

CHEMICAL KINETICS

The branch of chemistry, which deals with the rate of chemical reactions, the factors affecting the rate of reactions and the mechanism of the reaction, is called **chemical kinetics**.

Chemical Reactions on the Basis of Rate of Reaction

1. Fast/instantaneous reactions - Chemical reaction which completes in less than 10⁻¹² s time, is known as fast reaction. It is practically impossible to measure the speed of such reactions, e.g., ionic reactions, organic substitution reactions.

2. Slow reactions Chemical reactions which complete in a long time from some minutes to some years are called slow reactions. e.g., rusting of iron, transformation of diamond etc.

3. Moderately slow reactions - Chemical reactions which are intermediate between slow and fast reactions are called moderately slow reactions.

Rate of Reaction :-

Rate of a chemical reaction is the change in the concentration of any one of the reactants or products per unit time. It is expressed in mol L⁻¹s⁻¹ or Ms⁻¹ or atm time⁻¹ units.

Rate of reaction = (decrease/increase in the concentration of reactant/product/time taken)

This rate of reaction is known as average rate of reaction (rav). (rav can be calculated by dividing the concentration difference by the time interval). For a chemical reaction,

Average rate :- The average rate of a chemical reaction is defined as the change in concentration of a reactant or product divided by time interval over which the change occurs.

$$\begin{aligned}\text{Average rate} &= \frac{\text{Change in concentration of a species}}{\text{change in time}} \\ &= \frac{\Delta C}{\Delta t}\end{aligned}$$

Instantaneous Rate of Reaction

Rate of a chemical reaction at a particular moment of time, is known as instantaneous rate of reaction.

To determine the instantaneous rate of a reaction, the progress of the reaction is followed by measuring the concentration of the reactant or product at different time intervals. It is seen that the concentration of the reactant decreases and concentration of the product increases with time. The change in concentrations are relatively faster in the beginning and then becomes slow.

The instantaneous rate mathematically is represented by replacing Δ by d in the expression of average rate.

$$\text{Instantaneous rate at time } t = - \frac{d[R]}{dt} = \frac{d[p]}{dt}$$

For reaction, Methods for measuring reaction rate (i) pH measurement, (ii) change in optical activity, (iii) change in pressure, (iv) change in conductance. Slowest step of a reaction was called rate determining step by van't Hoff.

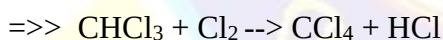
Factors influencing Rate of a reaction:-

1. **Concentration:-** As concentration of reactant increase, rate of reaction also increases.
2. **Temperature:-** Rate of reaction increases with increase of temperature mostly reaction rate double with rise of 100 temperature.
3. **Catalyst:-** Catalyst generally increase the rate of reaction without undergoing in the reaction, it also help in attaining the equilibrium quickly without disturbing the equilibrium state in reversible reaction.
4. **Surface area of reactant:-** If surface area of reactant increase, increases the rate of reaction.
5. **Radiations**
6. **Pressure of gas**

Rate Law: -

Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each terms raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balance chemical reaction.

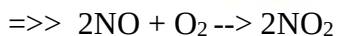
EX:- Reaction --> Experimental rate expression



$$\text{Rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$$



$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]_1 [\text{H}_2\text{O}]^0$$



Rate Law Expressions -

According to the law of mass action, For a chemical reaction, $aA + bB \rightarrow \text{Products}$

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

$$= k [A]^a [B]^b$$

But experimentally, it is observed that the rate of reaction is found to depend upon 'α' concentration terms of A and 'β' concentration terms of B. Then,

$$\begin{aligned}\text{Rate} &\propto [A]^{\alpha} [B]^{\beta} \\ &= k [A]^{\alpha} [B]^{\beta}\end{aligned}$$

where, [A] and [B] molar concentrations of A and B respectively and k is the velocity constant or rate constant. The above expression is known as rate law.

Rate Constant:-

In the above expression, k is called rate constant or velocity constant. Rate constant may be defined as the specific rate of reaction when the molar concentrations of

the reactants is taken to be unity, i.e.,

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

Units of rate constant or specific reaction rate for a nth order reaction is given as

$$K = (1/\text{Time}) \times (1/[\text{Conc.}]^{n-1})$$

Characteristics of rate constant: -

1. Greater the value of rate constant, faster is the reaction.
2. Each reaction has a particular value of rate constant at a particular temperature.
3. The value of rate constant for the same reaction changes with temperature.
4. The value of rate constant for a reaction doesn't depend upon the concentration of the reactants.

Application of the rate law -

- 1) The rate law can be used to estimate the rate of a reaction for any given composition of the reaction mixture.
- 2) It can be used to estimate the concentration of the reactant and products at any time during the course of the reaction.
- 3) The rate law is useful to predict the mechanism of a complex reaction.

Order of a reaction:- The sum of powers of the concentration of the reactants in the rate of law expression is called as the order of that chemical reaction.

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

$$\text{Order} = x + y$$

Order of reaction may be 0, 1, 2, 3 or even in fraction, Zero order reaction is independent of conc

Units of Rate constant of reaction :-

$$\text{Also, } k = \frac{\text{Rate}}{[A]^x[B]^y} = \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{conc.})^n} = \frac{(\text{Concentration})^{1-n}}{\text{time}}$$

$$\text{In SI, unit of } k = \frac{(\text{Mol L}^{-1})^{1-n}}{\text{s}}$$

For zero order reaction, Order = $n = 0$

$$\text{Unit of } k = \frac{(\text{Mol L}^{-1})^{1-0}}{\text{s}} = \frac{\text{Mol L}^{-1}}{\text{s}}$$

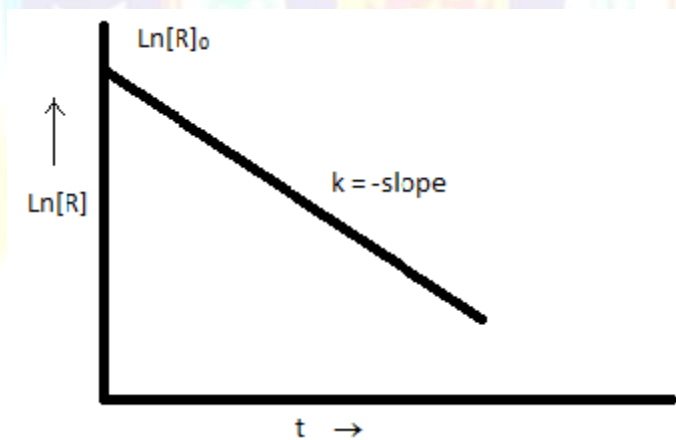
For first order, $n = 1$

$$\text{Unit of } k = \frac{(\text{Mol L}^{-1})^{1-1}}{\text{s}} = \frac{(\text{Mol L}^{-1})^0}{\text{s}} = \frac{1}{\text{s}} = \text{s}^{-1}$$

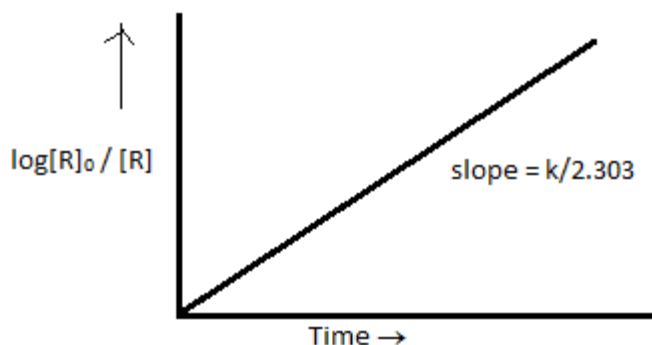
For second order, $n = 2$

$$\text{Unit of } k = \frac{(\text{Mol L}^{-1})^{1-2}}{\text{s}} = \frac{(\text{Mol L}^{-1})^{-1}}{\text{s}} = \text{Mol}^{-1} \text{ L s}^{-1}$$

Graph:• A plot between $\ln[R]$ and t for a first order reaction



A plot between $\log[R]^0 / [R]$ and time for a first order reaction



Integral rate equation: -

1. **Zero order reaction:** - The reaction whose rate is independent of the reactant concentration and remain constant throughout the course of the reaction.

consider a reaction-



The rate law of the reaction is given by

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

On rearrangement becomes $d[A] = -k dt$

on integration of the equation limit $[A] = [A]_0$ at $t = 0$ and $[A] = [A]_t$ at $t = t$ we get

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

Hence , $[A]_{[A]_0}^{[A]_t} = -k [t]_0^t$

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

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

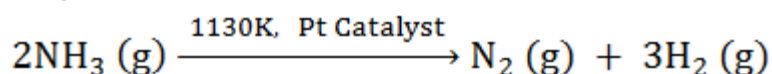
$$k = \frac{[A]_0 - [A]_t}{t}$$

This is the integrated rate equation of the zero order reaction.

OR

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

Example:



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

2. Integrated rate law for first order reaction - Consider a reaction-



The differential rate law for this first order reaction is

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

Where [A] is the concentration of the reactant A that remain unreacted at time t and $-\frac{d[A]}{dt}$ is the rate of the reaction measured at time t at which A is converted to the product. By rearranging and integrating the equation between the limit [A] = [A]₀ at t = 0 and [A] = [A]_t at t = t we write ,

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

where [A]₀ is the initial concentration of A at t = 0 and [A]_t is the concentration of A that remains unreacted at t

$$\ln [A]_t - \ln [A]_0 = -kt$$

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

$$k t = \ln \frac{[A]_0}{[A]_t}$$

$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t}$$

Converting ln to log₁₀ the integrated rate law becomes

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

This equation is the integrated rate law for the first order reaction .

Half life of a reaction: -The half life of a reaction is defined as the time needed for the reactant concentration to fall to one half of its initial value .

i. zero order reaction: - Rate constant is given by –

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

At $t = t_{1/2}$,

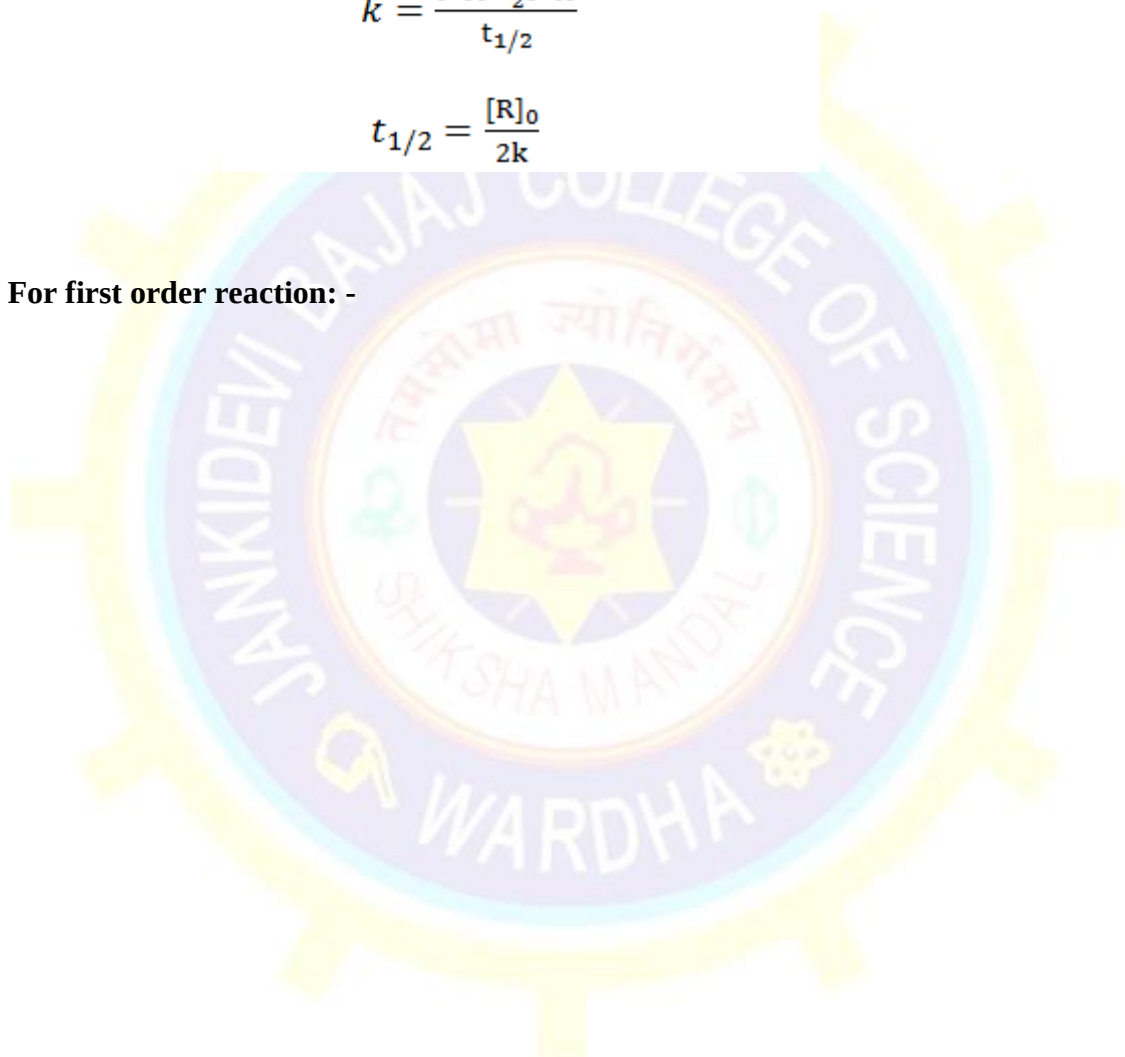
$$[R] = \frac{1}{2} [R]_0$$

The rate constant at $t_{1/2}$ becomes,

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

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

ii. For first order reaction: -



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

At, $t = t_{1/2}$

$$[R] = \frac{1}{2} [R]_0$$

The rate constant at $t_{1/2}$ becomes,

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

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

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

$$= \frac{2.303}{k} \times 0.3010$$

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

Molecularity of a reaction: - The no. of reacting species (atoms, ions, 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.

Pseudo First Order Reaction

Chemical reactions which appear to be of higher order but actually are of the lower order are called pseudo order reactions.

In case of pseudo first order reaction, chemical reaction between substances takes place and one of the reactant is present in excess. e.g., hydrolysis of ester, Inversion of cane sugar (Sucrose)

Methods to Determine Order of Reaction

1)Graphical method

(ii) Initial rate method In this method, the order of a reaction is determined by varying the concentration of one of the reactants while others are kept constant.

(iii) Integrated rate law method In this method out different integrated rate equation which gives the most constant value for the rate constant corresponds to a specific order of reaction.

(iv) Half-life period ($t_{1/2}$) method In general half-life period ($t_{1/2}$) of a reaction of nth order is related to initial concentration of the reactant as

This method is employed only when the rate law involved only one concentration term.(v)

Ostwald's isolation method This method is employed in determining the order of complicated reactions by isolating one of the reactants so far as its influence on the reaction rate is concerned.

Rate determining Step – A slowest step in the reaction mechanism is called a rate determining step

Reaction intermediate – Some additional species other than reactant and products is produced in the mechanism, such a species is called reaction intermediate.

Temperature dependence of the rate of a reaction: -

Most of chemical reactions are accelerated by increase in temperature. It has been found that for a chemical reaction with rise in temperature by 10° , the rate constant is nearly double.

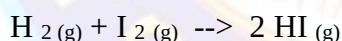
The temperature dependence of a chemical reaction can be accurately explained by Arrhenius equation-

$$k = A e^{-E_a/RT} \dots\dots\dots(1)$$

Where, A is Arrhenius factor or frequency factor, R is gas constant

E_a is activation energy measured in joules/mole (J mol^{-1})

Also, in this reaction-



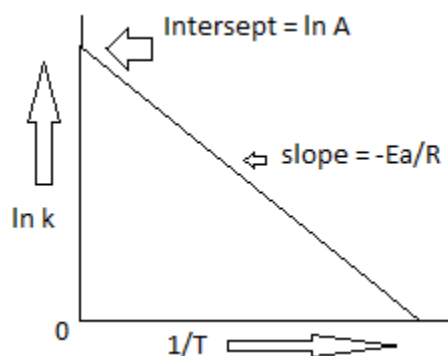
According to Arrhenius, This reaction can take place only when a molecule of hydrogen and molecule of iodine collide to form an unstable intermediate. It exist for a very short time and then break up to form two molecule of hydrogen iodide.

The energy required to form this intermediate, called 'activation complex' (C), is known as activation energy (E_a).

Also, taking natural logarithm of both side of equation (1), we get

$$\ln k = \frac{-E_a}{RT} + \ln A \dots\dots\dots(2)$$

The plot of 'ln k' vs '1/T' gives a straight line according to equation (2)



In figure, slope = $-E_a/R$ and Intercept = $\ln A$

So, we can calculate E_a and A using these values. At temperature T_1 , equation (2) is-

$$\ln k_1 = \frac{-E_a}{RT_1} + \ln A \quad \dots \dots \dots (3)$$

At temperature T_2 , equation (2) is-

$$\ln k_2 = \frac{-E_a}{RT_2} + \ln A \quad \dots \dots \dots (4)$$

Substrate eq. (3) & (4) We get,

$$\begin{aligned} \ln k_2 - \ln k_1 &= \frac{E_a}{RT_1} - \frac{E_a}{RT_2} \\ \ln \frac{k_2}{k_1} &= \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \\ \log \frac{k_2}{k_1} &= \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots \dots \dots (5) \end{aligned}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots \dots \dots (6)$$

Arrhenius equation is a mathematical expression to give a quantitative relationship between rate constant and temperature, and the expression is where, A = frequency or Arrhenius factor. It is also called pre-exponential factor

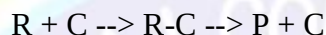
R = gas constant

E_a = activation energy

Effect of catalyst:-

A catalyst which alters the rate a reaction without itself undergoing any permanent chemical change. The action of a catalyst can be explained by **intermediate complex theory**.

According to this theory, A catalyst participate in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex and decompose to yield products and catalyst.



Reactant + catalyst $\rightarrow$ intermediate complex $\rightarrow$ product + catalyst

Collision theory of chemical reactions:-

According to this theory **“The reactant molecules are assume to be hard spheres and reaction is postulated to occur when molecule collide with each other”**

$\Rightarrow$ “The no. of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z)”

$\Rightarrow$ Another factor which affects the rate of a chemical reaction is activation energy for a bimolecular elementary reaction.



Rate of reaction can be expressed as

$$\text{Rate} = ZAB e^{-E_a/RT}$$

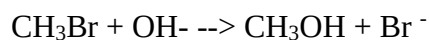
Where, ZAB represents the collision frequency of the reactants, A & B and

$e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a.

$\Rightarrow$ All collision do not lead to the formation of product. the collision in which molecule collide with sufficient kinetic energy (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 collision.

Note:- Threshold energy = Activation energy + Energy possessed by reacting species.

EX:- Formation of methanol from bromoethane



Activated complex (or transition state)

Activated complex is the highest energy unstable intermediate between the reactants and products and gets decomposed immediately (having very short life), to give the products. In this state, bonds of reactant are not completely broken while the bonds of products are not completely formed.

Threshold energy (E_T) The minimum amount of energy which the reactant must possess in order to convert into products is known as threshold energy.

Activation energy (E_a) The additional amount of energy, required by the reactant so that their energy becomes equal to the threshold value is known as activation energy.

$$\Rightarrow E_a = E_T - E_R$$

Lower the activation energy, faster is the reaction. Different reactions have different rates because their activation energies are different. Larger the value of E_a , smaller the value of rate constant and greater is the effect of a given temperature rise on K

Photochemical Reactions

Chemical reactions that occur on exposure to visible radiation are called photochemical reaction

1. The rate of a photochemical reaction is affected by the intensity of light.
2. Temperature has little effect on photochemical reactions.

Quantum yield or quantum efficiency of a photochemical reaction,

$\phi = (\text{number of reactant molecules reacting in a given time} / \text{number of photons (quanta) of light absorbed in the same time})$

Important points about Arrhenius equation

- (i) If k_2 and k_1 are rate constant at temperature T_2 and T_1 ; then
- ii) Fraction of molecules with energy equal to or greater than the activation energy is called

Boltzmann factor and is given by

(iii) E_a is constant for a particular reaction.

(iv) E_a doesn't depend on temperature, volume, pressure, etc., but gets affected by catalyst.

In the Arrhenius equation, when $T \rightarrow \infty$ then $\mathfrak{R} = Ae^0 = A$ when $E_a = 0$, $k = A$ and the rate of Reaction becomes independent temperature.

Role of Catalyst in a Chemical Reaction

A catalyst is a chemical substance which alters the rate of a reaction without itself undergoing any permanent chemical change. In the chemical reactions, 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.

Theory of Reaction Rates

Collision Theory

According to this theory, the reactant molecules are assumed to be hard spheres and the reaction is postulated to occur, when molecules collide with each other. The number of collisions between the reacting molecules taking place per second per unit volume is known as collision frequency (Z_{AB}). But only those collisions in which the colliding species are associated with certain minimum amount of energy and collide in proper orientation result in the product formation, such collisions are called fruitful collisions or effective collision.

Here, rate = $-(dv/dt) = \text{collision frequency} \times \text{fraction of effective collision}$

$$= Z_{AB} \times f = Z_{AB} \times e^{-\frac{E_a}{RT}}$$

where, Z_{AB} represents the collision frequency of reactants, A and B $e^{-E_a/RT}$

$e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a .

So, to account for effective collisions, another factor, P called the probability or steric factor is introduced. So, rate = $PZ_{AB}e^{-E_a/RT}$

The Activated Complex Theory or Transition State Theory



This theory is based on the fact that bond cleavage and bond formation, involved in a chemical

reaction, must occur simultaneously. Hence, the reactants are not converted directly into the products. There is an energy barrier or activated complex [intermediate product with partially formed bond] between the reactants and products. The reactants must cross this energy barrier before converting into products. The height of the barrier determines the threshold energy.

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Note :- Mathematical problem see in the text book