). Since K_a is a true equilibrium constant so the equilibrium mole fraction (x_i) of the reacting components are changed. However, the catalyst is added to a very small amount so the equilibrium composition is also very small.

(5) A catalyst not only accelerates the forward process, but also it accelerates the backward process to the same extent.

We have $K_{eq} = k_f/k_b$, where k_f and k_b are the rate constants of the forward and backward processes respectively of a reaction. If the catalyst increases the rate of the forward process, k_f is increased. Thus, in order to keep K_{eq} constant, k_b is also increased to the same extent. So the catalyst enhances the rates of both the forward and backward processes and it helps to attain the equilibrium much more quickly.

For example, H^+ which accelerates the hydrolysis of ester is also an accelerator for the esterification of the organic acids.

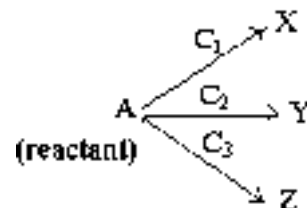


This suggests that the catalyst not only lowers the activation energy of the forward process but also it lowers the activation energy of the backward process to the same extent.

(6) The action of a catalyst is specific.

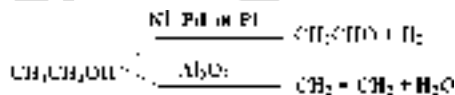
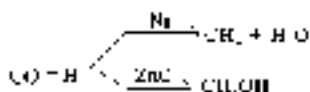
A catalyst can catalyse only a specific reaction and cannot be used for many reactions. For example, MnO_2 can catalyse the decomposition of $KClO_3$ but not KNO_3 or $KClO_4$. Highly specific action of a catalyst can be compared to the specific use of a key which can open a particular lock and not every lock (Emil Fisher).

This specific action of the catalyst helps to eliminate undesirable side products when several products are possible for same reactants. A catalyst can lower the activation energy of a specific path. Thus it is possible to select and direct the course of then reaction in a specific path. This specificity and selectivity property of a catalyst is very much useful to change the direction of the reaction.



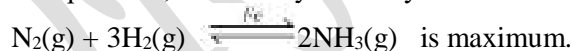
The catalyst C_1 reduces the activation energy of the path $A \rightarrow X$ and does not affect the formation of products Y and Z . Similar cases also happen in other two paths.

Examples:



(7) There is optimum temperature at which the efficiency of a catalyst is notably high.

For example, at 770 K temperature, the activity of catalyst Fe in the Haber's process:



This is because at this temperature, N_2 is chemisorbed on the surface of Fe powder and N_2 is dissociated into N-atoms by the heat of adsorption (dissociative adsorption) and thereby it favours the formation of NH_3 .

In case of enzyme catalyst, the efficiency increases exponentially with temperature and when sufficient temperature is raised, the efficiency falls down due to coagulation of the enzyme from the colloidal state. The optimum temperature of the catalyst is between 25 °C and 45 °C.

(8) Some substances, known as promoters, can activate the efficiency of a catalyst. They act as catalyst

for the catalyst. In the Haber's process, $N_2(g) + 3H_2(g) \xrightarrow[Fe]{(K_2O+Al_2O_3)} 2NH_3(g)$, Al_2O_3 acts as barrier that prevents the tiny particles of Fe from joining together (sintering). Since formation of large crystals decreases the surface area of the catalyst, Fe and thereby catalytic activity is also diminished.

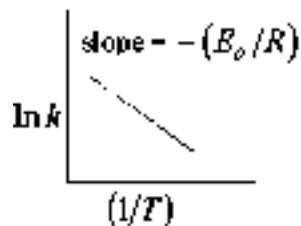
(9) Some substances can destroy the activity of the catalyst and these are called 'catalyst poison'.

For example in the contact process, $2SO_2(g) + O_2(g) \xrightarrow[As_2S_3]{Pt catalyst} 2SO_3(g)$.

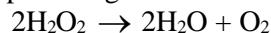
A small amount of As destroys the efficiency of the catalyst Pt by forming Pt-arsenide. These substances adsorb on the reactive site of the catalyst and form strong bond, and thus block for the reaction. These poisons may be present along with the reactants as impurities or formed as by-product from the reaction. They include compounds of S, N, P, As etc having lone pair of electrons and also certain metals like Pb, Hg, etc. Pb is catalyst poison and so lead-free gasoline is used in the car.

Lowering of activation energy by the catalyst

Activation energy (E_a) of a reaction (both catalysed and uncatalysed) can be experimentally determined by Arrhenius plot of the $\ln k$ vs. $\frac{1}{T}$ in the equation $\ln k = \ln A - \left(\frac{E_a}{R}\right)\frac{1}{T}$ or by $E_a = RT^2 \left(\frac{d \ln k}{dT}\right)$.



Different catalysts lower the activation energy of the same reaction to different extent. Some examples are given for the reaction of decomposition of H_2O_2



Activation energies: 17.0 kcal/mol when uncatalysed
 13.6 kcal/mol when catalysed by I⁻
 12.0 kcal/mol when catalysed by colloidal Pt particles
 10.0 kcal/mol when catalysed by Fe^{+3}
 2.0 kcal/mol when catalysed by enzyme liver catalase.

A decrease from 17.0 to 2.0 kcal/mol in E_a increases the rate constant by 10^{11} times at room temperature assuming the factor A is not significantly changed.

$$\frac{k_{cat}}{k_{uncat}} = \frac{Ae^{-E_{cat}/RT}}{Ae^{-E_{uncat}/RT}} = e^{(E_{uncat}-E_{cat})/RT} = e^{(17.0-2.0)/(2 \times 10^{-3} \times 300)} = 7.2 \times 10^{10} \approx 10^{11}$$

Question: A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation energy barrier by 20 kJ mol^{-1} . [IIT – JAM Sample]

Answer: $R_{uncat} = k_{uncat}[S] = Ae^{-E_{uncat}/R \times 500}[S]$ at 500 K and $R_{cat} = k_{cat}[S] = Ae^{-E_{cat}/R \times 400}[S]$ at 400 K.

But these two rates are same, so $Ae^{-E_{cat}/R \times 400}[S] = Ae^{-E_{uncat}/R \times 500}[S]$

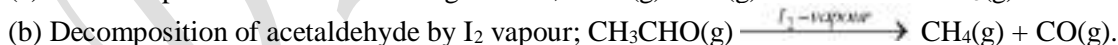
$$\text{or, } \left(\frac{E_{uncat} - 20 \text{ kJ mol}^{-1}}{400}\right) = \frac{E_{uncat}}{500} \quad \text{or, } E_{uncat} = 100 \text{ kJ mol}^{-1}$$

Type of catalysed reactions

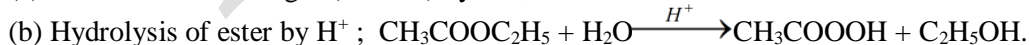
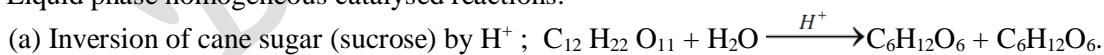
Catalysed reactions can be classified as:

(A) **Homogeneous catalysed reactions:** The catalyst remains in the same phase as the reacting substances.

(1) Gas phase homogeneous catalysed reaction:

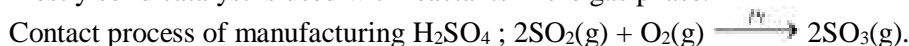


(2) Liquid phase homogeneous catalysed reactions:

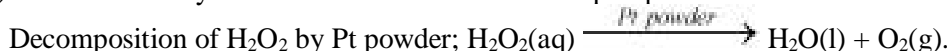


(B) **Heterogeneous catalysed reactions:** The catalyst is present in different phases from the reactants.

(1) Mostly solid catalyst is used with reactants in the gas phase.



(2) Also solid catalyst is used with reactants in the liquid phase:



(C) Micro heterogeneous catalysed reactions:

Enzyme catalysts are used in colloidal state having dimensions 10^3 to 10^4 Å and kinetic behaviour is similar to that of heterogeneous catalysed reactions. So this is sometimes called heterogeneous catalysed reactions.



Theory of homogeneous catalysis

It is now a known fact that for a chemical reaction to occur, it is essential that the reacting substances must possess addition minimum energy, called activation energy.

Function and criteria of catalyst:

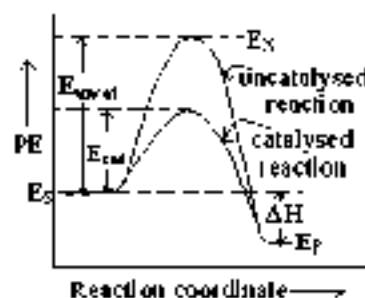
According to the theory of homogeneous catalysis, the function of a catalyst is to provide an alternative path in which the activation energy is lowered. Lesser activation energy permits larger amount of reactants to react in a given time.

For example, the uncatalysed decomposition of ethyl ether is found to be a unimolecular reaction with activation energy 53 kcal/mole. When iodine vapour is used as catalyst, the reaction becomes bimolecular with activation energy 35 kcal/mole. The rate equation is given as: $-\frac{d[\text{ether}]}{dt} = k[\text{ether}][\text{I}_2]$.

Catalyst is like a tunnel in chemical reaction:

That the activation energy in catalysed reaction (E_c) is less than that in uncatalysed reaction (E_{uc}) can be obtained from the Arrhenius plot for the reaction in absence of the catalyst and in presence of the catalyst.

This function of the catalyst can be compared to that of a tunnel in crossing mountain. In order to cross a mountain at its full height, there requires more energy. But catalyst provides an alternative route to the reaction similar to the tunnel at some lower height. This requires less energy to cross the mountain.



Postulates of the theory:

The postulates of the theory of homogeneous catalysis are given below:

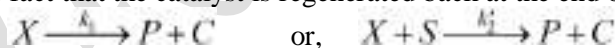
- (i) The catalyst (C) first combines with the substrate (S) to intermediate (X). This postulate complies with the fact that catalyst participates in the reaction and does not react with any substrate (selectivity)



where k_2 and k_{-1} are the rate constants of the forward bimolecular and backward unimolecular reaction.

- (ii) The intermediate compound (X) then breaks down to the product (P) and the catalyst (C) in unimolecular reactions. In bimolecular reactions, the intermediate (X) reacts with another substrate (S) to form product (P) and catalyst (C)

This step also supports the fact that the catalyst is regenerated back at the end of the reaction.



- (iii) The catalyst (C) is regenerated in the last step and may further undergo steps (i) and (ii) to form more and more products. Thus the turn over number of the catalyst is very high.

Formulation of the rate law:

The rate of formation of the product, $\frac{d[P]}{dt} = k_1[X]$. Using the steady-state approximation for the reactive

intermediate X , we have $\frac{d[X]}{dt} = k_2[S][C] - k_{-1}[X] - k_1[X] = 0$ or, $[X] = \frac{k_2[S][C]}{k_{-1} + k_1}$.

Inserting in the rate expression, we get $\frac{d[P]}{dt} = \frac{k_1 k_2 [S][C]}{k_{-1} + k_1} = \left(\frac{k_1 k_2}{k_{-1} + k_1} \right) [S][C]$ or, $\frac{d[P]}{dt} = k_c [S][C]$,

where k_c is the catalytic coefficient of the catalyst. It is characteristic constant of the catalyst for the reaction.

Thus, it is seen that the catalysed reaction becomes bimolecular though the uncatalysed reaction is unimolecular ($S \rightarrow P$). Again the rate equation shows that the rate of the catalysed reaction depends on the conc. of the catalyst although it is neither produced nor consumed in the reaction. This has been confirmed by experiments.

Examples: Oxidation of SO_2 catalysed by NO is $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{\text{NO}(\text{g})} 2\text{SO}_3(\text{g})$.

The reaction follows the above mechanism as $\text{O}_2 + 2\text{NO} \rightarrow 2\text{NO}_2$; $2\text{SO}_2 + 2\text{NO}_2 \rightarrow 2\text{SO}_3 + 2\text{NO}$
The net reaction is $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$. The existence of the intermediate, NO_2 is experimentally confirmed.

Success of the theory: This mechanism explains the following criteria of the catalyst.

- (1) Catalyst participates in the reaction (criteria 1)
- (2) Catalyst is regenerated at the end (criteria 2)
- (3) It shows that it provides an alternative path of lower activation energy (4) It shows the selective nature of the catalyst as C does not form intermediate with any substrate (criteria 5).
- (5) This explains that the rate of catalysed reaction depends on the conc. of catalyst.

Failure of the theory:

(1) This theory fails to explain the heterogeneous catalysis. (2) This also fails to explain the action of catalyst poison and catalyst promoters.

Question: In a homogeneous catalysed reaction, 1.9 (M) substrate and 1.0 μ (M) of a catalyst yields 1.0 m(M) of a product in 10 sec. The turn-over frequency (TOF) of the reaction (sec^{-1}) is

- (A) 10^{-2} (B) 10^2 (C) 10^3 (D) 10^{-3} [IIT – JAM Sample]

Answer: The correct option is (B).

Hints:
$$TOF = \frac{[\text{Product}]}{[\text{Catalyst}] \times \text{time}} = \frac{1.0 \text{ m(M)}}{1.0 \mu(\text{M})} \times \frac{1}{10 \text{ sec}} = \frac{1.0 \times 10^{-3} (\text{M})}{1.0 \times 10^{-6} (\text{M})} \times \frac{1}{10 \text{ sec}} = 10^{-2} \text{ sec}^{-1}.$$

Question: The pseudo first order rate constant for the cobalt-catalysed auto-oxidation of toluene in acetic acid at 87 °C at different conc. of Co(III) are

[Co(III)]/M	→ 0.053	0.084	0.118	0.172
$k/10^{-5} \text{ s}^{-1}$	→ 1.47	2.93	5.68	11.58

for $[\text{toluene}]_0 = 0.5 \text{ M}$. The order with respect to $[\text{Co(III)}]$ is

- (1) 2 (2) 1.5 (3) 1 (4) 0.5 [NET(CSIR – UGC), 2015 (I)]

Answer: The correct option is (2). Hints: The pseudo first order rate constant, $k = k_c [C]^n$, where n is the order with respect to the catalyst Co(III) and k_c is the catalytic constant. Putting the first and second set data in the above equation, we get

$$\frac{2.93 \times 10^{-5} \text{ s}^{-1}}{1.47 \times 10^{-5} \text{ s}^{-1}} = \left(\frac{0.084}{0.053} \right)^n. \text{ Solving the equation, } n = 1.5.$$

Question: Sucrose is hydrolyzed to glucose and fructose in presence of H^+ as catalyst. At any initial conc. of sucrose, the half lives at pH = 5 and pH = 4 are 500 min and 50 min respectively. Find out the values of the exponents 'a' and 'b' in the rate law expression

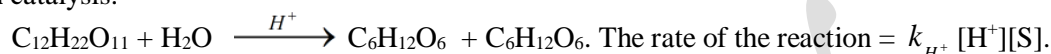
$$-d[\text{sucrose}]/dt = k[\text{sucrose}]^a [\text{H}^+]^b \quad \text{[Calcutta Univ. 2013]}$$

Acid – Base Catalysis [An example of homogeneous catalysis]

Acids and bases are very popular in their activity to catalyse the variety types of chemical reactions. Some of the examples are given below in brief:

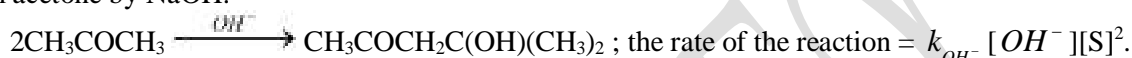
(1) Specific H^+ ion catalysed reactions:

Oswald found that inversion of cane sugar is catalysed by acids to different extent depending on the strength of the acids. Later, it is explained that this is due to the fact that these reactions are catalysed by H^+ ions only and different acids produce different $[H^+]$ in solution depending on their strength. This is called specific H^+ ion catalysis.



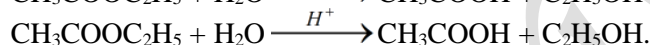
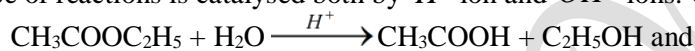
(2) Specific OH^- ion catalysed reactions:

These reactions are catalysed by OH^- only. One example of this type is the formation of diacetone alcohol from acetone by NaOH.



(3) Specific H^+ ion and OH^- ion catalysed reactions:

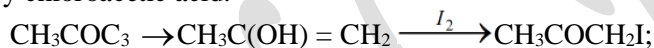
This type of reactions is catalysed both by H^+ ion and OH^- ions. One example is the hydrolysis of ester.



The rate of the reaction is $= k_{H^+} [H^+][S] + k_{OH^-} [OH^-][S] + k_{H_2O} [H_2O][S]$.

(4) Generalized acid catalysed reactions:

These reactions are catalysed by H^+ , HA and the cations of weak bases. One example is the iodination of acetone catalysed by chloroacetic acid.



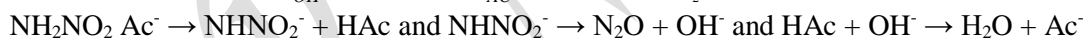
rate of the reaction $= k_{H^+} [H^+][S] + k_{HA} [HA][S] + k_{H_2O} [H_2O][S]$.

(5) Generalized base catalysed reactions:

These reactions are catalysed by OH^- , BOH and anions of weak acids. One example is the decomposition of nitramide by OH^- , Ac^- and H_2O .



the rate $= k_{OH^-} [OH^-][S] + k_{Ac^-} [Ac^-][S] + k_{H_2O} [H_2O][S]$.



(6) Generalized acid –base catalysed reactions:

All acids and bases like H^+ , OH^- , HA, BOH, anions of weak acids and cations of weak bases have catalysed effect on the reaction. One example is the mutarotation of glucose.



The rate $= k_{OH^-} [OH^-][S] + k_{H^+} [H^+][S] + k_{Ac^-} [Ac^-][S] + k_{HAc} [HAc][S] + k_{H_2O} [H_2O][S]$.

The catalytic constants determined experimentally have values,

$$k_{OH^-} = 6 \times 10^3, k_{H^+} = 1.4 \times 10^{-1}, k_{Ac^-} = 2.7 \times 10^{-2}, k_{HAc} = 2 \times 10^{-3} \text{ and } k_{H_2O} = 6 \times 10^{-3}.$$

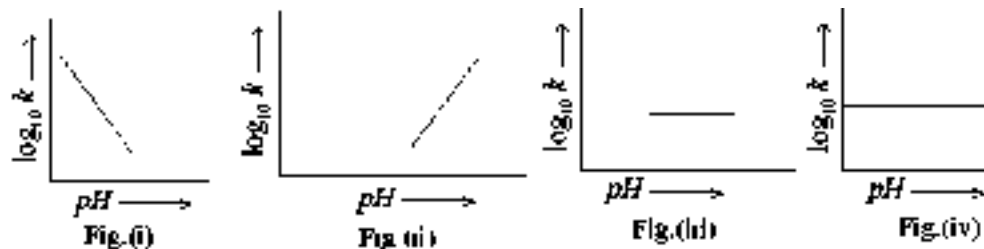
Question: The rate constant of a reaction catalysed by H_3O^+ and OH^- ions, and also occurring spontaneously is

$$k = k_0 + k_{H_3O^+} [H_3O^+] + k_{OH^-} [OH^-], \text{ where } k_0 = \text{rate constant for the uncatalysed reaction.}$$

What should be the plot of $\log_{10} k$ vs. pH for

- (i) sufficiently acid solution (ii) sufficiently basic solution (iii) solutions when there is no catalysis in either the acid or the basic region, and (iv) the uncatalysed reaction. **[Burdwan Univ 1992]**

- Answer:** (i) In sufficiently acidic solution, $[H_3O^+] \gg [OH^-]$, we can neglect both k_0 and $k_{OH^-}[OH^-]$ in comparison to $k_{H^+}[H_3O^+]$. The rate constant $k = k_{H^+}[H_3O^+]$ or, $\log_{10} k = \log_{10} k_{H^+} - pH$
- (ii) In sufficiently alkaline solution, $k = k_{OH^-}[OH^-]$ or, $\log_{10} k = \log_{10} k_{OH^-} + \log_{10}[OH^-]$
or, $\log_{10} k = \log_{10} k_{OH^-} + \log_{10} K_w + pH$.
- (iii) The region of the acid and bases where the reaction is not catalysed will be around the neutral region i.e., around $pH = 7.0$ and the rate constant, $\log_{10} k = \log_{10} k_0$
- (iv) for the uncatalysed reaction, $k = k_0$ and $\log_{10} k = \log_{10} k_0$.



Question: Decomposition of a compound A is catalysed by OH^- ions. If the rate constant is 1.35×10^{-2} lit mol $^{-1}$ sec $^{-1}$ at 30 °C in aqueous solution, calculate the half life of A in a solution of $pH = 10$.

[Burdwan Univ. 1996]

Answer: Rate = $k_{OH^-}[OH^-][A]$ and the rate constant $k_{OH^-} = 1.35 \times 10^{-2}$ lit mol $^{-1}$ sec $^{-1}$. But the reaction is conducted at $pH = 10$ so $pOH = 14 - 10 = 4$ and $[OH^-] = 10^{-4}$ (M).

The rate constant $k = k_{OH^-}[OH^-] = 1.35 \times 10^{-2} \times 10^{-4}$ lit mol $^{-1}$ sec $^{-1} \times$ mol lit $^{-1} = 1.35 \times 10^{-6}$ sec $^{-1}$.

The reaction is 1st order as rate constant is independent of time, so the half life of A is,

$$t_{1/2} = 0.693/k = 0.693/(1.35 \times 10^{-6} \text{ sec}^{-1}) = 5.13 \times 10^{-7} \text{ sec}.$$

Question: Hydrolysis of ester is simultaneously catalysed by both H^+ and OH^- ions. The reaction is first order

with respect to each species. Show that the rate is minimum when $[H^+] = \left(\frac{k_{OH^-} \cdot K_w}{k_{H^+}} \right)^{1/2}$.

[Calcutta Univ, 2011, Burdwan Univ. 1997]

Answer: Rate of the reaction, $R = k[E]$. But rate = $(k_{H^+}[H^+] + k_{OH^-}[OH^-])[E]$, where $[E]$ is conc. of ester

and $k = k_{H^+}[H^+] + k_{OH^-}[OH^-] = k_{H^+}[H^+] + \frac{k_{OH^-} \times K_w}{[H^+]}$. Differentiating with respect to $[H^+]$,

$$\text{we get } \frac{dk}{d[H^+]} = k_{H^+} - \frac{k_{OH^-} \times K_w}{[H^+]^2} \text{ or, } k_{H^+} - \frac{k_{OH^-} \times K_w}{[H^+]^2} = 0 \text{ or, } [H^+] = \left(\frac{k_{OH^-} \cdot K_w}{k_{H^+}} \right)^{1/2}.$$

When the rate is minimum, k is also minimum at the $[H^+]$ and the condition this is $(dk/d[H^+]) = 0$.

Question: Find the appropriate pH in the above problem at which the minimum rate is observed at room temperature, if $k_{OH^-}/k_{H^+} = 100$.

[Burdwan Univ. 2010]

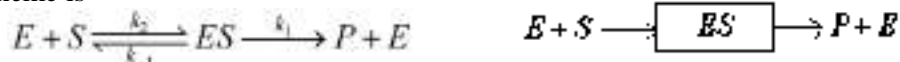
Answer: We have $[H^+] = \left(\frac{k_{OH^-} \cdot K_w}{k_{H^+}} \right)^{1/2} = (100 \times 10^{-14})^{1/2}$ or, $[H^+] = 10^{-6}$ (M) or, $pH = -\log 10^{-6} = 6$.

The overall reaction is



with rate constant k which is determined by experiment.

Michaelis – Menten scheme is



This is done catalytic cycle performed by the reactive centre of the enzyme.

The enzyme-bound substrate (ES) is short lived and so reactive intermediate. It maintains steady value of conc. during the reaction. Thus steady-state approximation can be applied to the conc. of ES.

$$\frac{d[ES]}{dt} = k_2[E][S] - k_{-1}[ES] - k_1[ES] = 0 \quad \text{or,} \quad [ES] = \frac{k_2[E][S]}{k_{-1} + k_1} = \frac{[E][S]}{(k_{-1} + k_1)/k_2} \quad \text{or,} \quad [ES] = \frac{[E][S]}{K_M},$$

where $(k_{-1} + k_1)/k_2 = K_M$, called **Michaelis constant** for the reaction. K_M value is different for different

enzyme-catalysed reaction. It may given a **significance** as $K_M = \frac{[E][S]}{[ES]}$, ----- (1)

K_M may called dissociation constant of enzyme –bound substrate for the reaction, $ES \rightleftharpoons E + S$.

The higher value of K_M signifies the higher dissociation of the enzyme-bound substrate to the substrate and enzyme instead of breaking into product (P). Thus higher value of K_M of the enzymolysis hampers the rate of the reaction.

For this reaction scheme, the enzyme exists either as free enzyme (E) or as part of enzyme-substrate complex (ES). Because enzyme is catalyst and is not consumed by the process, so sum of these two conc. is constant and equal to the total conc. of enzyme taken initially, $[E]_0$ but this is not so in case of substrate as it is consumed during the process. Thus, $[E] + [ES] = E_0$, a constant through out the reaction. Since only a little enzyme is added, the total conc. of the substrate is approximately equal to the conc. of unbound substrate i.e. $[S] + [ES] \approx [S]$. Typical values are $[E] = 10^{-9}$ M and $[S] = 10^{-5}$ M to moderate the speed of enzymolysis. These reactions are very fast and to maintain steady-state condition of [ES], $[S]/[E]$ is kept very large about 10^4 . Since [E] varies during the reaction, it is generally replaced by $[E]_0 - [ES]$. So using the expression of steady conc. of [ES], we have

$$[ES] = \frac{([E]_0 - [ES])[S]}{K_M} \quad \text{or,} \quad [ES] \times K_M = ([E]_0 - [ES])[S] \quad \text{or,} \quad [ES] = \frac{[E]_0[S]}{K_M + [S]}.$$

The overall rate of the reaction according to Michaelis – Menten mechanism when one substrate undergoes

$$\text{enzymolysis, Rate (R),} \quad \frac{d[P]}{dt} = k_1[ES] \quad \text{or,} \quad R = \frac{k_1[E]_0[S]}{K_M + [S]} \quad \text{----- (2)}$$

This rate equation shows that

- (i) For a fixed conc. of substrate $[S]_0$, the rate of formation of product is proportional to the initial conc. of enzyme taken, $[E]_0$.
- (ii) For a given $[E]_0$, at low $[S]$, $[S] \ll K_M$ the rate, $R = (k_1/K_M)[E]_0[S]$ and the reaction is 1st order with respect to substrate, S. This $(k_1/K_M) = k_{cat}$, called catalytic coefficient of the enzymolysis.

Higher the value of k_{cat} , greater is the efficiency of the enzyme for the reaction.

- (iii) For a given $[E]_0$, at high $[S]$, $[S] \gg K_M$, the rate, $R = k_1[E]_0$. The reaction is zero order with respect to the substrate. This is the maximum rate (R_{max}) of the enzymolysis for a given initial conc. of enzyme.

These characteristic features of enzymolysis are experimentally verified thus Michaelis mechanism is universally accepted.

Initial rate of enzymolysis:

The mechanism is actually given as $E + S \rightleftharpoons ES \rightleftharpoons P + E$. But during the initial period, [P] is small so the rate of the reaction $P + E \rightarrow ES$ is also very small hence it can be neglected. The reaction thus follows as



The initial rate R^0 is not the rate at $t = 0$, there is a short induction period after which the steady-state condition is attained. However, the induction period is generally too short to detect. Usually the reaction is followed only to a few % completion and initial rate (R^0) is determined.

Determination of constants of the rate equation:

The rate equation as formulated by Michaelis and Menten at the starting time is $R^0 = \frac{k_1[E]_0[S]_0}{K_M + [S]_0}$ ----- (3),

where R^0 is the initial rate of the reaction when the substrate conc. is $[S]_0$.

When the initial rate (R^0) is plotted against $[S]_0$, it is a straight line when $[S]_0$ is low and when $[S]_0$ is high R^0 attains a limiting value at given initial conc. of enzyme. This is the maximum rate of the reaction and it is

$$R_{\max}^0 = k_1[E]_0. \text{ Putting this expression of } R_{\max}^0 \text{ in the equation (3), the rate is } R^0 = \frac{R_{\max}^0 [S]_0}{K_M + [S]_0} \text{ -----(4)}$$

For each initial conc. of S, initial rate is determined and the curve is shown given below:

At very high value of $[S]_0$, the rate is maximum and $R_{\max}^0 = k_1[E]_0$.

Thus from the value of R_{\max}^0 from the curve and known $[E]_0$,

it is possible to determine k_1 . This k_1 is called turn-over number

of the enzyme. It is the number of substrate molecules that are converted into product by one molecule of enzyme in unit time.

It is also defined as the maximum number of moles of product produced in unit time by one mole of enzyme.

Turn Over Number (TON) = $R_{\max}^0 / [E]_0$, provided one enzyme molecule contains one reactive centre only.

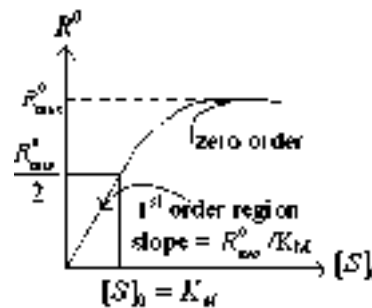
Turn-over number of an enzymes ranges from 10^{-2} to 10^6 molecules per sec with 10^3 sec^{-1} being typical.

For example, one molecule of enzyme carbonic anhydrase will dehydrate 6×10^6 molecules of H_2CO_3 per sec. This reaction, $\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2$, is important in the excretion of CO_2 from capillaries of lungs.

For comparison of efficiency of enzyme, the turn-over number of heterogeneous catalyst is 1 sec^{-1} .

Michaelis constant (K_M) can be evaluated from the value of $[S]_0$ when the rate (R^0) is half of its R_{\max}^0 .

This is shown as $R^0 = \frac{R_{\max}^0 [S]_0}{K_M + [S]_0}$, but when $R^0 = \frac{R_{\max}^0}{2}$, we have $\frac{R_{\max}^0}{2} = \frac{R_{\max}^0 [S]_0}{K_M + [S]_0}$ and $[S]_0 = K_M$.



Question: The condition for which the reaction rate of an enzymolysis that follows Michaelis-Menten kinetics, is half its maximum value, is

- (1) $[S] \ll K_M$ (2) $[S] = K_M$ (3) $[S] = K_M/2$ (4) $[S] \gg K_M$ [BHU Adm. Test, 2011]

Answer: The correct option is (2).

Question: The rate constant k_1 , k_{-1} and k_2 for the enzyme catalysed reaction

are 0.1, 0.01 and 0.05 sec^{-1} respectively. The Michaelis constant for the reaction is

- (1) 0.6 (2) 1.6 (3) 0.0066 (4) 2.25 [BHU Adm. Test, 2013]

Answer: The correct option is (1).

Lineweaver-Burk Plot:

However, for many enzyme-catalysed reactions, it is not possible to obtain data close enough to the plateau region to determine R_{\max}^0 . In this case, alternative method is used to determine R_{\max}^0 and K_M . The rate equation (4) is rearranged in such a way so that a straight line can be obtained by suitable choice of variables. This is done as

$$\frac{1}{R^0} = \frac{K_M + [S]_0}{R_{\max}^0 [S]_0} \quad \text{or,} \quad \frac{1}{R^0} = \frac{K_M}{R_{\max}^0} \frac{1}{[S]_0} + \frac{1}{R_{\max}^0} \quad \text{----- (5)}$$

The plot of $\frac{1}{R^0}$ vs. $\frac{1}{[S]_0}$ gives a straight line and its slope = $\frac{K_M}{R_{\max}^0}$,

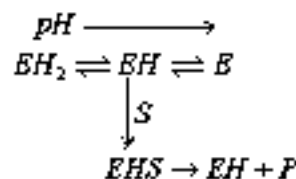
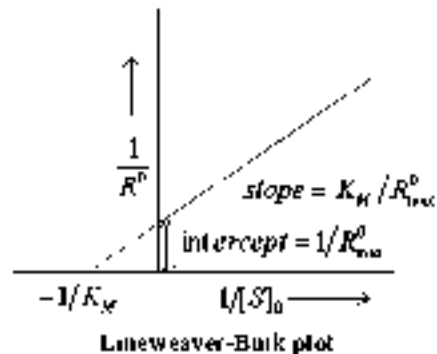
and intercept = $\frac{1}{R_{\max}^0}$. Thus $R_{\max}^0 = \frac{1}{\text{intercept}}$ and $K_M = \frac{\text{slope}}{\text{intercept}}$

while $[E]_0$ is kept fixed in the reaction for which the plot is drawn.

Effect of pH on the activity of the enzyme catalyst:

The catalytic activity of an enzyme generally passes through maximum at a certain pH. This can be explained by assuming that there are three forms of enzyme remaining in equilibrium with each other.

Among the three forms, only EH can combine with substrate (S) and yield EHS that can form product (P). The other intermediates EH_2S and ES do not form product. Since the conc. of EH passes through at a particular pH, the activity of the enzyme becomes maximum also.



Catalytic Efficiency of an Enzyme:

The catalytic efficiency (ε) is defined as $\varepsilon = k_1 / K_M$. Higher the value of ε , the more efficient is the enzyme.

The catalytic efficiency as the effective rate constant, also called catalytic rate constant (k_{cat}) when the conc. of

S is low. This is shown as: $R = \frac{k_1[E]_0[S]}{K_M + [S]}$, but at low $[S]$, $R = \left(\frac{k_1}{K_M}\right)[E]_0[S] = k_{cat}[E]_0[S]$. k_{cat} attains

maximum when k_1 is high and K_M is low. In that case, enzyme is said to attain catalytic perfection.

For example, the enzyme catalase has $k_{cat} = 4 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$.

The structure of active centre is specific to the reaction that it catalyses. For example, the active centre of the catalase has d-metal ions for binding of the substrate and for mediating the electron transfer reactions that lead to decomposition of H_2O_2 . Thus, an enzyme is biological molecule which has evolved to a specific job with great efficiency.

Problem: In an enzymolysis, the intercept and slope of $1/R^0$ vs. $1/[S]_0$ are given below:

Intercept = $8 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ min}$ and slope = 94.88 min . Find R_{\max}^0 and Michaelis constant (K_M) of the enzyme reaction. **[Solution:** $R_{\max}^0 = 1.25 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$ and $K_M = 1.19 \times 10^{-3} \text{ mol dm}^{-3}$].

Question: The slope and intercept of the plot $1/R^0$ vs. $1/[S]_0$ are $3.5 \times 10^2 \text{ s}$ and $5 \times 10^4 \text{ mol}^{-1} \text{ L s}$ respectively, where R^0 and $[S]_0$ are the initial rate and initial substrate conc. of an enzyme catalysed reaction obeying Michaelis-Menten kinetics. Estimate the K_M and the turn-over number when the initial enzyme conc. $[E]_0 = 2.5 \times 10^{-9} \text{ mol L}^{-1}$. **[Calcutta Univ. 2008]**

Answer: $K_M = \text{slope} / \text{intercept} = 3.5 \times 10^2 \text{ s} / 5 \times 10^4 \text{ mol}^{-1} \text{ L s} = 7.0 \times 10^{-3} \text{ mol L}^{-1}$.

$R_{\max}^0 = 1 / \text{intercept} = 1 / (5 \times 10^4 \text{ mol}^{-1} \text{ L s}) = 2 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$. But $R_{\max}^0 = k_1 [E]_0$

or, $k_1 = (2 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}) / (2.5 \times 10^{-9} \text{ mol L}^{-1}) = 8.0 \times 10^3 \text{ s}^{-1}$.

Question: For an enzyme catalysed reaction, a Lineweaver –Burk plot give the following data:

slope = 40 s, intercept = 4 (mmol dm⁻³ s⁻¹)⁻¹. If the initial conc. of enzyme is 2.5 × 10⁻⁹ mol dm⁻³, what is the catalytic efficiency (in dm⁻³ mol s⁻¹) of the reaction?

(1) 10⁵ (2) 10⁶ (3) 10⁷ (4) 10⁴ [NET(CSIR – UGC) 2011(I)]

Answer: $R_{\max}^0 = 1 / \text{intercept} = k_1 [E]_0$ or, $k_1 = 1 / (\text{intercept} \times [E]_0)$ and $K_M = \text{slope} / \text{intercept}$. Thus,

$$k_{\text{efficiency}} = k_1 / K_M = \frac{1}{\text{intercept} \times [E]_0} / \frac{\text{slope}}{\text{intercept}} = \frac{1}{\text{slope} \times [E]_0}$$

$$= \frac{1}{40 \text{ s} \times 2.5 \times 10^{-9} \text{ mol dm}^{-3}} = 10^{-7} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}. \text{ So the correct option is (3).}$$

Question: In the Michaelis-Menten mechanism for enzyme kinetics, the expression obtained as

$$\frac{v}{[E]_0[S]} = 1.4 \times 10^{12} - \frac{10^4 v}{[E]_0}$$

The values of k_3 (k_{cat} , mol⁻¹ L sec⁻¹) and k_M (Michaelis constant, mol L⁻¹) respectively are

(1) (1.4 × 10¹², 10⁴) (2) (1.4 × 10⁸, 10⁴) (3) (1.4 × 10⁸, 10⁻⁴) (4) (1.4 × 10¹², 10⁻⁴).

[NET(CSIR – UGC) 2010]

Answer: The rate equation is $v = \frac{k_1[E]_0[S]}{K_M + [S]}$ or, $v(K_M + [S]) = k_1[E]_0[S]$ or, $v \times K_M = k_1[E]_0[S] - v[S]$.

Dividing by $K_M [E]_0 [S]$, we get $\frac{v}{[E]_0[S]} = \frac{k_1}{K_M} - \frac{1}{K_M} \left(\frac{v}{[E]_0} \right)$. Comparing with equation given,

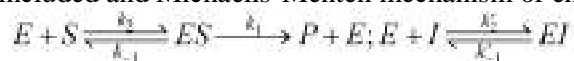
$1/K_M = 10^4$ so, $K_M = 10^{-4}$ and $k_1/K_M = k_{\text{cat}} = 1.4 \times 10^{12}$. The correct option is (4).

Question: Plot $R^0/[S]_0$ against R^0 and find the value of R_{\max}^0 and K_M . [See above form].

Answer: $\frac{R^0}{[S]_0} = \frac{k_1[E]_0}{K_M} - \frac{R^0}{K_M}$ or, $\frac{R^0}{[S]_0} = \frac{R_{\max}^0}{K_M} - \frac{R^0}{K_M}$. The plot gives slope = $\frac{R_{\max}^0}{K_M}$ and intercept = $\frac{1}{K_M}$.

Enzyme Inhibition:

The ability of enzyme to catalyse a reaction can be hindered by inhibitor molecules. One of the mechanism is that the inhibitor molecule competes with the substrate molecule for binding to the active site of enzyme. This inhibition reaction can be included and Michaelis-Menten mechanism of enzyme reaction is modified.



In the last equation, I is the inhibitor molecule and EI is the enzyme-inhibitor complex. We consider this

reaction is in rapid equilibrium so equilibrium constant, $K = \frac{[EI]}{[E][I]}$ or, $[EI] = K[E][I]$.

Using the steady-state approximation to [ES], we get $[ES] = \frac{[E][S]}{K_M}$. K_M is Michaelis constant = $\frac{(k_{-1} + k_2)}{k_1}$.

So, $[E_0] = [E] + [ES] + [EI] = [E] + \frac{[E][S]}{K_M} + K[E][I] = [E] \left(1 + \frac{[S]}{K_M} + K[I] \right)$

or, $E = [E]_0 / \left(1 + \frac{[S]}{K_M} + K[I] \right)$ or, $[ES] = \frac{[E]_0[S]}{K_M (1 + [S]/K_M + K[I])} = \frac{[E]_0[S]}{K_M + [S] + K_M K[I]}$.

The rate of the reaction is $\frac{d[P]}{dt} = k_2[ES]$ or, $R = \frac{k_2[E]_0[S]}{K_M + [S] + K_M K[I]} = \frac{k_2[E]_0[S]}{(K_M + K[I]) + [S]}$.

Let $K'_M = K_M + K[I]$, then rate equation in the enzyme inhibition reaction is $R = \frac{k_2[E]_0[S]}{K'_M + [S]}$.----- (6)

This shows that when $[I] \rightarrow 0$, rate equation becomes $R = \frac{k_2[E]_0[S]}{K_M + [S]}$ same as deduced in absence of inhibitor.