CHEMICAL KINETICS

A brief review of the basic concepts

SECTION- A

1. Chemical kinetics: The branch of chemistry which deals with the study of reaction rates and the mechanism by which they occur is called chemical kinetics.

2. Fast, very slow and slow reactions: from the kinetic point of view, the chemical reactions can be categorized as follows.

i) Fast or ionic reactions: these reactions take place almost instantaneously and get completed in about $10^{-16}10^{-14}$ seconds. Such reactions are very fast and take place between ions. For example,

$$Ag^+No^-{}_3 + Na + cl^- \rightarrow AgCl + Na^+NO^-{}_3$$

The rates of such reactions can not be measured conveniently by the commonly used techniques.

ii) Very slow reactions: these reactions take place very slowly and may take very several months for their completion. Rusting of iron is an example of this type of reactions. These reactions are so slow that their rates can not be measured easily.

iii) Slow or molecular reactions: between very fast and very slow reactions; we have a large number of molecular reactions whose rates can be measured conveniently. For example, reactions involved in the formation of ammonia, etherification, hydrolysis of ester, decomposition of N_2O_5 are the reactions of this type. Such reactions are termed as slow reactions or molecular reactions.

3. Rate of a chemical reaction: the rate of a chemical reaction may be defined as the change in concentration of any of the reactants or any of the products per unit time.

Following two types of rates of a chemical reaction are defined.

i) **average rate of a reaction:** the change in concentration of any of the reactants or any of the products per unit time over a specified interval of time is called the average rate of the reaction i.e.

Average rate of a reaction = $\dfrac{change in concentration of a reac\tan t or a product}{time \text{ int } erval involved \text{ int } he change}$

For example, for the reaction A $\rightarrow$ B, we have

Average rate of reaction = $\dfrac{\Delta[A]}{\Delta t} = \dfrac{\Delta[B]}{\Delta t}$

Where, $\Delta[A]$ =decrease in the conc. Of A in mol L-1,

$\Delta[B]$ =increase in the conc. Of [B] in mol L-1, and

Δt = time interval involved in the change.

It is to be noted that ΔA is a negative quantity because concentration of [A] decreases with time. Since the rate of a reaction is always expressed as a positive quantity, a negative sign (-) is put before ΔA to make the rate positive.

The average rate of a reaction can be obtained by dividing the rate of disappearance of any of the reactants or the rate of appearance of any of the products by its stoichiometric coefficient. For example,

aA + bB $\rightarrow$ cC + dD

the average rate of reaction = $\dfrac{1}{a}\dfrac{\Delta[A]}{\Delta t} = -\dfrac{1}{b}\dfrac{\Delta[B]}{\Delta t} = \dfrac{1}{c}\dfrac{\Delta[C]}{\Delta t} = \dfrac{1}{d}\dfrac{\Delta[D]}{\Delta t}$

ii) **Instantaneous rate of a reaction:** the rate of change of concentration of any of the reactants or products at a particular instant of time is called the instantaneous rate of the given reaction at that instant.

For the determination of instantaneous rate, the time interval Δt is taken as small as possible. Thus, the instantaneous rate can be expressed as

Instantaneous rate = $\lim_{x\to\infty}\dfrac{\Delta x}{\Delta t} = \dfrac{dx}{dt}$

Where dx represents an infinitesimally small change in concentration for any of the reactants or products occurred in an infinitesimally small time dt.

For the reaction, aA + bB → cC + dD , the instantaneous rate can be expressed as

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Units of rate of reaction: The rate of a reaction is usually expressed in the units of mol L^{-1} s^{-1}. when the reactants and products are in the gaseous state and their concentrations are expressed in terms of their partial pressures, the rate of reaction is expressed in the units of atm s^{-1}

4. Reaction life time: the time taken by a reaction to got to completion is difficult to be measured because most of the reactions become very slow at the verge of their completion. Therefore, usually time take for 98% completion is measured. This time is referred to as reaction life time. Shorter the reaction life time, faster is the reaction. The time taken for 50% completion of the reaction is half life of the reaction. During the half life of a reaction, the concentrations of reactants are reduced to half of their original value.

5. Factors which affect the reaction rate:

- **Nature of reactants:** the reactions involving polar and ionic substances are quite fast whereas those involving covalent compounds are much slower.

- **Concentration of reactants:** in general, the rate of a reaction increases on increasing the concentration of reactants. This is due to an increase in the probability of molecular collisions.

- **Temperature:** the rate of a reaction usually increases on increasing the temperature. For most of the homogeneous reactions, the rate becomes doubled to for each 10^0 rise in temperature.

- **Presence of a catalyst:** a catalyst provides an alternate path with a lower energy barrier and thus enables a larger number of reactant molecules to cross it and to take party in the reaction. Therefore, a catalyst increases the rate of a reaction.

- Surface area: if one of the reactants is a solid, the rate of reaction increases with an increase in the surface area of the reactant. An increase in surface area enhances the rate of encounters between the reactant molecules and consequently the rate of reaction increases.

6. Rate law and rate constant: The law of mass action is unable to predict the observed dependence of the rate of a chemical reaction on the molar concentrations of the reactants involved in the reaction in several cases. In fact, the true rate expression for a reaction can not be written just by seeing the balanced equation. It has to be derived on the basis of experimental facts.

The expression which describes the experimentally observed dependence of the reaction rate on the molar concentrations of the reactants is called the rate law or rate equation.

The rate law describes the true dependence of the rate of reaction on the molar concentration of the reactants. In the rate law, the rate of reaction is expressed in terms of the product of molar concentrations of reactants, with each concentration term raise to the power describing the true dependence of the rate on the concentration. This power may or may not be t he same as the stoichiometric coefficient of the reactant in the balanced chemical equation. The rate laws of some reactions are given below.

[redacted]

Rate constant (specific reaction rate): the constant k appearing in the expression for the rate law of a reaction is called the rate constant or velocity constant or specific reaction rate of the reaction. It may be defined as equal to the rate of reaction when the concentration of each of the reactant is unity.

The rate constant of a reaction has a definite value at a particular temperature. Its value increases with increase in temperature. It does not depend upon the initial concentrations of reactants.

Units of rate constant: The units of rate constant depend upon the overall sum of the powers to which the concentration of the reactants is raise in the rate law. If for a general reaction

aA + bB → cC → products. The rate law is

Rate = $k[A]^p[B]^q[C]^r$

And p+q+r = n then,

$$k= \frac{rate}{(conc. of reac\tan ts)^n} = \frac{molL^{-1}s^{-1}}{(molL-1)^n} molL^{1-n}L^{n-1}s^{-1}$$

Here, in general, the units of rate constant are $molL^{1-n}L^{n-1}s^{-1}$, where n represents the sum of powers appearing in the rate law. For a gaseous reaction, units of rate constant will be $atm^{1-n}s^{-1}$

Characteristics of rate constant:

i) It is a measure of the rate of reaction. Higher the value of k, greater is the rate of reaction.
ii) A particular reaction has a definite value of k at a particular temperature.
iii) The value of rate constant increases with an increase in temperature.
iv) it does not depend upon the initial concentrations of reactants.
v) Its units depend upon the overall order of reaction.

7. Order of a reaction: the power to which the concentration term of a particular reactant in the rate law is raised is called the order of reaction with respect to that reactant and the sum of all the powers to which all the concentration terms in the rate law are raise to express the observed rate of reaction is called the overall order of reaction.

For example, if for the general reaction

aA + bB → cC + dD ,

Rate = k $[A]^p[B]^q$ the experimentally observed then the reaction is said to be of order p with respect to A and of order q with respect to B. the overall order of the reaction is given by

Overall order of reaction = p + q

When the overall order of a reaction is 1, the reaction is said to be a first order reaction.
When the overall order is 2, the reaction is said to be a second order reaction.
In case the overall order is 3, the reaction is referred to as a third order reaction.

It is to be noted that the order of a reaction is purely an experimental quantity and can not be known just by seeing the equation. The stoichiometric coefficients present in the balanced chemical equation have nothing to do with the order of the reaction.

The order of a reaction is usually a whole number. However, it can be zero or fractional also.

8. Reactions of different orders and the units of their rate constants:

i) First order reactions: a reaction of a type A → products is said to be of first order, if its rate law is given by

Rate = k $[A]^1$

Obviously, in a first order reaction, the rate is directly proportional to the concentration of the reactant. If the concentration of reactant A is doubled, the rate of reaction also gets double, some examples of first order reactions are as follows:

$$PCl_5 \rightarrow PCl_3 + Cl_2; rate = k[PCl_5]$$

$$NH_4NO_2 \rightarrow N_2 + 2H_2O; rate = k[NH_4NO_2]$$

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2; rate = k[N_2O_5]$$

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2; rate = k[H_2O_2]$$

$$SO_2Cl_2 \rightarrow SO_2 + Cl_2; rate = k[SO_2Cl_2]$$

The units of rate constant for a first order reaction are time^{-1} i.e. s^{-1} , or min^{-1} , or hour^{-1}.

ii) Second order reactions: a reaction of the type A → products is said to be of second order , if its rate law is given by

Rate = k $[A]^2$

Obviously, in a second order reaction, the rate depends upon the square of the concentration of reactants. When the concentration of reactants is doubled, the rate increases by four times. Some examples of second order reactions are as follows.

$$2NO_2 \rightarrow 2NO + O_2; rate = k[NO_2]^2$$
$$H_2 + I_2 \rightarrow 2HI; rate = k[H_2][I_2]$$
$$NO + O_3 \rightarrow NO_2 + O_2; rate = k[NO][O_3]$$
$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH; rate = k[CH_3COOC_2H_5][NaOH]$$

The units of rate constant for a second order reaction are $conc^{-1}$. i.e. $mol^{-1}\ ls^{-1}$. For a gaseous reaction the units of k will be $atm^{-1}\ s^{-1}$.

iii) Third order reactions: when the rate of a reaction depends upon the cube of the concentration of reactants, the reaction is said to be of third order. In such a case, when the concentration is doubled, the rate of reaction increases by eight times.

The most common third order reactions are of the following type;

$2A + B \rightarrow$ Products : rate k $[A]^2$ [B]

In this case, the reaction is of order 2 with respect to A

Order 1 with respect to B.

The overall order is 2+1 = 3.

Some examples of third order reactions are as follows;

$$2NO + O_2 \rightarrow 2NO_2; rate = k[NO]^2[O_2]$$
$$2NO + Cl_2 \rightarrow 2NOCl; rate = k[NO]^2[Cl_2]$$
$$2NO + Br_2 \rightarrow 2NOBr; rate = k[NO]^2[Br_2]$$

The units of rate constant for a reaction of third order are $conc^{-2}\ time^{-1}$ i.e. $mol^{-2}\ L^2\ s^{-1}$. for a gaseous reaction the units will be $atm^{-2}s^{-1}$.

iv) Zero order reactions: a reaction A $\rightarrow$ products is said to be of zero order when its rate law is given by

Rate =k [A]0 = k

Obviously, in a zero order reaction, the rate does not depend upon the concentration of reactants and remains constant throughout the course of reaction when the concentration of a reactant is changed, the rate does not change i.e. the reaction proceeds with a constant rate. Some examples of zero order reactions are as follows.

$$H_2 + Cl_2 \rightarrow 2HCl; rate = k[H_2]^0[Cl_2]^0 = k$$
$$2NH_3 \rightarrow N_2 + 3H_2; rate = k[NH_3]^0 = k$$

The units of rate constant for a zero order reaction are conc. $Time^{-1}$ ie.e. mol $L^{-1}\ s^{-1.}$ For a gaseous reaction the units are atm s^{-1}.

v) **Reaction of fractional order:** some examples of reactions having fractional orders are as follows.

$$CH_3CHO \rightarrow CH_4 + CO; rate = k[CH_3CHO]^{3/2} order = 3/2$$
$$H_2 + Br_2 \rightarrow 2HBr; rate = k[H_2][Br_2]^{1/2} order = 3/2$$
$$COCl_2 \rightarrow CO + Cl_2; rate = k[COCl_2]^{3/2} order = 3/2$$
$$CO + Cl_2 \rightarrow COCl_2; rate = k[CO]^2[Cl_2]^{1/2} order = 5/2$$

9. First order reactions: some more details of the first order reactions are as follows;

a) Rate equation for a first order reaction: a first order reaction is an exponential process and the concentration of the reactant decreases exponentially with time. Let us consider the following reaction which is of first order.

A $\rightarrow$ products

If, $[A]_0$ = initial concentration of A, and [A] = concentration of A after a time interval of t , we have

$[A] = [A]_0\ e^{-kt}$ ……………..(i)

Where, k is the rate constant of the reaction.

The above equation can also be written as

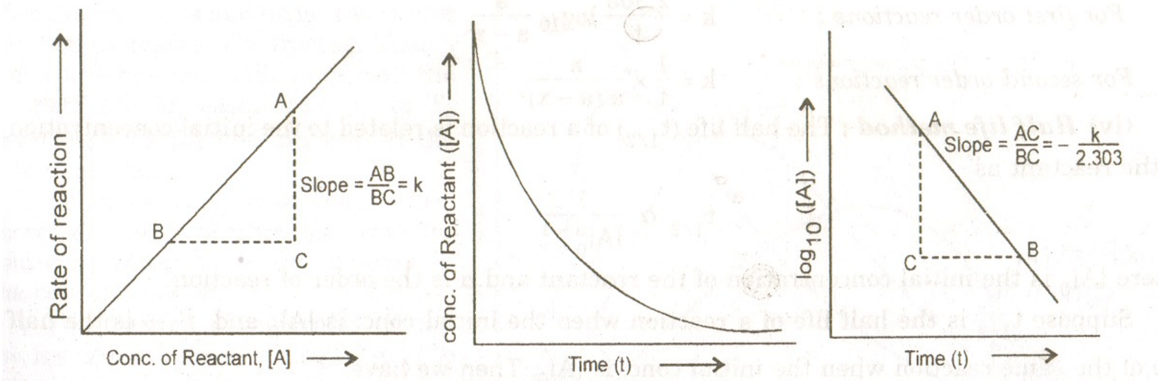
$$K = \frac{2.303}{t}\log\frac{[A]_0}{[A]} \qquad \text{..............(ii)}$$

This equation represents the rate equation of a first order reaction.
If the initial concentration of A is a mol L^{-1} and x moles of it change into products during time interval t, we have $[A]_0$= a mol L^{-1} and [A] = a – x mol L^{-1}. Thus, the above equations can also be written as

$$\frac{2.303}{t}\log_{10}\frac{a}{a-x} \text{........(iii)}$$

Eqs. (ii) and (iii) are also referred to as integrated rate law or integrated rate equations for a first order reaction.

b) Graphical representation of a first order reaction: following are the different graphical representations of a first order reaction:



c) Half life of a first order reaction: it is given by

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

Where, k is the rate constant of the reaction. The half life of a first order reaction is independent of the initial concentration of the reactant.

d) Characteristics of a first order reaction: i) the rate of reaction is directly proportional to the concentration of the reactant i.e. rate α [A]
ii) The rate constant has the units of time^{-1}
iii) A first order reaction obeys equations. (i), (ii) and (iii) given above.
iv) A plot of **log [A]** against **t** is a straight line with slope equal to –k/2.303.
v) The half life of first order reaction is independent of the initial concentration.
vi) The time taken for the completion of any fraction of a first order reaction is independent of initial Concentration.

10. Determination of order of a reaction: following methods are used to determine the order of a reaction.

i) Graphical method: this method is used when the reaction involves only one reactant. The method is based on the fact that for a reaction of order n,

Rate α [A] n

For a first order reaction, n =1, Hence, rate α [A]. Thus a plot of rate of reactions Vs conc. Will be a Straight line

For a second order reaction, n=2. Hence rate α $[A]^2$. Thus a plot of rate of reaction Vs conc. will be a Straight line.

ii) Initial rate method: in this method, the rate law of the reaction is determined by determining the orders of reaction with respect to all the reactants one by one. This is done by changing the initial concentration of only one reactant keeping the concentrations of all other reactants constant and measuring the rate of the reaction. The procedure is repeated with respect to each reactant and the order determined. The overall order of the reaction can be obtained by summing up the indi8vidual orders of reaction with respect to the reactants involved.

iii) Integrated rate law method: in this method, the data obtained from an experiment is fed into the rate equation of a particular order and the values of k are calculated for different sets of observations. If the values of k are found to be constant for all the sets, the reactions is supposed to obey that particular rate law and follows the order suggested by that integrated rate law. In case, the values of k are not constant, the data is used in the rate equation of other order. The rate equation for first and second order reactions are as follows.

For first order reactions: $k = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$

For second order reactions: k = $\frac{1}{t} X \frac{x}{(a-x)}$

iv) Half life method: the half life (t1/2) of a reaction is related to the initial concentration of the reactant as

$$t_{1/2} \alpha \frac{1}{[A]^{n-1}{}_{0}}$$

Where $[A]^0$ is the initial concentration of the reactant and n is the order of reaction.
Suppose t1/2 is the half life of a reaction when the initial conc. Is $[A]^0$ and $\mathbf{t_{1/2}}$ is the half life of the same reaction when the initial conc. Is $[A]^0$. Then we have

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

Thus, the order n of the reaction can be determined.

11. Effect of temperature on reaction rate: the rate of a chemical reaction is significantly affected by a change in temperature. For most of the chemical reactions, the rate increases with increase in temperature. The rate usually becomes doubled for each 10º rise in temperature.

a) Temperature coefficient: it is defined as the ratio of the rate constant of a reaction at two different temperatures separated by 10 C. the two temperatures generally taken are 35 C and 25 C. thus,

$$\text{Temperature coefficient} = \frac{k_{35C}}{k_{25C}}$$

For most of the homogeneous reactions, the value of temperature coefficient lies between 2 and 3.

b) Collision theory of reaction rate: this theory was proposed to explain the effect of temperature on reaction rates. The salient features of the theory are as follows.

i) A reaction occurs only when the reactant molecules undergo collisions with one another.

ii) All collisions between the reaction molecules are not effective in producing a chemical change. Only a fraction of total number of collisions is effective and leads to the formation f products.

iii) The collisions between the reaction molecules are effective only when they acquire a definite amount of energy. The minimum amount of energy which must be possessed by the reacting molecules to make effective collisions is called threshold energy.

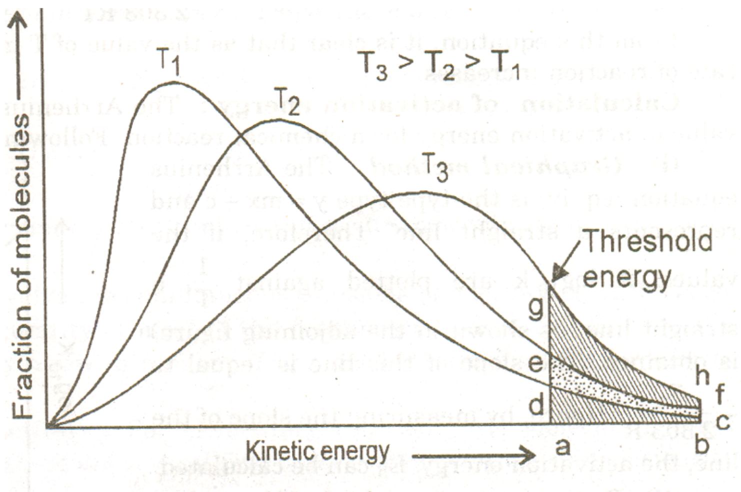
Effective collisions are those collisions which lead to the formation of products. The number of effective collision is governed by the following two factors.

i) Energy barrier: the collisions are effective only when the molecules possess energy greater than or equal to the threshold energy.

ii) Orientation barrier: the reactant molecules must collide with favorable orientation in order to facilitate the breaking of old bond and formation of new bonds.

c) Qualitative of increase in reaction rate with temperature: the following figure shows the energy distribution curves at temperature T_1, T2 and T_3 such that $T_3 > T_2 > T_1$. At temperature T_1, the fraction of molecules enclosed in the shaded are a b c d possesses kinetic energy greater than or equal to the threshold energy and is capable of making effective collisions. As the temperature increases from T_1 to T_2. The fraction of molecules having kinetic energy greater than the threshold energy increase. Thus effective collisions and hence the rate of reaction increases. The fraction of such molecules becomes still larger as the temperature increases from T_2 to T_3 resulting in a further increase in the rate of reaction.

Thus, an increase in temperature increases the number of effective collisions resulting in an increase in the rate of reaction.
The fraction of molecules having energy greater than or equal to the threshold energy increases appreciably even with a small rise in temperature. Hence, the rate of a reaction increase appreciably even with a small rise in temperature.

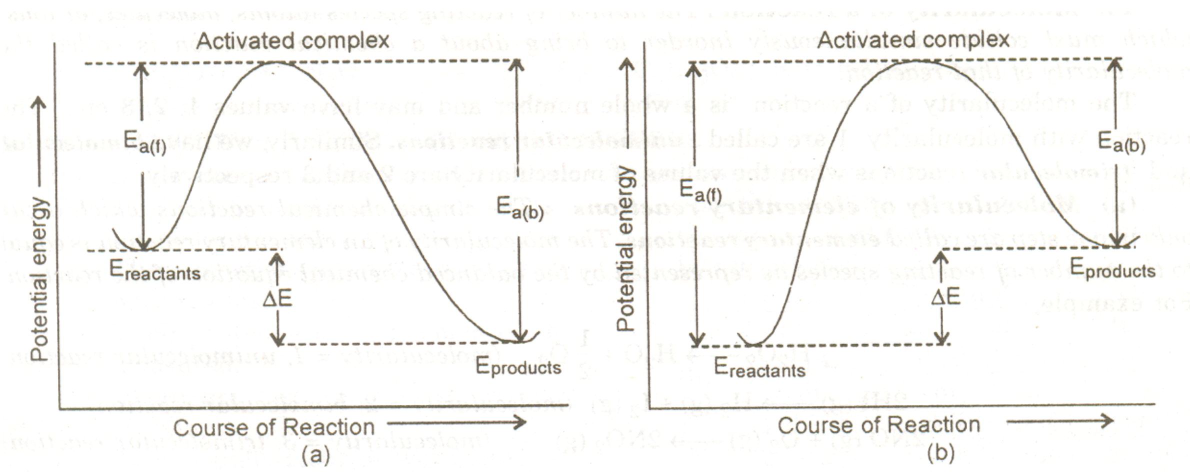


12. Activation energy: the excess energy that the reactant molecules must acquire in order to cross the energy barrier and to change into the products is called the activation energy of the reaction.

Activation energy = threshold energy-average energy possessed by reactant molecules.

Each reaction has a definite value of activation energy. The value of activation energy decides the fraction of collisions which are effective. Smaller the activation energy of the reaction, higher is the number of molecules capable of crossing the energy barrier and consequently the greater is the rate of reaction.

The activation energies for forward and backward reactions in a reversible reaction are shown in the following figures.



$K = A\, e^{-Ea/RT}$

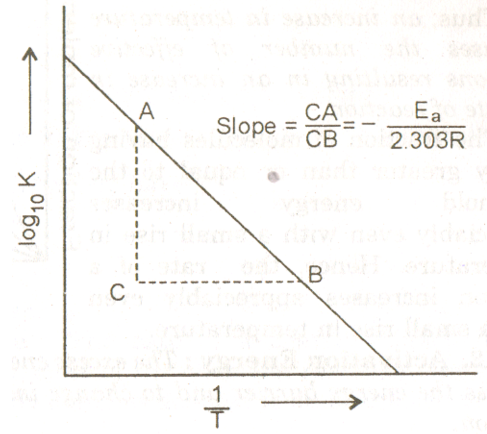
Where A is a constant known as frequency factor and gives the frequency of binary collisions of reactant molecules per second per liter. Ea is the energy of activation, R is gas constant and T represents the temperature of the system. k is the rate constant of the reaction

Arrhenius equation can also be expressed as

$$\log_{10} k = \frac{E_a}{2.303RT} + \log_{10} A \ldots\ldots\ldots\ldots \text{(iv)}$$

From this equation, it is clear that as the value of T increases, the value of k and hence the rate of reaction increases.

Calculation of activation energy: the Arrhenius equation enables us to calculate the value of activation energy for a chemical reaction. Following two methods may be used.



i) Graphical method: the Arrhenius equation (iv) is the type, type **y = mx + c** and represents a straight line.

Therefore, if the values of **log k** are plotted against 1/T, a straight line is obtained. The slope of this line is equal to the - $-\frac{E_a}{2.303R}$. Hence, by measuring the slope of the line, the activation energy Ea can be calculated.

ii) Rate constant method: if k_1 and k_2 are the rate constants measured at temperatures T_1 and T_2 respectively, then on the basis of Arrhenius equation, we can have

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Thus, knowing the values of rate constant, k_1 and k_2 of a reaction measured at two different temperatures T_1 and T_2 respectively. The energy of activation Ea of the reaction can be calculated with the help of the above equation.

13. Molecularity of a reaction: the number of reacting species which must collide simultaneously in Order to bring about a chemical reaction is called the molecularity of that reaction.

The molecularity of a reaction is a whole number and may have values 1, 2, 3 etc.
The reactions with molecularity 1 are called unimolecular reactions.
Similarly, we have bimolecular and trimolecular reactions when the values of molecularity are 2 and 3 respectively.

a) Molecularity of elementary reactions: The simple chemical reactions which occur only in one step are called elementary reactions. The molecularity of an elementary reaction is equal to the number of reacting species as represented by the balanced chemical equation of the reaction, for example.

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 (molecularity = 1, unimolecularreaction)$$

$$2HI \rightarrow H2 + I2 (molecularity = 2, bimolecularreaction)$$

$$2NO + O_2 \rightarrow 2NO_2 (molecularity = 3, trimolecularreaction)$$

b) Molecularity of complex reactions: the reactions which occur in two or more steps are called complex reactions.

Complex reactions proceed through a series of steps, each involving one, two, or at the most three molecules. Each step is an elementary reaction and has its own rate. The overall rate of a complex reaction is governed by the rate of the slowest elementary step called the rate determining step.

The number of reacting species taking part in the slowest elementary step of a complex reaction is called the molecularity of the complex reaction.

For example, the reaction 2NO +$2H_2 \rightarrow N_2 + H_2O$ is a complex reaction and takes place in the following two steps.

Step1. $2NO + H_2 \rightarrow N_2 + H_2O_2 (slow)$

Step2. $H_2O_2 + H_2 \rightarrow 2H_2O\ (fast)$

Obviously, step 1 is the rate determining step and therefore the molecularity of the overall complex reaction is 3.

Most of the chemical reactions involve the simultaneous collisions of one, two or at the most three molecules. Therefore, the molecularity of most of the reactions is either 1 or 2. Even the reactions with molecularity 3 are only a few in number. The reactions with higher molecularity are rare.

14. Pseudo-unimolecular reactions: for elementary reactions, the molecularity and order are usually the same. However, there are several first order reactions in which molecularity differs from the order.

The first order reactions having molecularity greater than one are called pseudo-unimolecular reactions.
A pseudo-unimolecular reaction is obtained when one of the reactants is present in large excess. The reactant present in large excess does not contributes to the rate of reactions. Its concentration remains almost constant during the course of reaction and therefore the rate of the reaction does not depend upon its concentration. Some examples of pseudo-unimolecular reactions are as follows.

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH; rate = k[CH_3COOC_2H_5]$$
$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6; rate = k[C_{12}H_{22}O_{11}]$$

15. Units of rate constant:

Units of rate constant

For a general reaction

$$aA + bB \rightarrow cC + dD$$
$$\text{Rate} = k\,[A]^x\,[B]^y$$

Where x + y = n = order of the reaction

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$
$$= \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concerntration})^n}$$

Taking SI units of concentration, mol L^{-1} and time, s, the units of k for different reaction order are listed in Table 4.3

Table 4.3: Units of rate constant

Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1}\text{s}^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1}\text{L s}^{-1}$

16. Zero order reaction:

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

As any quantity raised to power zero is unity

$$\text{Rate} = -\frac{d[R]}{dt} = k \times 1$$

$$d[R] = -k\,dt$$

Integrating both sides

$$[R] = -kt + I \qquad (4.5)$$

where, I is the constant of integration.

At $t = 0$, the concentration of the reactant $R = [R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation (4.5)

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation (4.5)

$$[R] = -kt + [R]_0 \qquad (4.6)$$

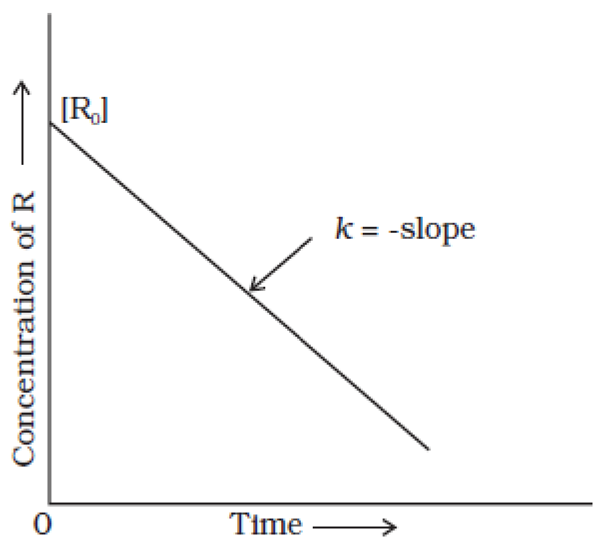


Fig. 4.3: Variation in the concentration vs time plot for a zero order reaction

17. Half life of zero order reaction:

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

For a zero order reaction, rate constant is given by equation 4.7.

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

$$\text{At } t = t_{1/2}, \quad [R] = \frac{1}{2}[R]_0$$

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

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

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

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

18. First order reaction:

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant R. For example,

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\text{or} \quad \frac{d[R]}{[R]} = -k\,dt$$

Integrating this equation, we get

$$\ln [R] = -kt + I \qquad (4.8)$$

Again, I is the constant of integration and its value can be determined easily.

When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation (4.8) can be written as

$$\ln [R]_0 = -k \times 0 + I$$

$$\ln [R]_0 = I$$

Substituting the value of I in equation (4.8)

$$\ln[R] = -kt + \ln[R]_0 \qquad (4.9)$$

Rearranging this equation

$$\ln\frac{[R]}{[R]_0} = -kt$$

$$\text{or } k = \frac{1}{t}\ln\frac{[R]_0}{[R]} \qquad (4.10)$$

At time t_1 from equation (4.8)

$$*\ln[R]_1 = -kt_1 + *\ln[R]_0 \qquad (4.11)$$

At time t_2

$$\ln[R]_2 = -kt_2 + \ln[R]_0 \qquad (4.12)$$

where, $[R]_1$ and $[R]_2$ are the concentrations of the reactants at time t_1 and t_2 respectively.

Subtracting (4.12) from (4.11)

$$\ln[R]_1 - \ln[R]_2 = -kt_1 - (-kt_2)$$

$$\ln\frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)}\ln\frac{[R]_1}{[R]_2} \qquad (4.13)$$

Equation (4.9) can also be written as

$$\ln\frac{[R]}{[R]_0} = -kt$$

Taking antilog of both sides

$$[R] = [R]_0\, e^{-kt} \qquad (4.14)$$

Comparing equation (4.9) with y = mx + c, if we plot ln [R] against t (Fig. 4.4) we get a straight line with slope = $-k$ and intercept equal to ln $[R]_0$

The first order rate equation (4.10) can also be written in the form

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} \qquad (4.15)$$

$$*\log\frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between log $[R]_0/[R]$ vs t, (Fig. 4.5), the slope = $k/2.303$

Hydrogenation of ethene is an example of first order reaction.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Rate = $k\,[C_2H_4]$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

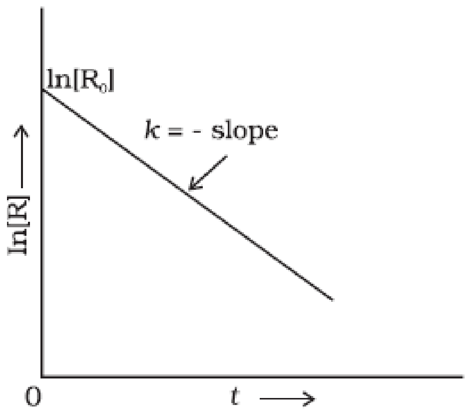


Fig. 4.4: A plot between ln[R] and t for a first order reaction

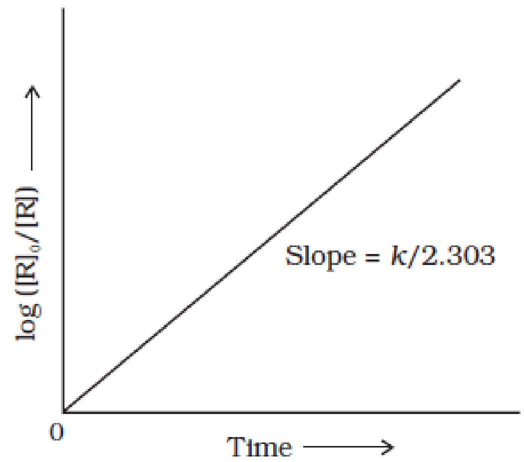


Fig. 4.5: Plot of log $[R]_0/[R]$ vs time for a first order reaction

$$^{226}_{88}Ra \rightarrow ^{4}_{2}He + ^{222}_{86}Rn$$

Rate = k [Ra]

Decomposition of N_2O_5 and N_2O are some more examples of first order reactions.

19. Half life of first order reaction:

For the first order reaction,

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

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

So, the above equation becomes

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

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

$$t_{1/2} = \frac{2.303}{k}\times 0.301$$

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

It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.

For zero order reaction $t_{1/2} \propto [R]_0$. For first order reaction $t_{1/2}$ is independent of $[R]_0$.

CHEMICAL KINETICS

SECTION-B

Q1.Express the rate of following reactions in terms of concentrations of reactants and products.

i) $PCl_5 \rightarrow PCl_3 + Cl_2$

ii) $2NO_2 \rightarrow 2NO + O_2$

Solution:

i) rate of reaction = $-\frac{d[PCl_5]}{dt} = \frac{d[PCl_3]}{dt} = \frac{d[Cl_2]}{dt}$

ii) Rate of reaction = $\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[NO]}{dt} = \frac{d[O_2]}{dt}$

Q2. The concentration of reactant R at different times are given below:

Time in seconds	[R] in mol L^{-1}
0	160×10^{-3}
5	80×10^{-3}
10	40×10^{-3}
20	10×10^{-3}
30	2.5×10^{-3}

Calculate the average rate of reaction R → P during the different intervals of time.

Solution:

$R_{ave} = -\frac{[R_2]-[R_1]}{\Delta t}$

$[R_1]$ X10^{-3}	$[R_2]$ X10^{-3}	t_1 Sec	t_2 Sec	R_{ave} mol/lit/sec
160	80	0	5	$-\frac{(80-160)x10^{-3})}{5-0} = 16x10^{-3}$
80	40	5	10	$-\frac{(40-80)x10^{-3})}{10-5} = 8x10^{-3}$
40	10	10	20	$-\frac{(10-40)x10^{-3})}{20-10} = 3x10^{-3}$
10	2.5	20	30	$-\frac{(2.5-10)x10^{-3}}{30-20} = 0.75x10^{-3}$

It can be seen that the average rate decreases from 16 X 10^{-3} to 0.75 X 10^{-3} mol/lit/sec During time interval 0 to 30 sec.

Q3. Ammonia and Oxygen reacted at high temperature as shown below.

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

The rate of formation of NO is 3.6 X 10^{-3} mol/lit/sec. calculate rate of disappearance of ammonia and rate of formation of water.

Solution:

Rate = $\frac{1}{4}\frac{d[NH_3]}{dt} = -\frac{1}{5}\frac{d[O_2]}{dt} = \frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$

i) Rate of disappearance of NH_3 = Rate of appearance of NO = 3.6 X 10^{-3} mol/lit/sec

ii) Rate of formation of H_2O = $\frac{d[H_2O]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt} = \frac{1}{4}\frac{d[NO]}{dt}$

Therefore $\frac{d[H_2O]}{dt} = \frac{6}{4}$ X 3.6 X 10^{-3} mol/lit/sec

Q4. The decomposition of N_2O_5 in CCl_4 solution at 318 K has been studied by monitoring the Concentration of N_2O_5 in the solution. Initially, the concentration of N_2O_5 is 2.33 M and after 184 minutes, it is reduced to 2.08 M. the reaction takes place according to the equation:

$2N_2O_5 \rightarrow 4NO_2 + O_2$

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO_2 during this period.

Solution:

Rate of reaction

$= -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = -\frac{1}{2}\frac{(2.08-2.33) molL^{-1}}{184 \min} = 6.79 \times 10^{-4}$ mol/lit/min

If time 184 = 3.067 hours

Rate = $-\frac{1}{2}\frac{(2.08-2.33) molL^{-1}}{3.067 hr} = 4.07 \times 10^{-2}$ mol/lit/hr

If time = 184 X 60 = 11040 sec

Rate = $-\frac{1}{2}\frac{(2.08-2.33) molL^{-1}}{11040 \sec} = 1.13 \times 10^{-5}$ mol/lit/sec

Rate = $\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$

$\frac{\Delta[NO_2]}{\Delta t}$ = 4 X rate

= 4 X 6.79 X 10^{-4} mol/lit/min

= 2.72 X 10^{-3} mol/lit/min

Q5. Calculate the overall order of reaction which has the rate expression:

i) Rate = $k[A]^{1/2}[B]^{3/2}$

ii) Rate = $k[A]^{3/2}[B]^{-1}$

iii) A + B → C is zero order, write rate equation.

Solution:

i) Order of reaction = $\frac{1}{2}+\frac{3}{2}=2$ Second order.

ii) Order of reaction = $\frac{3}{2}+(-1) = \frac{1}{2}$ Half order.

iii) For zero order reaction

A + B → C

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

Order of the reaction = 0 + 0 = 0 Zero order.

Q6. i) If the concentration of A and B are expressed in terms of mole dm^{-3} and time in minutes, calculate the units for rate constant for the following reaction:

A + B → AB

ii) What are the units for Zero order reaction?

Solution:

i) for the reaction A + B → AB

Rate = k[A][B]

The rate is change in concentration with time. The time and concentration are expressed in minutes and dm^{-3} respectively.

$\frac{moldm^{-3}}{\min} = k(moldm^{-3})(moldm^{-3})$ or

K= $(mol\ dm^{-3})^{-1} (min^{-1}) = mol^{-1}\ dm^3\ min^{-1}$

ii) For zero order reaction, the rate is independent of the concentration:

Rate = k

Units of k are : k = Rate = $\frac{mol^{-1}}{s}$ mol /lit/sec

Q7. Write the rate constant for a nth order reaction. Deduce from this the units of rate constant for a i) half order reaction ii) 3/2th order reaction iii) third order reaction.

Solution:

The units of the rate constant for nth order reactions are:

Rate = $k[A]^n$

$\frac{mol^{-1}}{s}$ = $k[mol\ L^{-1}]^n$ $k=(mol\ L^{-1})^{1-n} s^{-1}$

i) $n = \frac{1}{2}$, units are : $mol^{1/2}\ L^{-1/2}\ s^{-1}$

ii) $n = \frac{3}{2}$ units are : $mol^{-1/2}\ L^{1/2}\ s^{-1}$

iv) n = 3 , units are: $mol^{-2}\ L^2\ s^{-1}$

Q8. The rate law of a reaction of A,B and C has been found to be rate = k [A][B][C]^2. How are the rate of reaction change when

i) concentration of C is doubled

ii) concentration of A is halved

iii) concentration of both B and C are doubled

iv) concentration of each of A, B, C and D are tripled?

Solution:

Suppose the initial concentrations are :

$[A] = a\ mol\ L^{-1}$,

$[B] = b\ mol\ L^{-1}$ Rate = $k\ abc^2$

$[C]= c\ mol\ L^{-1}$

i) New[C] = 2c

Rate = $k\ ab(2c)^2 = 4kabc^2$

Rate of reaction is four folded (4 times).

ii) New[A] = a/2

Rate = $k[\frac{a}{2}]bc = \frac{1}{2}kabc$

Rate of reaction is halved.

iii) New[B] = 2b New[C] = 2c

Rate = $ka(2b)(2c)^2 = 8kabc^2$

Rate of reaction increased to 8 times.

iv) New [A] = 3a, [B] = 3b, [C] = 3c

Rate = $k(3a)(3b)(3c)^2 = 81kabc^2$

Rate increased to 81 times.

Q9. The decomposition of hydrogen peroxide in the presence of iodide ion has been found to be first order in H_2O_2:

$2H_2O_2 \rightarrow 2H_2O + O_2$

The rate constant has been found to be 1.01 X 10^{-2} min$^-$, calculate the rate of reaction when i) $[H_2O_2]$ = 0.4 mol/lit ii) $[H_2O_2]$ = 0.15 mol/lit

iii) What concentration of $[H_2O_2]$ would give rate of 1.12 X10^{-2} mol/lit /min

Solution:

The reaction is of first order in H_2O_2 so that

Rate = $k[H_2O_2]$

i) $k = 1.01X10^{-2}min^{-1}$, $[H_2O_2] = 0.4\ mol/L^{-1}$

Rate = $(1.01X10^{-2}min^{-1})X(0.4\ mol\ L^{-1})$

ii) When $[H_2O_2] = 0.15\ mol\ L^{-1}$

Rate =$(1.01X10^{-2}min^{-1}X(0.15\ mol\ L^{-1})$

$=1.5X10^{-3}\ mol\ L^{-1}\ min^{-1}$

iii) To obtain concentration of H_2O_2 when rate

$=1.12X10^{-2}\ mol\ L^{-1}\ min^{-1}$

$[H_2O_2] = \frac{Rate}{k} = \frac{1.12X10^{-2} molL^{-1} \min^{-1}}{1.01X10^{-2} \min^{-1}}$
$= 1.11$ mol L^{-1}

Q10. For the reaction

$2A + B + C \rightarrow A_2B + C$

The rate law has been found to be

Rate = $k[A][B]^2$ with k = 2.0 X 10^{-6} mol $^{-2}$ L^2 s^{-1}

For this reaction, determine the initial rate of reaction with[A]=0.1 mol L^{-1},[B]=0.2 mol L^{-1},[C] =0.8 mol L^{-1}.Determine the rate after 0.04 mol L^{-1} of A has been reacted.

Solution:

Rate law is :
Rate = $k[A][B]^2$
Where k= 2.0 X 10^{-6} mol^{-2} L^2 s^{-1}
Initial concentration,
[A] = 0.1 mol L^{-1},[B]=0.2 mol L^{-1},[C]=0.8 mol L^{-1}
Rate = (2.0X10^{-6} mol^{-2} L^2 s-1)(0.1 mol L^{-2})(0.2 mol $L^{-1})^2$
=8X10^{-9} mol L^{-1} s^{-1}
Conc. Of A after 0.04 mol L^{-1} of A has been reacted
[A] = 0.1-0.04 = 0.06 mol L^{-1}
Now , we know that when 2 moles of A are consumed then one mole of B gets consumed.
Therefore , moles of B consumed when 0.04 moles of A have been consumed=0.04X1/2 = 0.02 mole
[B] = 0.2 – 0.02 = 0.18 mol L^{-1}
Rate = (2.0X10^{-6} mol^{-2} L^2 s-^{2})X(0.06 mol L^{-1})X(0.18 mol $L^{-1})^2$
=3.89X10^{-9} mol L^{-1} s^{-1}

Q11. Following reaction takes place in one step:

$2NO + O_2 \rightarrow 2NO_2$

How will the rate of the above reaction change if the volume of the reaction vessel is Diminished to one third of its original volume? Will there be any change in the order of the reaction with reduced volume?

Solution:

Before the volume of the reaction vessel is changed, the rate of reaction is expressed as:
R =$k[NO]^2[O_2]$……………(i)
When the volume is reduced to $\frac{1}{3}$,the concentration of each reactant is increased by 3 times.
$R^1 = k[3NO]^2[3O_2]$…………(ii)
=27 $k[NO]^2[O_2]$
$\frac{R^1}{R} = 27$. Rate became 27 times.
It is clear the order of reaction remained same.

Q12. How will rate of a reaction change when $[A]_0$ is doubled and tripled for

i) zero order reaction

ii) second order reaction

Solution:

When $[A]_0$ is doubled
i) The rate of zero order reaction remains unchanged.
ii) The rate of second order reaction becomes four times.
When $[A]_0$ is tripled
i) The rate of zero order reaction remains unchanged
ii) The rate of second order reaction becomes 9 times.

Q13. Why is the use of instantaneous rate of reaction preferred over average rate of reaction?

Solution:

The rate of reaction continuously decreases with time (except for zero order reaction) and Therefore, average rate has no significance for the reaction.

Q14. What is the order of a reaction whose rate constant has same units as the rate of the

Reaction?
Solution:
Zero order reaction.

Q15. A spontaneous reaction is not necessarily a fast reaction. Why?
Solution:
A spontaneous reaction means that it has tendency to occur of its own. But this reaction may take very small time or extremely large time.

Q16. A reaction is found to be zero order. Will its molecularity be zero?
Solution:
No, molecularity of a reaction cannot be zero.

Q17. Is there any reaction whose rate does not fall with the progress of the reaction?
Solution:
Zero order reaction.

Q18. Why does the rate of reaction not remain constant throughout?
Solution:
Because the rate of reaction depends upon concentration of reactants which keeps on decreasing.

Q19. How rate is constant related to concentration of the reactants?
Solution:
Rate constant does not depend upon the concentration of the reactants.

Q20. For a reaction:
$A + H_2O \rightarrow B$, rate α [A]
What is its i) molecularity ii) order of reaction
Solution:
i) Pseudo unimolecular ii) Order of reaction = 1.

Q21. For the reaction: $3H_2 + N_2 \rightarrow 2NH_3$, how are the rate of reaction expressions $-\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$ interrelated?
Solution:
$$-\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

Q22. Identify the reaction order from each of the following rate constants:
i) $k = 6.2 \times 10^{-5}\ L\ mol^{-1}\ s^{-1}$
ii) $k = 4.0 \times 10^{-4}\ s^{-1}$
Solution:
Order can be predicted by the inspection of units of rate constant
i) second order reaction
ii) first order reaction

Q23. For the reaction: Ester + $H^+ \rightarrow$ Acid + Alcohol, rate=k[Easter]$[H^+]^0$. Find the order of reaction.
Solution:
Order=1

Q24. For the assumed reaction: $X_2 + 2Y_2 \rightarrow 2XY_2$, write the rate equation in terms of the rate of disappearance of Y_2.
Solution:
$$\frac{1}{2}\frac{d[Y_2]}{dt} = k[X_2][Y_2]^2$$
$$\frac{d[Y_2]}{dt} = 2k[X_2][Y_2]^2$$

Q25. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is
i) Doubled ii) reduced to ½ ?

Solution:
Rate=k[A]^2
i) When concentration of reactant is doubled, the rate becomes 4 times.
ii) When concentration of reactant is reduced to ½ the rate becomes ¼ times.

Q26. The decomposition of N_2O_5 at 320K according to the following equation follows first order reaction:

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

The initial concentration of N_2O_5 was $1.24X10^{-2}$ mol L^{-1} and that after 60 minutes uas $0.20X10^{-2}$ mol L^{-1}. Calculate the rate constant of the reaction at 320K.
Solution:
For a first order reaction

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

T=60 min.$[R]_0$ =$1.24X10^{-2}$ mol L^{-1},[R] =$0.20X10^{-2}$ mol L^{-1}

$$k=\frac{2.303}{60}\log\frac{1.24X10^{-2}molL^{-1}}{0.20X10^{-2}molL^{-1}}$$

$$=\frac{2.303}{60}\log 6.2$$

$$=\frac{2.303}{60}X\,0.7924=0.0304\min^{-1}$$

Q27. The rate of decomposition of hydrogen peroxide at a particular temperature was measured by titrating its solution with acidic $KMnO_4$ solution. Following results were obtained:

Time, t (min)	0	10	20
Mol ($KMnO_4$)	22.8	13.8	8.3

Show that the reaction is of first order.
i) Calculate the rate constant.
Solution:
Volume of $KMnO_4$ used is proportional to the amount of H_2O_2 present. If the reaction is of first order, it must obey the equation.

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

or

$$k=\frac{2.303}{t}\log\frac{V_0}{V_t}$$

Here V_0 = 22.8 and the value of k can be calculated by substituting the concentration of V_t at different temperatures.
T=10 min, V_t =13.8

$$k=\frac{2.303}{10}\log\frac{22.8}{13.8}$$

$$=0.05022\min^{-1}$$

$$t=20\min, V_t=8.3$$

$$k=\frac{2.303}{20}\log\frac{22.8}{8.3}$$

$$=0.05053\min^{-1}$$

i) Since the value of k comes out to be almost constant, the reaction therefore, is of First order.

ii) The mean value of k=0.05037 min^{-1}

Q28. The following data were obtained during the first order thermal decomposition of N_2O_5 (g) at constant volume,

$2N_2O_5$ (g) → $2N_2O_4$ (g) + O_2 (g)

Time (s)	**0**	**100**
Total pressure(atm)	**0.500**	**0.512**

Calculate the rate constant.

Solution:

Let the pressure of N_2O_5 decreases by 2x atm. Since 2 moles of N_2O_5 decompose to give 2 moles of N_2O_4 and 1 mole of O_2 , then the pressure of N_2O_4 (g) increases by 2x atm and that of O_2(g) increases by x atm.

	$2N_2O_5$ (g) →	$2N_2O_4$ (g) +	O_2 (g)
At time, t=0	0.5 atm	0	0
At time t(100 s)	(0.5-2x)atm	2x atm	x atm

Total pressure, p_t=0.5-2x+2x+x=0.5+x

At=100 s, p_t=0.512 atm

Or x= p_t-0.5=0.512-0.5=0.012 atm

Now $p(N_2O_5)$=0.5-2x=0.5-2X0.012=0.476 atm

For a first order reaction,

$$k = \frac{2.303}{t}\log\frac{p(N_2O_5)_0}{p(N_2O_5)_t}$$

$$= \frac{2.303}{100}\log\frac{0.5atm}{0.476atm}$$

$$= \frac{2.303}{100}\log 1.504$$

$$= \frac{2.303}{100} X 0.0214$$

$$= 4.93 X 10^{-4} s^{-1}$$

Q29. The following data were obtained for the reaction:

2NO(g) + Br(g) → 2NOBr(g)

Experiment	**initial conc [NO]**	**[Br_2]**	**initial rate (mol L-^{1} min $^{-1}$)**
I	**0.10**	**0.10**	**$1.3X10^{-6}$**
II	**0.20**	**0.10**	**$5.2X10^{-6}$**
III	**0.20**	**0.30**	**$1.56X10^{-5}$**

Determine i) the orders with respect to NO and Br_2 ii) the rate law and iii) Rate constant.

Solution:

The rate law may be written as:

Rate=$k[NO]^p[Br_2]^q$

The initial rate becomes

$(Rate)_0 = k[NO]_0^p[Br_2]^q$

Comparing experiment I and II, we get

$(Rate)_1=k(0.1)^p(0.1)^q=1.3X10^{-6}$

$(Rate)_2=k(0.2)^p(0.1)^q=5.2X10^{-6}$

Dividing Eq. (ii) by Eq. (i)

$$\frac{(Rate)_2}{(Rate)_1}=\frac{k(0.2)^p(0.1)^q}{k(0.1)^p(0.1)^q}=\frac{5.2X10^{-6}}{1.3X10^{-6}}$$

Or $(2)^p = 4$ or $(2)^p = 2^2$

P=2.

Thus, order with respect to NO is 2.

Comparing experiments II and III

$(Rate)_2\ k(0.2)^p(0.1)^q = 5.2X10^{-6}$

$(Rate)_3=k(0.2)^p(0.3)^q=1.56X10^{-5}$

Divding Eq. (iv) by Eq.(iii), we get:

$$\frac{k(0.2)^p(0.3)^q}{k(0.2)^p(0.1)^q}=\frac{1.56X10^{-5}}{5.2X10^{-6}}$$

Or $(3)^q = 3$

Or q=1

Thus, order with respect can be calculated by substituting the values of rate, [NO] and $[Br_2]$ for any experiment

$$k=\frac{Rate}{[NO]^2[Br_2]}=\frac{1.3X10^{-6}}{(0.1)^2(0.1)}$$

$=1.3X10^{-3}\ mol^{-2}L^2s^{-1}$

Q30. The following data were obtained for the reaction

$2NO_2(g) + F_2 \rightarrow 2NO_2F$

Experiment	initial conc $[NO_2]_0$	$[F_2]_0$	initial rate $[Br_2]$ (mol L^{-1} min^{-1})
I	0.20	0.05	6.0 $X10^{-3}$
II	0.40	0.05	$1.2X10^{-2}$
III	0.80	0.10	$4.8X10^{-2}$

Determine i) Order of reaction ii) rate law iii) rate of reaction when $[NO_2]$=0.50 mol/lit and $[F_2]$=0.60 mol/lit

Q31. A reaction that is of first order with respect to reactant A has a rate constant 6 min^{-1}. if we start with [A]=5.0 mol L^{-1}, when would [A] reach the value of 0.05 mol L^{-1}?

Solution:

For the first order reaction,

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

$[A]_0 = 5.0$ mol L^{-1},[A]=0.05 mol L^{-1}, k =6 min^{-1},

$$t=\frac{2.303}{6}\log\frac{5.0}{0.05}$$

$$=\frac{2.303}{6}\log 100 = 0.768\,min$$

Q32. The initial rate of a reaction is

A + 5B + 6C → 3L + 3M

Has been determined by measuring the rate of appearance of A under the following conditions.

Expt. No.	$[A]_0$ M	$[B]_0$ M	$[C]_0$ M	Initial rate M/min-^{1}
1.	0.02	0.02	0.02	$2.08X10^{-3}$
2.	0.01	0.02	0.02	$1.04X10^{-3}$
3.	0.02	0.04	0.02	$4.16X10^{-3}$
4.	0.02	0.02	0.04	$8.32X10^{-3}$

Determine the order of reaction with respect to each reactant and overall order of reaction.

What is the rate constant? Calculate the initial rate of reaction when the concentration of all the reactions is 0.01M. Calculate the initial rate of change in concentration of B and L.

Q33. The rate constant for the first order reaction is 60 sec. how much time will it take to reduce the concentration to 1/16 th value?

Solution:

Let the initial conc.$[A]_0$ = a Final concentration = $\frac{1}{16}a$

Rate constant =60 s^{-1}

$$t=\frac{2.303}{k}\log\frac{[A]_0}{[A]} = =\frac{2.303}{60}\log\frac{a}{a/16} = \frac{2.303}{60}\log 16 == \frac{2.303}{60}X1.204 = 0.046\sec$$

Q34. Calculate the half life period of a first order reaction where the specific rate constant is i) $200s^{-1}$ ii) 2 min $^{-1}$ iii) 4 years^{-1}

Solution:

For the first order reaction,

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

$$i)k=200s^{-1}$$

$$t_{1/2}=\frac{0.693}{200}=3.465X10^{-3}s$$

$$ii)k=2\min^{-1}$$

$$t_{1/2}=\frac{0.693}{2}=0.3465\min$$

$$iii)k=4year^{-1}$$

$$t_{1/2}=\frac{0.693}{2}=0.1732year$$

Q35. A first order reaction is found to have rate constant $k=5.5X10^{-14}S^{-1}$. Find half life period of the reaction?

Solution:

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

$$=\frac{0.693}{5.5X10^{-14}s^{-1}}$$

$$=1.26X10^{13}s$$

Q36. The half life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact contained wood had only 80% of ^{14}C found in a living tree. Estimate the age of sample.

Solution:

$$Decaycons\tan t,k=\frac{0.693}{t_{1/2}}$$

$$t_{1/2}=5730year$$

$$\therefore k=\frac{0.693}{5730y}=1.209X10^{-4}year^{-1}$$

$$Sincetherateofcountsisproportionaltothenumberof\,^{14}Catom\sin thesample,$$

$$N_0=100, N=80$$

$$Now, t=\frac{2.303}{k}\log\frac{N_0}{N}$$

$$=\frac{2.303}{1.209X10^{-4}}\log\frac{100}{80}$$

$$=\frac{2.303}{1.209X10^{-4}}X0.0969$$

$$=1846years.$$

Q37. For a first order reaction, calculate the ratio between the time taken to complete three-Fourth of the reaction and the time taken to complete half of the reaction.

Solution:

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

For ¾ of a reaction to take place, t =$t_{3/4}$,[A]=$[A]_0$-$\frac{3}{4}$$[A]_0$

$\frac{1}{4}$$[A]_0$

Thus, $t_{3/4} = \frac{2.303}{k}\log\frac{[A]_0}{1/4[A]_0} = \frac{2.303}{k}\log 4$

Now, for half of a reaction

T=$t_{1/2}$;[A]=1/2$[A]_0$

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

$$\frac{t_{3/4}}{t_{1/2}} = \frac{\log 4}{\log 2} = \frac{0.6020}{0.3010} = 2$$

Hence time required for $3/4^{th}$ of reaction to occur is two times that required for half of the reaction.

Q38. Show that in case of first order reaction the time taken for the completion of 99.9% reaction is 10times time required for half change of a reaction.

Solution:

$$[R] = [R]_0 - \frac{99.9}{100}[R]_0$$

$$= 0.001[R]_0$$

$$= \frac{2.303}{k}\log\frac{[R]_0}{0.001[R]_0}$$

$$= \frac{2.303}{k}\log 10^3$$

$$= \frac{2.303 X 3}{k}$$

When half of the reaction is completed

$$t_{1/2} = \frac{2.303}{k}\log\frac{[R]_0}{0.5[R]_0}$$

$$= \frac{2.303}{k}\log 2$$

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

Dividing $t_{99.9\%}$ by $t_{1/2}$

$$\frac{t_{(99.9\%)}}{t_{1/2}} = \frac{3}{0.3010} = 10 times$$

Q 39. The specific rate constant for the combination of H_2 and I_2 to form HI is 2.34 X 10-3 mol/lit/sec. at 673 K and 7.50 X10-2 mol/lit/sec at 773K. Calculate the activation energy for the reaction.

Solution:

The Arrhenius equation is:

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

$$\log\frac{7.50X10^{-2}}{2.34X10^{-3}}=\frac{E_a}{2.303R}[\frac{1}{673}-\frac{1}{773}]$$
$$\log 32.05=\frac{E_a}{2.303X8.314}(\frac{773-673}{673X773})$$
$$1.506=\frac{E_a}{2.303X8.314}X\frac{100}{673X773}$$
$$Ea=\frac{1.506X2.303X673X773X8.314}{100}$$
$$=1.51X10^4\ j/mol=15.1kJ/mol$$

Q40. The rate constant s of a reaction at 700K and 760K are 0.011Ms^{-1} and 0.105Ms^{-1} respectively. Calculate Arrhenius parameters.

Solution:

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}[\frac{1}{T_1}-\frac{1}{T_2}]$$
$$\log\frac{0.105}{0.011}=\frac{E_a}{2.303R}[\frac{1}{700}-\frac{1}{760}]$$
$$\log 9.595=\frac{E_a}{2.303X8.314}(\frac{760-700}{760X700})$$
$$0.9798=\frac{E_a}{2.303X8.314}X\frac{60}{700X760}$$
$$Ea=\frac{0.9798X2.303X8.314X700X760}{60}$$
$$=166.342X10^3\ j/mol=166.0kJ/mol$$

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

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

Log A = log 0.011+ $\frac{166.342X10^3}{2.303X8.314X700}$

= - 1-9586 + 12.411

= 10.4524

A= 2.834X10^{10}M^{-1}s^{-1}

Q41. The first order rate constant for the decomposition of ethyl iodide by the reaction:
$C_2H_5I \rightarrow C_2H_4 + HI$
At 600 K is 1.60X 10^{-5} s^{-1}. its energy of activation is 209 kJ mol^{-1}. calculate the rate constant of the reaction at 700K.

Solution:

$$\log\frac{k_2}{1.60X10^{-5}}=\frac{209X10^3}{2.303X8.314}[\frac{700-600}{700X600}]$$
$$\log\frac{k_2}{1.60X10^{-5}}=2.599$$
$$\frac{k_2}{1.60X10^{-5}}=397.19$$
$$k_2=397.19X1.60X10^{-5}$$
$$=6.36X10^{-3}s^{-1}$$

Q42. Can activation energy for reactions be zero?

Solution:

In the Arrhenius equation,
$K=Ae^{-Ea/RT}$
If E_a is zero then k=A
i.e, every collision between molecules leads to chemical reaction. Which is not possible hence E_a can not be zero.

Q43. What value of k is predicted for the rate constant by Arrhenius equation if T → α ? Is this value physically reasonable?
Solution:
From the equation, $k=A_e^{-Ea/RT}$,if T → α; k → A so that E_a=0. This is not feasible.

Q44. Why ∆G is positive for photochemical reactions?
Solution:
This is because a part of light energy absorbed by the reactants gets converted into free energy.

Q45. What is the main difference between a photo sensitizer and a catalyst?
Solution:
A catalyst only changes the speed of the reaction, while a photo sensitizer only initiates the reaction.

Q46. Give the damaging effect of photochemistry.
Solution:
The color of fabrics fades away on exposure to sunlight.

Q47. The half life period of a first order reaction is x and three-fourth of the same reaction is y. how are x and y related to each other?
Solution:
Y is twice of x because the time required for $3/4^{th}$ of a reaction to occur is two times that required for half of the reaction.

Q48. After five half life periods for a first order reaction what fraction of reactant remains?
Solution:
$\frac{1}{32}$

Q49. A substance with initial concentration Co follows zero order kinetics. How long will this reaction take to got to completion?
Solution:
For zero order reaction,
Co = C +kt
For the reaction to be completed C = 0
Co=kt or $t=\frac{C_0}{k}$

Q50. The rate law for a reaction is Rate = $k[A]\,[B]^{3/2}$
Can the reaction be an elementary process? Explain.
Solution:
No. An elementary process would have a rate law with orders equal to its molecular ties and, Therefore, must be integers.

Q51. A reaction is first order in A and second order in B.
i) Write differential rate equation.
ii) How is the rate affected when concentration of B is tripled?
iii) How is the rate affected when concentration of both A and B is doubled?
Solution:
i) Rate – $k[A][B]^2$
ii) Rate becomes $(3)^2$= 9 times
iii) Rate becomes $(2)(2)^2$ =8 times

Q52. Reaction between NO_2 and F2 to give NO_2F takes place by the following mechanism:
$NO_2 + F_2 \rightarrow NO_2F + F$
$NO_2 + F \rightarrow NO_2F$

Write the rate expression for the reaction.
Solution:
Since the slow step is the rate determining: Rate=k $[NO_2][F_2]$

Q53. It has been found that for a reaction a large number of colliding molecules has energy more than threshold value, yet the reaction is slow. Why?
Solution:
This is because the colliding molecules may not have proper orientation at the time of collision, which is also a necessary condition for effective collisions.

Q54. What are zero order reactions? Give an example. What are units of k for zero order reaction?
Solution:
A zero order reaction is one in which rate of reaction remains unchanged by change in concentration of reactants. The rate of reaction remains constant throughout the course of reaction. e.g.

$$H_2 + I_2 \xrightarrow{h\nu} 2HI$$

Rate = $K[H_2]^0\,[I_2]^0$ order = 0

Rate = $K\,[A]^0$

∴ Unit of k = mol L^{-1} s^{-1}

Q55. Calculate the order of reaction from following data -
Rate [A] [B] $r_1 = 1\times10^{-2}$ 0.10 0.10 $r_2 = 8\times10^{-2}$ 0.20 0.20 $r_3 = 2\times10^{-2}$ 0.10 0.20

Solution:

Let rate = $K[A]^x\,[B]^y$

Order of reaction = $x + y$

$$\frac{r_2}{r_3} = \frac{8\times10^{-2}}{2\times10^{-2}} = \frac{(0.20)^x\,(0.20)^y}{(0.10)^x\,(0.20)^y}$$

$(2)^x = 4 \quad \therefore\ x = 2$

$$\frac{r_3}{r_1} = \frac{2\times10^{-2}}{1\times10^{-2}} = \frac{(0.2)^2\times(0.2)^y}{(0.1)^x\,(0.1)^y}$$

$\therefore\ (2)^y = 2 \quad \therefore\ y = 1$

Order of reaction = $x + y = 2 + 1 = 3$

Q56. The activation energy of reaction was found to be 12.49 k cal mol^{-1}. If temperature is Increased from 295K to 305K. Find the increase in rate of reaction.
Solution:
Given R = 0.002 K cal K^{-1} mol^{-1}

$$\log\frac{k_2}{k_1} = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{k_2}{k_1} = \frac{12.49}{2.303\times0.002}\left[\frac{305 - 295}{305\times295}\right]$$

= 0.301

$\frac{k_2}{k_1} = 2.00$

$k_2 = 2k_1$

Increase in rate = $(2.00 - 1)k_1 = 1.00k_1$

Increase in rate = $\frac{1.00k_1 \times 100}{k_1} = 100\%$

Q57. 75% of first order reaction is completed in 36 minutes. How long will it take to complete 50% of reaction?

Solution:

K = $\frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$

K = $\frac{2.303}{36} \log\left(\frac{100}{100-75}\right)$

K = 0.0639 log 4

K = 0.0639×0.602

= 0.0384

K = $\frac{2.303}{t} \frac{\log a}{a-x}$

0.0384 = $\frac{2.303}{t} \log \frac{100}{100-50}$

0.0384 = $\frac{2.303}{t} \log \frac{100}{50}$

0.0384 = $\frac{2.303}{t} 0.3010$

Or $0.0384 \times t$ = 0.6932

t = $\frac{0.6932}{0.0384}$

= 18.24 minutes

Q58. Write differences between molecularity and order of reaction.

Solution:

Molecularity	**Order**
1. It is the total number of molecules as present in balanced chemical reaction leading to formation of products.	It is the total number of molecule whose concentration changes.
2. Molecularity of reaction can never be in fractions.	Order of reaction can be in fractions.
3. Molecularity of reaction cannot be zero.	Order of reaction can be zero.

Q59. Find the activation energy of reaction given that —

$T_1 = 300k,\ T_2 = 340k,\ k_1 = 2 \times 10^{-2},\ k_2 = 8 \times 10^{-2}$

Solution:

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

or $\log \frac{8 \times 10^{-2}}{2 \times 10^{-2}} = \frac{Ea}{2.303 \times 8.314}\left[\frac{340 - 300}{300 \times 340}\right]$

or log 4 = $\frac{Ea}{19.14} \times \frac{40}{102000}$

or 0.602 = $\frac{40\ Ea}{1952280}$

∴ $Ea = \frac{0.602 \times 1952280}{40}$

= 29381.814 J/mol.

Q60. The half-life period of reaction is 10 minutes. How long it will take for concentration of reactant to be reduced to 10% of original.

Solution:

$\frac{0.693}{t_{1/2}} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$

t = $\frac{2.303}{t_{1/2}} \log \frac{a}{a-x}$

t = $\frac{2.303}{0.0693} \log \frac{100}{10}$

t = $33.23 \times \log 10$

t = $33.23 \times 1 = 33.23$ minutes

Q61. The slope of a line in the graph of $\log_{10} k$ verses $\frac{1}{T}$ for a reaction is –5642k. Calculate the activation energy for this reaction.

Solution:

Slope = $\frac{E_a}{2.303R}$

$E_a = slope \times 2.303 \times R$

$= -(-5642) \times 2.303 \times 8.314$

$= 108028.18\ J\ mol^{-1}$

$= 108.0\ kJ\ mol^{-1}$

Q62. The reaction $2A + B + C \rightarrow$ Product, is found to be first order with respect to A, second order with respect to B and zero order with respect to C.

(i) Write rate law for above reaction.

(ii) What will happen to rate of reaction when concentration of A, B and C are doubled.

Solution:

(i) Rate = $K[A]^1[B]^2[C]^0$

or $\frac{dx}{dt} = K[A][B]^2$

(iii) Let the rate of reaction r_1

$r_1 = K[A][B]^2$

When concentration of A, B and C are doubled, let the rate = r_2

$r_2 = k[2A][2B]^2[2C]^0$

$= k[2A] \times 4(B)^2$

$= 8k[A][B]^2 = 8r_1$

Q64. Rate of formation of product for certain reaction is $9.5 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}$. The initial concentration of reactant was found to 0.01 mol/L. Calculate the rate constant for the given second order reaction.

Solution:

For second order reaction-

Rate = $k[conc.]^2$

$9.5 \times 10^{-5} = k(0.01)^2$

k = $\frac{9.5 \times 10^{-5}}{(0.01)^2}$

$= 0.95\ mol^{-1} L\ s^{-1}$

Q65. In a first order reaction, 75% of reactants disappeared in 1.386 hrs. Calculate the rate constant of the reaction.

Solution:

$t = 1.386\ hrs \quad = 1.386 \times 60 \times 60\ sec = 4989.6\ sec$

K = $\frac{2.303}{t} \log \frac{a}{a-x}$

$= \frac{2.303}{4989.6} \log \frac{100}{25}$

$= 4.615 \times 10^{-4} \log 4$

$= 4.615 \times 10^{-4} \times 0.602$

$= 2.78 \times 10^{-4} s^{-1}$

Q66. $2X \rightleftharpoons 4Y + Z$ For the above change if concentration of y increases by 5×10^{-3} in 10 sec. Calculate the rate of appearance of y and rate of disappearance of x.

Solution:

Rate of reaction = $-\frac{1}{2}\frac{\Delta[x]}{\Delta t} = \frac{1}{4}\frac{[y]}{\Delta t} = \frac{\Delta[z]}{\Delta t}$

Rate of appearance of y = $\frac{\Delta y}{\Delta t} = \frac{5\times10^{-3}}{10}$

= $5\times10^{-4}\, mol\, L^{-1}\, s^{-1}$

Rate of disappearance of x = $\frac{-\Delta[x]}{\Delta t} = \frac{1}{2}\frac{[\Delta y]}{\Delta t} = \frac{1}{2}\times5\times10^{-4}$

= $2.5\times10^{-4} mol\, L^{-1}s^{-1}$

Q67. Write the expression for average and instantaneous rates for the following reaction- $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Solution:

Average rate = $-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$

Instantaneous rate = $-\frac{1}{4}\frac{d[NH_3]}{dt} = -\frac{1}{5}\frac{d[O_2]}{dt} = \frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$

Q68. A reaction $A \rightarrow$ Product is found to be third order reaction. What will happen to rate of reaction when concentration of A is doubled?

Solution:

$r_1 = k[A]^3$ (Given)

Conc. of A is doubled.

∴ It becomes 2A.

∴ $r_2 = k\,[2A]^3 = 8[A]^3 = 8r_1$

∴ Rate of reaction will increase by factor of 8.

Q69. Find the unit of k for n^th order reaction.

Solution:

For nth order reaction-

Rate = $k(conc)^n$

k = $\frac{rate}{[conc.]^n}$

Units of k = $\frac{mol/L\ sec}{(mol/L)n} = mol^{1-n}\, L^{n-1}\, s^{-1}$

Q70. For a reaction $X \rightarrow$ Products. The rate of reaction doubles when concentration of A is increased by 4. What is the order of reaction?

Solution:

Let order of reaction = n

$r = k[A]^n$ __________ (1)

$2r = k[4A]^n$ __________ (2)

Divide eq. (2) by eq. (1)

Q.71 Define (i) Activation energy (ii) Collision frequency

Solution:

(i) Activation energy: Activation energy is the excess energy that the reactant molecule must acquire in order to cross energy barrier and change into products.

Activation energy = Threshold energy –Average energy of reactant molecule

(ii) Collision frequency: The number of collisions per second per unit volume of reaction mixture is known as collision frequency.

$$\frac{2r}{r} = \frac{k[4A]^n}{k[A]^n}$$

$$= 2^{2n} \quad \therefore n = \frac{1}{2}$$

Q.72 $N_2O_5\,(in\ CCl_4) \rightarrow 2NO_2 + \frac{1}{2}O_2$

This reaction is of first order and rate constant of reaction is $6.2 \times 10^{-4}\,s^{-1}$.

Solution:

Rate = $k[N_2O_5]$

$= 6.2 \times 10^{-4} \times 1.75$

$= 10.93\,mol\,L^{-1}s^{-1}$

Q.73 The rate constant of a reaction is $5.0 \times 10^{-5}\,L$ mol^{-1} min^{-1}. What is the order of reaction?

Solution:

The units of reaction are (mol L^{-1})$^{-1}$ min^{-1} i.e. conc.$^{-1}$ time^{-1}. These are the units of k for second order reaction.

The order of reaction is 2.

Q74.The rate constant for first order reaction has the value $5.7 \times 10^{-3}\ sec^{-1}$. Find value of $t_{1/2}$

Solution:

$$k = \frac{0.0693}{t_{1/2}}$$

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

$$= \frac{0.693}{5.7 \times 10^{-3}}$$

= 121.5 s

Q.75 What is

(i)Ratelawexpression?

(ii) Rate determining step?

Solution:

(i) Rate law expression is the expression in which rate is given in terms of molar concentration of reactants with each term raised to power which is experimentally determined.

(ii) Rate determining step - The slowest step in a multiple step reaction which determines the overall rate of reaction is called rate-determining step.

Q.75 How does change in temperature effects rate constant? Write the relationship, which explains the temperature dependence of a reaction.
Solution:

For a chemical reaction, every 10? rise in temperature, nearly doubles the rate constant. Arrhenius established the relationship between rate constant and temperature of reaction.
$k = Ae^{-E_a/RT}$

Where, A = Arrhenius factor / frequency factor

E_a = Activation energy in J mol^{-1}

Q76. DDT on exposure to water decomposes. Half-life = 10 years. How much time will it take for its 90% decomposition?
Solution:
70 years

Q77. In the reaction 2A + B → a_2B, if the concentration of A is doubled and that of B is halved then the rate of reaction will:
Solution:
Increase by 2 times
Initially rate = $k[A]^2[B] = a^2b$, new rate = $k(2a)^2$ $(b/2)2ka^2b$

Q78. The chemical reaction was carried out at 300K and 280k. The rate constants were found to be K_1& K_2 respectively. Then
Solution:
$K_2 = 0.25K_1$

For every 10^0 rise in temperature, rate constant is doubled. Hence for 20^0 rises in the temperature rate constant will become 4 times.

Q79. In Arrhenius plot, intercept =
Solution:
ln A

$\ln k = -(E_a/RT) + \ln A$. Hence intercept = ln A

Q80. If I is the intensity of absorbed light and C is the concentration of AB for the Photochemical reaction AB + hν → AB* the rate of formation of AB* is directly proportional to:
Solution:
Rate of photochemical reaction is directly proportional to the Intensity of light.

Q81. When a biochemical reaction is carried out in laboratory from outside of human body in absence of enzyme then the rate of reaction obtained is 10^{-6} times then activation energy of reaction in presence of enzyme is:
Solution:
Different from E_a obtained in the laboratory
Rates are different due different activation energies.

Q82. 75% of the first order reaction was completed in 32 minutes. 50% was

Solution:
16
75% of the reaction is completed in two half lives.

Q82. The rate of gaseous reaction is given by the expression k[A][B]. If the volume of reaction

vessel is suddenly reduced to 1/4 of the initial volume the reaction rate relating to the original rate will be:

Solution:

16

rate=Kab when volume is reduced to 1/4 concentrations will become = 4 times. New rate =k (4a) (4b) =16kab=16 times.

SECTION-C (CHEMICAL KINETICS)

Q1. Give an example of pseudo order reaction.

Solution:

An example of pseudo order reaction is the hydrolysis of cane-sugar in the presence of mineral acid H_2SO_4 or HCl .

$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

An example of pseudo order reaction is the hydrolysis of easter in the presence of mineral acid H_2SO_4 or HCl .

$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

Q2. A reaction is first order in A and second order in B.

i) Write differential rate equation.

ii) How is the rate affected if the concentration is tripled.

iii) How is the rate affected when the concentration of both A and B are doubled?

iv) What is the significance of rate constant in the rate expression?

Solution:

i) Differential rate equation is:

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

ii) If the concentration of B is tripled the rate becomes 9 times

$\text{Rate} = k[A][3B]^2$

$= 9k[A][B]^3$

iii) If the concentration of both A and B are doubled the rate becomes 8 times.

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

$= 8k[A][B]^3$

iv) Significance: a) The value of rate constant (k) is independent of concentration but depends on temperature T

b) At fixed temperature, k is constant and characteristic of the reaction.

c) k is proportionality constant ,If both [A] and [B] are 1M each then rate of reaction is equal to k.

Q3 Express the relation between the half life period of a reactant and its initial concentration for a reaction of n^{th} order.

Solution:

$$t_{1/2} = \frac{1}{k[A_0]^{n-1}}$$

Q4. Is there any reaction for which reaction rate does not decrease with time?

Solution:

For a zero order reaction, the reaction rate does not decrease with time because it is independent of concentration of the reactants.

Q5. Express the relation between the half life of a reaction and its initial concentration if the reaction involved is of second order.

Solution:

For second order reaction $t_{1/2} \; \alpha \; \frac{1}{a}$, a is initial concentration.

Q6. A first order reaction takes 69.3 min for 50% completion. Setup an equation for determining the time need for 80% completion of this reaction.

Solution:

First order reaction: In first case

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$k = \frac{2.303}{t}\log\frac{100}{100-50}$$

$$k = \frac{2.303}{69.3}\log 2$$

In second case

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$k = \frac{2.303}{t}\log\frac{100}{100-80}$$

$$k = \frac{2.303}{t}\log 5$$

$$\frac{2.303}{t}\log 5 = \frac{2.303}{69.3}\log 2$$

$$t = \frac{2.303\log 5}{\frac{2.303}{69.3}\log 2}$$

$$= \frac{69.3\log 5}{\log 2} = 160.93\,\text{min}$$

Q7. A certain reaction is 50% complete in 20 minutes at 300Kand the same reaction is again 50% complete in five minutes at 350K.Calculate the activation energy if it is a first order reaction.(R= 8.314j/k/mol. And log 4 = 0.602)

Solution:

$$k_1 = \frac{0.693}{20\,\text{min}} = 0.03465\,\text{min}^{-1}$$

$$k_2 = \frac{0.693}{5\,\text{min}} = 0.1386\,\text{min}^{-1}$$

T_1 = 300K T_2 = 350K

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}[\frac{T_2-T_1}{T_1T_2}]$$
$$\log\frac{0.1386}{0.03465}=\frac{E_a}{2.303X8.314}[\frac{350\ -300}{350X300}]$$
$$log 4=\frac{E_a}{19.147}[\frac{50}{350x300}]$$
$$E_a=\frac{\log 4x19.147x350x300}{50}$$
$$=\frac{0.602x19.147x350x300}{50}$$
$$=\frac{1210281.87}{50}$$
$$=24205.6J/mol$$
$$=24.205kj/mol$$

Q8. **For the reaction A → B, the rate of reaction becomes 20 times when the concentration is increased 3 times. What is the order of the reaction?**

Solution:

R = $k[A]^n$ …….Eq (i)

27R = $k[3A]^n$ ……Eq(ii)

Dividing the above (ii) by (i)

$27 = 3^n$ n = 3

Hence the order of reaction is 3.

Q9. **The rate of a particular reaction triples when the temperature changes from 50^0C to 100^0C. Calculate the activation energy of reaction.(log 3 =0.4771.R = 8.314J/K/mol.**

Solution:

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}[\frac{T_2-T_1}{T_1T_2}]$$
$$E_a=2.303XRX[\frac{T_2XT_1}{T_1-T_2}]\log\frac{k_2}{k_1}$$
$$E_a=2.303X8.314JK^{-1}X[\frac{323KX373K}{(373-323)K}]\log 3$$
$$E_a=2.303X8.314X[\frac{323X373}{50}]X0.4771J/mol$$
$$E_a=2201.76J/mol$$
$$=22.012kJ/mol$$

Q.10 **Cl_2 + 2NO → 2NO, the rate law is expressed as rate =$k[Cl_2][NO]^2$ What is the over all order of this reaction?**

Solution: 3

Q11. **The decomposition of NH_3 of platinum surface $2NH_3$ → N_2 + $3H_2$ is zero order reaction with k = 2.5 $X10^{-4}$ mol/sec.What are the rates of production of N_2 and H_2?**

Solution:

$2NH_3$ → N_2 + $3H_2$

For a zero order reaction, Rate of the reaction = k

$$= \frac{rateofreactionofN_2}{1} = \frac{RateofproductionofH_2}{3}$$

$$RateofproductionofN_2 = K = 2.5X10^{-4}\,mol/\sec.$$

$$RateofproductionofH_2 = \frac{K}{3} = \frac{2.5X10^{-4}}{3}$$

$$= 0.83X10^{-4}\,mol/\sec.$$

Q12. What is meant by elementary reaction?

Solution:

Elementary reaction is the reaction which takes place in one step. For example

H_2 + I_2 → 2HI

Q13. Following reaction takes place in one step. How will the rate of this reaction change if volume of the reaction vessel is diminished to one-third of its original volume?

2NO + O_2 ↔ $2NO_2$

Solution:

The rate of the reaction 2NO + O_2 ↔ $2NO_2$ is given by

Rate (r) = k $[NO]^2[O_2]$

If the volume of the vessel is reduced to one-third of its original volume the rate of the reaction will be raised to 27 times.

$$r^1 = k(3[NO])^2(3[O_2]) = 27k[NO]^2[O_2] = 27r$$

Q14. Give the examples of pseudo first order reaction.

Solution:

Hydrolysis of cane sugar in the presence of mineral acids like HCl or H_2SO_4

$C_{12}H_{22}O_{11}$ + H_2O → $C_6H_{12}O_6$ + $C_6H_{12}O_6$

An example of pseudo order reaction is the hydrolysis of ester in the presence of mineral acid H_2SO_4 or HCl .

$CH_3COOC_2H_5$ + H_2O → CH_3COOH + C_2H_5OH

Q15. Express the relation between half life period of reactant and its initial concentration for a reaction of n^{th} order.

Solution:

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

Where n is the order of reaction.

Q16. The activation energy of a reaction is 75 .2kJ/mol in the absence of catalyst and 50.14kj/mol with a catalyst, how many times the rate of reaction grows in the presence of the catalyst if the reaction proceeds in the presence of catalyst at 25^0 C?

Solution:

$$l\,n\,k_1 = lnA - \frac{E_a}{RT}$$

$$l\,n\,k_2 = lnA - \frac{E_a}{RT}$$

$$lnk_2 - lnk_1 = \frac{E_{a1}}{RT} - \frac{E_{a2}}{RT}$$

$$ln\frac{k_2}{k_1} = \frac{1}{RT}(E_{a1} - E_{a2})$$

$$2.302 l\,og\frac{k_2}{k_1} = \frac{1}{298KX\,8.314JK^{-1}mol^{-1}}(75.2kJ/mol - 50.14kJ/mol)$$

$$log\frac{k_2}{k_1} = \frac{25.06X\,1000J/mol}{2.303X\,298KX\,8.314JK^{-1}mol^{-1}}$$

$$\log\frac{k_2}{k_1} = \frac{25060}{5705.8} = 4.40$$

$$\frac{k_2}{k_1} = Anti\log 4.40$$

$$= 2.5 \text{ X } 10^4$$

Hence rate of reaction raised by 25000 times in the presence of the catalyst.

Q17. A reaction is 50% complete in 2hours and 75% complete in 4 hours. What is the order of reaction.

Solution: First order

Q18. Express the rate of following reaction in terms of disappearance of hydrogen in the reaction. $3H_2 + N_2 \longrightarrow 2NH_3$

Solution:

$$Rate = \frac{1}{3}\frac{d[H_2]}{dt}$$

Q19. The rate constant for a first order reaction is $60s^{-1}$ .How much time will it takes to reduce the concentration of the reactant to $\frac{1}{10}^{th}$ of its initial value?

Solution:

$$t = \frac{2.303}{k}\log\frac{[R_0]}{[R]}$$

$$= \frac{2.303}{60}\log\frac{[1\ ]}{[1/1]}$$

$$= 0.038s$$

$$= 3.8X10^{-2}s.$$

Q20. State the condition at which a bimolecular reaction may become kinetically of first order reaction.

Solution:

A bimolecular reaction may become kinetically of first order reaction if any one of the reactant is taken in excess and the other is taken significantly low.

SECTION- D (CHEMICAL KINETICS)

1. Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide:
$2\ NO(g) + O_2(g) \rightarrow 2NO_2(g)$
The rate law for this reaction is
Rate=k $[NO]_2\,[O_2]$.
Propose a mechanism for the above reaction.

2. The decomposition of a compound is found to follow a first-order rate law. If it takes 15 minutes for 20 percent of original material to react, calculate i) the specific rate constant, ii) the time at which 10 percent of the original material remains un reacted, iii) the time it takes for the next 20 percent of the reactant left to react first 15 minutes.

3. Find the two-third life, $t_{2/3}$, of a first order reaction in which k=5.4 x 10 -14 s -1

4. First order reaction is 15% complete in 20 minutes. How long will it take to be 60% complete?

5. The catalyst decomposition of hydrogen peroxide was studied by titrating it at different intervals with $KMnO_4$. calculate the rate constant from the following data, assuming the reaction to be of first order:

t(sec)	0	600	1,200
$KMnO_4$ (ml)	22.8	13.8	8.2]

6. The decomposition of phosphene, 4 PH_3 (g) $\rightarrow$ P_4 + 6H_2 (g) has rate law, rate K [PH_3]. The rate constant is 6.0x 10^{-4} at 300K and activation energy is 3.05x 10^5 j/mol. What is the value of rate constant at 300K (R=8.314j/k/mol).

7. A first order reaction is 20% complete in10 mints. Calculate time for75%completion of the reaction.

8. In general it is observed that the rate of a chemical reaction doubles for every 10^0. If this generalization holds good for the reaction in the temperature range 295 – 305K, what would be the value of activation energy for this reaction.

9. What are photochemical reactions? Give an example to illustrate the course of a photo chemical reaction.

10. For a first order reaction, show that time require for the completion of 99.9% of reaction is 3 times time required for completion of 90% of the reaction.

11. A certain reaction is 50% complete in 20 mnts at 300K and the same reaction is again 50% complete in 5 minutes in 350K. Calculate the energy of activation if it is the reaction of first order.

12. The rate constant K of a reaction varies with temperature according to the equation: Log k = constant – E_a / 2.303 R T where Ea is activation energy for the reaction. When a graph is plotted for log k versus 1/T a straight line with a slope -6670 k is obtained. Calculate the activation energy for this reaction. State the units (R=8.314j/k/mol).

13. State the role of activated complex in a reaction and state its relation with activation energy.

14. For a certain reaction, it takes 5 minutes for the initial concentration of 0.5 moles per litre to become 0.25 mole per litre and another 5 minutes to become 0.125 made per liter. What is the order of this reaction and why it is so? Calculate the rate constant for the reaction.

15. The reaction is SO_2Cl_2 + SO_2 + Cl_2 is first order reaction with k = 2.2X10^{-5} at 320^0 C. what % of SO_2Cl_2 is decomposed on heating this gas for 90 minutes.

16. A certain reaction X + Y $\rightarrow$ products, is first order with respect to each reactant with k = 5 x 10^{-3} L/ mol/ s. Calculate the concentration of X remaining after 100 sec. If initial concentration of X was 0.100M and that of Y was 10M. State any approximation that you will make in obtaining the result.

17. Write stoichiometric equation whose mechanism is detailed bellow $A_2 \leftrightarrow 2A$ $k_f = 10^{10}$ sec^{-1} ,$k_b=10^{10}$ $M^{-1}sec^{-1}$. Write i) value of equilibrium constant for the first step ii) The rate law equation for the overall reaction in terms of initial concentrations.

18. The rate constant for the decomposition of N2O5 at various temperatures are given bellow Plot log k against 1/ T and calculate the energy of activation. Predict the reaction rate at 303K and 343K.

Temperature in centigrade	**Rate constant k**

0	7.87×10^{-7}
20	1.70×10^{-5}
40	2.57×10^{-4}
60	1.78×10^{-3}
80	2.14×10^{-2}

19. The reaction $2NO (g) + Cl_2 (g) \leftrightarrow 2NOCl$ was studied at - 10^0C, and the following data were obtained: Initial concentrations (mol L^{-1}) Initial rate of formation of NOCl mol L^{-1} min $^{-1}$)

Run	[NO]	[Cl_2]	
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.44

i) What is the order of reaction with respect to NO and with respect to Cl_2?
ii) What is the numerical value of the rate constant at 10^0 C?

20. The inversion of sucrose was studied in 1M HCl at 298 K. The following data were obtained for optical rotation at different time intervals.

Time (Min.)	0.0	10.0	20.0	30.0	-
Rotation (degrees)	24.5	22.3	20.3	18.4	-10.7

Calculate i) rate constant of the reaction, and ii) half-life period. Also show that the reaction follows the first order kinetics.

21. The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is 1st order reaction. i) After 55 seconds at 400K, the pressure of Cl_2o_7 falls from 0.062 to 0.044atm. Calculate the rate constant. ii) Calculate the pressure of Cl_2O_7 after 100 sec of decomposition at this temperature.

22. The rate of decomposition of N_2O_5 is 1.3×10^{-4} mol L^{-1} $_s^{-1}$ when [N_2O_5] concentration is 0.22M. What is the value of k for this first order reaction?

23. A gas phase decomposition of dimethyl either follows the first order kinetics

$$CH3 - O - CH_3(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 500^0 C and has a half life period of 14.5 min. Initially only dimethyl either is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 min? Assume ideal behavior.

24. A first order reaction $A \rightarrow B$ requires activation energy of 70 kj mol^{-1} . When 20% solution of A was kept at 25^0 C for 20 minutes, 25% of decomposition took place what will be the percentage decomposition of 30% solution at 40^0C in the same time.. Assume activation energy remains constant in this range of temperature.

25. The half-time for the decomposition of nitramide is 2.1 hour at 15^0C.
$NH_2NO_2(aq) \rightarrow N_2O(g) + H_2O(l)$ If 6.2 g of NH_2NO_2 is allowed to decompose, calculate: i) time taken for NH_2NO_2 to decompose 99% ii) volume of dry N_2O produced at this point measured at N.T.P.

26. Consider the data for the reaction between A and B

[A] (mol L^{-1})	**[B] (mol L^{-1})**	**Initial rate (mol L^{-1} s^{-1})**	
		T 300 K	**At 320 K**
2.5×10^{-4}	3.0×10^{-5}	5×10^{-4}	2×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4×10^{-3}	-----------
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	------------

Calculate i) Order w.r.t. A and B ii) rate constant at 300 K iii) the energy of activation iv) the pre-exponential factor

27. The rate constant of a first order reaction is 6 times when the temperature is increased from 350K to 410K. Calculate the energy of activation for the reaction.(R= 8.314 jk^{-1} mil^{-1}).

28. Consider the following data for the reaction A + B → products

Conc.of A (mol L^{-1})	Conc.of B (mol L^{-1})	Initial rate (mol L^{-1} s^{-1})
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	1.0×10^{-2}
0.5	0.5	1.0×10^{-2}

Calculate: i) the order w.r.t. A and B ii) the rate constant iii) reaction rate when the concentration of A and B are 0.2 M and 0.35 M respectively.

29. At 380^0 C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation is 200 kj / mol. Calculate the time required for 75% decomposition at 450^0 C.

30. The ionization constant of NH_4^+ ion in water is 5.6×10^{10} at 25^0C. The rate constant for the reaction between OH^- and NH_4^+ to form NH_3 and H_2O at 25^0C is 3.4×10^{10} L/ mol/ s. calculate the rate constant for proton transfer from H_2O to NH_3.

31. The rate constant for the first order decomposition of certain reaction is described by the equation

Log k(s^{-1})= 14.34 – (1.25×10^4K) / T

i) What is the energy of activation for this reaction?

ii) At what temperature will the half life period be 256 min?

32. Consider the following data for the reaction: A + B → products. Determine the overall order w.r.t.A and B.

Conc.of A (mol L^{-1})	**Conc.of B (mol L^{-1})**	**Initial rate (mol L^{-1} s^{-1})**
0.1 M	1.00 M	2.1×10^{-3}
0.2 M	1.00 M	8.4×10^{-3}
0.2 M	2.00 M	8.4×10^{-3}

33. The time required for 10% completion of a first order reaction at 298 K is equal to that required for it 25% completion at 308K if pre-exponential factor of reaction is 3.56×10^{9} s^{-1}. Calculate the rate constant at 318K and also energy of activation.

34. The rate constant of a reaction is 1.5×10^7 at 50^0 C and $4.5 \times 10^7 s^{-1}$ at 100^0C. Evaluate the Arrhenius parameters A and Ea.

35. For the reaction $N_2O_5 \rightarrow 2NO_2 + 0.5\ O_2$. Calculate the mole fraction of N_2O_5 decomposed at constant volume and temperature if initial pressure is 600 mm of Hg and the pressure at any time is 960mm of Hg. Assuming the gas to be ideal.

36. The rate constant for an iso-merization reaction is A → B 4.5×10^{-3} $min.^{-1}$. If initial concentration of A is 1M. Calculate the rate of reaction after one hour.

37. The vapour pressure of two miscible liquids A and B are 300 and 500 mm of Hg respectively. In a flask 10 moles of A is mixed with 12 moles of B. However, as soon as B is added, A starts polymerizing into a insoluble solid. The polymerization follows first order kinetics. After 100 minutes, 0.525 mole of a solute is dissolved which arrests the polymerization completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerization reaction. Assume negligible volume changes on mixing and polymerization and ideal behaviour for the final solution.

38. For the reaction, A + B → products, the following initial rates were obtained at various given initial concentrations

S.No.	**[A] mol L^{-1}**	**[B] mol L^{-1}**	**Rate (mol L^{-1} s^{-1})**
1	0.1	0.1	0.05
2	0.2	0.1	0.10
3	0.1	0.2	0.05

Write the rate law and find the rate constant of the above reaction.