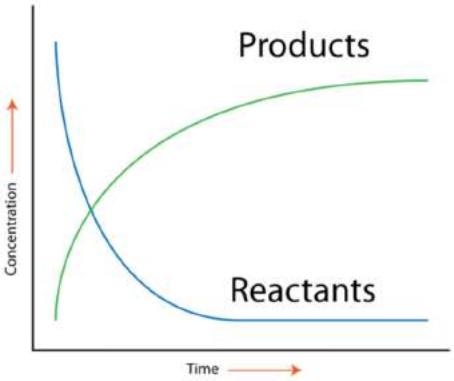
Chapter 4

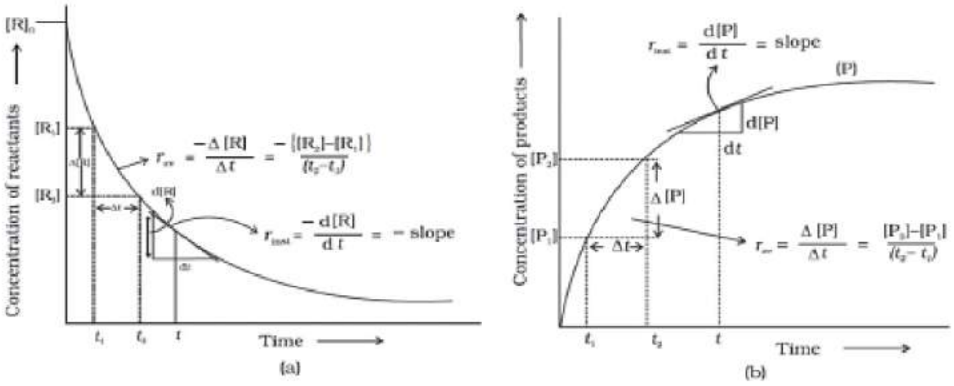
Chemical Kinetics

Rate of a Chemical Reaction and Factors Affecting Rate

Rate of a Reaction



- The rate of reaction refers to the speed at which the products are formed from the reactants in a chemical reaction.
- It gives some insight into the time frame under which a reaction can be completed. For example, the reaction rate of the combustion of cellulose in fire is very high and the reaction is completed in less than a second.
- In general, for a reaction : R → P, 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 for the reaction R → P:

$$r_{av} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

where $\Delta[R]$ and $\Delta[P]$ represents the change in the concentrations of 'R' and 'P' 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 'R' of 'P' on this graph at the time instants t_f and t_i as shown.
If $[R]_f$ and $[R]_i$ are the concentrations of the reactant 'A' at the time instants t_f and t_i then:

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

Similarly from the plot of 'P' as a function of 't', we have: $r_{av} = \left(\frac{[P]_f - [P]_i}{t_f - t_i}\right)$

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, $[R]_i$) or (t_f, $[P]_f$) and (t_i, $[P]_i$) as shown.

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

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

$$r_{inst.} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Note:

- The above expression for $r_{inst.}$ is equivalent to the slope of the tangent from the plot of the concentration of 'R' or 'P' 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 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.

Units of rate of a reaction:

Units of rate are concentration time^{-1}. For example, if concentration is in mol L^{-1} and time is in seconds then the units will be mol L^{-1}s^{-1}. However, in gaseous reactions, when the concentration of gas is expressed in terms of their partial pressures, then the units of the rate equation will be atm s^{-1}.

Relation between various rates:

In general for a reaction: $aA + bB \rightarrow cC + dD$
The rate of reaction can be expressed as follows:

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt} = k_r[A]^m[B]^n$$

What is Chemical Kinetics?

This branch of chemistry which 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)
Chemical reaction kinetics deals with the rates of chemical processes. Any chemical process may be broken down into a sequence of one or more single-step processes known either as elementary *processes*, *elementary reactions*, or *elementary steps*. Elementary reactions usually involve either a single reactive collision between two molecules, which we refer to as a a *bimolecular* step, or dissociation/isomerization of a single reactant molecule, which we refer to as a *unimolecular* step.
Very rarely, under conditions of extremely high pressure, a *termolecular* step may occur, which involves simultaneous collision of three reactant molecules. An important point to recognize is that many reactions that are written as a single reaction equation in actual fact consist of a series of elementary steps. This will become extremely important as we learn more about the theory of chemical reaction rates.
As a general rule, elementary processes involve a transition between two atomic or molecular states separated by a potential barrier. The potential barrier constitutes the *activation energy* of the process, and determines the rate at which it occurs. When the barrier is low, the thermal energy of the reactants will generally be high enough to surmount the barrier and move over to products, and the reaction will be fast. However, when the barrier is high, only a few reactants will have sufficient energy, and the reaction will be much slower.

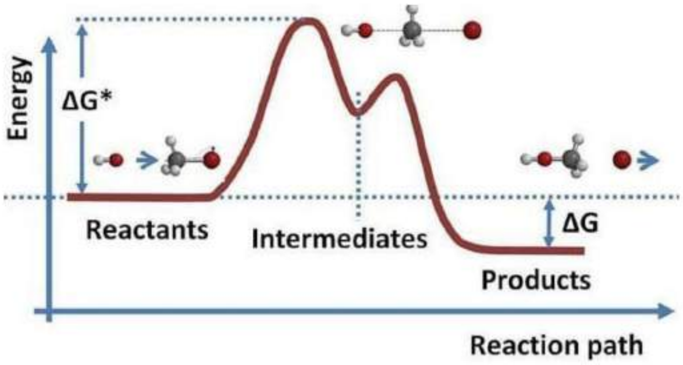


Fig: Chemical kinetics

The presence of a potential barrier to reaction is also the source of the temperature dependence of reaction rates. The huge variety of chemical species, types of reaction, and the accompanying potential energy surfaces involved means that the timescale over which chemical reactions occur covers many orders of magnitude, from very slow reactions, such as iron rusting, to extremely fast reactions, such as the electron transfer processes involved in many biological systems or the combustion reactions occurring in flames.
A study into the kinetics of a chemical reaction is usually carried out with one or both of two main goals in mind:
1. Analysis of the sequence of elementary steps giving rise to the overall reaction. i.e. the *reaction mechanism.*
2. Determination of the absolute rate of the reaction and/or its individual elementary steps.

Factors Affecting the Rate of Reaction

The various factions that can affect the rate of a chemical reaction are listed in this subsection.

Nature of the reaction

- The rate of reaction highly depends on the type and nature of the reaction. As mentioned earlier, few reactions are naturally faster than others while some reactions are very slow.
- The physical state of reactants, number of reactants, complexity of reaction and other factors highly influence the reaction rate as well.
- The rate of reaction is generally slower in liquids when compared to gases and slower in solids when compared to liquids. Size of the reactant also matters a lot. The smaller the size of reactant, the faster the reaction.

Effect of concentration on reaction rate

- According to the collision theory, the rate of reaction increases with the increase in the concentration of the reactants.
- As per the law of mass action, the chemical reaction rate is directly proportional to the concentration of reactants.
- This implies that the chemical reaction rate increases with the increase in concentration and decreases with the decrease in the concentration of reactants.
- Time plays a major role in changing the concentration of reactants and products. Therefore, even time is a vital factor affecting the reaction rate.

Pressure factor

- Pressure increases the concentration of gases which in turn results in the increase of the rate of reaction. The reaction rate increases in the direction of less gaseous molecules and decreases in the reverse direction.
- Thus, it can be understood that pressure and concentration are interlinked and that they both affect the rate of reaction.

How does temperature affect the reaction rate?

- According to collision theory, a chemical reaction that takes place at a higher temperature generates more energy than a reaction at a lower temperature.
- This is because colliding particles will have the required activation energy at high temperature and more successful collisions will take place.
- There are some reactions that are independent of temperature. Reactions without an activation barrier are examples of chemical reactions that are independent of temperature.

Solvent

The rate of reaction also depends on the type of solvent. Properties of solvent and ionic strength highly affect the reaction rate.

Order

The order of reaction manages how the reactant pressure or concentration affects the rate of reaction.

Electromagnetic Radiation

Electromagnetic radiation is a form of energy and its presence at the chemical reaction may increase the rate of reaction as it gives the particles of reactants more energy.

Intensity of Light

Even the intensity of light affects the rate of reaction. Particles absorb more energy with the increase in the intensity of light thereby increasing the rate of reaction.

Presence of Catalyst

- A catalyst can be defined as a substance that increases the rate of the reaction without actually participating in the reaction. The definition itself describes its effect on chemical reactions.
- The presence of a catalyst increases the speed of reaction in both forward and reverse reaction by providing an alternate pathway which has lower activation energy.

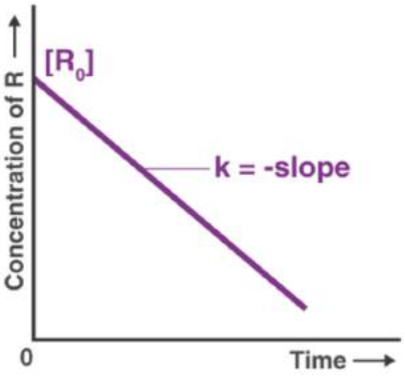
Surface Area of the Reactants

The surface area of reactants affects the rate of reaction. If the size of a particle is small, the surface area will be more and this increases the speed of heterogeneous chemical reactions.

Integrated Rate Equations: Zero, First & Second Order Reactions

Zero Order Reactions

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



$$A \longrightarrow \text{product}$$

$t=o \quad a = [A]_o \quad o$

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

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

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

$$-\int_{[A]_o}^{[A]} d[A] = k\int_{o}^{t} dt$$

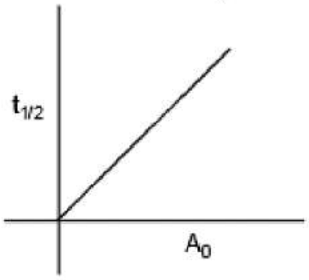
$$[A]_o - [A] = kt$$

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

Half-life ($t_{1/2}$) of Zero Order Reaction

Time in which half of initial amount is left.

$$\underset{t = o}{[A]_o} \longrightarrow \underset{t = t_{1/2}}{[A]_o/2}$$



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

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

Thus, for a Zero order reaction, half-life is directly proportional to the 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.

Example:

(1) Photochemical Reactions, Photosynthesis

(2) $CH_4\ Cl_2 \xrightarrow{h\nu}$

$Cl - Cl \longrightarrow Cl$

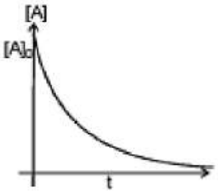
$CH_4 + Cl \longrightarrow CH_3Cl + H^\bullet$

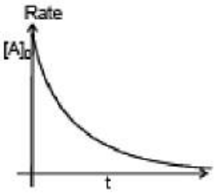
First Order reaction

$A \longrightarrow$ product

$t = o$ $[A]_o$ -

$t = t$ $[A]$ $[P]$





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

$$-\int_{[A]_o}^{[A]} d[A]/[A] = k\int_o^t dt$$

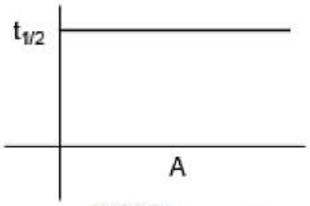
$$\ln [A]_o/[A] = kt$$

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

Half life ($t_{1/2}$) of First Order Reaction

$t = t_{1/2}$ $[A] = [A]_o/2$

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



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

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

$[A] = \frac{[A]_o}{2^n}$ where, n = number of half lifes.

Average life

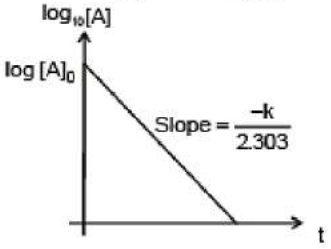
$t_{av} = 1.44\ t_{1/2} = \frac{1}{K}$

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)
Note that plot of $\log_{10}$ A vs t is linear.



Example:
(1) Radioactive disintegration.
(2) $PCl_5(g) \rightarrow PCl_3(g)\ Cl_2(g)$
(3) $H_2O_2 \rightarrow H_2O + 1/2O_2$
(4) $NH_4NO_2 \rightarrow N_2 + 2H_2O$

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

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

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

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

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

$$2.303\log_{10}\frac{A_1}{A_2} = k(t_1 - t_2)$$

Thus, k can be evaluated.

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

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

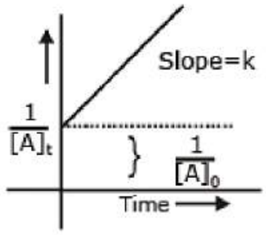
(a) Calculate the order of reaction.
(b) Find the rate constant.
(c) Find the initial rate if $[NO] = [H_2] = 8.0 \times 10^{-3}$ M

Assuming rate law can be expressed as follows:
rate = $k[NO]^x\ [H_2]^y$
By analyzing the data:
From observation 1 and 2, we see that $[H_2]$ is constant and when [NO] is tripled, the rate is also tripled.
$\Rightarrow$ 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:
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.
Initial rate = $k[NO][H_2] = 2.4 \times (8 \times 10^{-3})^2 = 1.536 \times 10^{-4}$ mol/L/s.

Second Order Reaction

Case I:

	A $\longrightarrow$	product
t = o	$[A]_o$	–
t = t	$[A]_t$	[P]



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

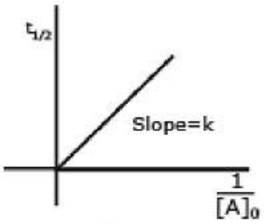
$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k\int_0^t dt$$

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

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

Half-life ($t_{1/2}$) of Second-Order Reaction

$$[A]_t = \frac{[A_0]}{2},\ k = 2/[A]_0 - 1/[A]_0$$



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

Example:

(1) Alkaline hydrolysis of esters.
(2) Self Cannizzaro's reactions,

Case (II):

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

	A	B	product
t = o	a	b	–
t = t	a–x	b – x	x

$$-\frac{d[A]}{dt} = k[A][B],\ \frac{dx}{dt} = k(a-x)(b-x)$$

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

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

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

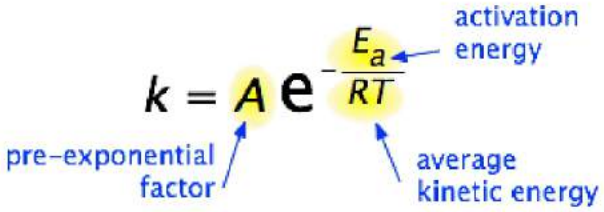
$$k = \frac{1}{t(b-a)} \left[\ln\left(\frac{a}{a-x} \times \frac{b-x}{b}\right)\right]$$

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

Arrhenius Equation & Pseudo First Order Reaction

What is the Arrhenius Equation?

The Arrhenius equation is an expression that provides a relationship between the rate constant (of a chemical reaction), the absolute temperature, and the A factor (also known as the pre-exponential factor; can be visualized as the frequency of correctly oriented collisions between reactant particles). It provides insight into the dependence of reaction rates on absolute temperature. The expression of the Arrhenius equation is:



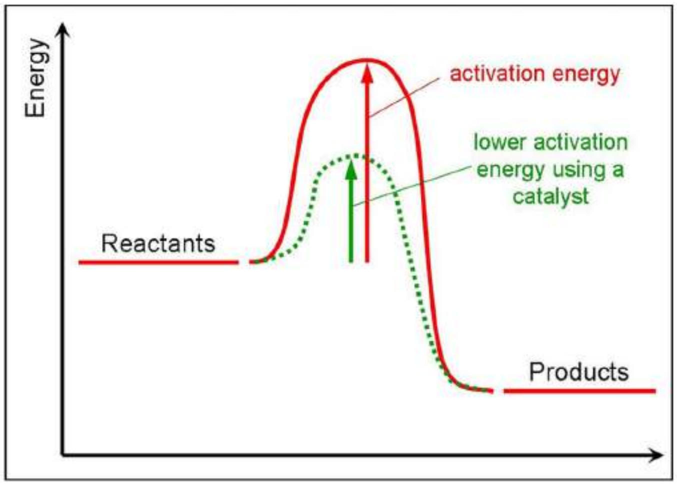
$$k = A e^{-\frac{E_a}{RT}}$$

- k denotes the rate constant of the reaction
- A denotes the pre-exponential factor which, in terms of the collision theory, is the frequency of correctly oriented collisions between the reacting species
- e is the base of the natural logarithm (Euler's number)
- E_a denotes the activation energy of the chemical reaction (in terms of energy per mole)
- R denotes the universal gas constant
- T denotes the absolute temperature associated with the reaction (in Kelvin)

If the activation energy is expressed in terms of energy per reactant molecule, the universal gas constant must be replaced with the Boltzmann constant (kB) in the

Arrhenius equation. The Arrhenius equation was put forward by the Swedish chemist Svante Arrhenius in the year 1889.

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 actuality, 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:

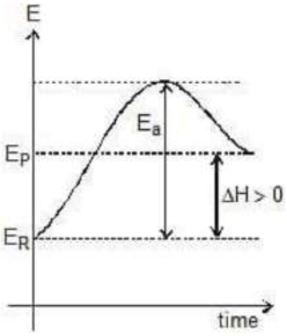
Effective collisions and In-effective collisions

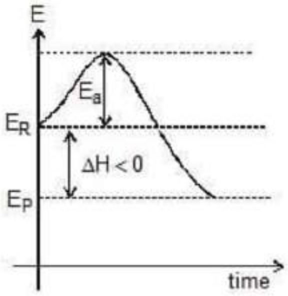
Effective collisions are collisions between the molecules that have energies equal to or above a certain minimum value. This minimum energy which must be possessed by the molecules in order to make an effective collision (i.e., to give a molecule of products) is called as *threshold energy.* So it is the effective collisions that 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: $NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$ is faster at ordinary temperature whereas the following reaction:

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ is slower at the same temperature as the value of E_a for the second reaction is much higher.

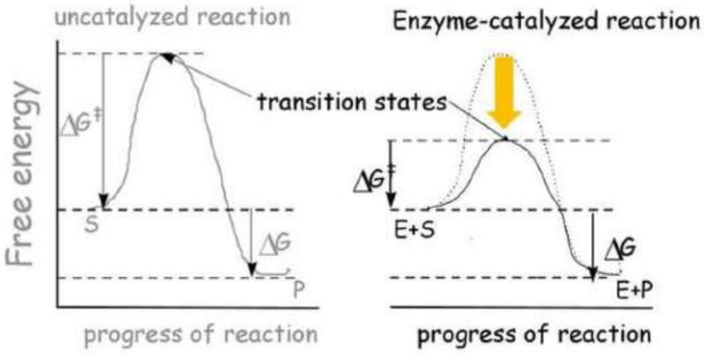
Factors Affecting Rate of Reaction

(a) Catalyst

The rate of reaction increased by addition of catalyst, because catalyst lowers, the activation energy and increased the rate of reaction. A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change. For example, MnO2 catalyses the following reaction so as to increase its rate considerably.

$2KClO3 \xrightarrow{MnO_2} 2\ KCl + 3O2$

The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called inhibitor. The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.



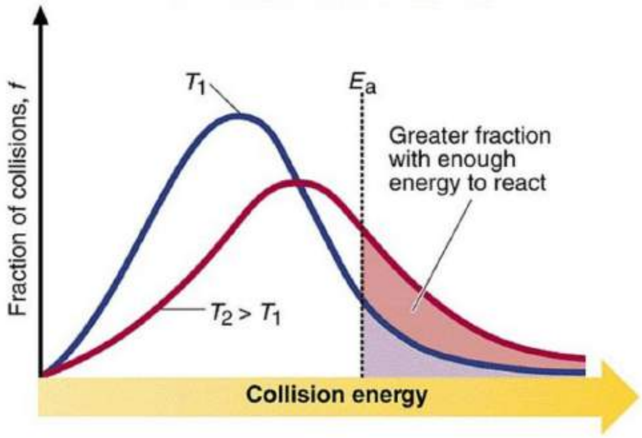
It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier as shown in Fig. It is clear from Arrhenius equation that lower the value of activation energy faster will be the rate of a reaction. A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter Gibbs energy, DG of a reaction. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions. It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

(b) Temperature

With increase in temperature the rate of reaction increases. It is generally found for every 10o increase in temperature. The rate constant double.

The ratio of rate constants with 10° difference in their temperature is called the temperature coefficient.

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



(c) Concentration

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

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:

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

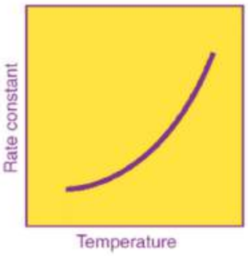
Increase in surface area increases the number of collisions and hence rate increases

(f) Radiation

Some reactions exposes to sunlight also increases the rate of reaction

Effect of temperature on Rate of Reaction

Temperature is one of the parameters that can affect the rate of a chemical reaction considerably. We have often seen milk boiling on a gas stove. The rate at which a specific quantity of milk boils depends on the flame of the stove. If the flame height is maximum, the milk boils in less time and if the flame height is minimum, the milk takes more time to boil. Here the flame height resembles temperature.



$k = A \bullet \exp(-E_a/RT)$
(Arrhenius equation)

E_a is the activation energy (J/mol)
R is the gas constant (8.314 J/K•mol)
T is the absolute temperature
A is the frequency factor

$\ln k = \frac{E_a}{R} \frac{1}{T} + \ln A$

Pseudo First Order Reaction

The order of a reaction is sometimes altered by conditions. Consider a chemical reaction between two substances when one reactant is present in large excess. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning ($t = 0$) and completion (t) of the reaction are given as under.

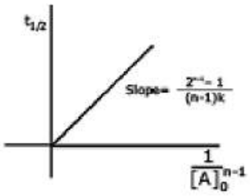
$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

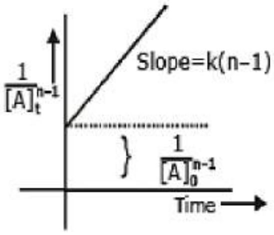
t = 0	0.01 mol	10 mol	0 mol	0 mol
t = t	0 mol	9.9 mol	0.01 mol	0.01 mol

The concentration of water does not get altered much during the course of the reaction. So, in the rate equation Rate = k'[$CH_3COOC_2H_5$] [H_2O] the term [H_2O] can be taken as constant. he equation, thus, becomes Rate = k[$CH_3COOC_2H_5$] where k = k'[H_2O] and the reaction behaves as first order reaction. 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 uni-molecular reactions.

$C_{12}H_{22}O_{11} + H_2O + H^+ \rightarrow C_6H_{12}O_6$(glucose) + $C_6H_{12}O_6$(fructose)
$CH_3COOC_2H_5$(ester) + $H_2O + H^+ \rightarrow CH_3COOH + C_2H_5OH$
(In both the reactions, H ion acts as a catalyst)

nth Order kinetics_
A $\longrightarrow$ product





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

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

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

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

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

Half-life ($t_{1/2}$) for n order reaction

at $t = t_{1/2}$, $[A]_t = \frac{[A]_0}{2}$

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

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

Q. For the non-equilibrium process, A + B → 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 $K = 10^{-2}$ litre^2 mol^{-2} sec^{-1}
Now $\text{rate}_{II} = 10^{-2} \times 0.5 \times (0.5)^2$
or New rate = **1.2×10^{-3} mol/L-sec**

Analysis of some important first-order reactions

Decomposition of Hydrogen peroxide (H_2O_2)

$H_2O_2(g) \rightarrow H_2O(g) + 1/2O_2(g)$
The rate of this first order reaction is measured by titrating a fixed volume of H_2O_2 (undecomposed) against a standard solution of $KMnO_4$. Here $KMnO_4$ acts as oxidising agent and H_2O_2 as reducing agent. The volumes of $KMnO_4$ used for H_2O_2 after regular intervals of time are as follows.

Time instants	t = 0	t_1	t2	t3	t4	t5
Vol. of $KMnO_4$	V_o	V_1	V_2	V_3	V_4	V_5

Volume of $KMnO_4$ at t = 0 corresponds to volume of H_2O_2 initially present.
$\Rightarrow A_0 \propto V_0$
Volume of $KMnO_4$ at time instants t_1, t_2, t_3, ... corresponds to volume of H_2O_2 remaining after t_1, t_2, t_3, ...
$\Rightarrow A \propto V_t$
Now it being a first order reaction, follows first order kinetics, so

$$k\,t = 2.303 \log_{10} \frac{V_0}{V_t}$$

Now using the above expression, if we calculate the values of k for different time intervals t_1, t_2, ... (for actual numerical data), the values of k should be same if the reaction follows first order kinetics.

Decomposition of ammonium nitrite (NH_4NO_2) and benzene diazonium chloride ($C_6H_5N = NCl$)

$NH_4NO_2(g) \rightarrow 2\,H_2O(g) + N_2(g)$
$C_6H_5 - N = N - Cl(g) \rightarrow C_6H_5 - Cl(g) + N_2(g)$
The rate of both the reaction is studied (measured) in similar manner. The volume of nitrogen (N_2) is collected after a regular interval of time as follows

Time instants	$t = 0$	ti	$^t2$	$^t3$	t_4	t
Vol. of N_2	0	V_1	V_2	V_3	V_4	$V\propto$

At $t = 0$, clearly the volume of $N_2 = 0$
Time instant $t = \infty$ means the end of a reaction i.e., when whole of NH_4NO_2 or $C_6H_5 - N = N - Cl$ is decomposed.
$\Rightarrow$ At $t = \infty$, V_∞ corresponds to the initial volume of NH_4NO_2 or $C_6H_5 - N = N - Cl$
(Note that the ratio of stoichiometric coefficient for both $N_2: NH_4NO_2$ or $N_2: C_6H_5N = NCl$ is 1: 1)
$\Rightarrow A_0 \propto V_\infty$
At $t = t_1, t_2, t_3$................ the volume of N_2 corresponds to concentration of product formed i.e., equal to x.
$\Rightarrow x \propto V_t$
$\Rightarrow A_0 - x \propto V_\infty - V_t$

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

Hydrolysis of Esters ($CH_3COOC_2H_5$)

$CH_3COOC_2H_5$ (ester) + H_2O + HCl (H^+) $\rightarrow CH_3COOH + C_2H_5OH$
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	$^t2$	$^t3$	t4	$t_\propto$
Vol. of NaOH	V_o	V_1	V_2	V_3	V_4	$V_\propto$

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 A t $t = \infty$, volume of CH_3COOH corresponds to volume of ester taken initially
$\Rightarrow A_0 \propto V_\infty - V_0$ (as V_0 = vol. of HCl)
At $t = t_1, t_2, t_3$............ V_1, V_2, V_3, ...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 ($C_{12}H_{22}O_{11}$)

$C_{12}H_{22}O_{11} + H_2O + H^+ \rightarrow C_6H_{12}O_6$(glucose) $+ C_6H_{12}O_6$ (fructose)
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_1 and r_∞ represent rotations at the start of reaction, after time t and at the end of reaction respectively,
then
$\Rightarrow A_0 \propto r_0 - r_\infty$ and $x \propto r_0 - r_t$
$A_0 - x \propto r_t - r_\infty$
$kt = 2.303 \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$

Decomposition of $AsH_3(g)$

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)

$AsH_3(g) \rightarrow As(s) + \frac{3}{2}H_2(g)$
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 $AsH_3(g)$ is P_0, if x is the decrease in pressure of $AsH_3(g)$ after time t.

	$AsH_3(g)$	→	As(s)	+	$H_2(g)$
$A_0 \equiv$ initial pressure	P_0		0		0
$A \equiv$ partial pressures	$P_0 - x$		0		$\frac{3}{2}x$

Arsenic is solid, so $P(AS) = 0$
After time t, let P_t be the total pressure, then

$P_t = P(AsH_3) + P(H_2) = (P_0 - x) + \frac{3}{2}x$

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

Now $A_0 \propto P_0$

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

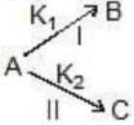
$\Rightarrow kt = 2.303 \log_{10} \frac{P_0}{3P_0 - 2P_t}$

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

1. $N_2O(g) \rightarrow N_2(g) + \frac{1}{2}O_2(g)$
2. $(CH_3)_3C - O - O - C(CH_3)\ (g) \rightarrow 2(CH_3)_2C = O(g) + C_2H_6(g)$

Complex (First order) kinetics

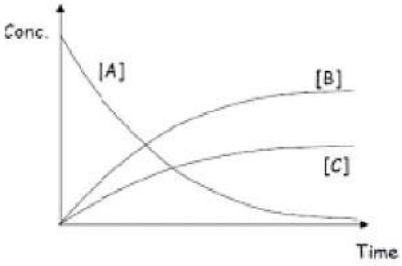
(A) Parallel Kinetics



Rate of change of A = [rate of change of A] $_{I}$ + [rate of change of A] $_{II}$

$-\frac{d[A]}{dt} = K_1[A] + K_2[A], \frac{dB}{dt} = k_1A, \frac{dC}{dt} = k_2A$

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



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

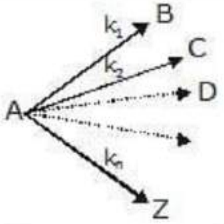
% of C in the = $\frac{k_2}{k_1 + k_2} \times 100$

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

$K_1 + K_2 = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$

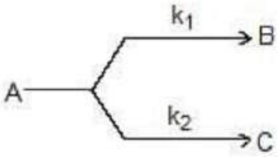
$$t_{1/2} = \frac{0.693}{K_1 + K_2}$$

Generalization



$$K_1 + K_2 + \cdots\cdots K_n = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}, \quad t_{1/2} = \frac{0.693}{K_1 + K_2 + \cdots K_n}$$

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



; $\frac{k_1}{k_2} = \frac{1}{9}$ **and** $k_1 = 1.3 \times 10^{-5}$ **sec**$^{-1}$**.**

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 $k_1 = 1.3 \times 10^{-5}$ sec^{-1} ; $k_2 = 9 \times 1.3 \times 10^{-5}$ sec^{-1} = 117×10^{-5} sec^{-1}

$(k_1 + k_2) = (1.3 \times 10^{-5}) + (11.7 \times 10^{-5})$ sec^{-1} = 13×10^{-5} sec^{-1} ....(1)

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

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

$\Rightarrow \ln\left[\frac{[A]_t + \frac{[C]_t}{9} + [C]_t}{[A]_t}\right] = (k_1 + k_2)t$ [from eq. (2)] $\Rightarrow \ln\left[1 + \frac{10}{9}\frac{[C]_t}{[A]_t}\right] = (k_1 + k_2)t$

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

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

Series Kinetics

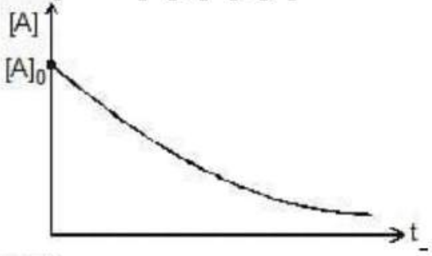
$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

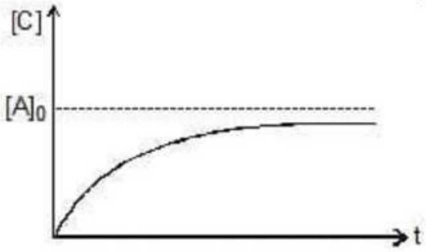
$$-\frac{d[A]}{dt} = K_1[A], \quad [A]_t = [A]_o \; e^{-k_1 t}$$

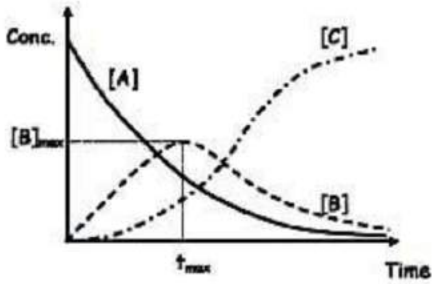
$$\frac{d[B]}{dt} = K_1[A] - K_2[B], \quad [B] = \frac{k_1[A]_o}{(k_2 - k_1)}\left[e^{-k_1 t} - e^{-k_2 t}\right]$$

$$\frac{d[C]}{dt} = K_2[B], \quad [C] = \frac{k_1 k_2 [A]_o}{k_1 - k_2}\left[\frac{(e^{-k_1 t} - 1)}{k_1} - \frac{(e^{-k_2 t} - 1)}{k_2}\right]$$

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



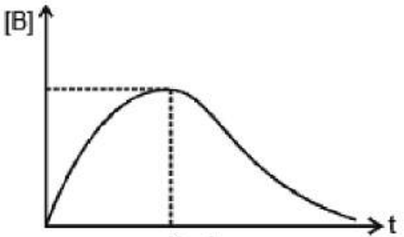




Time when [B] is maximum

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

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



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

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

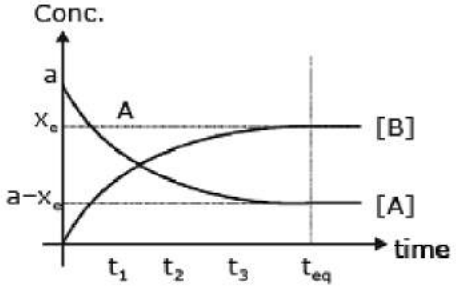
$$e^{(k_2 - k_1)t} = \frac{k_2}{k_1}$$

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

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

Reversible Kinetics

	A	$\rightleftharpoons$	B
$t = 0$	a		0
$t = t_1$	$a - x_1$		x_1
$t = t_2$	$a - x_2$		x_2
$t = t_3$	$a - x_3$		x_3
- - -	- - -	- - -	- - -
- - -	- - -	- - -	- - -
$t = t_{eq}$	$a - x$		x



$0 < t < t_{eq} \longrightarrow$ **Chemical kinetics,** $t_{eq} \leq t < \infty \longrightarrow$ **Chemical Equilibrium**

At equilibrium, $r_f = r_b$, $k_1 [A]_{\text{equilibrium}} = k_2 [B]_{\text{equilibrium}}$, $\frac{k_1}{k_2} = \frac{[B]_{eq.}}{[A]_{eq.}}$

$$\frac{k_1}{k_2} = \frac{[A]_b - [A]_{\text{equilibrium}}}{[A]_{\text{equilibrium}}} = \frac{[A]_b}{[A]_{eq}} - 1, \quad \frac{k_1 + k_2}{k_2} = \frac{[A]_b}{[A]_{eq}}$$

$$[A]_{\text{equilibrim}} = \frac{k_2\,[A]_o}{k_1 + k_2} \quad \text{............ (I)}$$

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

$$= (k_1 + k_2)\left[-[A] + \frac{k_2}{k_1 + k_2}[A]_o\right]$$

By substituting the value from equation (I)

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

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

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

Q. For a reversible first order reaction,

$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$; $K_f = 10^{-2}\ \text{sec}^{-1}$

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.

$$\begin{array}{lcl} A_0 & \rightarrow & B \\ 0.01 & & 0 \\ 0.01 - x_{eq} & & x_{eq} \end{array}$$

$$\frac{[B]_{eq}}{[A]_{eq}} = \frac{10^{-2}}{K_b} = 4 = \frac{[x]_{eq}}{0.01 - [x]_{eq}}$$

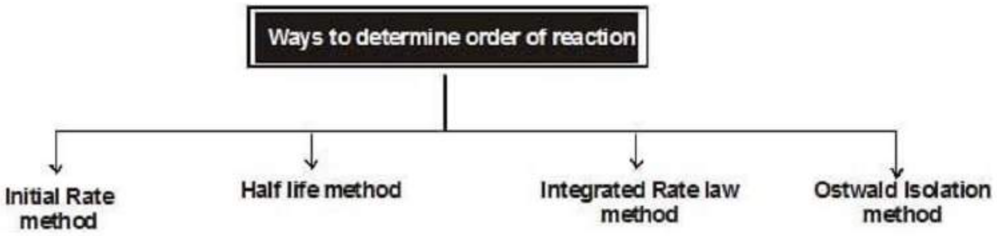
Therefore, $K_b = 0.25 \times 10^{-2}$ and $x_{eq} = \frac{0.04}{5} = 0.008$

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

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

Therefore, $\frac{0.008}{0.008 - x} = 1.455$

Therefore, $x = 2.50 \times 10^{-3}$



(1) Initial Rate Method

$A + B \longrightarrow$ product

rate = $k\,[A]^m\,[B]^n$; Order = $m + n$

	[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)

$$\frac{2\times10^{-3}}{4\times10^{-3}} = \frac{k\,[0.1]^m\ [0.1]^n}{k\,[0.1]^m\ [0.2]^n}$$

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

$n = 1$

Experiment (1) and Experiment (3)

$$\frac{2\times10^{-3}}{32\times10^{-3}} = \frac{k\,[0.1]^m\ [0.1]^n}{k\,[0.2]^m\ [0.1]^n}$$

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

$m = 4$

Order $(m + n) = 4 + 1 = 5$

(2) Half - life method

$t_{1/2}$	$[A]_o$
1 hr	0.1
2 hr	0.2

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

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

$$n = 1 + \frac{\log (t_{1/2})_2 / (t_{1/2})_1}{\log [A]_{o_1} / [A]_{o_2}}$$

(3) Integrated Rate law Method

$$A \longrightarrow \text{product}$$

t = 0 1000 M

t = 60 sec 100 M

t = 120 sec 10 M

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

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

n = 1

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

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

(4) Ostwald Isolation method

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

Experiment 1: [A] = In small quantity; [B], [C], [D] - - - - - - - in excess

The rate equation reduces to

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] - - - - - - ⇒ in excess.

rate = $k' [B]^n \rightarrow$ repeated

Order of reaction = m + n + o + p + - - - - - - - -

Order & Molecularity of a Reaction

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: $aA + bB \rightarrow cC + dD$. The differential rate law is written as:

Rate = $-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt} = k_r[A]^m[B]^n$

where k_r is called as **rate constant of the reaction** or **velocity constant** or **specific Reaction rate.**
k is a characteristic of a reaction at a given temperature. It changing only when the temperature changes.
The powers *m* and *n* are integers or fractions. *m* is called as order of reaction with respect to A and *n* is called as order of reaction with respect to B The overall order of reaction = m n

Hence, the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

- 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
- Order can be fractional, zero or negative.

For example consider the following reaction :
(i) $H_2(g)$ $Br_2(g) \rightarrow 2\ HBr\ (g)$ rate = $k[H_2]\ [Br_2]^{1/2}$ (by experiment), order of reaction = 1 1/2 = 3/2
(ii) $CH_3CHO(g) \rightarrow CH_4(g)$ $CO(g)$, rate = $k[CH_3CHO]^{3/2}$, order of reaction = 3/2

Units of k:

In general, the rate law for a n^th^ order reaction can be taken as : $\frac{dc}{dt} = -kc^n$
where k : rate constant; c : concentration and n : order of reaction

$\Rightarrow$ $k = \frac{dc/dt}{c^n}$ **⇒ Units of k º $(mol/L)^{1-n}$ $(time)^{-1}$**
For a 'zero' order reaction (n = 0): Units of k = $(mol/L)^1$ $(time)^{-1}$ or mol/L/sec
For a first order reaction (n = 1): Units of k º $(time)^{-1}$ e.g. sec^{-1}, min^{-1}, hrs^{-1} etc.
For a second order reaction (n = 2): Units of k º $(mol/L)^{-1}$ $(time)^{-1}$ or L/mol/sec.

Molecularity

As already discussed, the order of a reaction is an experimental concept.
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 number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
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

1. Cyclopropane → propene
2. $O_3(g) \rightarrow O_2(g) + O(g)$
3. $N_2O_5(g) \rightarrow N_2O_4(g) + 1/2O_2(g)$

Bimolecular

1. $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$
2. $2HI(g) \rightarrow H_2(g)\ I_2(g)$

Termolecular

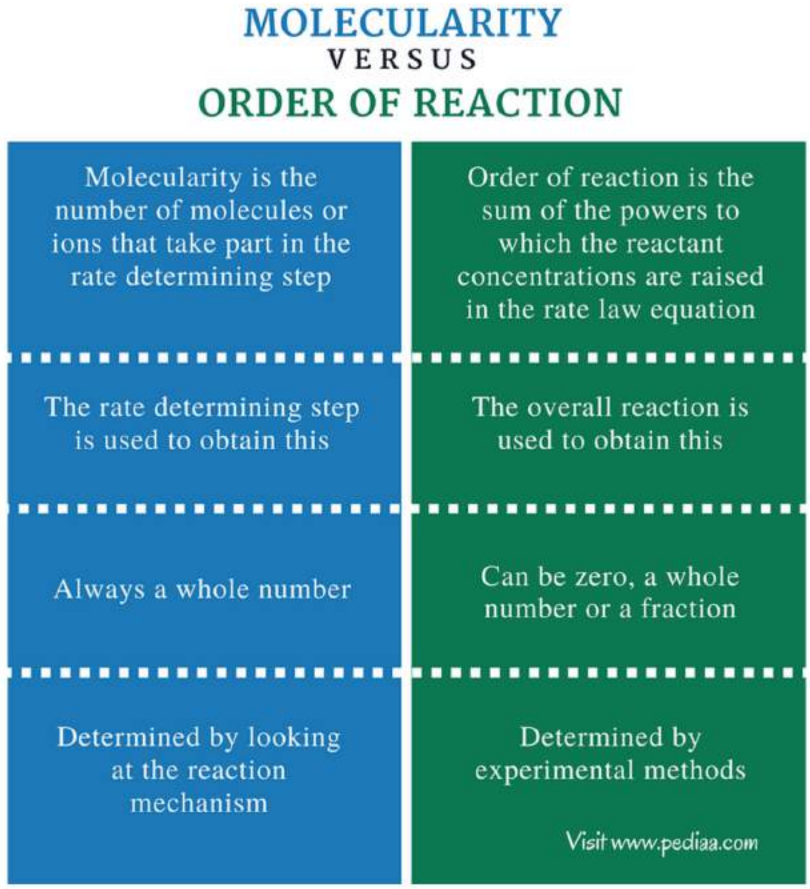
1. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed. It is, therefore, evident that complex reactions involving more than three molecules in the stoichiometric equation must take place in more than one step.
$KClO_3 + 6FeSO_4 + 3H_2SO_4 \rightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O$
This reaction which apparently seems to be of tenth order is actually a second order reaction. This shows that this reaction takes place in several steps. Which step controls the rate of the overall reaction? The question can be answered if we go through the mechanism of reaction, for example, chances to win the relay race competition by a team depend upon the slowest person in the team. Similarly, the overall rate of the reaction is controlled by the slowest step in a reaction called the rate determining step.
(i) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.

(ii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning. 103 Chemical Kinetics
(iii) For complex reaction, order is given by the slowest step and molecularity of the slowest step is same as the order of the overall reaction.

- For a reaction: $A \rightarrow B$ in the rate law: rate = $k[A]^m [B]^n$

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 and 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).



MOLECULARITY
VERSUS
ORDER OF REACTION

Molecularity is the number of molecules or ions that take part in the rate determining step	Order of reaction is the sum of the powers to which the reactant concentrations are raised in the rate law equation
The rate determining step is used to obtain this	The overall reaction is used to obtain this
Always a whole number	Can be zero, a whole number or a fraction
Determined by looking at the reaction mechanism	Determined by experimental methods

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Problem 1:

The rate of formation of NO(g) in the reaction $NOBr(g) \rightarrow NO(g)\ Br_2(g)$ is found to be 1.6×10^{-4} M/s. Find the rate of overall reaction rate and rate of consumption of NOBr.

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

First write a balanced chemical equation. $2NOBr(g) \rightarrow 2NO(g)\ Br_2(g)$

Now, Rate of overall reaction = $-\frac{1}{2}\frac{d[NOBr]}{dt} = +\frac{1}{2}\frac{d[NO]}{dt} = \frac{1}{1}\frac{d[Br_2]}{dt} = 0.8 \times 10^{-4}$ M/s

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

Problem 2:

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

Sol. $PV = nRT \Rightarrow P = cRT$ (c: concentration in mol/L)

Substitute R = 0.0821 L-atm/mol/K ; T = 273 K ; P = 1 atm ⇒ c = 0.04462 mol/L

$\Rightarrow k = \frac{3 \times 10^{-5}}{0.04462} = 6.73 \times 10^{-4}$ 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:

(i) $2HCrO_4^- + 6I^- + 14H \rightarrow 2Cr^3 + 3I_2 + 8H_2O$, Rate = $k[HCrO_4^-]\ [I^-]^2\ [H\ ]^2$

(ii) $H_2O_2 + 2I^- + 2H \rightarrow I_2 + 2H_2O$, Rate = $k[H_2O_2]\ [I^-]$

Sol. (i) The order of the reaction with respect to $[HCrO_4^-]$ is 1; with respect to $[I^-]$ is 2 and with respect to [H] is 2. The overall order of the reaction is 1 +2 +2 = 5

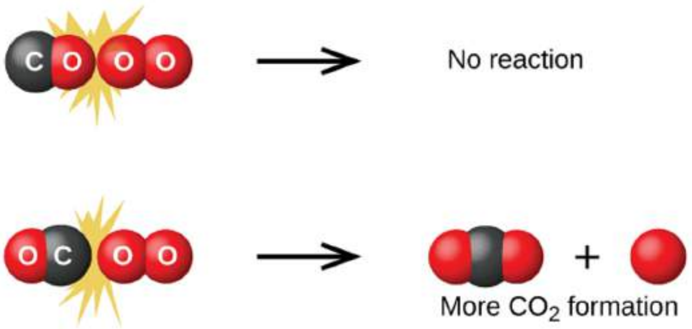
(ii) The order of the reaction with respect to $[H_2O_2]$ is 1 and with respect to $[I^-]$ is 1. The overall order of the reaction is 1 +1= 2.

- 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.

Collision Theory & Variations in Arrhenius Equation

Collision Theory of Chemical Reaction

- Though the Arrhenius equation is applicable under a wide range of circumstances, collision theory, which was developed by Max Trautz and William Lewis in 1916 -18, provides greater insight into the energetic and mechanistic aspects of reactions. It is based on the kinetic theory of gases.
- According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.
- The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z). Another factor that affects the rate of chemical reactions is activation energy (as we have already studied). For a bimolecular elementary reaction.



A + B → Products rate of reaction can be expressed as

Rate = $Z_{AB}e^{-E_a/RT}$ ....(1)

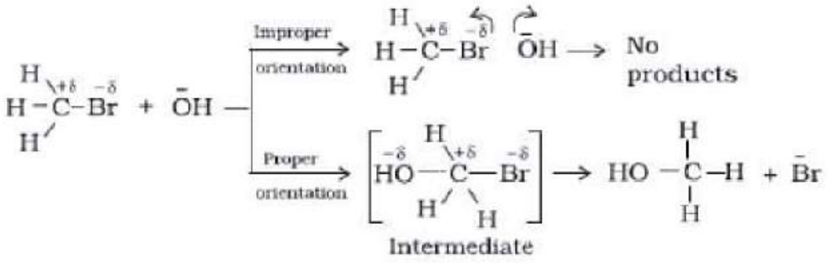
where Z_{AB} represents the collision frequency of reactants, A and B

and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than Ea. Comparing (1) with Arrhenius equation, we can say that *A* is related to collision frequency. Equation (1) predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy (called threshold energy*) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as **effective collisions**.

To account for effective collisions, another factor P, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e., Rate = $PZ_{AB}e^{-E_a/RT}$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

$CH_3Br + \bar{O}H \longrightarrow CH_3OH + \bar{B}r$



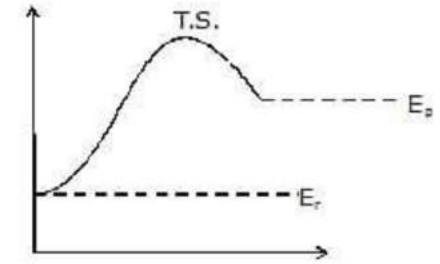
Mechanism of Reaction

Reactions can be divided into

Elementary/Simple/single step
Complex/multi-step

Elementary Reaction

These reaction take place in single step without formation of any intermediate



For elementary reaction we can define molecularity of the reaction which is equal to no of molecules which make transition state or activated complex because of collisions in proper orientation and with sufficient energy
molecularity will always be a natural no
1 = unimolecular one molecular gets excited (like radioactivity)
2 = bimolecular
3 = trimolecular
Molecularity ≤ 3 because the probability of simultaneous collision between 4 or mor molecules in proper orientation is very low

For elementary reaction there is only single step and hence it is going to be rate determining step so order of an elementary reaction is its molecularity
Order of elementary reaction w.r.t reactant = stoichiometric co-efficient of the reactant

$H_2 + I_2 \square\ 2HI \rightarrow$ Simple reaction

rate = k $[H_2]$ $[I_2]$

$2H_2 + 2I_2 \square\ 4HI$ (no elementary)

reaction obtained by multiplying and elementary reaction with some no will not be of elementary nature

$H_2 + Cl_2 \square\ 2HCl$

order = 0

Complex Reaction

Reaction which proceed in more than two steps or having some mechanism. (sequence of elementary reaction in which any complex reaction proceeds)
For complex reaction each step of mechanism will be having its own molecularity but molecularity of net complex reaction will not be defined.
Order of complex reaction can be zero fractions whole no, even negative w.r.t some species.
Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction generally using rate determine step (R.D.S) if given.
Rate law of a reaction is always written in terms of conc. of reactant, products or catalysts but never in terms of conc. of intermediates.
The mechanism of any complex reaction is always written in terms of elementary steps, so molecularity of each of these steps will be defined but net molecularity of complex reaction has no meaning.
The mechanism of most of the reaction will be calculated or predicted by using mainly the following approximation.

The Rate-Determining-Step Approximation %

In the rate-determining-step approximation (also called the rate-limiting-step approximation or the equilibrium approximation), the reaction mechanism is assumed to consist of one or more reversible reactions step, which in turn is followed by one or more rapid reactions. In special cases, there may be no equilibrium steps before the rate-determining step or no rapid reactions after the rate-determining step.
When steps 2 B $\square$ (C) is assumed to be the rate-determining step. For this assumption to be valid, we must have $k_{-1} >> k_2$. The slow of $B \rightarrow C$ compared with $B \rightarrow A$ ensures that most B molecules go back to A rather than going to C,

thereby ensuring that step 1(A □ B) remains close to equilibrium. Further-more, we must have $k_3 >> k_2$ and $k_3 >> k_{-2}$ to ensure that step 2 acts as a"bottleneck" and that product D is rapidly formed from C. The overall rate is then controlled by the rate-determining step $B \rightarrow C$. (Note that since $k_3 >> k_{-2}$, the rate-limiting step is not in equilibrium.) Since we are examining the rate of the forward reaction $A \rightarrow D$, we further assume that $k_2[B] >> k_{-2}[C]$. During the early stage of the reaction, the concentration of C will be low compared with B, and this condition will hold. Thus we neglect the reverse reaction for step 2. Since the rate-controlling step is taken to be essentially irreversible, it is irrelevant whether the rapid steps after the rate-limiting step are reversible or not. The observed rate law will, depends only on the nature of the equilibrium that precede the rate-determining step and on this step itself.

Arrhenius Equation

Number of effective collisions = Number of collision x fraction.

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

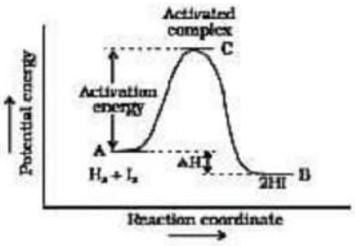
Where, k = rate constant of reaction

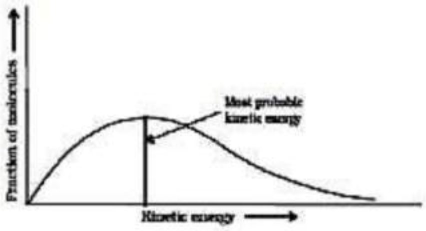
A = Pre exponential factor or Arrhenius constant or Frequency factor.

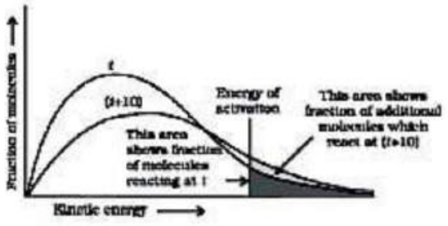
E_a = Activation energy

R = Universal gas constant

T = Absolute temperature.



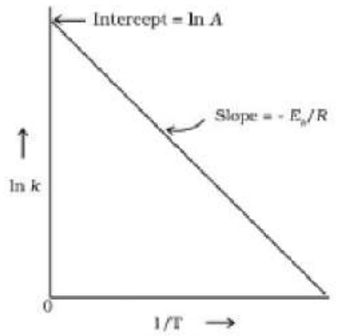




⇒ **Fraction of molecules undergoing effective collision** $= e^{-Ea/RT} = \frac{K}{A}$

Variation in Arrhenius equation

Type -1 :



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

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

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

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

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

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

Type -2: Temperature Variation:

$r_1 \longrightarrow K_1 \longrightarrow T_1$

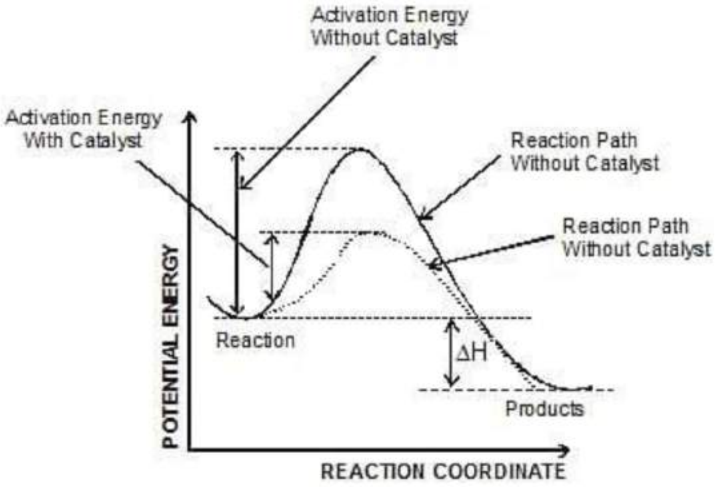
$r_2 \longrightarrow K_2 \longrightarrow T_2$

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

$\log k_1 = \log A - \frac{E_a}{2.303\,RT_1}$, $\log k_2 = \log A - \frac{E_a}{2.303\,RT_2}$

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

Type -3: Addition of Catalyst:



$$r_1 \longrightarrow k_1 \longrightarrow \text{no catalyst} \longrightarrow E_a \longrightarrow T$$

$$r_2 \longrightarrow k_1 \longrightarrow \text{catalyst} \longrightarrow E_{ac} \longrightarrow T$$

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

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

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

Type -4: Both Catalyst and Temperature:

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

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

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

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

Therefore, $t_{0.75} = \frac{1.386}{0.693} \times 118.24 =$ **236.48 min**

Q. The activation energy of the reaction: A + B → 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

At $T_1 : r_1 = k_1[A]^x[B]^y$

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.

$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \Rightarrow \log_{10} \frac{k_2}{k_1} = \frac{102.9 \times 10^3}{2.303 \times 8.31}\left(\frac{40}{313 \times 353}\right)$

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

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

Q. 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:

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

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. $k = Ae^{-E_a/RT}$
2. $k_c = Ae^{-E_a/RT}$

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

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

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

Q. A first order reaction A → 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%

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

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

Using Arrhenius equation find k at 40°C.

$$\log_{10} \frac{k_{40^\circ}}{k_{25^\circ}} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

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

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

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

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

$\Rightarrow x = 67.1 \equiv 67.1\%$ decomposition of A at 40°C.

Q. The rate constant of a reaction is 1.5 x 10^7 sec^{-1} at 50°C and 4.5 x 10^7 sec^{-1} at 100°C. Evaluate the Arrhenius parameters A and E_a.

Sol. Therefore, $2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

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

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

Therefore, A = 5.42 x 10^{10}

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

Sol. Given, $T_2 = 60 + 273 = 333$ K, $T_1 = 30 + 273 = 303$ K,

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

$r = k[\,]^n$ (at a temperature T)

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

$\frac{r_2}{r_1} = 5$ Therefore, $\frac{K_2}{K_1} = 5$

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

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 kcal mol⁻¹**

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

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

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

Therefore, E_a^f = **1258.68 cal**

Now, equilibrium constant at 300 K = K'

Equilibrium constant at 310 K = K' + 3/100 x 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, $\Delta H = 549.89$ cal

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

Therefore, $549.89 = 1258.68 - E_a^b$

Therefore, E_a^b = **708.79 cal**

Q. 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. $K_1 = 0.693/360$ min^{-1} at 653 K and
$E_a = 200 \times 10^3$ J, $K_2 = ?$ at 723 K, R = 8.314 J
Therefore, From $2.303 \log_{10} (K_2 / K_1) = (E_a/R) [(T_2 - T_1)/(T_1T_2)]$
$K_2 = 0.068$ min^{-1}
Now, $t = \frac{2.303}{0.068} \log_{10} \frac{100}{25}$ = **20.39 minute**

Solved Subjective Problems: Chemical Kinetics

<u>subjective solved problems</u>

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

Sol. We have,
$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{3}\frac{d[D]}{dt}$ = rate of reaction
Therefore, $\frac{d[C]}{dt} = 1.0$ mol litre^{-1} sec^{-1}
Therefore, $-\frac{d[A]}{dt} = \frac{d[C]}{dt}$ = **1.0 mol L^{-1}sec^{-1}**
$-\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{2}$ = **0.5 mol L^{-1} sec^{-1}**
$\frac{d[D]}{dt} = \frac{3}{2}\frac{d[C]}{dt} = \frac{3}{2}\times 1$ = **1.5 mol L^{-1} sec^{-1}**
Also,
Q Rate = $\frac{1}{2}\frac{d[C]}{dt}$
Therefore, Rate = $\frac{1}{2} \times 1$ = **0.5 mol L^{-1} sec^{-1}**

Problem: 2
For the reaction A B → 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 1×10^{-4} mol litre^{-1} 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 9.0×10^{-4} mol litre^{-1} minute^{-1}.

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

Sol. Let Rate = $K[A]^m[B]^n$
(a) $r_1 = 1 \times 10^{-4} = K\,[0.1]^m\,[0.1]^m$ ...(1)
$r_2 = 9 \times 10^{-4} = K[0.1]^m[0.3]^n$ ...(2)
$r_3 = 2.7 \times 10^{-3} = K[0.3]^m[0.3]^m$ ...(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, Rate = $\mathbf{K[A]^1[B]^2}$
(b) Also by Eq. (1), $1 \times 10^{-4} = K[0.1]^1\,[0.1]^2$
$K = \mathbf{10^{-1} = 0.1\ L^2\ mol^{-2}\ min^{-1}}$

Problem: 3
The chemical reaction between $K_2C_2O_4$ and $HgCl_2$ is;
$2HgCl_2\ K_2C_2O_4 \rightarrow 2KCl\ 2CO_2\ Hg_2Cl_2$
The weights of Hg_2Cl_2 precipitated from different solutions in given time were taken and expressed as following:

Let the rate law be written as: $r = k[HgCl_2]^x\,[K_2C_2O_4]^y$

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

Problem : 4
The reaction given below, involving the gases is observed to be first order with rate constant
$7.48 \times 10^{-3}\ sec^{-1}$. 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.
$2A(g) \rightarrow 4B(g)\ C(g)$

Sol. $2A(g) \rightarrow 4B(g)\ C(g)$
initial $P_0 = 0$
at time t P_0 - P¢ 2P¢ P¢/2

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

P¢ = $\frac{2}{3}$ (0.145 - 0.1) = 0.03 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 sec

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_{total} = 0.1 $\frac{3}{2}$ (0.080) ≃ **0.22 atm.**

Problem: 5
The net rate of reaction of the change:
$[Cu\ (NH_3)_4]^2\ H_2O \rightleftharpoons [Cu(NH_3)_3H_2O]^2\ NH_3$ is,
$\frac{dx}{dt} = 2.0 \times 10^{-4}$ $[Cu\ (NH_3)_4]^2 - 3.0 \times 10^5 [Cu(NH_3)_3H_2O]^2\ [NH_3]$

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 = $2.0 \times 10^{-4}\ [Cu\ (NH_3)_4]^2\ [H_2O]$
Rate of backward reaction = $3.0 \times 10^5\ [Cu\ (NH_3)_3H_2O]^2\ [NH_3]$
(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: 6

The rate law for the decomposition of gaseous N_2O_5,

$N_2O_5(g) \rightarrow 2NO_2(g)\ \frac{1}{2}\ O_2(g)$

is observed to be

$$r = -\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

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

$N_2O_5(g) \overset{k}{\rightleftharpoons} NO_2(g)\ NO_3(g)$ (fast equilibrium)

$NO_2(g) + NO_3(g) \xrightarrow{k_1} NO_2(g)\ NO(g)\ O_2(g)$ (slow)

$NO(g)\ NO_3(g) \xrightarrow{k_2} 2NO_2(g)$ (fast)

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

Since the slow step is the rate determining step, hence

$r = k_1[NO_2]\ [NO_3]$ ...(1)

and from the fast equilibrium step,

$$K = \frac{[NO_2][NO_3]}{[N_2O_5]}$$

Thus, $[NO_2]\ [NO_3] = K[N_2O_5]$ ...(ii)

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

$r = k_1K[N_2O_5] = k[N_2O_5]$ where $k = k_1K$

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

Problem: 7

The half life of first order decomposition of nitramide is 2.1 hour at 15°C.

$NH_2NO_2(aq) \rightarrow N_2O(g)\ H_2O\ (l)$

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:

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

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

(b) 6.2 gm of $NH_2NO_2 \equiv 0.1$ mol

and 1 mole NH_2NO_2 º 1 mole of N_2O

As 99% of NH_2NO_2 is decomposed

$\Rightarrow$ 0.099 mol of NH_2NO_2 is decomposed

0.099 mol of N_2O are produced º $22.4 \times 0.099 = 2.217$ L of N_2O at STP.

Problem: 8

The reaction A OH$^-$ → 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 $K = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

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

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

Problem: 9

A certain reaction A B → products; is first order w.r.t. each reactant with $k = 5.0 \times 10^{-3}$ M^{-1}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 → products

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

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

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

Thus, the reaction is now of first order.

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

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

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

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

Problem: 10

Dimethyl ether decomposes according to the following reaction:

$CH_3 - O - CH_3(g) \rightarrow CH_4(g)\ CO(g)\ H_2(g)$

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

(i) Show that the reaction is first order.

(ii) Compute the pressure of CO(g) after 25 minutes.

Sol. $CH_3 - O - CH_3\ (g) \rightarrow CH_4(g)\ CO(g)\ H_2(g)$ (all are gases)

$\Rightarrow P_t = P_0\ 2x$

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

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

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.

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

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

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

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

$\Rightarrow P_t = 648.46$ mm $\Rightarrow x = 114.23$ mm

Problem: 11

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

$2N_2O_5(g) \rightarrow 4NO_2(g)\ O_2\ (g)$

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.

Sol. $2N_2O_5(g) \rightarrow 4NO_2(g)\ O_2(g)$

P_0: initial pressure; Let P_t: pressure at 30 min and $P_{¥}$: pressure at the end of decomposition.

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

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

For the first order kinetics

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

A_0: initial concentration; A: final concentration

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

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

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

Problem: 12

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. $2N_2O_5(g) \rightarrow 4NO_2(g)\ O_2(g)$

Initial Pressure (at t = 0) P_0 0 0

At equilibrium P_0 - 2x 4x x

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, $\Delta P_{N_2O_5} = \frac{2}{3}(P_{t1} - P_{t2})$ 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: 13

5 ml of ethylacetate was added to a flask containing 100 ml f 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:

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

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

Time $V_\propto$- V_t k_1

75 min $21.05 - 12.10 = 8.95$ $\frac{2.303}{75}\log\frac{11.43}{8.95} = 0.003259\ min^{-1}$

119 min $21.05 - 13.10 = 7.95$ $\frac{2.303}{119}\log\frac{11.43}{7.95} = 0.003051\ min^{-1}$

183 min $21.05 - 14.75 = 6.30$ $\frac{2.303}{183}\log\frac{11.43}{6.30} = 0.003254\ min^{-1}$

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

Problem: 14

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:

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 $a_0 = r_0 - r_¥ = 32.4 - (-11.1) = 43.5$

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

Time	**r_t**	**$r_t - r_¥$**	**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: 15

The hydrolysis of ethyl acetate

$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$

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**
$k_1 \times 10^{-4} s^{-1}$	**1.1**	**11**	**110**

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

Sol. Rate = $k[CH_3COOC_2H_5]^a[H\ ]^b$

[H] is constant through out the reaction

$k_1 = k[H\ ]^b$

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

$b = 1$

$k_1 = k\,[H\ ]$

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

Problem: 16

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

Let temperature co-efficient be a

$\frac{R_{35}}{R_{25}} = \frac{K_{35}}{K_{25}} = a \quad \frac{R_{45}}{R_{35}} = \frac{K_{45}}{K_{35}} = a$

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

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

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

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** [Therefore, $(R_{25})_{I} = (R_{25})_{II}$]

Problem: 17

For the reaction:

$C_2H_5I + OH^- \rightarrow C_2H_5OH + I^-$

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

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

$k_1 = 6.71$ mol^{-1} dm^3 s^{-1} at $T_1 = 333$ 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, $E_a = 88.914$ 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, $k_1 = 0.35$ mol^{-1} dm^3 s^{-1}

Problem: 18

A secondary alkyl halide (RX) is hydrolysed by alkali simultaneously by S_N1 and

S_N2 pathways. A plot of $-\frac{1}{[RX]}\frac{d[RX]}{dt}$ vs $[OH^-]$ is a straight line with slope equal to 1.0×10^{-3} mol^{-1} L min^{-1} and intercept equal to 2.0×10^{-3} min^{-1}. Calculate initial rate of consumption of RX when [RX] = 0.5 M and $[OH^-]$ = 1.0 M.

Sol. 1.5×10^{-3} mol L^{-1} min^{-1}

For S_N1 pathway:

$-\frac{d[RX]}{dt} = K_1[RX]$ K_1 = 1st order rate constant

For S_N2 pathway:

$-\frac{d[RX]}{dt} = K_2[RX][OH^-]$ K_2 = 2nd order rate constant

Thus, the overall rate of consumption of RX is as given below:

$-\frac{d[RX]}{dt} = K_1[RX]\ K_2[RX][OH^-]$

or $-\frac{1}{[RX]}\frac{d[RX]}{dt} = K_1\ K_2[OH^-]$

According to this equation as plot of $-\frac{1}{[RX]}\frac{d[RX]}{dt}$ vs [OH|-] will be a straight line of the slope equal to K_2 and intercept equal to K_1. Thus, from question.

$K_1 = 2.0 \times 10^{-3}$ min^{-1}

$K_2 = 1.0 \times 10^{-3}$ min^{-1} L min^{-1}

Thus, $-\frac{d[RX]}{dt} = 2.0 \times 10^{-3} \times 0.5\ 1.0 \times 10^{-3} \times 0.5 \times 1$

$= 1 \times 10^{-3}\ 0.5 \times 10^{-3}$

$= 1.5 \times 10^{-3}$ mol L^{-1} min^{-1}

Problem: 19

A polymerisation reaction is carried out at 2000 K and the same reaction is carried out at 4000 K with catalyst. The catalyst increases the potential barrier by 20 KJ but the rate of the reaction remains same. Find activation energy of the reaction.

(Assuming all other parameters to be same.)

Sol. 0020

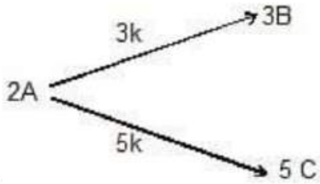
$k = Ae^{-Ea/R\times2000} = Ae^{-\left(\frac{Ea+20}{R\times4000}\right)}$

$\frac{Ea}{R\times2000} = \frac{(Ea+20)}{R\times4000}$

$2Ea = Ea\ 20$

$Ea = 20$ kJ

Problem : 20



Consider the following first order parallel reaction.
The concentration of C after time t is :

Sol. $\frac{25}{16}[1-e^{-16kt}]$

$-\frac{1}{2}\frac{dA}{dt}=\frac{1}{3}\frac{dB}{dt}+\frac{1}{5}\frac{dC}{dt} = 3k[A]\ 5k[A] = 8kA$

$-\frac{dA}{dt}=8kA\times 2 = 16\ kA$

$A = A_0\ e^{-16\ kt}$

$\frac{1}{3}\frac{dB}{dt}=3kA,\ \frac{dB}{dt} = 9kA = 9kA_0\ e^{-16kt}$

$B = \frac{9}{16}[1-e^{-16kt}]$

Similarly

$\frac{25}{16}[1-e^{-16kt}]$