

CHEMICAL KINETICS

This branch of chemistry deals with the study of rates of chemical reactions and the mechanism by which they occur. While studying reaction, one deals with :

- (a) how fast (or slow) the reactants get converted into products
- (b) the steps or paths through which the products are formed (reaction mechanism)

★



$$t = 0 \quad a \quad 0$$

$$t = t_1 \quad a - x_1 \quad x_1$$

$$t = t_2 \quad a - x_2 \quad x_2$$

$$t = t_3 \quad a - x_3 \quad x_3$$

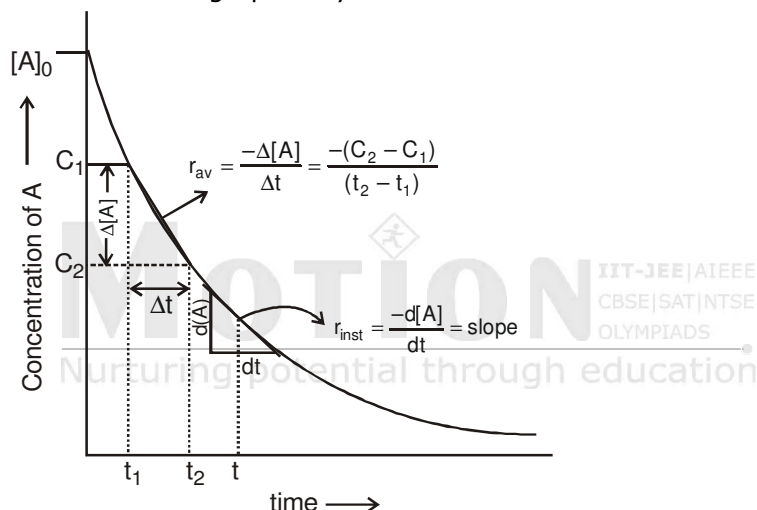
$$t = t_{eq} \quad a - x \quad x$$

$$0 < t < t_{eq} \longrightarrow \text{CHEMICAL KINETICS}$$

$$t_{eq} \leq t < \infty \longrightarrow \text{CHEMICAL EQUILIBRIUM}$$

RATE OF A REACTION

In general, for a reaction : $A \rightarrow B$, the behaviour of the concentration of the reactant and product, as the reaction proceeds is shown graphically

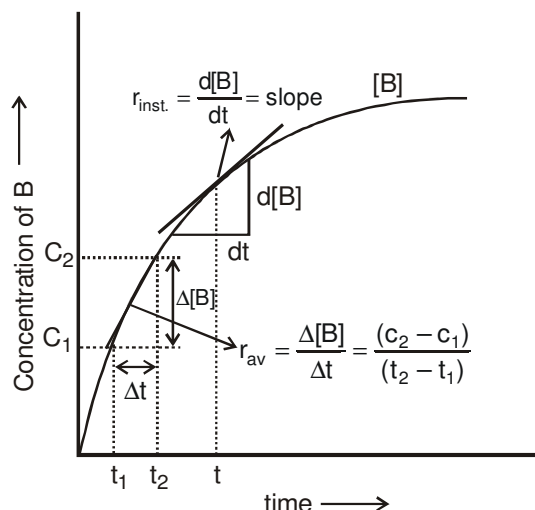


From the graph, it is clear that the concentration of the reactant decreases and that of the product increases as the reaction proceeds and the rate of the change of the concentration of the reactant as well as that of the product is also changing.

Rate of a reaction can, now, be defined in two ways :

Average Rate of reaction (r_{av}) given by :

$$r_{av} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$



where $\Delta[A]$ and $\Delta[B]$ represents the change in the concentrations of 'A' and 'B' respectively over a time interval Δt

The average rate of the reaction between a time interval ($t_f - t_i = \Delta t$) can be determined from the above graph by locating the concentration of 'A' or 'B' on this graph at the time instants t_f and t_i as shown.

If $[A]_f$ and $[A]_i$ are the concentrations of the reactant 'A' at the time instants t_f and t_i then :

$$r_{av} = -\left(\frac{[A]_f - [A]_i}{t_f - t_i}\right)$$

Similarly from the plot of 'B' as a function of 't', we have :

$$r_{av} = \left(\frac{[B]_f - [B]_i}{t_f - t_i}\right)$$

Note :

➤ The above expression for r_{av} is equivalent to the slope of the line joining the points $(t_f, [A]_f)$ and $(t_i, [A]_i)$ or $(t_f, [B]_f)$ and $(t_i, [B]_i)$ as shown.

Instantaneous Rate of reaction ($r_{inst.}$) can be calculated from r_{av}

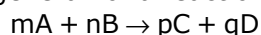
in the limit $\Delta t \rightarrow 0$ and is represented as :

$$r_{inst.} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

Note : ➤ The above expression for $r_{inst.}$ is equivalent to the slope of the tangent from the plot of the concentration of 'A' or 'B' at any time instant 't'.

- The rate of the reaction ($r_{inst.}$ or r_{av}) is always calculated as a positive quantity.
- The rate of the change of the concentration of the reactant will be a negative quantity since its concentration is decreasing with time.
- The rate of the change of the concentration of the product will be a positive quantity since its concentration is increasing with time.
- The magnitude of the rates of the change of the concentration of reactants and products will be equal in this case, as one mole of 'A' gives one mole of 'B' in the above reaction.
- The rate of a reaction at any temperature depends on the concentration of the reactants and sometimes on the concentration of some foreign substances (e.g a catalyst being used in the reaction as well. The representation of this dependence of the rate of the reaction on the concentrations is known as rate law and this rate law is determined experimentally.)
- The above expression for $r_{inst.}$ is called as differential rate law.

In general for a reaction :



The rate of reaction can be expressed as follows :

$$\text{Rate} = -\frac{1}{m} \frac{d[A]}{dt} = -\frac{1}{n} \frac{d[B]}{dt} = +\frac{1}{p} \frac{d[C]}{dt} = +\frac{1}{q} \frac{d[D]}{dt}$$

Problem 1 :

The rate of formation of NO(g) in the reaction $\text{NOBr(g)} \rightarrow \text{NO(g)} + \text{Br}_2\text{(g)}$ is found to be $1.6 \times 10^{-4} \text{ M/s}$. Find the rate of overall reaction and rate of consumption of NOBr .

We have : $\frac{d[\text{NO}]}{dt} = 1.6 \times 10^{-4} \text{ M/s}$.

First write a balanced chemical equation. $2\text{NOBr(g)} \rightarrow 2\text{NO(g)} + \text{Br}_2\text{(g)}$

Now, Rate of overall reaction = $-\frac{1}{2} \frac{d[\text{NOBr}]}{dt} = +\frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{1}{1} \frac{d[\text{Br}_2]}{dt} = 0.8 \times 10^{-4} \text{ M/s}$

Rate of consumption of $\text{NOBr} = -\frac{d[\text{NOBr}]}{dt} = +1.6 \times 10^{-4} \text{ M/s}$

LAW OF MASS ACTION

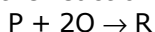
Rate $\propto [\text{A}]^a [\text{B}]^b$

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

Law of mass action states that the rate of reaction is directly proportional to the concentration of reacting species raised to the power of stoichiometric coefficients. But this is valid only for elementary reactions.

ORDER OF A REACTION

By performing a reaction in actual in laboratory and carefully examining it, it is possible to express the rate law as the product of concentrations of reactants each raised to some power. For example consider the reaction :



The differential rate law is written as :

$$\text{Rate} = -\frac{d[\text{P}]}{dt} = -\frac{1}{2} \frac{d[\text{Q}]}{dt}$$

Also, Rate can be expressed as $\text{Rate} = k[\text{P}]^m[\text{Q}]^n$

where k is called as rate constant or velocity constant or specific reaction rate.

k is a characteristic of a reaction at a given temperature. It changes only when the temperature changes.

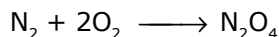
The powers m and n are integers or fractions. m is called as order of reaction with respect to P and n is called

as order of reaction with respect to Q .

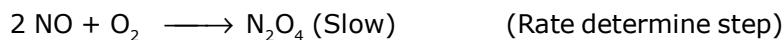
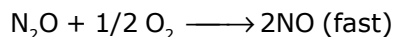
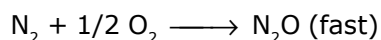
The overall order of reaction = $m + n$

Note :

➤ The values of m and n are calculated from the experimental data obtained for a reaction and the powers m and n are not related to the stoichiometric coefficients of the reactants

★ **Why difference in experimental rate equation & theoretical rate equation**

Theoretical rate = $k [\text{N}_2]^1 [\text{O}_2]^2$; order = $1 + 2 = 3$



rate = $K [\text{NO}]^2 [\text{O}_2]^1$; Order = $2 + 1 = 3$

NOTE :

(1) Order can be fractional

(2) Order can be zero.

(3) Order can be negative with respect to any one quantity but can not be negative for whole reaction.



rate = $k [\text{A}]^a [\text{B}]^b \longrightarrow$ Theoretical Rate equation

rate = $k [\text{A}]^m [\text{B}]^n \longrightarrow$ Experimental Rate equation

Case (I) :

$$a = m, b = n$$

Elementary reaction

Single step reaction

Case (II) :

(i) $a = m$; $b \neq n$

or (ii) $a \neq m$; $b = n$

or (iii) $a \neq m$; $b \neq n$

Complex reaction

multiple step reaction

Units of k :

In general, the rate law for a n^{th} order reaction can be taken as :

$$\frac{dc}{dt} = -kc^n \quad \left[\text{Note : } r_{\text{inst}} = -\frac{dc}{dt} = kc^n \right]$$

where k : rate constant; c : concentration and n : order of reaction

$$\Rightarrow k = \frac{dc/dt}{c^n}$$

$$\Rightarrow \text{Units of } k \equiv (\text{mol/L})^{1-n} (\text{time})^{-1}$$

For a 'zero' order reaction ($n = 0$) :

$$\text{Units of } k = (\text{mol/L})^1 (\text{time})^{-1}$$

$$\Rightarrow \text{Units are : mol/L/sec}$$

For a first order reaction ($n = 1$) :

$$\text{Units of } k \equiv (\text{time})^{-1}$$

$$\Rightarrow \text{Units are : sec}^{-1}, \text{min}^{-1}, \text{hrs}^{-1} \text{ etc.}$$

For a second order reaction ($n = 2$) :

$$\text{Units of } k \equiv (\text{mol/L})^{-1} (\text{time})^{-1}$$

$$\Rightarrow \text{Units are : L/mol/sec.}$$

Problem 2 :

The rate constant for a given reaction is $k = 3 \times 10^{-5} \text{ s}^{-1} \text{ atm}^{-1}$. Express it in units of $\text{L mol}^{-1} \text{ sec}^{-1}$.

Try to express concentration of 1 atm into mol/L using gas law ($PV = nRT$)

$$PV = nRT \Rightarrow P = cRT \quad (c : \text{concentration in mol/L})$$

Substitute $R = 0.0821 \text{ L-atm/mol/K}$;

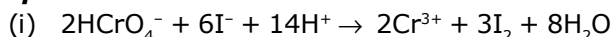
$$T = 273 \text{ K} ; \quad P = 1 \text{ atm}$$

$$\Rightarrow c = 0.04462 \text{ mol/L}$$

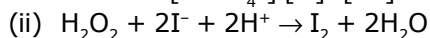
$$\Rightarrow k = \frac{3 \times 10^{-5}}{0.04462} = 6.73 \times 10^{-4} \text{ L/mol/s.}$$

Problem 3 :

From the rate laws for the reactions given below, determine the order with respect to each species and the overall order :



$$\text{Rate} = k[\text{HCrO}_4^-] [\text{I}^-]^2 [\text{H}^+]^2$$



$$\text{Rate} = k[\text{H}_2\text{O}_2] [\text{I}^-]$$

(i) The order of the reaction with respect to $[\text{HCrO}_4^-]$ is 1; with respect to $[\text{I}^-]$ is 2 and with respect to $[\text{H}^+]$ is 2. The overall order of the reaction is $1 + 2 + 2 = 5$

(ii) The order of the reaction with respect to $[\text{H}_2\text{O}_2]$ is 1 and with respect to $[\text{I}^-]$ is 1. The overall order of the reaction is $1 + 1 = 2$.

- Note :** ➤ In (i) stoichiometric coefficient of I^- is 6 whereas the power coefficient (n) in the rate law is 2.
- Reaction (i) may not take place in a single step. It may not be possible for all the 22 molecules to be in a state to collide with each other simultaneously. Such a reaction is called a complex reaction.
- A complex reaction takes place in a series of a number of elementary reactions.

MOLECULARITY

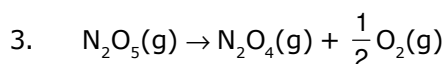
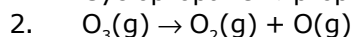
As already discussed, the order of a reaction is an experimental concept. The theoretical aspect of chemical kinetics is molecularity.

A complex chemical reaction is understood in terms of various indirect steps called elementary processes. The study of a reaction in terms of elementary processes is called as reaction mechanism. Now various elementary steps occur at different rates. **The slowest elementary process in the reaction mechanism is called as rate determining step.**

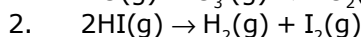
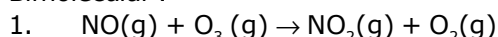
Molecularity is defined as the number of ions or molecules or atoms taking part in an elementary process of the reaction mechanism.

In the rate determining step, when one molecule takes part, it is said to be a unimolecular reaction ; two molecules take part, it is said to be a bimolecular reaction; three molecules take part, it is said to be a termolecular reaction.

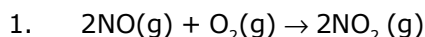
Unimolecular :



Bimolecular :



Termolecular :

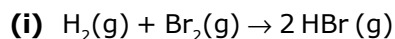


Note : ➤ For a reaction : $\text{A} \rightarrow \text{B}$ in the rate law : $\text{rate} = k[\text{A}]^m [\text{B}]^n$

Neither the order of reaction ($m + n$) nor the molecularity of a reaction can be predicted from stoichiometric coefficient of a balanced reaction. The order of reaction is always to be determined experimentally

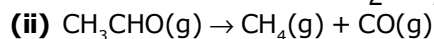
molecularity is determined theoretically after studying the reaction mechanism. However as a theoretical idea sometime, we can have an approximate order of reaction equal to molecularity (i.e., the number of molecules taking part in slowest elementary for complex reactions).

➤ Order of a reaction can be fraction also. For example consider the following reaction :



$$\text{rate} = k[\text{H}_2][\text{Br}_2]^{1/2} \quad (\text{determined experimentally})$$

$$\text{order of reaction} = 1 + \frac{1}{2} = \frac{3}{2}$$



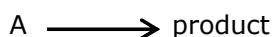
$$\text{rate} = k[\text{CH}_3\text{CHO}]^{3/2} \quad (\text{determined experimentally})$$

$$\text{order of reaction} = \frac{3}{2}$$

Also note that sum of stoichiometric coefficient ($1 + 1 = 2$) is not equal to the order of reaction.

TYPES OF REACTION BASED ON KINETICS

(1) ZERO ORDER REACTION;



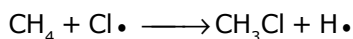
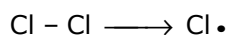
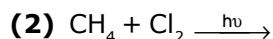
$$\text{Rate} = K [\text{A}]^0 = k$$



$$\text{Rate} = K [\text{A}]^0 [\text{B}]^0 \text{ or } K [\text{A}]^1 [\text{B}]^{-1}$$

Example :

(1) Photochemical Reactions, Photosynthesis



All reactions occurring by free radical mechanism.

(2) FIRST ORDER REACTION :



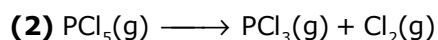
$$\text{Rate} = K [\text{A}]^1$$



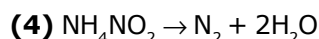
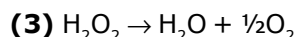
$$\text{Rate} = K [\text{A}]^2 [\text{B}]^{-1}$$

Example :

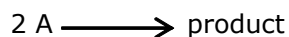
(1) Radioactive disintegration.



Gaseous phase decomposition



(3) SECOND ORDER REACTION :



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

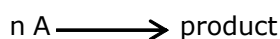


$$\text{Rate} = k [A]^1 [B]^1$$

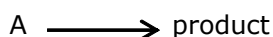
Example :

(1) Alkaline hydrolysis of esters.

(2) Self Cannizzaro's reactions,

(4) n^{th} ORDER REACTION :

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

Zero Order Reactions :The rate law for zero order reactions ($n = 0$) is written as :

$$t=0 \quad a = [A]_0 \quad 0$$

$$t=t \quad a - x = [A] \quad x$$

$$\text{Rate of reaction} = - \frac{d[A]}{dt} \quad \dots\dots\dots(1)$$

$$\text{Rate of reaction} = k [A]^0 \quad \dots\dots\dots(2)$$

From equation (1) and (2)

$$- \frac{d[A]}{dt} = k [A]^0$$

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

$$- \int_{[A]_0}^{[A]} d[A] = k \int_0^t dt$$

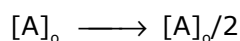
$$[A]_0 - [A] = kt$$

$$k = \frac{[A]_0 - [A]}{t} = \frac{x}{t}$$

★

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

Time in which half of initial amount is left.



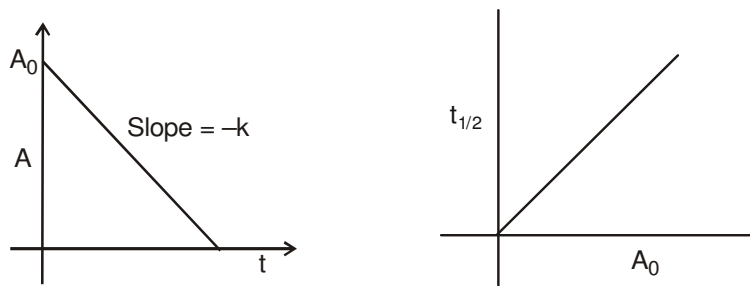
$$t = 0 \quad t = t_{1/2}$$

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

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

Thus, for a Zero order reaction, half life is directly proportional to initial concentration of the reactant. Clearly, zero order reactions are those, whose rates are not affected by change in concentrations of reactants (i.e., independent of concentration). The rates of such reactions only depend upon temperature. Most of photochemical reactions are zero order reactions. Other examples are : decomposition of HI over the surface of gold and NH_3 over tungsten.

Equation (i) can be rearranged and integrated to get the variation of the concentration of the reactants as a function of time.



➤ From the above expression, it is clear that if we plot A as a function of time (t) then it will be a straight line with a negative slope = - k and Y - Intercept of A_0

FIRST ORDER REACTION



$$t = 0 \quad [A]_0$$

$$t = t \quad [A]$$

$$\text{Rate of reaction} = - \frac{d[A]}{dt} \dots\dots\dots(1)$$

$$\text{Rate of reaction} = k [A]^1 \dots\dots\dots(2)$$

From equation (1) & (2)

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

$$- \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = k \int_0^t dt$$

$$\ln [A]_0/[A] = kt$$

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

★ **Half life ($t_{1/2}$) :**

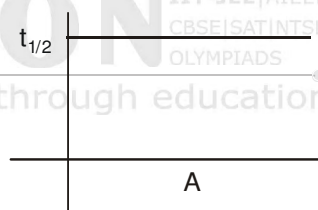
$$t = t_{1/2} \quad [A] = [A]_0/2$$

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A]_0}{[A]_0/2} = \frac{2.303}{t_{1/2}} \log 2$$

$$t_{1/2} = \frac{2.303}{k} \log_{10} 2$$

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

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



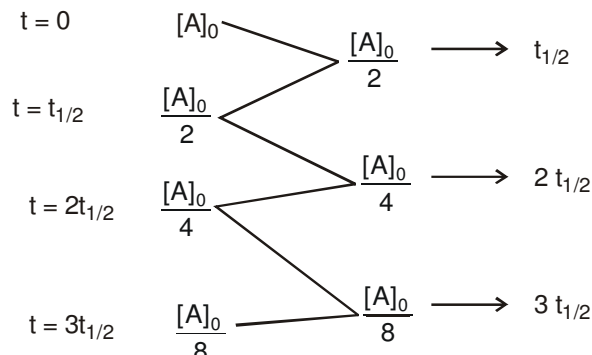
★ **Average life :**

$$Kt = \ln \frac{[A]_0}{[A]}$$

$$[A]_0 = [A] e^{Kt}$$

$$[A] = [A]_0 e^{-kt}$$

$$[A] = \frac{[A]_0}{2^n} \quad \text{where } n = \text{number of half lifes.}$$



$$t_{av} = \frac{\frac{[A]_0}{2} t_{1/2} + \frac{[A]_0}{4} 2 t_{1/2} + \frac{[A]_0}{8} 3 t_{1/2} + \dots}{[A]_0}$$

$$t_{av} = \left[\frac{1}{2} + \frac{2}{2^2} + \frac{3}{2^3} + \frac{4}{2^4} + \dots \right] t_{1/2}$$

$$t_{av} = 1.44 \quad t_{1/2} \quad \text{here } t_{1/2} = \frac{0.693}{k}$$

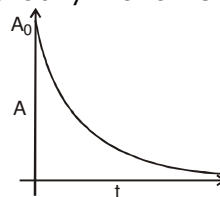
$$t_{av} = \frac{1.44 \times 0.693}{K}$$

$$\Rightarrow t_{av} = \frac{1}{K}$$

Features of a First Order Reaction :

1. A first order reaction must follow above form of rate law for all time instants. This means if we are given value of A_0 and values of x at different time instants [i.e. $(A_0 - x)$ as value of reactants after t], the values of k can be calculated for different time instants by using the above first order law.
If the reaction for which the data were given is a first order reaction, then all values of k will approximately equal to each other.
2. **The time for half reaction for a first order reaction is independent of initial concentration of reactants.**
3. The concentration of reactants in a first order reaction decreases exponentially with time (see figure) $[A = A_0 e^{-kt}]$ from (ii)
Note that plot of $\log_{10} A$ vs t is linear. It is important to note that

equation of this straight line is of the form :

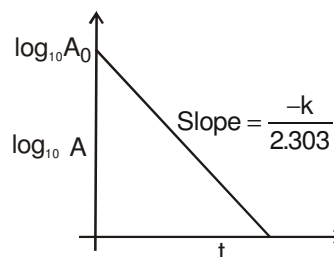


$y = mx + C$. Comparing it with 1st order rate law as follows :

$$kt = 2.303 \log_{10} \frac{A_0}{A}$$

$$\Rightarrow \log_{10} A = \left(\frac{-k}{2.303} \right) t + \log_{10} A_0 \text{ is the equation of line.}$$

Note that slope of the line $\left(\frac{-k}{2.303} \right)$ and Y-intercept (OA) = $\log_{10} A_0$



➤ **Rate constant of a first order reaction can also be calculated by measuring the concentration of the reactants at two time instants (if the initial concentration is not known).**

If A_1 and A_2 are the reactant's concentrations at two time instants ' t_1 ' and ' t_2 ' respectively, then we have :

$$2.303 \log_{10} \frac{A_0}{A_1} = kt_1 \quad \dots (iii)$$

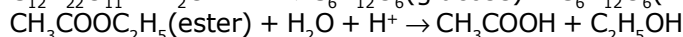
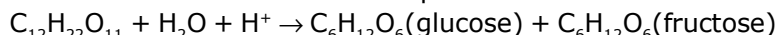
$$\text{and } 2.303 \log_{10} \frac{A_0}{A_2} = kt_2 \quad \dots (iv)$$

Subtracting (iv) from (iii), we get :

$$2.303 \log_{10} \frac{A_1}{A_2} = k(t_1 - t_2) \quad \text{Thus, } k \text{ can be evaluated.}$$

The molecularity of acidic hydrolysis of sucrose and esters is 2, whereas their order is 1. In both the reactions water is in excess so that its concentration remains constant throughout the reaction.

The rate of reaction therefore depends only on the concentration of sucrose and ester in two reactions respectively. So the reactions in which the molecularity is 2 or 3 but they conform to the first order kinetics are known as pseudo first order reactions OR pseudo unimolecular reactions.



(In both the reactions, H^+ ion acts as a catalyst)

Problem : 4

For a reaction $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$; the following data were obtained.

	$[NO] \text{ (mol/L)}$	$[H_2] \text{ (mol/L)}$	Rate (mol/L/s)
1.	5×10^{-3}	2.5×10^{-3}	3×10^{-5}
2.	15×10^{-3}	2.5×10^{-3}	9×10^{-5}
3.	15×10^{-3}	10×10^{-3}	3.6×10^{-4}

(a) Calculate the order of reaction.

(b) Find the rate constant.

(c) Find the initial rate if $[NO] = [H_2] = 8.0 \times 10^{-3} M$

Assuming rate law can be expressed as follows :

$$\text{rate} = k[NO]^x [H_2]^y$$

By analysing the data :

From observation 1 and 2, we see that $[H_2]$ is constant and when $[NO]$ is tripled, the rate is also tripled.

$$\Rightarrow \text{rate} (r) \propto [NO] \Rightarrow x = 1$$

From observations 2 and 3, we see that $[NO]$ is constant; when $[H_2]$ is increased four times, the rate also increases four times :

$$\text{rate} \propto [H_2] \Rightarrow y = 1$$

$$\Rightarrow r = k[NO][H_2O]$$

\Rightarrow The order of reaction w.r.t No and H_2 is 1 and the overall order of reaction is $1 + 1 = 2$.

$$\text{Initial rate} = k[NO][H_2] = 2.4 \times (8 \times 10^{-3})^2 = 1.536 \times 10^{-4} \text{ mol/L/s.}$$

Problem : 5

The rate of change of concentration of C in the reaction $2A + B \rightarrow 2C + 3D$ was reported as $1.0 \text{ mol litre}^{-1} \text{ sec}^{-1}$. Calculate the reaction rate as well as rate of change of concentration of A, B and D.

Sol. We have,

$$-\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt} = \frac{1}{3} \frac{d[D]}{dt} = \text{rate of reaction}$$

$$\therefore \frac{d[C]}{dt} = 1.0 \text{ mol litre}^{-1} \text{ sec}^{-1}$$

$$\therefore -\frac{d[A]}{dt} = \frac{d[C]}{dt} = \mathbf{1.0 \text{ mol L}^{-1} \text{ sec}^{-1}}$$

$$-\frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt} = \frac{1}{2} = \mathbf{0.5 \text{ mol L}^{-1} \text{ sec}^{-1}}$$

$$\frac{d[D]}{dt} = \frac{3}{2} \frac{d[C]}{dt} = \frac{3}{2} \times 1 = \mathbf{1.5 \text{ mol L}^{-1} \text{ sec}^{-1}}$$

Also,

$$\therefore \text{Rate} = \frac{1}{2} \frac{d[C]}{dt}$$

$$\therefore \text{Rate} = \frac{1}{2} \times 1 = \mathbf{0.5 \text{ mol L}^{-1} \text{ sec}^{-1}}$$

Problem : 6

For the reaction $A + B \rightarrow C$, the following data were obtained. In the first experiment, when the initial concentrations of both A and B are 0.1 M , the observed initial rate of formation of C is $1 \times 10^{-4} \text{ mol litre}^{-1} \text{ minute}^{-1}$. In the second experiment when the initial concentrations of A and B are 0.1 M and 0.3 M , the initial rate is $9.0 \times 10^{-4} \text{ mol litre}^{-1} \text{ minute}^{-1}$.

(a) Write rate law for this reaction

(b) Calculate the value of specific rate constant for this reaction.

Sol. Let $\text{Rate} = K[A]^m[B]^n$

$$(a) \quad r_1 = 1 \times 10^{-4} = K[0.1]^m [0.1]^n \quad \dots(1)$$

$$r_2 = 9 \times 10^{-4} = K[0.1]^m [0.3]^n \quad \dots(2)$$

$$r_3 = 2.7 \times 10^{-3} = K[0.3]^m [0.3]^n \quad \dots(3)$$

By Eqs. (1) and (2),

$$\frac{r_1}{r_2} = \frac{1 \times 10^{-4}}{9 \times 10^{-4}} = \left(\frac{1}{3}\right)^n$$

$$\therefore n = 2$$

By Eqs. (2) and (3),

$$\frac{r_2}{r_3} = \frac{9 \times 10^{-4}}{27 \times 10^{-4}} = \left(\frac{1}{3}\right)^m \quad m = 1$$

$$\therefore \text{Rate} = K[A]^1[B]^2$$

$$(b) \text{ Also by Eq. (1), } 1 \times 10^{-4} = K[0.1]^1 [0.1]^2$$

$$K = \mathbf{10^{-1} = 0.1 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}}$$

Problem : 7

The chemical reaction between $K_2C_2O_4$ and $HgCl_2$ is ;



The weights of Hg_2Cl_2 precipitated from different solutions in given time were taken and expressed as following :

Time (minutes)	HgCl ₂ (M)	K ₂ C ₂ O ₄ (M)	Hg ₂ Cl ₂ formed (M)
60	0.0418	0.404	0.0032
65	0.0836	0.404	0.0068
120	0.0836	0.202	0.0031

Let the rate law be written as : $r = k[\text{HgCl}_2]^x [\text{K}_2\text{C}_2\text{O}_4]^y$

$$1. \frac{0.0032}{60} = k[0.0418]^x [0.404]^y$$

$$2. \frac{0.0068}{65} = k[0.0836]^x [0.404]^y$$

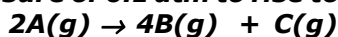
$$3. \frac{0.0031}{120} = k[0.0836]^x [0.202]^y$$

Solving the above equations, we get :

$x = 1$ and $y = 2 \Rightarrow$ order of reaction w.r.t $x = 1$ and $y = 2$ and overall order is 3.

Problem : 8

The reaction given below, involving the gases is observed to be first order with rate constant $7.48 \times 10^{-3} \text{ sec}^{-1}$. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm also find the total pressure after 100 sec.



Sol.

	$2\text{A(g)} \rightarrow$	$4\text{B(g)} +$	C(g)
initial	P_0	0	0
at time t	$P_0 - P'$	$2P'$	$P'/2$

$$P_{\text{total}} = P_0 - P' + 2P' + P'/2 = P_0 + \frac{3P'}{2}$$

$$P' = \frac{2}{3}(0.145 - 0.1) = 0.03 \text{ atm}$$

$$k = \frac{2.303}{2t} \log \frac{P_0}{P_0 - P'}$$

$$t = \frac{2.303}{7.48 \times 10^{-3} \times 2} \log \left(\frac{0.1}{0.07} \right)$$

$$t = 23.84 \text{ sec}$$

$$\text{Also, } k = \frac{2.303}{2t} \log \left(\frac{0.1}{P_0 - P'} \right)$$

$$7.48 \times 10^{-3} = \frac{2.303}{2 \times 100} \log \left(\frac{0.1}{0.1 - P'} \right)$$

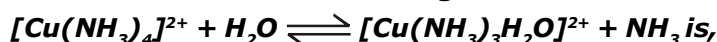
$$0.1/0.1 - P' = 5$$

$$P' = 0.08$$

$$P_{\text{total}} = 0.1 + \frac{3}{2}(0.080) \approx 0.22 \text{ atm.}$$

Problem : 9

The net rate of reaction of the change :



$$\frac{dx}{dt} = 2.0 \times 10^{-4} [\text{Cu}(\text{NH}_3)_4]^{2+} - 3.0 \times 10^{-5} [\text{Cu}(\text{NH}_3)_3\text{H}_2\text{O}]^{2+} [\text{NH}_3]$$

calculate :

(i) rate expression for forward and backward reactions.

(ii) the ratio of rate constant for forward and backward reactions.

(iii) the direction of reaction in which the above reaction will be more predominant.

Sol. (i) Rate of forward reaction = $2.0 \times 10^{-4} [\text{Cu}(\text{NH}_3)_4]^{2+} [\text{H}_2\text{O}]$
 Rate of backward reaction = $3.0 \times 10^5 [\text{Cu}(\text{NH}_3)_3\text{H}_2\text{O}]^{2+} [\text{NH}_3]$

(ii) Also, $K_f = 2.0 \times 10^{-4}$
 $K_b = 3.0 \times 10^5$

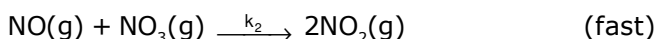
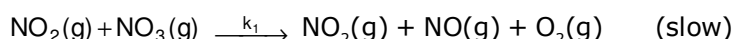
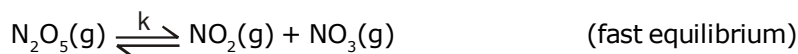
$$\therefore \frac{K_f}{K_b} = \frac{2.0 \times 10^{-4}}{3.0 \times 10^5} = 6.6 \times 10^{-10}$$

(iii) More predominant reaction is **backward reaction**.**Problem : 10****The rate law for the decomposition of gaseous N_2O_5** 

is observed to be

$$r = -\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$

A reaction mechanism which has been suggested to be consistent with this rate law is



Show that the mechanism is consistent with the observed rate law.

Since the slow step is the rate determining step, hence

$$r = k_1[\text{NO}_2][\text{NO}_3] \quad \dots(1)$$

and from the fast equilibrium step,

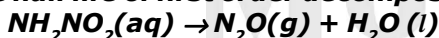
$$K = \frac{[\text{NO}_2][\text{NO}_3]}{[\text{N}_2\text{O}_5]}$$

$$\text{Thus, } [\text{NO}_2][\text{NO}_3] = K[\text{N}_2\text{O}_5] \quad \dots(ii)$$

Using (ii) in (i), we get :

$$r = k_1 K [\text{N}_2\text{O}_5] = k [\text{N}_2\text{O}_5] \quad \text{where } k = k_1 K$$

This shows that the mechanism is consistent with the observed rate law.

Problem : 11**The half life of first order decomposition of nitramide is 2.1 hour at 15°C .****If 6.2 gm of NH_2NO_2 is allowed to decompose, find :****(a) time taken for nitramide to decompose 99%;****(b) volume of dry N_2O gas produced at this point at STP.****Sol.** (a) Using first order kinetics, we have :

$$kt = 2.303 \log_{10} \frac{A_0}{A}$$

$$\Rightarrow \frac{0.693}{2.1} \times t = 2.303 \log \frac{100}{100-99} \quad \Rightarrow t = 13.96 \text{ hours}$$

(b)

$$6.2 \text{ gm of } \text{NH}_2\text{NO}_2 \equiv 0.1 \text{ mol}$$

$$\text{and } 1 \text{ mole } \text{NH}_2\text{NO}_2 \equiv 1 \text{ mole of } \text{N}_2\text{O}$$

As 99% of NH_2NO_2 is decomposed

$$\Rightarrow 0.099 \text{ mol of } \text{NH}_2\text{NO}_2 \text{ is decomposed}$$

$$0.099 \text{ mol of } \text{N}_2\text{O} \text{ are produced} \equiv 22.4 \times 0.099 = 2.217 \text{ L of } \text{N}_2\text{O} \text{ at STP.}$$

Second Order kinetics★ **Case I :**

$$t = 0 \quad [A]_0$$

$$t = t \quad [A]_t$$

$$\text{Rate of reaction} = - \frac{d[A]}{dt} \dots\dots\dots(1)$$

$$\text{Rate of reaction} = k [A]^2 \dots\dots\dots(2)$$

From equation (1) & (2)

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

$$- \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k \int_0^t dt$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = Kt$$

$$K = \frac{1/[A] - 1/[A]_0}{t}$$

★ **Half-life ($t_{1/2}$) :** $[A]_t = \frac{[A]_0}{2}$

$$K = 2/[A]_0 - 1/[A]_0$$

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

In this half life is inversely proportional to initial concentration

★ **Case (II):**

$$t = 0 \quad a \quad b$$

$$t = t \quad a-x \quad b-x$$

$$\text{Rate of reaction} = - \frac{d[A]}{dt} \dots\dots\dots(1)$$

$$\text{Rate of reaction} = k [A] [B] \dots\dots\dots(2)$$

From equation (1) & (2)

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

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

$$\int_0^x \frac{dx}{(a-x)(b-x)} = k \int_0^t dt$$

$$\int_0^x \frac{dx}{(b-a)(a-x)} + \int_0^x \frac{dx}{(a-b)(b-x)} = k \int_0^t dt$$

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

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

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

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

nTH ORDER KINETICS

A \longrightarrow product

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

$$\text{rate} = k [A]^n \quad \dots\dots\dots(2)$$

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

$$\Rightarrow - \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^n} = k \int_0^t dt$$

$$\Rightarrow \frac{1}{(n-1)} \left[\frac{1}{[A]^{n-1}} \right]_{[A]_0}^{[A]_t} = kt$$

$$\Rightarrow \frac{1}{(n-1)} \left[\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right] = kt$$

$$\Rightarrow k = \frac{1}{(n-1)t} \left[\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$$

★ **Half-life ($t_{1/2}$) :** at $t = t_{1/2}$, $[A]_t = \frac{[A]_0}{2}$

$$\Rightarrow k = \frac{1}{(n-1)t_{1/2}} \left[\frac{2^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$$

$$\Rightarrow t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k [A]_0^{n-1}} \quad \Rightarrow \quad t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

Problem : 12

For the non-equilibrium process, $A + B \rightarrow \text{Products}$, the rate is first order w.r.t A and second order w.r.t. B. If 1.0 mole each of A and B are introduced into a 1 litre vessel and the initial rate were 1.0×10^{-2} mol/litre-sec, calculate the rate when half of the reactants have been used.

Sol. Rate = $K[A][B]^2$
 $\therefore 10^{-2} = K[1][1]^2$
 or $K = 10^{-2} \text{ litre}^2 \text{ mol}^{-2} \text{ sec}^{-1}$
 Now rate_{II} = $10^{-2} \times 0.5 \times (0.5)^2$
 or New rate = $1.2 \times 10^{-3} \text{ mol/L-sec}$

Problem : 13

The reaction $A + OH^- \rightarrow \text{Products}$, obeys rate law expression as,

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

If initial concentrations of [A] and [OH⁻] are 0.002 M and 0.3 M respectively and if it takes 30 sec for 1% A to react at 25°C, calculate the rate constant for the reactions.

Sol.

A	+	OH ⁻	→	Products
t = 0		0.002		0.3
t = 30		$\left[0.002 - \frac{0.002 \times 1}{100}\right]$		$\left[0.3 - \frac{0.002 \times 1}{100}\right]$

Using $K = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

$$K = \frac{2.303}{30 \times (0.002 - 0.3)} \log_{10} \frac{0.3 \times \left[0.002 - \frac{0.002 \times 1}{100}\right]}{0.002 \left[0.3 - \frac{0.002 \times 1}{100}\right]}$$

$$K = 1.12 \times 10^{-3} \text{ L mol}^{-1} \text{ sec}^{-1}$$

Problem : 14

A certain reaction $A + B \rightarrow \text{products}$; is first order w.r.t. each reactant with $k = 5.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Calculate the concentration of A remaining after 100s if the initial concentration of A was 0.1 M and that of B was 6.0 M. State any approximation made in obtaining your result.

Sol. $A + B \rightarrow \text{products}$

Given : Rate = $k[A][B]$ (2nd Order reaction)

Now, since $[B] \gg [A]$, [B] can be assumed to remain constant throughout the reaction. Thus, the rate law for the reaction, becomes :

$$\text{Rate} \approx k_0[A] \quad \text{where } k_0 = k[B] = 5.0 \times 10^{-3} \times 6.0 \text{ s}^{-1} = 3.0 \times 10^{-2} \text{ s}^{-1}$$

Thus, the reaction is now of first order.

$$\text{Using, } 2.303 \log_{10} \frac{A_0}{A} = k_0 t$$

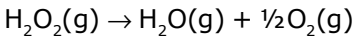
$$\Rightarrow 2.303 \log_{10} \frac{0.1}{A} = k_0 t = 3$$

$$\Rightarrow \log_e \frac{0.1}{A} = 3 \quad [\because \log_e x = 2.303 \log_{10} x]$$

$$\Rightarrow A = \frac{0.1}{e^3} = 5 \times 10^{-3} \text{ M}$$

ANALYSIS OF SOME IMPORTANT FIRST-ORDER REACTIONS

Decomposition of Hydrogen peroxide (H₂O₂)



The rate of this first order reaction is measured by titrating a fixed volume of H₂O₂ (undecomposed) against a standard solution of KMnO₄. Here KMnO₄ acts as oxidising agent and H₂O₂ as reducing agent. The volumes of KMnO₄ used for H₂O₂ after regular intervals of time are as follows.

Time instants	t = 0	t ₁	t ₂	t ₃	t ₄	t ₅
Vol. of KMnO ₄	V ₀	V ₁	V ₂	V ₃	V ₄	V ₅

Volume of KMnO₄ at t = 0 corresponds to volume of H₂O₂ initially present.

⇒ A₀ ∝ V₀

Volume of KMnO₄ at time instants t₁, t₂, t₃, corresponds to volume of H₂O₂ remaining

a f t e r
t₁, t₂, t₃,

⇒ A ∝ V_t

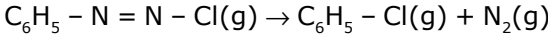
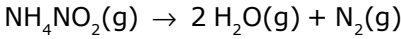
Now it being a first order reaction, follows first order kinetics, so

k t = 2.303 log₁₀ $\frac{V_0}{V_t}$

Now using the above expression, if we calculate the values of k for different time intervals t₁, t₂, (for actual numerical data), the values of k should be same if the reaction follows first order kinetics.

Decomposition of ammonium nitrite (NH₄NO₂)

and benzene diazonium chloride (C₆H₅N = NCl)



The rate of both the reaction is studied (measured) in similar manner. The volume of nitrogen (N₂) is collected after a regular interval of time as follows :

Time instants	t = 0	t ₁	t ₂	t ₃	t ₄	t
Vol. of N ₂	0	V ₁	V ₂	V ₃	V ₄	V _∞

At t = 0, clearly the volume of N₂ = 0

Time instant t = ∞ means the end of a reaction i.e., when whole of NH₄NO₂ or C₆H₅ - N = N - Cl is decomposed.

⇒ At t = ∞, V_∞ corresponds to the initial volume of NH₄NO₂ or C₆H₅ - N = N - Cl

(Note that the ratio of stoichiometric coefficient for both N₂ : NH₄NO₂ or N₂ : C₆H₅N = NCl is 1 : 1)

⇒ A₀ ∝ V_∞

At t = t₁, t₂, t₃, the volume of N₂ corresponds to concentration of product formed i.e., equal to x.

⇒ x ∝ V_t

⇒ A₀ - x ∝ V_∞ - V_t

⇒ k t = 2.303 log₁₀ $\frac{V_\infty}{V_\infty - V_t}$

Hydrolysis of Esters ($\text{CH}_3\text{COOC}_2\text{H}_5$)

The reaction rate is measured by titrating the acid (CH_3COOH) produced against a standard alkali solution. Note that when a test sample is prepared from the reacting mixture, there are two acids : one is mineral acid H^+ (HCl or any other) and second is CH_3COOH produced. So volume of alkali used gives titration value for both acids. The data is collected in the following manner.

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t_∞
Vol. of NaOH	V_0	V_1	V_2	V_3	V_4	V_∞

At $t = 0$, V_0 is the volume NaOH used to neutralise the mineral acid present (H^+) being used as catalyst. (At $t = 0$, no CH_3COOH is yet produced)

At $t = \infty$ (i.e., at the end of hydrolysis), V_∞ is the volume of NaOH used to neutralise whole of CH_3COOH plus vol. of HCl present. At $t = \infty$, volume of CH_3COOH corresponds to volume of ester taken initially

$$\Rightarrow A_0 \propto V_\infty - V_0 \text{ (as } V_0 \equiv \text{ vol. of HCl)}$$

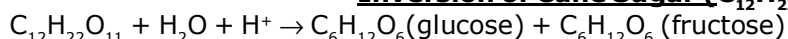
At $t = t_1, t_2, t_3, \dots, V_1, V_2, V_3, \dots$ corresponds to vol. of HCl plus vol. of CH_3COOH being produced.

$$\Rightarrow x \propto V_t - V_0$$

$$\Rightarrow A_0 - x \propto (V_\infty - V_0) - (V_t - V_0)$$

$$\Rightarrow A_0 - x \propto V_\infty - V_t$$

$$\Rightarrow kt = 2.303 \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$$

Inversion of Cane Sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)

The rate is measured by measuring the change in the angle of rotation (optical activity) by a polarimeter. Sucrose is dextro-rotatory, glucose is dextro-rotatory and fructose is leavo-rotatory. The change produced in rotatory power in time t gives a measure of x , the quantity of sucrose decomposed in that time. The total change in the rotatory power produced at the end of the reaction gives the measure of A_0 , the initial concentration of sucrose.

If r_0 , r_t and r_∞ represent rotations at the start of reaction, after time t and at the end of reaction respectively,

then

$$\Rightarrow A_0 \propto r_0 - r_\infty \text{ and } x \propto r_0 - r_t$$

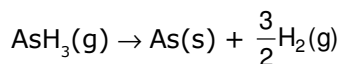
$$\Rightarrow A_0 - x \propto r_t - r_\infty$$

$$\Rightarrow kt = 2.303 \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

DECOMPOSITION OF $\text{AsH}_3(\text{g})$

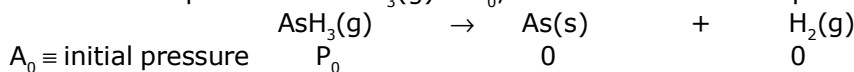
In first-order reactions involving gases, sometime measuring the pressure of the reaction mixture is very good method for measuring reaction rates.

For example consider decomposition of arsine gas (AsH_3)



The rate of reaction is measured as the *increase* in pressure of the reaction mixture. Note that there is an increase in number of moles of the gaseous products to the right, so as the reaction proceeds, there will be an increase in pressure of contents ($P \propto n$).

Let the initial pressure of $\text{AsH}_3(\text{g})$ is P_0 , if x is the decrease in pressure of $\text{AsH}_3(\text{g})$ after time t .



Arsenic is solid, so $P(\text{As}) = 0$

After time t , let P_t be the total pressure, then

$$P_t = P(\text{AsH}_3) + P(\text{H}_2) = (P_0 - x) + \frac{3}{2}x$$

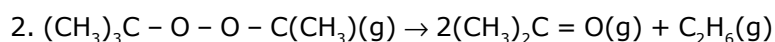
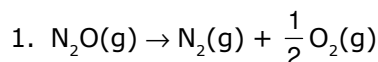
$$\Rightarrow P_t = P_0 + \frac{1}{2}x \quad \Rightarrow \quad x = 2(P_t - P_0)$$

Now $A_0 \propto P_0$

and $A \propto P_0 - x \equiv P_0 - 2(P_t - P_0) \equiv 3P_0 - 2P_t$

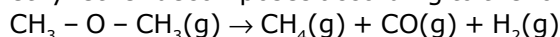
$$\Rightarrow kt = 2.303 \log_{10} \frac{P_0}{3P_0 - 2P_t}$$

On similar pattern, please try to write the expression for 1st order rate law for following first-order reactions. (in terms of P_0 and P_t)



Problem : 15

Dimethyl ether decomposes according to the following reaction :



At a certain temperature, when ether was heated in a closed vessel, the increase in pressure with time was noted down.

Time (min)	0	10	20	30
Pressure (mm Hg)	420	522	602	678

- (i) Show that the reaction is first order.
 (ii) Compute the pressure of $\text{CO}(\text{g})$ after 25 minutes.

Sol.



time	$\text{CH}_3-\text{O}-\text{CH}_3$	CH_4	CO	H_2
$t = 0$	$C_0 \equiv P_0$	0	0	0
$t = t$	$C_t \equiv P_0 - x$	x	x	x

$$\Rightarrow P_t = P_0 + 2x$$

$$\Rightarrow x = \frac{1}{2}(P_t - P_0)$$

$$\Rightarrow \frac{A_0}{A} = \frac{P_0}{P_0 - x} = \frac{2P_0}{3P_0 - P_t}$$

Now find k_1 , k_2 and k_3 using the first order kinetics

$$kt = 2.303 \log_{10} \frac{2P_0}{3P_0 - 2P_t}$$

$$k_1 = \frac{2.303}{10} \log_{10} \frac{2(420)}{3(420) - 522} = 0.0129 \text{ min}^{-1}$$

$$k_2 = \frac{2.303}{20} \log_{10} \frac{2(420)}{3(420) - 602} = 0.0122 \text{ min}^{-1}$$

$$k_3 = \frac{2.303}{30} \log_{10} \frac{2(420)}{3(420) - 678} = 0.0123 \text{ min}^{-1}$$

As $k_1 \sim k_2 \sim k_3$, the reaction is first order.

$$k_{\text{average}} = \frac{1}{3}(k_1 + k_2 + k_3) = 0.0127 \text{ min}^{-1}$$

$$P_{\text{CO}} = x = \frac{1}{2}(P_t - P_0)$$

Find P after $t = 25$ min using first order kinetics with $k = 0.0127 \text{ min}^{-1}$

$$\Rightarrow \log_{10} \frac{2(420)}{3(240) - P_t} = 0.0127 \times 25$$

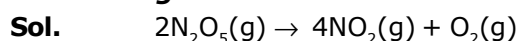
$$\Rightarrow P_t = 648.46 \text{ mm} \Rightarrow x = 114.23 \text{ mm}$$

Problem : 16

The decomposition of N_2O_5 according to following reaction is first order reaction :



After 30 min. from start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.



$2\text{N}_2\text{O}_5$	4NO_2	O_2
P_0	0	0
$P_0 - 2x$	$4x$	x

P_0 : initial pressure ; Let P_t : pressure at 30 min and P_∞ : pressure at the end of decomposition.

$$\Rightarrow P_t = P_0 + 3x \quad \Rightarrow \quad x = \frac{1}{3}(P_t - P_0)$$

$$\text{and } P_\infty = 2P_0 + \frac{1}{2}P_0 = \frac{5}{2}P_0 \Rightarrow P_0 = \frac{2}{5}P_\infty$$

For the first order kinetics

$$k_{\text{eff}} t = 2.303 \log_{10} \frac{A_0}{A}$$

A_0 : initial concentration ; A : final concentration

$$\text{Now } \frac{A_0}{A} = \frac{P_0}{P_0 - 2x} = \frac{\frac{1}{5}P_\infty}{\frac{1}{5}P_\infty - 2 \frac{P_t - 2/5P_\infty}{3}} \Rightarrow \frac{A_0}{A} = \frac{3}{5} \left(\frac{P_\infty}{P_\infty - P_t} \right)$$

$$\Rightarrow k_{\text{eff}} = \frac{1}{30} \times 2.303 \log_{10} \frac{3}{5} \times \frac{584.5}{584.5 - 284.5} = 5.204 \times 10^{-3} \text{ min}^{-1}$$

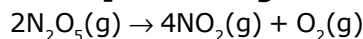
$$k \text{ for the reaction} = \frac{5.204}{2} \times 10^{-3} = 2.602 \times 10^{-3} \text{ min}^{-1}$$

Problem : 17

The gas phase decomposition of N_2O_5 to NO_2 and O_2 is monitored by measurement of total pressure. The following data are obtained.

P_{total} (atm)	0.154	0.215	0.260	0.315	0.346
Time (sec)	1	52	103	205	309

Find the average rate of disappearance of N_2O_5 for the time interval between each interval and for the total time interval. [Hint : Integrated rate law is NOT to be used]

Sol.

Initial Pressure (at $t = 0$) P_0 0 0

At equilibrium $P_0 - 2x$ $4x$ x

$$\text{Now: } P_t = (P_0 - 2x) + 4x + x \Rightarrow x = \frac{1}{3}(P_t - P_0)$$

$$P_{N_2O_5} = P_0 - 2x = \frac{1}{3}(5P_0 - 2P_t)$$

Thus, $\Delta P_{N_2O_5} = \frac{2}{3}(P_{t_1} - P_{t_2})$ where P_{t_2} and P_{t_1} are the total pressures at time instants t_2 and t_1 ($t_2 > t_1$) respectively

P_{total} (atm)	Time (sec)	$\frac{\Delta P_{N_2O_5}}{\Delta t}$ = Avg. Rate of disappearance of N_2O_5
0.154	1	$\frac{(0.154 - 0.215)}{(52 - 1)} = -1.20 \times 10^{-3}$
0.215	52	$\frac{(0.215 - 0.260)}{(103 - 52)} = -0.88 \times 10^{-3}$
0.260	103	$\frac{(0.260 - 0.315)}{(205 - 103)} = -0.54 \times 10^{-3}$
0.315	205	$\frac{(0.315 - 0.346)}{(309 - 205)} = -0.30 \times 10^{-3}$
0.346	309	

Problem : 18

5 ml of ethylacetate was added to a flask containing 100 ml of 0.1 N HCl placed in a thermostat maintained at 30°C. 5 ml of the reaction mixture was withdrawn at different intervals of time and after chilling, titrated against a standard alkali. The following data were obtained :

Time (minutes)	0	75	119	183	∞
Volume of alkali used in ml	9.62	12.10	1.10	14.75	21.05

Show that hydrolysis of ethyl acetate is a first order reaction.

Sol. The hydrolysis of ethyl acetate will be a first order reaction if the above data confirm to the equation.

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Where V_0 , V_t and V_∞ represent the volumes of alkali used at the commencement of the reaction, after time t and at the end of the reaction respectively, Hence

$$V_\infty - V_0 = 21.05 - 9.62 = 11.43$$

Time	$V_{\infty} - V_t$	k_1
75 min	$21.05 - 12.10 = 8.95$	$\frac{2.303}{75} \log \frac{11.43}{8.95} = 0.003259 \text{ min}^{-1}$
119 min	$21.05 - 13.10 = 7.95$	$\frac{2.303}{119} \log \frac{11.43}{7.95} = 0.003051 \text{ min}^{-1}$
183 min	$21.05 - 14.75 = 6.30$	$\frac{2.303}{183} \log \frac{11.43}{6.30} = 0.003254 \text{ min}^{-1}$

A constant value of k shows that hydrolysis of ethyl acetate is a **first order** reaction.

Problem : 19

The optical rotations of sucrose in 0.5N HCl at 35°C at various time intervals are given below. Show that the reaction is of first order :

Time (minutes)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	-11.1

Sol. The inversion of sucrose will be first order reaction if the above data confirm to the equation, $k_1 =$

$$\frac{2.303}{t} \log \frac{r_0 - r_{\infty}}{r_t - r_{\infty}}$$

Where r_0 , r_t and r_{∞} represent optical rotations initially, at the commencement of the reaction after time t and at the completion of the reaction respectively

In the case $a_0 = r_0 - r_{\infty} = +32.4 - (-11.1) = +43.5$

The value of k at different times is calculated as follows :

Time	r_t	$r_t - r_{\infty}$	k
10 min	+28.8	39.9	$\frac{2.303}{10} \log \frac{43.5}{39.9} = 0.008625 \text{ min}^{-1}$
20 min	+25.5	36.6	$\frac{2.303}{10} \log \frac{43.5}{36.6} = 0.008625 \text{ min}^{-1}$
30 min	+22.4	33.5	$\frac{2.303}{30} \log \frac{43.5}{33.5} = 0.008694 \text{ min}^{-1}$
40 min	+19.6	30.7	$\frac{2.303}{40} \log \frac{43.5}{30.7} = 0.008717 \text{ min}^{-1}$

The constancy of k_1 indicates that the inversion of sucrose is a **first order** reaction.

Problem : 20

The hydrolysis of ethyl acetate



in aqueous solution is first order with respect to ethyl acetate. Upon varying the pH of the solution the first order rate constant varies as follows.

pH	3	2	1
$k_1 \times 10^{-4} \text{ s}^{-1}$	1.1	11	110

what is the order of the reaction with respect of H^+ and the value of the rate constant?

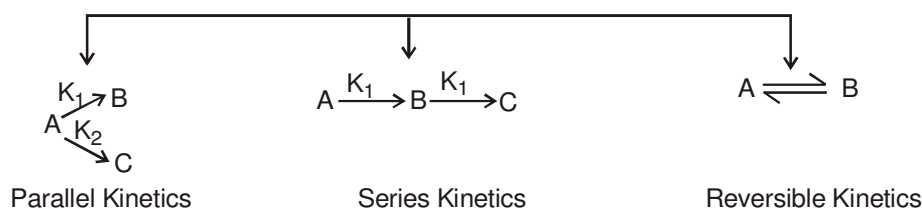
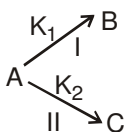
Sol. Rate = $k[\text{CH}_3\text{COOC}_2\text{H}_5]^a[\text{H}^+]^b$
 $[\text{H}^+]$ is constant through out the reaction
 $k_1 = k[\text{H}^+]^b$

$$\text{Hence, } \left(\frac{k_1}{k_1'} \right) = \left(\frac{[\text{H}^+]_1}{[\text{H}^+]_2} \right)^b \quad \frac{1.1}{11} = \left(\frac{10^{-3}}{10^{-2}} \right)^b$$

$$b = 1$$

$$k_1 = k[\text{H}^+]$$

$$1.1 \times 10^{-4} = k(10^{-3}) \Rightarrow k = 1.1 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

COMPLEX (FIRST ORDER) KINETICS**PARALLEL KINETICS**

$$t = 0 \quad [A]_0$$

$$t = t \quad [A]$$

$$\text{Rate of change of A} = [\text{rate of change of A}]_I + [\text{rate of change of A}]_{II}$$

$$-\frac{d[A]}{dt} = K_1 [A] + K_2 [A]$$

$$\frac{dB}{dt} = k_1 A, \quad \frac{dC}{dt} = k_2 A$$

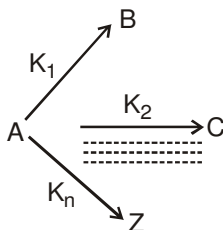
$$\Rightarrow \frac{[B]}{[C]} = \frac{k_1}{k_2}$$

$$\% \text{ of B in the mix of A \& B} = \frac{k_1}{k_1 + k_2} \times 100$$

$$\% \text{ of C in the} = \frac{k_2}{k_1 + k_2} \times 100$$

$$-\frac{d[A]}{dt} = (K_1 + K_2) [A]$$

$$K_1 + K_2 = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t} \quad t_{1/2} = \frac{0.693}{K_1 + K_2}$$

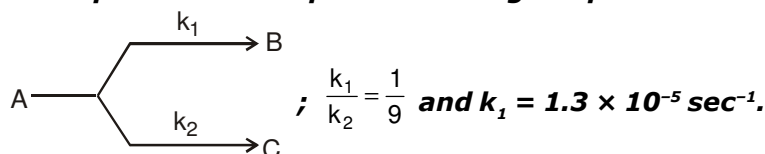
GENERALIZATION

$$K_1 + K_2 + \dots + K_n = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

$$t_{1/2} = \frac{0.693}{K_1 + K_2 + \dots + K_n}$$

Problem : 21

An organic compound A decomposes following two parallel first order mechanisms :



Calculate the concentration ratio of C to A, if an experiment is allowed to start with only A for one hour.

Sol. $\frac{k_1}{k_2} = \frac{1}{9}$

But $k_1 = 1.3 \times 10^{-5} \text{ sec}^{-1}$; $k_2 = 9 \times 1.3 \times 10^{-5} \text{ sec}^{-1} = 11.7 \times 10^{-5} \text{ sec}^{-1}$
 $(k_1 + k_2) = (1.3 \times 10^{-5}) + (11.7 \times 10^{-5}) \text{ sec}^{-1} = 13 \times 10^{-5} \text{ sec}^{-1}$ (1)

Also $\frac{[B]_t}{[C]_t} = \frac{1}{9} \Rightarrow [B]_t = \frac{[C]_t}{9}$ (2)

For parallel first order reaction :

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

$$\Rightarrow - \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = (k_1 + k_2) \int_{t=0}^{t=t} dt$$

$$\Rightarrow \ln \frac{[A]_0}{[A]_t} = (k_1 + k_2)t ; \ln \left[\frac{[A]_t + [B]_t + [C]_t}{[A]_t} \right] = (k_1 + k_2)t$$

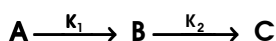
$$\Rightarrow \ln \left[\frac{[A]_t + \frac{[C]_t}{9} + [C]_t}{[A]_t} \right] = (k_1 + k_2)t \text{ [from eq. (2)]}$$

$$\Rightarrow \ln \left[1 + \frac{10 [C]_t}{9 [A]_t} \right] = (k_1 + k_2)t$$

$$\Rightarrow \ln \left[1 + \frac{10 [C]_t}{9 [A]_t} \right] = 13 \times 10^{-5} \times 60 \times 60 = 0.468 \text{ [from eq. (1)]}$$

$$\Rightarrow 1 + \frac{10 [C]_t}{9 [A]_t} = 1.5968 ; \quad \frac{[C]_t}{[A]_t} = 0.537$$

(2) SERIES KINETICS



$$-\frac{d[A]}{dt} = K_1 [A]$$

$$\frac{d[B]}{dt} = \text{Rate at which B is produced} - \text{Rate at which B is consumed}$$

$$\frac{d[B]}{dt} = \text{Rate at which A is consumed} - \text{Rate at which B is consumed}$$

$$\frac{d[B]}{dt} = K_1 [A] - K_2 [B]$$

$$\begin{aligned} \frac{d[C]}{dt} &= \text{Rate at which C is produced} \\ &= \text{Rate at which B is consumed} \end{aligned}$$

$$\frac{d[C]}{dt} = K_2 [B]$$

$$-\frac{d[A]}{dt} = K_1 [A]$$

$$[A]_t = [A]_0 e^{-k_1 t}$$

$$\frac{d[B]}{dt} = K_1 [A] - K_2 [B]$$

$$\frac{d[B]}{dt} + K_2 [B] = K_1 [A]_0 e^{-k_1 t}$$

$$\frac{dy}{dx} + P(x)y = Q(x)$$

$$y \times e^{\int P(x) dx} = \int Q(x) \cdot e^{\int P(x) dx} dx + C$$

$$[B] e^{\int k_2 dt} = \int K_1 [A]_0 e^{-k_1 t} e^{\int k_2 dt} dt + C$$

$$[B] e^{k_2 t} = k_1 [A]_0 \int e^{-k_1 t} e^{k_2 t} dt + C$$

$$[B] e^{k_2 t} = k_1 [A]_0 \int e^{(k_2 - k_1)t} dt + C$$

$$[B] e^{k_2 t} = k_1 [A]_0 \frac{e^{(k_2 - k_1)t}}{(k_2 - k_1)} + C$$

$$\text{At, } t = 0, [B] = 0$$

$$0 = \frac{k_1[A]_0}{k_2 - k_1} + C \Rightarrow C = \frac{-k_1[A]_0}{(k_2 - k_1)}$$

$$[B]e^{k_2 t} = k_1 [A]_0 \frac{e^{(k_2 - k_1)t}}{(k_2 - k_1)} - \frac{k_1 [A]_0}{(k_2 - k_1)}$$

$$[B] = \frac{k_1 [A]_0}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}]$$

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

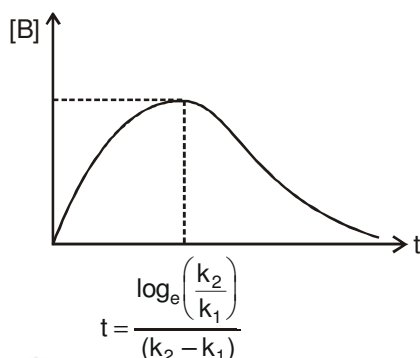
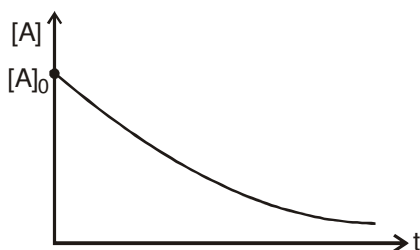
$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A]_0}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}]$$

$$[C] = \frac{k_1 k_2 [A]_0}{k_2 - k_1} \left[\frac{e^{-k_1 t}}{-k_1} - \frac{e^{-k_2 t}}{-k_2} \right]_0^t$$

$$[C] = \frac{k_1 k_2 [A]_0}{k_1 - k_2} \left[\frac{e^{-k_1 t}}{k_1} - \frac{e^{-k_2 t}}{k_2} - \frac{1}{k_1} + \frac{1}{k_2} \right]$$

$$[C] = \frac{k_1 k_2 [A]_0}{k_1 - k_2} \left[\frac{(e^{-k_1 t} - 1)}{k_1} - \frac{(e^{-k_2 t} - 1)}{k_2} \right]$$

★

Graph of [A], [B], [C] Vs t:

$$[B] = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

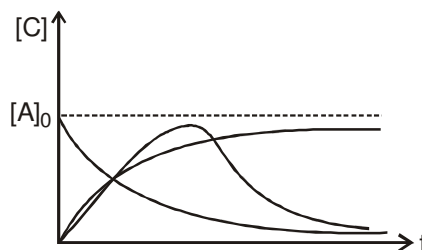
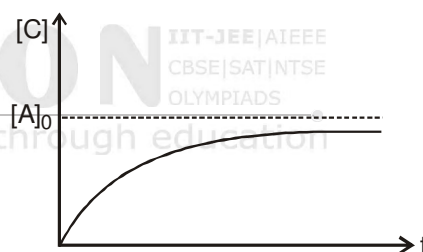
$$\frac{d[B]}{dt} = \frac{k_1 [A]_0}{k_2 - k_1} [-k_1 e^{-k_1 t} - (-k_2) e^{-k_2 t}] = 0$$

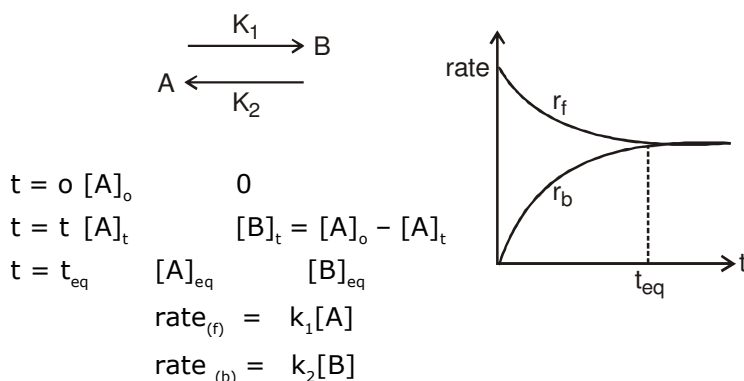
$$k_1 e^{-k_1 t} = k_2 e^{-k_2 t}$$

$$e^{(k_2 - k_1)t} = \frac{k_2}{k_1}$$

$$(k_2 - k_1)t = \log_e \frac{k_2}{k_1}$$

$$t = \frac{\log_e (k_2/k_1)}{k_2 - k_1}$$



REVERSIBLE KINETICS

At equilibrium, $r_f = r_b$

$$k_1 [A]_{\text{equilibrium}} = k_2 [B]_{\text{equilibrium}}$$

$$\frac{k_1}{k_2} = \frac{[B]_{\text{equilibrium}}}{[A]_{\text{equilibrium}}}$$

$$\frac{k_1}{k_2} = \frac{[A]_0 - [A]_{\text{equilibrium}}}{[A]_{\text{equilibrium}}} = \frac{[A]_0}{[A]_{eq}} - 1$$

$$\frac{k_1 + k_2}{k_2} = \frac{[A]_0}{[A]_{eq}}$$

$$[A]_{\text{equilibrium}} = \frac{k_2 [A]_0}{k_1 + k_2} \quad \dots\dots\dots (I)$$

$\frac{d[A]}{dt}$ = Rate at which A disappears
 + Rate at which A is produced.

$$\begin{aligned}
 \frac{d[A]}{dt} &= -k_1 [A] + k_2 [B] & \frac{d[A]}{dt} &= -k_1 [A] + k_2 [[A]_0 - [A]] \\
 &= -(k_1 + k_2) [A] + k_2 [A]_0 & &= (k_1 + k_2) \left[-[A] + \frac{k_2}{k_1 + k_2} [A]_0 \right]
 \end{aligned}$$

By substituting the value from equation (I)

$$\frac{d[A]}{dt} = (k_1 + k_2) [[A]_{eq} - [A]] \Rightarrow \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]_{eq} - [A]} = (k_1 + k_2) \int_0^t dt$$

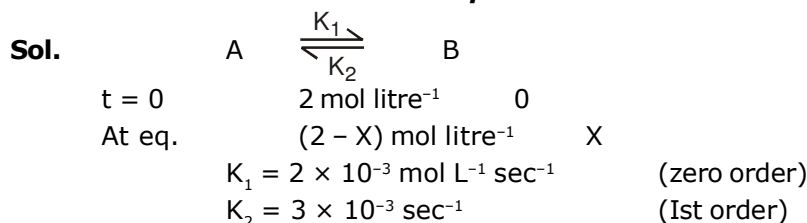
$$\log_e \frac{[A]_{eq} - [A]_0}{[A]_{eq} - [A]_t} = (k_1 + k_2) t$$

$$(k_1 + k_2) = \frac{2.303}{t} \log_{10} \frac{[A]_{eq} - [A]_0}{[A]_{eq} - [A]_t}$$

$$[B]_t = [A]_0 - [A]_t$$

Problem : 22

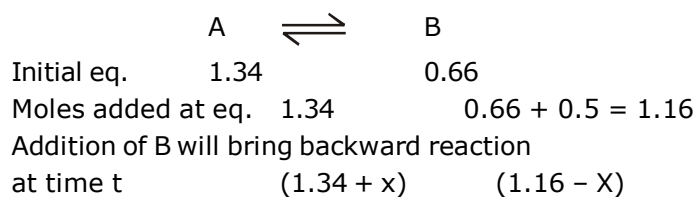
For the reversible reaction in equilibrium : $A \xrightleftharpoons[K_2]{K_1} B$. The values of K_1 and K_2 are $2 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}$ and $3 \times 10^{-3} \text{ sec}^{-1}$ respectively. If we add 0.5 moles of B in the equilibrium mixture, initially containing 2 moles of A. Calculate the time taken for concentration of B to become equal to $3/4$ of the concentration of A initial equilibrium. The volume of mixture is 1 L and remains constant.



$$\frac{dX}{dt} = K_1[A]^0 - K_2[B]^1$$

At equilibrium $\frac{dx}{dt} = 0 \therefore 0 = K_1 - K_2 [X]_{\text{eq}}$

$$\therefore [X]_{\text{eq}} = \frac{K_1}{K_2} = \frac{2 \times 10^{-3}}{3 \times 10^{-3}} = 0.66 \text{ mol litre}^{-1} = K_c$$



$$\therefore [B] = \frac{3}{4}[A]_{\text{eq}} = \frac{3}{4} \times 1.34 = 1.005$$

$$(1.16 - X) = 1.005$$

$$\therefore X = 0.155$$

Now, $\frac{dX}{dt} = K_1 - K_2[X] = 0.66K_2 - K_2X = K_2 [0.66 - X]$

$$\therefore \frac{dX}{(0.66 - X)} = K_2 \cdot dt$$

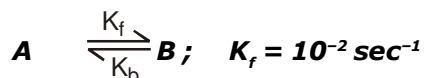
or $-2.303 \log (0.66 - X) = K_2 \cdot t + C$

at t = 0, X = 0

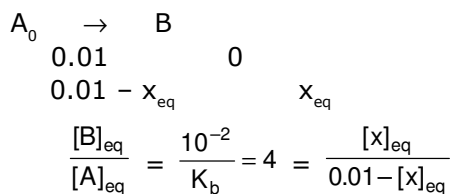
$$\therefore C = -2.303 \log 0.66$$

$$\therefore K_2 \cdot t = 2.303 \log \frac{0.66}{0.66 - X}$$

$$\therefore t = \frac{2.303}{3 \times 10^{-3}} \log \frac{0.66}{0.66 - 0.155} = \mathbf{89.24 \text{ sec}}$$

Problem : 23 For a reversible first order reaction,

and $\frac{B_{eq}}{A_{eq}} = 4$; If $A_0 = 0.01 \text{ ML}^{-1}$ and $B_0 = 0$, what will be concentration of B after 30 sec ?

Sol.

$$\therefore K_b = 0.25 \times 10^{-2} \quad \text{and} \quad x_{eq} = \frac{0.04}{5} = 0.008$$

$$t = \frac{2.303}{(K_f + K_b)} \log \frac{[x]_{eq}}{[x]_{eq} - x}$$

$$30 = \frac{2.303}{1.25 \times 10^{-2}} \log \frac{0.008}{(0.008 - x)}$$

$$\therefore \frac{0.008}{0.008 - x} = 1.455 \quad \therefore \quad x = 2.50 \times 10^{-3}$$

Ways to determine order of reaction

Initial Rate method

Half life method

Ostwald Isolation method

Integrated Rat law method

(1) Initial Rate Method



	[A]	[B]	rate
Experiment 1	0.1	0.1	2×10^{-3}
Experiment 2	0.1	0.2	4×10^{-3}
Experiment 3	0.2	0.1	32×10^{-3}

Experiment (1) and Experiment (2)

$$\frac{2 \times 10^{-3}}{4 \times 10^{-3}} = \frac{k [0.1]^m [0.1]^n}{k [0.1]^m [0.2]^n}$$

$$\left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^n$$

$$n = 1$$

Experiment (1) and Experiment (3)

$$\frac{2 \times 10^{-3}}{32 \times 10^{-3}} = \frac{k [0.1]^m [0.1]^n}{k [0.2]^m [0.1]^n}$$

$$\left(\frac{1}{2}\right)^4 = \left(\frac{1}{2}\right)^m$$

$$m = 4$$

$$\text{Order } (m + n) = 4 + 1 = 5$$

(2) Half - life method

$t_{1/2}$	$[A]_0$	
1 hr	0.1	$t_{1/2} \propto \frac{1}{[A]^{n-1}}$
2 hr	0.2	

$$\frac{[t_{1/2}]_1}{[t_{1/2}]_2} = \left(\frac{1}{2}\right)^{-1} = \frac{[0.1]^{n-1}}{[0.2]^{n-1}}$$

$$\left(\frac{1}{2}\right)^{-1} = \left(\frac{1}{2}\right)^{n-1}$$

$$n = 0$$

$$n = 1 + \frac{\log(t_{1/2})_2 / (t_{1/2})_1}{\log[A]_{0_1} / [A]_{0_2}}$$

(3) Ostwald Isolation method

$$\text{rate} = k[A]^m [B]^n [C]^o [D]^p \text{ - - - - -}$$

Experiment 1 :

[A] = In small quantity ; [B], [C], [D] - - - - - in excess

The rate equation reduces to

$$\text{rate} = k' [A]^m \Rightarrow r_1 = k' [A]_1^m$$

$$r_2 = k' [A]_2^m$$

$$\frac{r_1}{r_2} = \left(\frac{[A]_1}{[A]_2}\right)^m$$

$$\log \left(\frac{r_1}{r_2}\right) = m \log \left(\frac{[A]_1}{[A]_2}\right)$$

$$m = \frac{\log(r_1/r_2)}{\log([A]_1/[A]_2)}$$

Experiment 2:**[B] = In small quantity .**& [A], [C], [D] - - - - - \Rightarrow in excess.rate = $k' [B]^n \rightarrow$ repeated**Order of reaction = m + n + O + p + - - - - -****(4) Integrated Rate law Method****A \longrightarrow product**

t = 0 1000 M

t = 60 sec 100 M

t = 120 sec 10 M

$$n = 0 \quad k = \frac{[A]_0 - [A]_t}{t} = \frac{1000 - 100}{60} = \frac{900}{60} = 15$$

$$k = \frac{1000 - 10}{120} = \frac{990}{120}$$

$$n = 1$$

$$k = \frac{2.303}{60} \log \frac{1000}{10} = \frac{2.303}{60}$$

$$k = \frac{2.303}{120} \log \frac{1000}{10} = \frac{2.303}{60}$$

ACTIVATION ENERGY (E_a)

A mixture of magnesium and oxygen does not react at room temperature. But if a burning splinter is introduced to the mixture, it burns vigorously. Similarly a mixture of methane and oxygen does not react at room temperature, but if a burning match-stick is put in the mixture, it burns rapidly. Why it happen like this, that some external agents has to be introduced in order to initiate the reaction ?

According to the theory of reaction rates "for a chemical reaction to take place, reactant molecules must make collisions among themselves". Now in actual, only a fraction of collisions are responsible for the formation of products, i.e., not all collisions are effective enough to give products. So the collisions among reactant molecules are divided into two categories :-

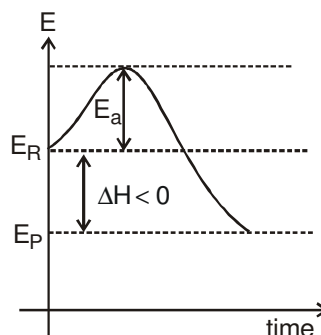
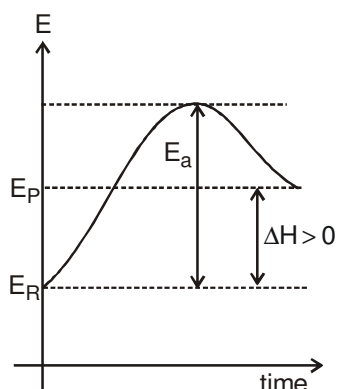
Effective collisions and In-effective collisions

Effective collisions are collisions between the molecules which have energies equal to or above a certain minimum value. This minimum energy which must be possessed by the molecules in order to make an effective collision (i.e., to give a molecule of products) is called as *threshold energy*. So it is the effective collisions which bring about the occurrence of a chemical reaction.

Ineffective collisions are the collisions between the molecules which does not posses the threshold energy. These can not result in a chemical reaction.

Now most of the times, the molecules of reactants do not possess the threshold energy. So in order to make effective collisions (i.e., to bring about the chemical reaction), an additional energy is needed to be absorbed by the reactant molecules. This additional energy which is absorbed by the molecules so that they achieve the threshold energy is called as energy of activation or simply activation energy. It is represented as E_a .

A reaction which needs higher activation energy is slow at a given temperature.

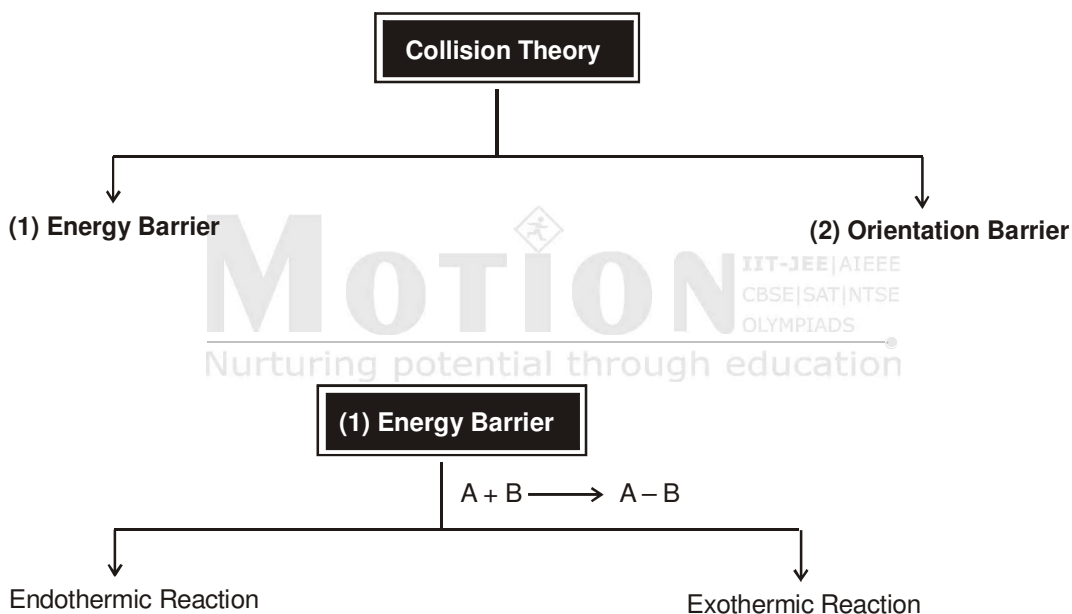


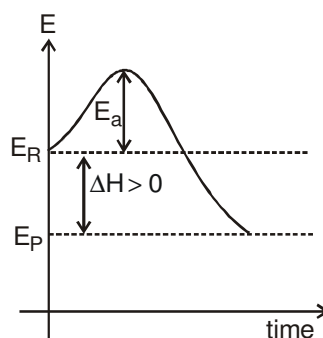
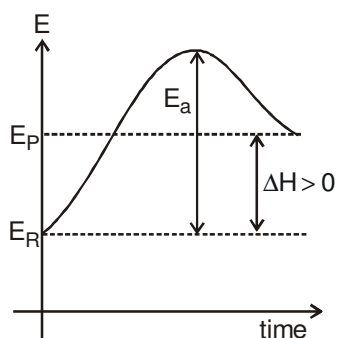
For example : $\text{NO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{NO}_2\text{(g)}$ is faster at ordinary temperature whereas the following reaction :

$\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ is slower at the same temperature as the value of E_a for the second reaction is much higher.

Note :

- The progress of the reaction can be studied in a graph with energy of the reacting system. You can find ΔH and E_a from graph. (see fig on left)





$$\begin{aligned}
 E_{af} &> E_{ab} \\
 H_f - H_i &= \Delta H_R \\
 E_{af} + H_i &= E_{ab} + H_f = E_{\text{threshold}} \\
 E_{af} &= E_{ab} + \Delta H_R
 \end{aligned}$$

$$E_{af} < E_{ab}$$

(2) Orientation Barrier



Improper orientation \Rightarrow no reaction.



Activated complex

Proper orientation \Rightarrow Reaction possible.

- For a reactant to change into product both the barriers should be crossed simultaneously.
- All those collisions which results into product are called **effective collisions**.

ARRHENIUS EQUATION

Number of effective collisions = Number of collision \times fraction.

$$K = A e^{-E_a/RT}$$

Where,

K = rate constant of reaction

- A** = Pre exponential factor
 = Arrhenius constant
 = Collision frequency
 = Frequency factor.
E_a = Activation energy
R = Universal gas constant
T = Absolute temperature.

➞ **Fraction of molecules undergoing effective collision** = $e^{-E_a / RT} = \frac{K}{A}$

Variation in Arrhenius equation

Type -1 :

$$\log k = 2 - \frac{5 \times 10^3}{T} ; A = ? \quad E_a = ?$$

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

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

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

$$\log_{10} A = 2 \Rightarrow A = 10^2 = 100$$

$$\frac{E_a}{2.303 RT} = \frac{5 \times 10^{-3}}{T} \Rightarrow E_a = 2.303 \times R \times 5 \times 10^{-3}$$

Type -2 : Temperature Variation :

$$r_1 \longrightarrow K_1 \longrightarrow T_1$$

$$r_2 \longrightarrow K_2 \longrightarrow T_2$$

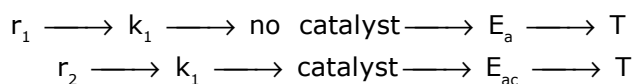
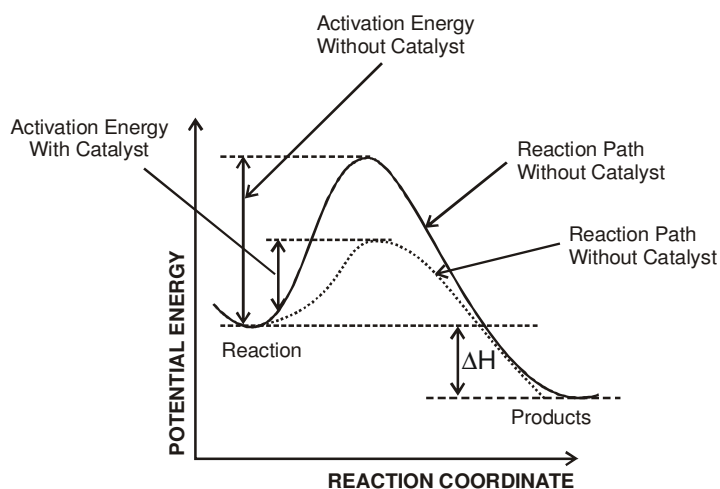
$$\frac{r_2}{r_1} = \frac{k_2}{k_1}$$

$$\log k_1 = \log A - \frac{E_a}{2.303 RT_1}$$

$$\log k_2 = \log A - \frac{E_a}{2.303 RT_2}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Type -3 : Addition of Catalyst :



$$\log k_1 = \log A - \frac{E_a}{2.303 RT}$$

$$\log k_2 = \log A - \frac{E_{ac}}{2.303 RT}$$

$$\log \frac{k_2}{k_1} = \frac{E_a - E_{ac}}{2.303 RT}$$

Type -4 : Both Catalyst and Temperature :

$$\log \frac{k_2}{k_1} = \frac{1}{2.303 R} \left[\frac{E_a}{T_1} - \frac{E_{ac}}{T_2} \right]$$

FACTORS AFFECTING RATE OF REACTION

- (a) Catalyst :** The rate of reaction increased by addition of catalyst, because catalyst lowers, the activation energy and increased the rate of reaction
- (b) Temperature :** With increase in temperature the rate of reaction increases. It is generally found for every 10° increase in temperature. The rate constant double.
The ratio of rate constants with 10° difference in their temperature is called temperature coefficient.

$$\frac{K_{T+10}}{K_T} = Q = \text{Temperature coefficient of reaction} \approx 2$$

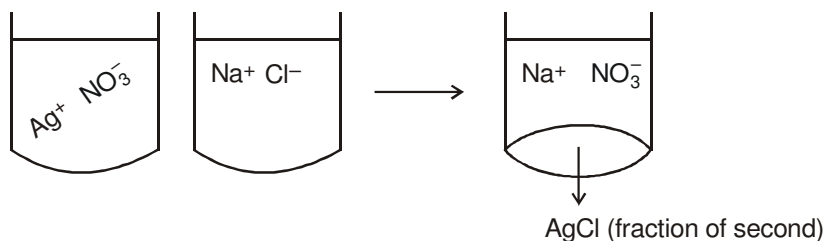
- (c) Concentration :**

$$\text{Rate} = A e^{-E_a/RT} [A]^m [B]^n \text{ - - - - -}$$

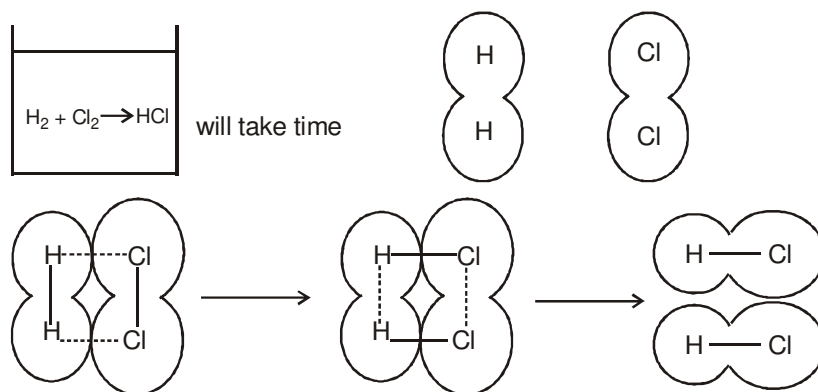
With increase in concentration of reactants the rate of the reaction increases because number of collision (effective collisions) increases.

(d) Nature of Reactants :

Ionic Reactants :



Covalent Reactants :



Generally ionic reactions in aq. media are fast than the reaction involving covalent reactants. As covalent reactants involving breaking of bond then formation of bond where as ionic reaction involve in single step.

(e) Surface Area : Increase in surface area increases the number of collisions and hence rate increases

(f) Effect of Sun light : Some reactions exposes to sunlight also increases the rate of reaction.

Problem : 24

At 278 °C the half life period for the first order thermal decomposition of ethylene oxide is 363 min and the energy of activation of the reaction is 52,00 cal/mole. From these data estimate the time required for ethylene oxide to be 75% decomposed at 450°C.

Sol. $\ln \frac{k_{450}}{k_{278}} = \frac{5200}{2} \left[\frac{1}{551} - \frac{1}{725} \right] = 1.122$

$$\frac{k_{450}}{k_{278}} = 3.07 = \frac{363}{t_{1/2}(\text{at } 450^\circ\text{C})} \quad t_{1/2}(\text{at } 450^\circ\text{C}) = 118.24 \text{ min.}$$

$$\text{Now } t_{0.75} = \frac{1}{k} \ln \frac{A_0}{A_0/4} = \frac{1}{k} \ln 4 = \frac{1.386}{k}$$

$$\therefore t_{0.75} = \frac{1.386}{0.693} \times 118.24 = \mathbf{236.48 \text{ min}}$$

Problem : 25

The activation energy of the reaction : $A + B \rightarrow \text{products}$ is 102.9 kJ/mol. At 40°C, the products are formed at the rate of 0.133 mol/L/min. What will be rate of formation of products at 80°C?

Sol. Let the rate law be defined as

$$\text{At } T_1 : r_1 = k_1[A]^x[B]^y$$

$$\text{At } T_2 : r_2 = k_2[A]^x[B]^y$$

$$\Rightarrow r_2 = r_1 \left(\frac{k_2}{k_1} \right)$$

Using Arrhenius equation find k at 40°C .

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \Rightarrow \log_{10} \frac{k_2}{k_1} = \frac{102.9 \times 10^3}{2.303 \times 8.31} \left(\frac{40}{313 \times 353} \right)$$

$$\Rightarrow \log_{10} \frac{k_2}{k_1} = 1.95 \Rightarrow \frac{k_2}{k_1} = 88.41$$

$$\Rightarrow r_2 = 0.133 \times 88.41 = 11.76 \text{ mol/L/min}$$

Problem : 26

The activation energy of a non-catalysed reaction at 37°C is 200 kcal/mol and the activation energy of the same reaction when catalysed decreases to only 6.0 kcal/mol . Calculate the ratio of rate constants of the two reactions.

Sol. We know that :

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

Let k = rate constant for non-catalysed reaction and k_c rate constant for catalysed reaction. Let E_a be the activation energy for non-catalysed reaction and E_{ac} be the energy of activation of catalysed reaction.

$$1. \quad k = A e^{-E_a/RT}$$

$$2. \quad k_c = A e^{-E_{ac}/RT}$$

$$\Rightarrow \frac{k}{k_c} = e^{\frac{1}{RT}(E_{ac} - E_a)}$$

$$\Rightarrow \log_{10} \frac{k}{k_c} = \frac{1}{2.303RT} (E_{ac} - E_a)$$

$$\Rightarrow \log_{10} \frac{k}{k_c} = \frac{1}{2.303 \times 2 \times 310} (6 \times 10^3 - 200 \times 10^3)$$

$$\Rightarrow \log_{10} \frac{k}{k_c} = -9.8 \Rightarrow \frac{k}{k_c} = 1.56 \times 10^{-10} \text{ or } \frac{k_c}{k} = 6.3 \times 10^9$$

Problem : 27

A first order reaction $A \rightarrow B$ requires activation energy of 70 kJ/mol . When 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C ? Assume that the activation energy remains constant in this range of temperature.

Sol. Note : It does not matter whether you take 20%, 30%, 40% or 70% of A.

At 25°C , 20% of A decomposes 25%

$$\Rightarrow kt = 2.303 \log_{10} \frac{A_0}{A}$$

$$\Rightarrow k(40) = 2.303 \log_{10} \frac{100}{75} \Rightarrow k(\text{at } 25^\circ\text{C}) = 0.0143 \text{ min}^{-1}$$

Using Arrhenius equation find k at 40°C .

$$\log_{10} \frac{k_{40^\circ}}{k_{25^\circ}} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log_{10} \frac{k_{40^\circ}}{0.0143} = \frac{70 \times 10^3}{2.303 \times 8.31} \left(\frac{40 - 25}{298 \times 313} \right) \Rightarrow k(\text{at } 40^\circ\text{C}) = 0.055 \text{ min}^{-1}$$

Now calculate % decomposition at 40°C using first order kinetics.

$$kt = 2.303 \log_{10} \frac{A_0}{A}$$

$$\Rightarrow 0.055 \times 40 = 2.303 \log_{10} \frac{100}{100 - x}$$

$$\Rightarrow x = 67.1 \approx 67.1\% \text{ decomposition of A at } 40^\circ\text{C}.$$

Problem : 28

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 .

Sol. $\therefore 2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

$$\therefore 2.303 \log_{10} \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{8.314} \left[\frac{373 - 323}{373 \times 323} \right]$$

$$\therefore E_a = 2.2 \times 10^4 \text{ J mol}^{-1}$$

Now, $K = Ae^{-E_a/RT} \quad \therefore 4.5 \times 10^7 = Ae^{-\frac{2.2 \times 10^4}{8.314 \times 373}}$

$$\therefore A = 5.42 \times 10^{10}$$

Problem : 29

A reaction proceeds five times more at 60°C as it does at 30°C . Estimate energy of activation.

Sol. Given, $T_2 = 60 + 273 = 333 \text{ K}$, $T_1 = 30 + 273 = 303 \text{ K}$,

$$R = 1.987 \times 10^{-3} \text{ kcal}$$

$$\therefore r = k []^n \text{ (at a temperature } T)$$

$$\therefore \frac{r_2}{r_1} = \frac{K_2}{K_1} \text{ (at temp. } T_2 \text{ and } T_1)$$

$$\therefore \frac{r_2}{r_1} = 5 \quad \therefore \frac{K_2}{K_1} = 5$$

$$\therefore 2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\therefore 2.303 \log_{10} 5 = \frac{E_a}{10^{-3} \times 1.987} \left[\frac{333 - 303}{333 \times 303} \right]$$

$$E_a = 10.757 \text{ kcal mol}^{-1}$$

Problem : 30

The rate constant of a reaction increases by 7% when its temperature is raised from 300 K to 310 K, while its equilibrium constant increases by 3%. Calculate the activation energy of the forward and reverse reactions.

Sol. Rate constant at 300K = k

$$\therefore \text{Rate constant at } 310 \text{ K} = k + \left[k \times \frac{7}{100} \right] = 1.07 k$$

Thus, $2.303 \log \frac{k_2}{k_1} = \frac{E_a^f}{R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$

$$2.303 \log \frac{1.07k}{k} = \frac{E_a^f}{2} \left[\frac{310 - 300}{310 \times 300} \right]$$

$$\therefore E_a^f = \mathbf{1258.68 \text{ cal}}$$

Now, equilibrium constant at 300 K = K'

$$\text{Equilibrium constant at 310 K} = K' + \frac{3}{100} \times K' = 1.03 K'$$

Using $2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

$$2.303 \log \frac{1.03K'}{K'} = \frac{\Delta H}{2} \left[\frac{310 - 300}{310 \times 300} \right]$$

$$\therefore \Delta H = 549.89 \text{ cal}$$

Since, $\Delta H = E_a^f - E_a^b$

$$\therefore 549.89 = 1258.68 - E_a^b$$

$$\therefore E_a^b = \mathbf{708.79 \text{ cal}}$$

Problem : 31

At 380°C, the half life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol⁻¹. Calculate the time required for 75% decomposition at 450°C. [IIT 1995]

Sol. $K_1 = 0.693/360 \text{ min}^{-1}$ at 653 K and $E_a = 200 \times 10^3 \text{ J}$, $K_2 = ?$ at 723 K, $R = 8.314 \text{ J}$
 \therefore From $2.303 \log_{10} (K_2 / K_1) = (E_a/R)[(T_2 - T_1)/(T_1 T_2)]$
 $K_2 = 0.068 \text{ min}^{-1}$

Now, $t = \frac{2.303}{0.068} \log_{10} \frac{100}{25} = \mathbf{20.39 \text{ minute}}$

Problem : 32

Two I order reactions having same reactant concentrations proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75°C

Sol. For I order reaction $r_1 = K[C]^1$

$$\therefore \frac{R_1}{R_2} = K_1 / K_2 = \text{temperature coefficient}$$

Let temperature co-efficient be a

$$\frac{R_{35}}{R_{25}} = \frac{K_{35}}{K_{25}} = a$$

$$\frac{R_{45}}{R_{35}} = \frac{K_{45}}{K_{35}} = a$$

$$\therefore \frac{R_{45}}{R_{25}} = a \times a = a^2$$

Similarly, $\frac{R_{75}}{R_{25}} = a^5$

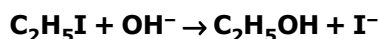
For I reaction $(R_{75})_1 = 2^5 \times (R_{25})_1$

For II reaction $(R_{75})_{II} = 3^5 \times (R_{25})_{II}$

$$\therefore \frac{(R_{75})_{II}}{(R_{75})_I} = \frac{3^5}{2^5} = 7.9537 \quad [\because (R_{25})_I = (R_{25})_{II}]$$

Problem : 33

For the reaction :



the rate constant was found to have a value of $5.03 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 289 K and $6.71 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 333 K. What is the rate constant at 305 K.

Sol. $k_2 = 5.03 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at $T_2 = 289 \text{ K}$

$k_1 = 6.71 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at $T_1 = 333 \text{ K}$

$$\log \left(\frac{6.71}{5.03 \times 10^{-2}} \right) = \frac{E_a}{2.303 \times 8.314} \left(\frac{333 - 289}{333 \times 289} \right)$$

On solving we get, $E_a = 88.914 \text{ kJ}$

The rate constant at 305 K may be determined from the relation :

$$\log \frac{k_1}{k_2} = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log \left(\frac{k_1}{5.03 \times 10^{-2}} \right) = \frac{88.914}{2.303 \times 8.314} \left(\frac{1}{298} - \frac{1}{305} \right)$$

On solving we get, $k_1 = 0.35 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

OBJECTIVE SOLVED PROBLEMS**Problem : 1**

In gaseous reactions important for understanding of the upper atmosphere H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ/mol at 500 K and $E_a = 77 \text{ kJ/mol}$, then E_a for two bimolecular recombination of 2OH radicals to form H_2O & O is

- (A) 3 kJ mol^{-1} (B) 4 kJ mol^{-1}
(C) 5 kJ mol^{-1} (D) 7 kJ mol^{-1}

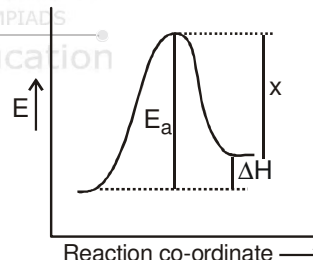
Sol. As ΔH is positive, therefore reaction is endothermic

This is the energy profile diagram for an endothermic reaction. Now when the products is converted back to reactant the energy of activation is x as shown in fig.

Evidently $x = E_a - \Delta H$

$$= (77 - 72) = 5 \text{ kJ mol}^{-1}$$

\therefore (C)

**Problem : 2**

In a certain reaction 10% of the reactant decomposes in the first hour, 20% in second hour, 30% in third hour and so on. What are the dimensions of rate constant.

- (A) hour^{-1} (B) $\text{mol lit}^{-1} \text{ sec}^{-1}$ (C) $\text{lit mol}^{-1} \text{ sec}^{-1}$ (D) mol sec^{-1}

Sol. If the amount of products formed which is 10%, 20% and 30% is plotted against time i.e., 1 hr, 2 hr and 3 hr respectively, it is a straight line passing through the origin.

\therefore it is a zero order reaction where $x = kt \Rightarrow \frac{x}{t} = k$

\therefore dimensions of $k = \text{moles lit}^{-1} \text{sec}^{-1}$

\therefore (B)

Problem : 3

Two substances A ($t_{1/2} = 5 \text{ mins}$) and B ($t_{1/2} = 15 \text{ mins}$) are taken in such a way that initially $[A] = 4[B]$. The time after which the concentration of both will be equal is

(A) 5 min

(B) 15 min

(C) 20 min

(D) concentration can never be equal

Sol. $t_{1/2}$ of A is 5 min

\therefore in 15 mins it will become $1/8$ of initial and $t_{1/2}$ of B is 15 mins

\therefore in 15 mins it will become $1/2$ of initial

\therefore ratio of $[A] : [B]$ after 15 min is 4 : 1

But given $[A] = 4[B]$

$\therefore [A] = [B]$ after 15 min

$\therefore [B]$

Problem : 4

The reaction $A(g) + 2B(g) \rightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.60$ and $P_B = 0.80 \text{ atm}$. When $P_C = 0.2 \text{ atm}$ the rate of reaction relative to the initial rate is

(A) 1/48

(B) 1/24

(C) 9/16

(D) 1/6

Sol. $A(g) + 2B(g) \rightarrow C(g) + D(g)$

$t = 0$ 0.60 0.80 0 0

$t = t$ $(0.6 - 0.2)$ $(0.8 - 2 \times 0.2)$ 0.2 0.2

$(\text{Rate})_i = k[A][B]^2 = k[0.6][0.8]^2$

$(\text{Rate})_t = k[0.4][0.4]^2$

$$\frac{R_t}{R_i} = \frac{k[0.4]^3}{k[0.6][0.8]^2} = \frac{1}{6}$$

$\therefore [D]$

Problem : 5

For a hypothetical reaction $A + B \rightarrow C + D$, the rate $= k[A]^{-1/2}[B]^{3/2}$. On doubling the concentration of A and B the rate will be

(A) 4 times

(B) 2 times

(C) 3 times

(D) none of these

Sol. $k = k[2]^{-1/2}[2]^{3/2} = k[2]^{3/2-1/2} = k[2]^1 = 2k$

$\therefore [B]$