CHEMICAL KINETICS

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(a) Effective collision

(b) Ineffective collision

THEORY

INTRODUCTION

Chemical Kinetics

(Kinesis : Movement)

The branch of chemistry which deals with the study of the rates of chemical reactions, the factors affecting the rates of the reactions and the mechanism by which the reactions proceed is called Chemical Kinetics.

Classification of reactions

On the basis of rates :

- Very fast reactions

    e.g. precipitation of AgCl

- Very slow reactions

    e.g. rusting of iron

- Reactions taking place at moderate speeds

    e.g. hydrolysis of starch

1. RATE OF A CHEMICAL REACTION

The rate of a reaction can be defined as the change in concentration of a reactant or a product in unit time.

1.1 Average rate

The rate of reaction measured over a definite time interval is called average rate of a reaction.

Consider a hypothetical reaction,

$$R \longrightarrow P$$

Average rate of reaction = (Decrease in concentration of R) / (Time taken)

$$= -[\Delta R] / \Delta t$$

Or = (Increase in concentration of P) / (Time taken)

$$= [\Delta P] / \Delta t$$

1.2 Instantaneous rate

Rate of change of concentration of any one of the reactants or products at that particular instant of time is called instantaneous rate.

As $\Delta t \rightarrow 0$ or $r_{inst} = \dfrac{-d\,[R]}{dt} = \dfrac{d\,[P]}{dt}$

IMPORTANT :

Rate of a reaction is always positive.

Since, $\Delta [R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with -1 to make the rate of the reaction a positive quantity.
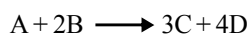
1.3 Units of rate of a reaction

Units of rate are concentration time^{-1}

e.g. mol L^{-1}s^{-1}; atm s^{-1} (for gaseous reactions)

1.4 Overall rate of a reaction

When there are several reactants and products the individual rates of the various components may differ as they would depend on the stoichiometric coefficients.

For a reaction,

$$A + 2B \longrightarrow 3C + 4D$$

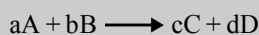Rate of disappearance of B = 2 × Rate of disappearance of A (2:1)

Rate of formation of C = 3 × Rate of disappearance of A (3:1)

Rate of formation of D = 4 × Rate of disappearance of A (4:1)

To define a unique value for the overall rate of the reaction we divide the individual rates by the respective coefficients and equate their signs.

Overall Rate $= -\,\Delta A / \Delta t = (-1/2)\,\Delta B / \Delta t = (+1/3)\,\Delta C / \Delta t = (+1/4)\,\Delta D / \Delta t$

Remember!!!

$aA + bB \longrightarrow cC + dD$

Overall Rate $= (-1/a) \ \Delta A / \Delta t = (-1/b) \ \Delta B / \Delta t$

$\qquad = (+1/c) \ \Delta C / \Delta t = (+1/d) \ \Delta D / \Delta t$

Instantaneous Rate $= (-1/a)dA/dt = (-1/b) \ dB/dt$

$\qquad = (+1/c) \ dC/dt = (+1/d) \ dD/dt$

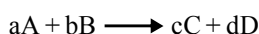## 2. DEPENDENCE OF RATE ON CONCENTRATION

Factors Influencing Rate of a Reaction

- concentration of reactants (pressure in case of gases),

- temperature and

- catalyst.

Dependence on Concentration :

2.1 Rate law

Consider a general reaction

$aA + bB \longrightarrow cC + dD$

The rate expression for this reaction is

Rate $\alpha \ [A]^x [B]^y$

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants.

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

$- d[R] \ / \ dt = k \ [A]^x [B]^y$

Above equation is known as **differential rate equation,**

k is a proportionality constant called **rate constant**.

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

IMPORTANT

Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.

e.g $\quad 2NO(g) + O_2(g) \rightarrow 2NO_2 \ (g) \quad$ Rate $= k \ [NO]^2[O_2]$

$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl \quad$ Rate $= k \ [CHCl_3] \ [Cl_2]^{1/2}$

2.2 Order of a Reaction

$aA + bB \longrightarrow cC + dD$

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

Sum of these exponents, i.e., x + y gives the overall order of a reaction where x and y represent the order with respect to the reactants A and B respectively.

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

Order of a reaction can be 0, 1, 2, 3 and even a fraction.

2.3 Units of rate constant

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

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

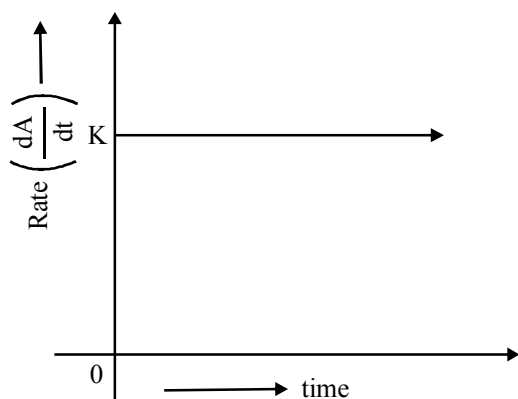| Reaction	Order	Units of rate constant
Zero order reaction	0	$\dfrac{mol \ L^{-1}}{s} \times \dfrac{1}{(mol \ L^{-1})^0}$ $= mol \ L^{-1} \ s^{-1}$
First order reaction	1	$\dfrac{mol \ L^{-1}}{s} \times \dfrac{1}{(mol \ L^{-1})^1} = s^{-1}$
Second order reaction	2	$\dfrac{mol \ L^{-1}}{s} \times \dfrac{1}{(mol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

3. INTEGRATED RATE EQUATIONS

3.1 Zero order reaction

The rate of the reaction is proportional to zero power of the concentration of reactants.

$R \rightarrow P$

Rate $= -[dR] \ / \ dt = kR^0$

Consider the reaction,

$$R \rightarrow P$$

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

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

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

Integrating both sides

$$[R] = -k\,t + I$$

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.
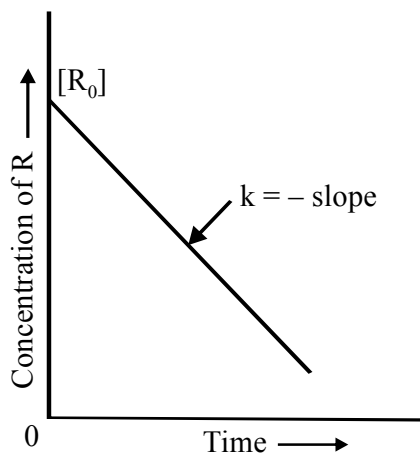
Substituting in equation

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

$$[R]_0 = I$$
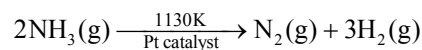
Substituting the value of I in the equation

$$[R] = -kt + [R]_0$$

$$\boxed{k = ([R]_0 - [R])/t}$$

e.g.

* The decomposition of gaseous ammonia on a hot platinum surface at high pressure.

$$2NH_3(g) \xrightarrow[\text{Pt catalyst}]{1130K} N_2(g) + 3H_2(g)$$

$$Rate = k\,[NH3]^0 = k$$

• Thermal decomposition of HI on gold surface

3.2 First order

The rate of the reaction is proportional to the first power of the concentration of the reactant R.

$$Rate = -d[R]/dt = k[R]$$

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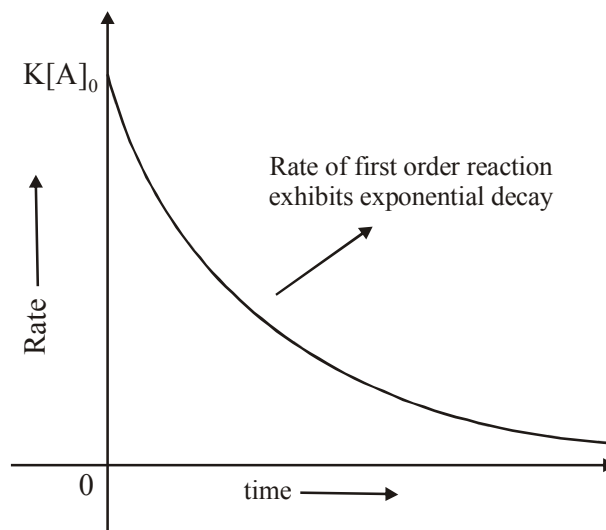
$$Rate = -\frac{d[R]}{dt} = k[R]$$

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

Integrating this equation, we get

$$\ln[R] = -kt + I \qquad ....(1)$$

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 can be written as

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

$\ln [R]_0 = I$

Substituting the value of I in equation

$\ln [R] = -kt + \ln [R]_0$ .... (2)

Rearranging this equation

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

or $k = \dfrac{1}{t} \ln \dfrac{[R]_0}{[R]}$ .... (3)

At time t_1 from equation (2)

$\ln [R]_1 = - kt_1 + \ln [R]_0$

At time t_2

$\ln [R]_2 = - kt_2 + \ln [R]_0$

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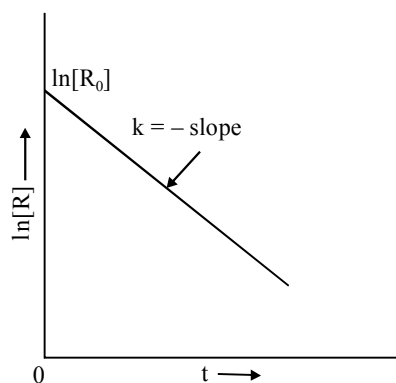
Subtracting

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

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

$$\boxed{k = \dfrac{1}{(t_2 - t_1)} \ln \dfrac{[R]_1}{[R]_2}}$$
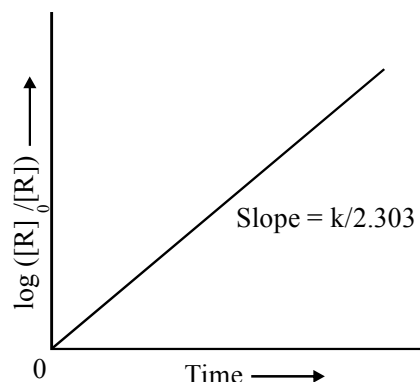
Comparing equation (2) with y = mx + c, if we plot $\ln [R]$ against t, we get a straight line with slope = –k and intercept equal to $\ln [R]_0$

The first order rate equation (3) can also be written in the form

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

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

e.g.

- Hydrogenation of ethane,

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

  Rate = k $[C_2H_4]$

- Decomposition of N_2O_5 and N_2O

3.3 Half-Life of a 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.

Represented as : $t_{1/2}$.

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

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

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

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

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

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

- For the first order reaction,

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

at $t_{1/2}$

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

So, the above equation becomes

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

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

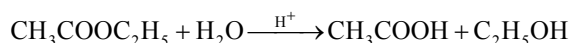$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

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

3.4 Pseudo First Order Reactions

Reactions which are not truly of the first order but under certain conditions become reactions of the first order.
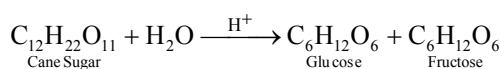
e.g.

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

Rate $= k \, [CH_3COOC_2H_5] \, [H_2O]$

The concentration of water does not get altered much during the course of the reaction. So, in the rate equation the term $[H_2O]$ can be taken as constant.

Rate $= k' \, [CH_3COOC_2H_5]$

where $k' = k [H_2O]$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{Glucose}{C_6H_{12}O_6} + \underset{Fructose}{C_6H_{12}O_6}$$
$$\underset{Cane\,Sugar}{}$$
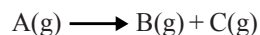
Rate $= k \, [C_{12}H_{22}O_{11}]$

3.5 Practical Analysis of First Order Reactions

Case - 1 : In gaseous phase reactions we prefer to measure the pressure of the gases or volume. For example the following reactions :

- For a first order gas phase reaction of the type :

$$A(g) \longrightarrow B(g) + C(g)$$

Let p_i be the initial pressure of A and p_t the total pressure at time 't'.

Integrated rate equation for such a reaction can be derived as :

Total pressure $p_t = p_A + p_B + p_C$ (pressure units) p_A, p_B and p_C are the partial pressures of A, B and C, respectively.

If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

$$
\begin{array}{cccc}
& A(g) & \rightarrow \quad B(g) & + \quad C(g) \\
At\ t=0 & p_i\ atm & 0\ atm & 0\ atm \\
At\ time\ t & (p_i - x)\ atm & x\ atm & x\ atm
\end{array}
$$
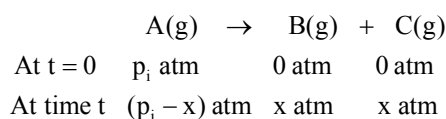
where, p_i is the initial pressure at time $t = 0$.

$p_t = (p_i - x) + x + x = p_i + x$

$x = (p_t - p_i)$

$p_A = p_i - x = p_i - (p_t - p_i)$

$= 2p_i - p_t$

$$k = \left(\frac{2.303}{t}\right)\left(\log \frac{p_i}{p_A}\right)$$

$$= \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

- For a first order gas phase reaction of the type :

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

The data given to us is:

Time	Pressure of gas C/Total Pressure
0	0
t	P_t
∞	P_∞

If we have to find the expression for k or verify that its a first order reaction then we will use the expression for k:

$$\ln \frac{a}{a-x} = kt$$

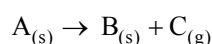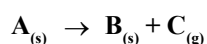But we don't know the values for a or a – x but we can find the above ratio by relating the given data with concentration values.

For gases, $P \propto$ number of moles

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

$t = 0$ a   0   0

$t = t$ a – x   x   x

$t = \infty$ 0   a   a

Now we can write:

$$\mathbf{P_t} \propto \mathbf{x}$$

$$P_\infty \propto \mathbf{a}$$

$$P_\infty - \mathbf{P_t} \propto \mathbf{a - x}$$

$$a/(a-x) = P_\infty / (P_\infty - P_t)$$

Now we can substitute this into the expression for k.

$$\mathbf{k = (1/t) \ln [\, P_\infty /(P_\infty - P_t)]}$$

The above expression can be used to evaluate the value of k from the pressure data and also verify that the reaction is of first order by checking 2-3 data points. In the above analysis the expression would have been same for the following reactions as well as the constants will cancel out.

$$\mathbf{A_{(s)} \rightarrow B_{(s)} + 2C_{(g)}}$$

$$\mathbf{A_{(s)} \rightarrow 2B_{(g)} + C_{(g)}} \text{ (if total pressure is given)}$$
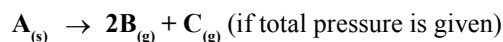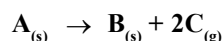
And the results will be same if the similar data is given in terms of volume.

Case 2 : If one of reactants is titrated with a red/ox reagent:

Suppose we have a reaction of the type:

$$A \rightarrow B + C$$
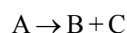
And suppose we detect the amount of A left by titrating it with some reagent and volume of that reagent reacting with the left over A is given at different time intervals:

Time	Volume of the reagent
0	V_0
t	V_t

Now the volume of the reagent will be proportional to the moles of A present. Therefore:

$$V_0 \propto a$$

$$V_t \propto a - x$$

We can evaluate k:

$$\mathbf{kt = \ln (V_0/V_t)}$$

If the same reagent reacts with all the reactants and products:

$$V_0 \propto a$$

$$V_t \propto a + x$$

$$2V_0 - V_t \propto a - x$$

$$\mathbf{kt = \ln (V_0/2V_0 - V_t)}$$

Reaction	Expression for rate constant
$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2a$	$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$ Here V_t = volume of O_2 after time t and V_∞ volume of O_2 after infinite time.
$NH_4NO_2 (aq) \rightarrow 2H_2O + N_2$	Same as above, here V_t and V_∞ are volumes of N_2 at time t and at infinite time respectively.
$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$	$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$ Here V_o and V_t are the volumes of $KMnO_4$ solution used for titration of same volume of reaction mixture at zero time (initially) and after time t.
$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH$ $+ C_2H_5OH$	$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$ Here V_0, V_t and V_∞ are the volumes of NaOH solution used for titration of same volume of reaction mixture after time, 0, t and infinite time respectively.
$\underset{d-sucrose}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{d-Glucose}{C_6H_{12}O_6} + \underset{\ell-Fructose}{C_6H_{12}O_6}$ (After the reaction is complete the equimolar mixture of glucose and fructose obtained is laevorotatory)	$k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$ Here, r_0, r_t and r_∞ are the polarimetric readings after time $0, t$ and infinity respectively.

3.6 Practical Methods of determining order of a reaction

i. Initial Rate Data Method:

We take different set of initial concentration and measure the initial rate. Then by keeping the concentration of one of the reactants constant and varying the other one we can study the effect on the rate and hence find out the order.

ii. Logarithmic data method:

For any order, be it fractional or integral, if we plot log (rate) vs log (concentration) graph it will always be a straight line for the reactions of the type:

$A \rightarrow$ products
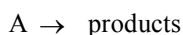
Rate, $r = k[A]^n$

log r = log k + n log [A]

We can take various data points and convert them to log values and plot them. We will obtain a straight line after curve-fitting with slope n and intercept log k. And hence we can find out the order and rate constant from the graph.
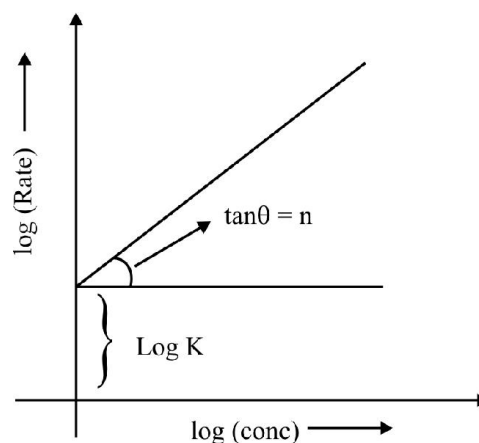
iii. Half Life Method:

If we take various concentrations of reactant and measure half life for all of them then we can find out the order of the reaction by mere observation or with the help of some calculations.

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

If simple observation is not possible then we can calculate the order of the reaction by taking two data points and using log for calculating n.

iv.   By integrated rate Equations:

If we have simple data of concentration and time we can use the integrated rate equations to find out the order. For this we will have to try and fit the data into the equation at various intervals and calculate the value of rate constants. If the values come out to be the same in all intervals then the data fits into the equation taken and we will know the order. For example, we have the following data:

Time: 0 t_1 t_2 t_3 .... t

Conc: A_0 A_1 A_2 A_3.......A_t

And if we assume that it can be of first order then we will calculate the values of k at minimum three data points by using the equation for first order:

$(1/t) \ln (A_0/A_t) = k$

Let these values be k_1, k_2 and k_3. If $k_1 = k_2 = k_3$ then it means that this data fits into the above equation hence the order is 1. If it doesn't we will have to try other equations as well.

v.   Isolation method:

In this method we try and eliminate one of the two reactants from the rate equation by taking it in excess. What happens is when the amount of a reactant is in excess its effect on the rate becomes marginal or negligible and then we can vary the concentration of the other reactant and observe its effect on rate and find out the order.

4. MOLECULARITY AND MECHANISM

4.1 Molecularity

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

Classification of reactions on the basis of Molecularity :

- **Unimolecular reactions :** when one reacting species is involved,

  for example, decomposition of ammonium nitrite.

  $NH_4NO_2 \rightarrow N_2 + 2H_2O$
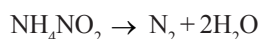
- **Bimolecular reactions :** involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

  $2HI \rightarrow H_2 + I_2$
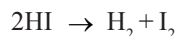
- **Trimolecular or termolecular reactions :** involve simultaneous collision between three reacting species, for example,

  $2NO + O_2 \rightarrow 2NO_2$
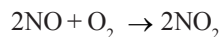
Reactions with molecularity greater than three are very rare.

4.2 Mechanism

The reactions taking place in one step are called **elementary reactions**.

When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called **complex reactions**.

The different steps in which the complex reaction takes place is called the **mechanism** of the reaction.

Rate determining step :

The overall rate of the reaction is controlled by the slowest step in a reaction called the **rate determining step**.

A complex reaction can be represented as a series of elementary steps.

For example

$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$
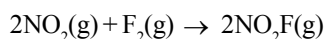
Experimentally, Rate of reaction $= k[NO_2][F_2]$

Probable mechanism :

Step-1:

$NO_2 + NO_2 \rightarrow NO + NO_3$ (slow)

Step-2 :

$NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)
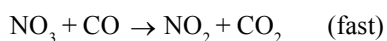
Slow step : bimolecular

Hence, a bimolecular reaction.

Reaction intermediates :

There are some species which are formed during the course of the reaction but do not appear in the overall reaction. They are called **reaction intermediates.**

e.g. NO_3 in the above example.

Distintion between Order and Molecularity of a reaction

Order

1. Order is the sum of the powers of the concentration of the reactants in the rate law expression.

2. It can be zero and even a fraction.

3. It is applicable to elementary as well as complex reactions.

4. It can be determined experimentally only and cannot be calculated.

5. For complex reaction, order is given by the slowest step.

Molecularity

1. Molecularity is the number of reacting species taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction.

2. It cannot be zero or a non integer.

3. It is applicable only for elementary reactions. For complex reaction molecularity has no meaning.

4. It can be calculated by simply adding the molecules of the slowest step.

5. Generally, molecularity of the slowest step is same as the order of the overall reaction.

5. TEMPERATURE DEPENDENCE

5.1 Activation Energy

According to collision theory, a reaction takes place because the reactant molecules collide with each other.

The minimum energy which the colliding molecules must have in order that the collision between them may be effective is called **threshold energy.**

The minimum extra amount of energy absorbed by the reactant molecules so that their energy becomes equal to threshold value is called **activation energy**.

Threshold energy = Activation energy + Energy possessed by the reactants

Less is the activation energy, faster is the reaction.

In order that the reactants may change into products, they have to cross an energy barrier (corresponding to threshold energy). Reactant molecules absorb energy and form an intermediate called activated complex which immediately dissociates to form the products.

e.g.

Intermediate
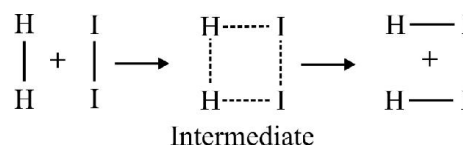
Reaction profile of an exothermic reaction
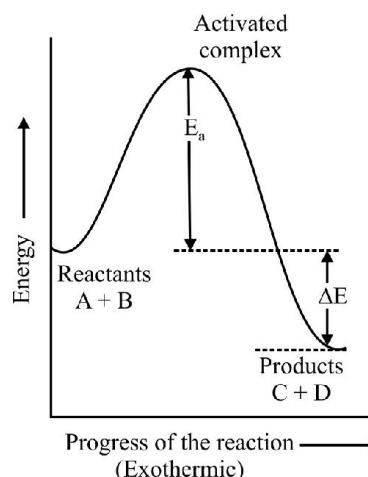
Reaction profile of an endothermic reaction
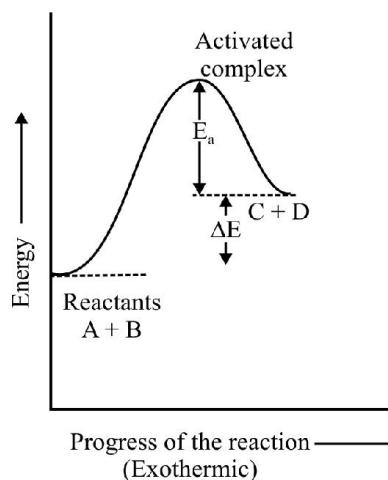
5.2 Temperature Dependence of the Rate of a Reaction

For a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.

Temperature coefficient = (Rate constant at $T + 10^0$) / (Rate constant at T^0)

Explanation :

At a particular temperature, if fractions of molecules are plotted versus corresponding kinetic energies, a graph of the type shown is obtained. The peak of the curve represents the kinetic energy possessed by the maximum fraction of molecules and is called **most probable kinetic energy**.
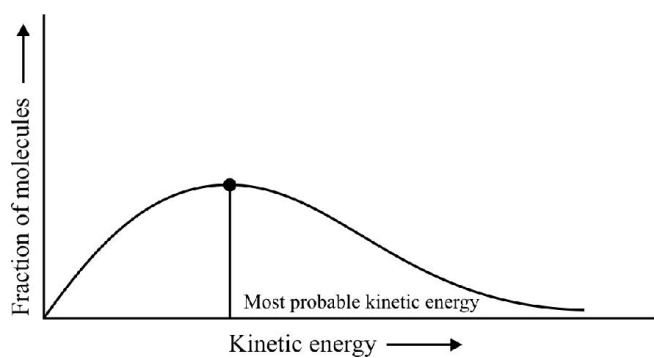
Distribution curve showing energies among gaseous molecules
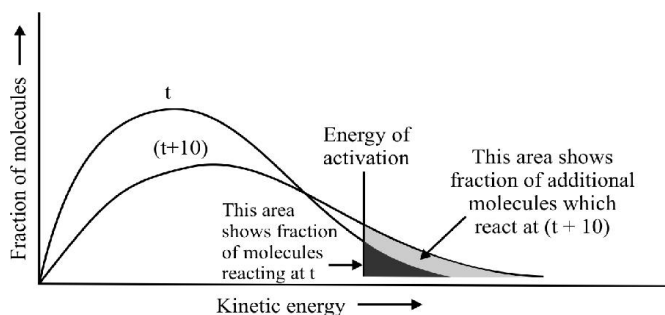
Distribution curve showing temperature dependence of rate of a reaction

With increase in temperature :

(i) maximum of the curve moves to the higher energy value i.e., most probable kinetic energy increases

(ii) the curve spreads to the right i.e., there is a greater proportion of molecules with much higher energies.

The area under the curve remains constant since total probability must be one at all times. At (t + 10), the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

Arrhenius equation

Quantatively, the temperature dependence of the rate of a chemical reaction can be explained by Arrhenius equation

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

where A is the Arrhenius factor or the frequency factor or pre-exponential factor. R is gas constant and E_a is activation energy measured in joules/mole.

The factor $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a.

Thus, it has been found from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

Taking natural logarithm of both sides of equation

$$\ln k = -\frac{E_a}{RT} + \ln A$$

The plot of ln k vs 1/T gives a straight line with slope $= -\frac{E_a}{R}$ and intercept = ln A.

At temperature T_1, equation

$$\ln k_1 = \frac{E_a}{RT_1} + \ln A$$

At temperature T_2, equation is

$$\ln k_2 = \frac{E_a}{RT_2} + \ln A$$

(since A is constant for a given reaction)

k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively.

Substracting equation form, we obtain

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

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

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

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

6. EFFECT OF CATALYST

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

e.g.

$$2KClO_3 \xrightarrow{MnO_2} 2\,KCl + 3O_2$$
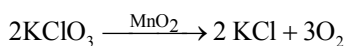
Action of the catalyst

According to intermediate complex theory, reactants first combine with catalyst to form intermediate complex which then decomposes to form the products and regenerating the catalyst.

$$
\begin{array}{l}
A + B + C \longrightarrow \quad A\cdots\cdots B \longrightarrow \quad A\!-\!B + C \\
\quad\quad \text{Catalyst} \quad\quad\quad\quad\quad\quad\quad \text{Product} \quad \text{Catalyst} \\
\text{Reactants} \quad\quad\quad\quad\quad C \quad\quad\quad\quad\quad\quad \text{(Regenerated)} \\
\quad\quad\quad\quad \text{Intermediate complex}
\end{array}
$$
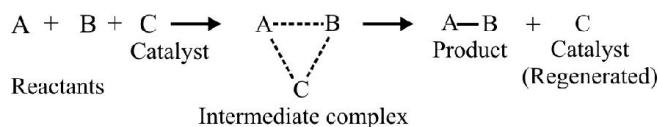
Effect of catalyst on activation energy
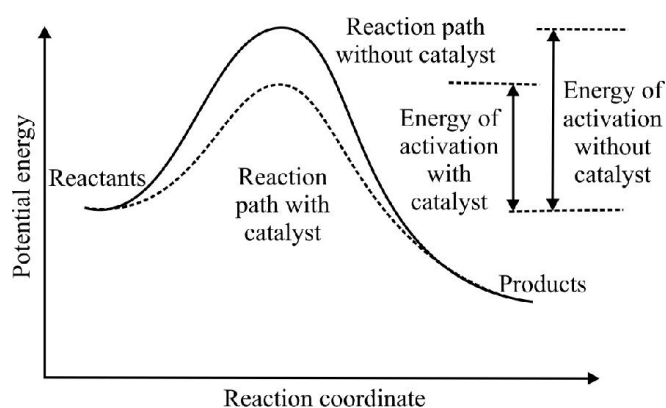
Catalyst provides an alternate pathway by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.

Important characteristics of catalyst :

❏ A small amount of the catalyst can catalyse a large amount of reactants.

❏ A catalyst does not alter Gibbs energy, ΔG of a reaction.

❏ It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.

❏ A catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster.

7. COLLISION THEORY OF CHEMICAL REACTIONS

According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.

Rate of reaction depends on the number of effective collisions which in turn depends on :

(i) Energy factor : colliding molecules must have energy more than threshold energy.

(ii) Steric or probability factor (P) : colliding molecules must have proper orientations at the time of collision.

Thus, the Arrhenius equation is modified to

$$\boxed{k = PZ_{AB}\, e^{-E_a/RT}}$$

8. IMPORTANT FORMULAE

8.1 Rate of Reactions

$(aA + bB \rightarrow cC + dD)$
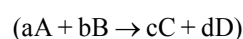
Instantaneous Rate $= -\dfrac{1}{a}\dfrac{dA}{dt} = -\dfrac{1}{b}\dfrac{dB}{dt} = \dfrac{1}{c}\dfrac{dc}{dt} = \dfrac{1}{d}\dfrac{dD}{dt}$

Average Overall Rate $= -\dfrac{1}{a}\dfrac{\Delta A}{\Delta t} = -\dfrac{1}{b}\dfrac{\Delta B}{\Delta t} = \dfrac{1}{c}\dfrac{\Delta C}{\Delta t} = \dfrac{1}{d}\dfrac{\Delta D}{\Delta t}$

8.2 Arrhenius Equation

$$k = Ae^{-\frac{E_a}{RT}}.$$

	Zero-Order	**First Order**	**Second Order**	**nth-Order**
Rate Law	$-\dfrac{d[A]}{dt} = k$	$-\dfrac{d[A]}{dt} = k[A]$	$-\dfrac{d[A]}{dt} = k[A]^2$	$-\dfrac{d[A]}{dt} = k[A]^n$
Integrated Rate Law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$	$\dfrac{1}{[A]^{n-1}} = \dfrac{1}{[A]_0^{n-1}} + (n-1)kt$ (Except first Order)
Units of Rate Constant (k)	$\dfrac{M}{s}$	$\dfrac{1}{s}$	$\dfrac{1}{M \cdot s}$	$\dfrac{1}{M^{n-1} \cdot s}$
Linear Plot to determine k	$[A]$ vs. t	$\ln([A])$ vs. t	$\dfrac{1}{[A]}$ vs. t	$\dfrac{1}{[A]^{n-1}}$ vs. t (Except first Order)
Half-life	$t_{1/2} = \dfrac{[A]_0}{2k}$	$t_{1/2} = \dfrac{\ln(2)}{k}$	$t_{1/2} = \dfrac{1}{[A]_0 k}$	$t_{1/2} = \dfrac{2^{n-1} - 1}{(n-1)k\,[A]_0^{n-1}}$ (Except first Order)

SOLVED EXAMPLES

Example - 1

What do you understand by 'Rate of reaction' ?

Sol. The change in the concentration of any one of the reactants or products per unit time is termed as the rate of reaction.

Example - 2

For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, how are the reaction expressions $-\dfrac{d[H_2]}{dt}$ and $\dfrac{d[NH_3]}{dt}$ interrelated ?

Sol. $-\dfrac{1}{3}\dfrac{d[H_2]}{dt} = +\dfrac{1}{2}\dfrac{d[NH_3]}{dt}$

Example - 3

For the assumed reaction $X_2 + 3Y_2 \rightarrow 2XY_3$, write the rate of equation in terms of rate of disappearance of Y_2.

Sol. Rate $= -\dfrac{d[X_2]}{dt} = -\dfrac{1}{3}\dfrac{d[Y_2]}{dt} = +\dfrac{1}{2}\dfrac{d[XY_3]}{dt}$

Rate of disappearance of $Y_2 =$

$$-\dfrac{d[Y_2]}{dt} = -3\dfrac{d[X_2]}{dt} = +\dfrac{3}{2}\dfrac{d[XY_3]}{dt}$$

Example - 4

Why is it that instantaneous rate of reaction does not change when a part of the reacting solution is taken out ?

Sol. Instantaneous rate is measured over a very small interval of time, hence, it does not change when a part of solution is taken out.

Example - 5

Define specific reaction rate or rate constant.

Sol. Specific reaction rate is the rate of reaction when the molar concentration of each of the reactants is unity.

Example - 6

The rate of decomposition of a substance A becomes eight times when its concentration is doubled. What is the order of this reaction ?

Sol. Rate law is,

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

$$r = k[A]^n \qquad \text{........ (i)}$$

$$8r = k[2A]^n \qquad \text{....... (ii)}$$

Dividing (ii) by (i), we get

$$\dfrac{8r}{r} = \dfrac{k[2A]^n}{k[A]^n}$$

$$8 = [2]^n$$

$$n = 3$$

The order of reaction is 3.

Example - 7

Rate of a reaction is given by the equation :

Rate $= k[A]^2[B]$

What are the units for the rate and the rate constant for this reaction ?

Sol. Units of rate $=$ **mol L^{-1} s^{-1}**

Units of k $= \dfrac{\text{Rate}}{[A][B]^2} = \dfrac{\text{mol } L^{-1}s^{-1}}{(\text{mol } L^{-1})(\text{mol } L^{-1})^2}$

$$= \textbf{L}^2 \textbf{ mol}^{-2} \textbf{ s}^{-1}.$$

Example - 8

$A + 2B \rightarrow 3C + 2D$. The rate of disappearance of B is 1×10^{-2} mol L^{-1} s^{-1}. What will be

(i) Rate of the reaction

(ii) Rate of change in concentration of A and C ?

Sol. (i) Rate $= -\dfrac{1}{2}\dfrac{d[B]}{dt} = \dfrac{1}{2} \times 1 \times 10^{-2}$

$$= \textbf{0.5} \times \textbf{10}^{-2} \textbf{ mol } \textbf{L}^{-1} \textbf{ s}^{-1}$$

(ii) Rate $= -\dfrac{d[A]}{dt} = -\dfrac{1}{2}\dfrac{d[B]}{dt} = +\dfrac{1}{3}\dfrac{d[C]}{dt}$

Rate of change in concentration of A

$$= -\dfrac{d[A]}{dt} = -\dfrac{1}{2}\dfrac{d[B]}{dt}$$

$$= 0.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

Rate of change in concentration of C

$$= +\dfrac{d[C]}{dt} = -\dfrac{3}{2}\dfrac{d[B]}{dt} = \dfrac{3}{2} \times 10^{-2}$$

$$= 1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

Example - 9

Calculate the overall order of a reaction which has the rate expression

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

Sol.   (a) Rate = k [A]^x [B]^y

order = x + y

So,   order $= \dfrac{1}{2} + \dfrac{3}{2} = 2$, i.e., **second order**

(b)   Order $= \dfrac{3}{2} + (-1) = \dfrac{1}{2}$ i.e., **half order.**

Example - 10

The specific reaction rate of a reaction is 6.2 × 10^{-3} mol lit^{-1} s^{-1}. What is the order of reaction ?

Sol.   Comparing with (mol L^{-1})$^{1-n}$ s^{-1}, we get

$$\text{mol}^{1-n} = \text{mol}^1$$

$$1 - n = 1$$

$$n = 0$$

i.e., **zero order reaction.**

Example - 11

The rate of reaction, 2NO + Cl$_2$ → 2NOCl is doubled when concentration of Cl$_2$ is doubled and it becomes eight times when concentration of both NO and Cl$_2$ are doubled. Deduce the order of the reaction.

Sol.   Let $r = k [NO]^x [Cl_2]^y$

$$2r = k [NO]^x [2Cl_2]^y \qquad \text{...... (i)}$$

$$8r = k [2NO]^x [2Cl_2]^y \qquad \text{........ (ii)}$$

Dividing (ii) by (i), we get

$$\dfrac{8r}{2r} = \dfrac{k[2NO]^x [2Cl_2]^y}{k [NO]^x [2Cl_2]^y}$$

$$2^2 = [2]^x$$

$$x = 2$$

Putting the value of x in (i), we get

$$2r = k [NO]^2 [2Cl_2]^y$$

Also $r = k [NO]^2 [Cl_2]^y$

$$\dfrac{2r}{r} = \dfrac{[2Cl_2]^y}{[Cl_2]^y}$$

$$2 = [2]^y$$

$$y = 1$$

$$\text{Rate} = k [NO]^2 [Cl_2]^1$$

Overall order of reaction = x + y = 2 + 1 = **3.**

Example - 12

Following reaction takes place in one step :

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$
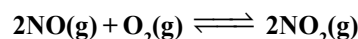
How will the rate of the above reaction change if the volume of the reaction vessel is diminished to one-third of its original volume ? Will there be any change in the order of the reaction with reduced volume ?

Sol.   Rate = k [NO]^2 [O$_2$]

Let initially, moles of NO = a, moles of O$_2$ = b, volume of the vessel = V. Then

$$[NO] = \dfrac{a}{V} \text{ M}, [O_2] = \dfrac{b}{V} \text{M}$$

$\therefore$ Rate (r$_1$) $= k\left(\dfrac{a}{V}\right)^2 \left(\dfrac{b}{V}\right) = k\dfrac{a^2 b}{V^3}$ .... (i)

Now, new volume $= \dfrac{V}{3}.$

$\therefore$ New concentrations : $[NO] = \dfrac{a}{V/3} = \dfrac{3a}{V}$

$$[O_2] = \dfrac{b}{V/3} = \dfrac{3b}{V}$$

$\therefore$ New rate $(r_2) = k\left(\dfrac{3a}{V}\right)^2 \left(\dfrac{3b}{V}\right) = \dfrac{27ka^2b}{V^3}$ .... (ii)

$\therefore$ $\dfrac{r_2}{r_1} = 27$ or $r_2 = 27\, r_1$ = rate becomes **27 times.**

Thus, there is no effect on the order of reaction.

Example - 13

For an elementary reaction $2A + B \rightarrow 3C$ the rate of appearance of C at time 't' is 1.3×10^{-4} mol L^{-1} s^{-1}.

Calculate at this time

(i) rate of the reaction.

(ii) rate of disappearance of A.

Sol. (i) $Rate = \dfrac{1}{3}\dfrac{d[C]}{dt} = \dfrac{1}{3} \times 1.3 \times 10^{-4}$

$= 0.43 \times 10^{-4}$ **mol L^{-1} s^{-1}**

(ii) $Rate = \dfrac{-d[A]}{dt} = \dfrac{2}{3} \times \dfrac{d[C]}{dt}$

$= 0.86 \times 10^{-4}$ **mol L^{-1} s^{-1}**

Example - 14

Differentiate between rate of reaction and reaction rate constant.

Sol. Rate of Reaction

1. Rate of reaction is the change in concentration of a reactant or product in a unit interval of time.

2. The rate of reaction at any instant of time depends upon the molar concentrations of the reactants at that time.

3. Its units are always mol litre^{-1} time^{-1}.

Reaction Rate Constant

1. It is the rate of reaction when the molar concentration of each of the reactants is unity.

2. The rate constant does not depend upon the concentrations of the reactants.

3. Its units depend upon the order of reaction.

Example - 15

A reaction : Reactant $\rightarrow$ Product is represented by
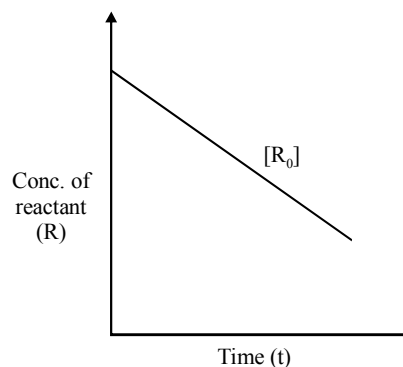
(i) the order of the reaction in this case.

(ii) What does the slope of the graph represent ?

Sol. (i) The reaction is of the zero order.

(ii) Slope of the straight line graph = $-k = \dfrac{d[R]}{dt}$.

Example - 16

What is meant by the 'rate constant, k' of a reaction ? If the concentration is expressed in mol L^{-1} units and time in seconds, what would be the units for k (i) for a zero order reaction and (ii) for a first order reaction ?

Sol. Rate constant is the rate of the reaction when the concentration of each reactant is taken as unity.

$\because$ rate = $k [A]^n$

$\therefore$ General unit of $k = \left(\dfrac{mol.}{lit.}\right)^{1-n} s^{-1}$

(i) For a zero order reaction $n = 0$

$\therefore$ Unit of $k = $ mol lit^{-1}s^{-1}

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

$\therefore$ Unit of $k = s^{-1}$

Example - 17

A first order reaction has a rate constant of 0.0051 min⁻¹. If we begin with 0.10 M concentration of the reactant, what concentration of reactant will remain in solution after 3 hours ?

Sol. For a first order reaction

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

$t = 3, h = 3 \times 60 \text{ min} = 180 \text{ min}$

$k = 0.0051 \text{ min}^{-1}, [R]_0 = 0.10 \text{ M}, [R] = ?$

$$180 \text{ min} = \frac{2.303}{0.0051 \text{ min}^{-1}} \log \frac{0.10}{[R]}$$

$$\log \frac{0.1}{[R]} = \frac{180 \text{ min} \times 0.0051 \text{ min}^{-1}}{2.303} = \frac{918}{2303}$$

$$\log \frac{0.1}{[R]} = 0.3986$$

$$\frac{0.1}{[R]} = \text{Anti log} (0.3986) = 2.503$$

$$[R] = \frac{0.1}{2.503} = 0.03995 M$$

[R] = 0.04 M

Example - 18

A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of reaction.

Sol. $$t_{20\%} = \frac{2.303}{k} \log \frac{a}{a - 0.2a}$$

$$t_{20\%} = \frac{2.303}{k} \log \frac{10}{8} = \frac{2.303}{k} \times .0969$$

$$t_{75\%} = \frac{2.303}{k} \log \frac{a}{a - 0.75a}$$

$$= \frac{2.303}{k} \log \frac{a}{0.25a} = \frac{2.303}{k} \log 4 = \frac{2.303}{k} \times 0.6021$$

$$\frac{t_{75\%}}{t_{20\%}} = \frac{2.303}{k} \times \frac{k}{2.303} \times \frac{0.6021}{0.0969}$$

$$\frac{t_{75\%}}{10} = \frac{0.6021}{0.0969}$$

$$t_{75\%} = \frac{10 \times 0.6021}{0.0969} = \textbf{62.13 min}$$

Example - 19

The reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ is a first order reaction with k = 2.2 × 10⁻⁵ at 320ºC. Calculate the percentage of SO_2Cl_2 that is decomposed on heating this gas for 30 minutes.

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

$$2.2 \times 10^{-5} = \frac{2.303}{30 \times 60} \log \frac{a}{a - x}$$

$$\log \frac{a}{(a-x)} = \frac{2.2 \times 10^{-5} \times 1800}{2.303} = 0.1719$$

$$\frac{a}{(a-x)} = \text{antilog} \, 0.1719 = 1.486$$

$a = 1.486a - 1.486x$

$0.486a = 1.486x$

$$\frac{x}{a} = \frac{0.486}{1.486} = 0.327 = \textbf{32.7\%}$$

Example - 20

Show that time required for the completion of three-fourths of a first order reaction is twice the time required for the completion of half reaction.

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

$$\frac{t_{3/4}}{t_{1/2}} = \frac{\frac{2.303}{k} \log \frac{a}{a - 3a/4}}{\frac{2.303}{k} \log \frac{a}{a - a/2}} = \frac{\log 4}{\log 2}$$

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

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

$$t_{3/4} = 2t_{1/2}$$

Example - 21

Show that in case of a first order reaction, the time required for 99.9% of the reaction to take place is about ten times than that required for half the reaction.

Sol.
$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{\dfrac{2.303}{k}\log\dfrac{100}{0.1}}{\dfrac{2.303}{k}\log\dfrac{100}{50}}$$

$$= \frac{\log 10^3}{\log 2}$$

$$= \frac{3\log 10}{0.3010} = \frac{30.0}{3.01}$$

$$t_{99.9\%} = 10t_{50\%}$$

Example - 22

The decomposition of $N_2O_5(g)$ is a first order reaction with a rate constant of 5×10^{-4} s^{-1} at 45ºC. i.e., $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. If initial concentration of N_2O_5 is 0.25M, calculate its concentration after 2 min. Also calculate half life for decomposition of $N_2O_5(g)$.

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

$$5\times 10^{-4} = \frac{2.303}{2\times 60}\log\frac{0.25}{[R]_t}$$

$$[R]_t = 0.23\ M$$

$$t_{1/2} = \frac{0.693}{5\times 10^{-4}}s = 1386s$$

Example - 23

The half-life for decay of radioactive ^{14}C is is 5730 years. An archaeological artefact containing wood has only 80% of the ^{14}C activity as found in living trees. Calculate the age of the artefact.

Sol.
$$t_{1/2} = 5730\ year$$

$$\therefore \qquad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} = 1.209\times 10^{-4}\ year^{-1}$$

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = \frac{2.303}{1.2\times 10^{-4}}\log\frac{100}{80}$$

$$t = \frac{2.303\times 10^4}{1.2}(\log 10 - \log 8) = \frac{2.303\times 10^4}{1.2}(1-3\log 2)$$

$$t = \frac{2.303}{1.2}\times 10^4\ (1-3\times 0.3010)$$

$$= \frac{2.303\times 0.097\times 10^4}{1.209}$$

t = 1847.7 years

Example - 24

Decomposition of phosphine (PH_3) at 120ºC proceeds according to the equation :

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

It is found that this reaction follows the following rate equation :

$$Rate = k\ [PH_3]$$

The half life of PH_3 in 37.9 s at 120ºC.

(i) How much time will be required for 3/4 of PH_3 to decompose ?

(ii) What fraction of the original amount of PH_3 will remain undecomposed after 1 minute ?

Sol. (i) Given $t_{1/2} = 37.95$

$$t_{1/2} = \frac{0.693}{k},\ k = \frac{0.693}{t_{1/2}} = 1.83\times 10^{-2}s^{-1}$$

$$k = \frac{0.693}{37.9}s^{-1},\ t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

$$t_{3/4} = \frac{2.303}{1.83 \times 10^{-2} s^{-1}} \log \frac{[A]_0}{\frac{[A]_0}{4}} = \frac{2.303}{1.83} \times 100 \log 2^2 \, s$$

$$t_{3/4} = \frac{2.303 \times 100 \times 2 \times 0.30105}{1.83} = \frac{138.64}{1.83} \, s$$

$$t_{3/4} = \mathbf{75.76 \, s}$$

(ii) $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{37.9} s^{-1} = 1.83 \times 10^{-2} s^{-1}$

$t = 1$ minute $= 60s$

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

$$60s = \frac{2.303}{1.83 \times 10^{-2} s^{-1}} \log \frac{[A]_0}{[A]}$$

$$\log \frac{[A]_0}{[A]} = \frac{60 \times 1.83 \times 10^{-2}}{2.303} = 0.4768$$

$$\log \frac{[A]_0}{[A]} = -0.4768 \, \overline{1}.5232$$

$$\frac{[A]}{[A]_0} = \text{Anti log } \overline{1}.5232 = 0.3336$$

$$\frac{[A]}{[A]_0} = \mathbf{0.334}$$

Example - 25

Hydrogen peroxide, H_2O_2 (aq) decomposes to H_2O(l) and O_2(g) in a reaction that is of first order in H_2O_2 and has a rate constant, $k = 1.06 \times 10^{-3}$ min^{-1}.

(i) How long will it take 15% of a sample of H_2O_2 to decompose ?

(ii) How long will it take 85% of a sample of H_2O_2 to decompose ?

Sol. (i) $t = \dfrac{2.303}{k} \log \dfrac{[A]_0}{[A]}$

Given : $k = 1.06 \times 10^{-3}$ min^{-1}, $\dfrac{[A]_0}{[A]} = \dfrac{100}{85}$

$$t = \frac{2.303}{1.06 \times 10^{-3} \text{min}^{-1}} \log \frac{100}{85} = \frac{2303}{1.06}$$

$$[2 \log 10 - \log 85] \text{ min}$$

$$t = \frac{2303}{1.06}[2 \times 1 - 1.9294] = \frac{2303 \times 0.0706}{1.06} = 153.39 \text{ min}$$

$$t = \mathbf{153.4 \ min.}$$

(ii) Given : $k = 1.06 \times 10^{-3}$ min^{-1}, $\dfrac{[A]_0}{[A]} = \dfrac{100}{15}$

$$t = \frac{2.303}{1.06 \times 10^{-3} \text{min}^{-1}}, \log \frac{100}{15} = \frac{2303}{1.06}$$

$$[2 \log 10 - \log 15] \text{ min}$$

$$= \frac{2303}{1.06}[2 \times 1 - 1.1761] = \frac{2303 \times 0.8239}{1.06} \text{ min}$$

$$t = \mathbf{1790 \ min.}$$

Example - 26
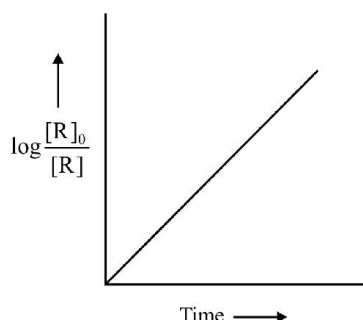
Answer the following questions on the basis of the above curve for a first order reaction $A \rightarrow P$:

(a) What is the relation between slope of this line and rate constant ?

(b) Calculate the rate constant of the above reaction if the slope is 2×10^{-4} s^{-1}.

Sol. (a) slope $= k/2.303$

(b) $k = 2.303 \times$ slope

$= 2.303 \times 2 \times 10^{-4}$

$= 4.606 \times 10^{-4}$ s^{-1}

Example - 27

What are zero order reactions ? Derive integrated rate equation for zero order reaction.

Sol. 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

$$[R] = -k\, t + I$$

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

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

$$[R]_0 = I$$

Substituting the value of I in the equation

$$[R] = -kt + [R]_0$$

Example - 28

What is half life period ? Show that the time required for the completion of half of the reaction is independent of intial concentration.

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

For the first order reaction,

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

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

So, the above equation becomes

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

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

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

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

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.

Example - 29

State any one condition under which a bimolecular reaction may be kinetically of first order.

Sol. A bimolecular reaction may become kinetically of first order if one of the reactants is present in excess.

Example - 30

What is meant by a pseudo first order reaction ? Give an example of a pseudo first order reaction and write the rate equation for the same.

Sol. A reaction which is of higher order but follows the kinetics of first order under special conditions is called a pseudo first order reaction.

Example, Acid hydrolysis of ethyl acetate.

$$CH_3-COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3-COOH + C_2H_5-OH$$
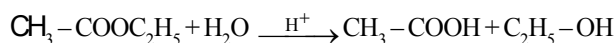
Here, the rate law is given by expression

$$\text{Rate} = k[CH_3-COOC_2H_5]$$

The concentration of H_2O is so large that it hardly undergoes any change during the reaction, therefore, it does not appear in the rate law.

Example - 31

What is meant by an elementary reaction ?

Sol. A reaction that takes place in one step is called an elementary reaction. Say, for example, reaction between H_2 and I_2 to form 2HI is an elementary reaction. Different steps of a complex reaction are each an elementary reaction.

Example - 32

When could order and molecularity of a reaction

(i) be the same and (ii) be different ?

Sol. (i) If the rate determining step involves all the reactants taking part in the reaction, i.e., it is a one-step reaction, then order and molecularity of the reaction is same.

(ii) If reaction involves more than one step, then order and molecularity are different.

Example - 33

Define the following terms giving an example for each :

(i) The order of a reaction

(ii) The molecularity of a reaction.

Sol. (i) Order of reaction may be defined as the sum of powers of the concentration of the reactants in the rate law expression.

For example consider the reaction

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$
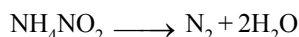
Experimentally, it is observed that the rate law for this reaction is

$$Rate = k\,[NH_4NO_2]$$

Hence, the order of reaction is 1.

(ii) Molecularity of a reaction may be defined as the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.

For example molecularity of the reaction

$2HI \longrightarrow H_2 + I_2$ is 2 as it involves simultaneous collision between two HI molecules.

Example - 34

Define the following :

(i) Elementary step in a reaction

(ii) Rate of a reaction

Sol. (i) **Elementary step :** Each step of a complex reaction is called an elementary step.

(ii) **Rate of reaction :** It is the change in the concentration of any of the reactants or products per unit time.

Example - 35

Distinguish between order and molecularity of reaction.

Sol. **Order**

1. Order is the sum of the powers of the concentration of the reactants in the rate law expression.
2. It can be zero and even a fraction.
3. It is applicable to elementary as well as complex reactions.
4. It can be determined experimentally only and cannot be calculated.
5. For complex reaction, order is given by the slowest step.

Molecularity

1. Molecularity is the number of reacting species taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction.
2. It cannot be zero or a non integer.
3. It is applicable only for elementary reactions. For complex reaction molecularity has no meaning.
4. It can be calculated by simply adding the molecules of the slowest step.
5. Generally, molecularity of the slowest step is same as the order of the overall reaction.

Example - 36

What is Arrhenius equation to describe the effect of temperature on rate of a reaction ?

Sol. The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation.

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

where A is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and Ea is activation energy measured in joules/mole (J mol^{-1}).

Example - 37

Define threshold energy of a reaction.

Sol. Threshold energy is the minimum energy which must be possessed by reacting molecules in order to undergo effective collision which leads to formation of product molecule.

Example - 38

Define collision frequency

Sol. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).

Example - 39

Define effective collision

Sol. The collisions in which molecules collide with sufficient kinetic energy and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

Example - 40

For a decomposition reaction, the values of rate constant k at two different temperatures are given below :

$k_1 = 2.15 \times 10^{-8}$ **L mol^{-1} s^{-1} at 650 K**

$k_2 = 2.39 \times 10^{-7}$ **L mol^{-1} s^{-1} at 700 K**

Calculate the value of activation energy for this reaction.

(R = 8.314 JK^{-1} mol^{-1})

Sol. $\log \dfrac{k_2}{k_1} = \dfrac{E_a}{2303R}\left(\dfrac{T_2 - T_1}{T_1\,T_2}\right)$

$E_a = \dfrac{2.303 \times R \times T_1 \times T_2}{T_2 - T_1}\log \dfrac{k_2}{k_1}$

$E_a = \dfrac{2.303 \times 8.314\,\text{J mol}^{-1}\text{K}^{-1} \times 650\text{K} \times 700\text{K}}{700\text{K} - 650\text{K}}\log \dfrac{2.39 \times 10^{-7}}{2.15 \times 10^{-8}}$

$E_a = \dfrac{19.147 \times 650 \times 700}{50}\log (23.9 - \log 2.15)\text{J mol}^{-1}$

$E_a = 174237.7\,(1.3783 - 0.3324)\text{J mol}^{-1}$

$E_a = 174237.7 \times 1.0459\,\text{J mol}^{-1} = 182235.2\,\text{J mol}^{-1}$

$E_a = \mathbf{182.24\ kJ\ mol^{-1}}$.

Example - 41

For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K, if k = 1.6 × 10^6 s^{-1} at 280 K ? [R = 8.31 JK^{-1} mol^{-1}]

Sol. Given $T_1 = 280$ K, $k_1 = 1.6 \times 10^6$ s^{-1}, $k_2 = ?$,

$\qquad\qquad E_a = 0$, $T_2 = 300$ K

By Arrhenius equation,

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

As, $E_a = 0$

$\therefore\qquad\qquad \log \dfrac{k_2}{k_1} = 0$

$\dfrac{k_2}{k_1} = 1 \qquad\qquad (\log 1 = 1\text{og }10^o = 0)$

$k_2 = k_1$

Thus, the rate constant at 300 K is $\mathbf{1.6 \times 10^6\ s^{-1}}$.

Example - 42

Rate constant k of a reaction varies with temperature according to the equation

$$\log k = \text{Constant} - \dfrac{E_a}{2.303\ RT}$$

where E$_a$ is the activation energy. When a graph is plotted for log k vs 1/T, a straight line with a slope − 6670 K is obtained. Calculate the energy of activation for the reaction in proper units. (R = 8.314 JK^{-1} mol^{-1})

Sol. $\text{Slope} = -\dfrac{E_a}{2.303\ R} = -6670\ k$

$E_a = 6670 \times 2.303 \times 8.314 = 127711.43\ \text{J mol}^{-1}$

$= \mathbf{127.711\ kJ\ mol^{-1}}$

Example - 43

In general it is observed that the rate of a chemical reaction doubles with every 10° rise in temperature, If this generalization holds good for a reaction in the temperature range 295 K and 305 K, what would be the value of activation energy for this reaction ?

(R = 8.314 JK^{-1} mol^{-1})

Sol. $T_1 = 295$ K $\quad k_1 = k$ (say), $T_2 = 305$K $\quad k_2 = 2k$

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

$\log \dfrac{2k}{k} = \dfrac{E_a}{2.303\ R}\dfrac{[305 - 295]}{305 \times 295}$

$$E_a = \frac{\log 2 \times 2.303 \times 8.314 \times 305 \times 295}{10}$$

$$= \frac{0.3010 \times 2.303 \times 8.314 \times 305 \times 295}{10}$$

$$= 51855.2 \text{ J mol}^{-1} = \textbf{51.855 kJ mol}^{-1}$$

Example - 44

The decomposition of phosphine

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

has the rate law, Rate = k [PH$_3$]

The rate constant is 6.0×10^{-4} s^{-1} at 300 K and activation energy is 3.05×10^5 J mol^{-1}. What is the value of rate constant at 310 K. [R = 8.314 JK^{-1} mol^{-1}]

Sol. $k_1 = 6.0 \times 10^{-4}$ s^{-1} $T_1 = 300$ K

$k_2 = ?$ $T_2 = 310$ K

$E_a = 3.05 \times 10^5$ J mol^{-1}

$$\log \frac{k_2}{k_1} = \frac{3.05 \times 10^5}{2.303 \times 8.314} \left[\frac{310 - 300}{310 \times 300}\right]$$

$$= \frac{3.05 \times 10^5 \times 10}{2.303 \times 8.314 \times 310 \times 300}$$

$$\log \frac{k_2}{k_1} = 1.718$$

$$\frac{k_2}{k_1} = \text{antilog } 1.718 = 51.62$$

$k_2 = 51.62 \times k_1 = 51.62 \times 6.0 \times 10^{-4}$ s^{-1} = $\textbf{3.1} \times \textbf{10}^{-2}$ s^{-1}

Example - 45

The rate of a particular reaction triples when temperatures changes from 50ºC to 100ºC. Calculate the activation energy of the reaction.

[log 3 = 0.4771; R = 8.314 JK^{-1} mol^{-1}]

Sol. $k_2 = 3k_1 \Rightarrow \frac{k_2}{k_1} = 3$

$T_2 = 50 + 273 = 323$ K, $T_2 = 100 + 273 = 373$ K

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

$$\log 3 = \frac{E_a}{2.303 \times 8.31} \left(\frac{373 - 323}{373 \quad 323}\right)$$

$$0.4771 = \frac{E_a}{19.147} \left(\frac{50}{120479}\right)$$

$$\Rightarrow E_a = \frac{0.4771 \times 19.127 \times 120479}{50}$$

$$\Rightarrow E_a = \left(\frac{50}{120479}\right) = \frac{0.4771 \times 19.127 \times 120479}{50}$$

$$\Rightarrow E_a = 22011.59 \text{J} \quad \Rightarrow \quad \textbf{E}_a = \textbf{22.0122 kJ mol}^{-1}$$

Example - 46

(a)   A reaction is of first order in A and of second order in B. Write the differential rate equation for this reaction.

(b)   The rate constant k of a reaction increases four fold when the temperature changes from 300 K to 320 K. Calculate the activation energy for the reaction. (R = 8.314 J mol^{-1} k^{-1})

Sol. (a)   Rate $= \frac{dx}{dt} = k[A][B]^2$

(b) $k_2 = 4k_1$ i.e. $\frac{k_2}{k_1} = 4$

$T_1 = 300$k $T_2 = 320$ k

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

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \left(\frac{320 - 300}{300 \times 320}\right)$$

$$2 \log 2 = \frac{E_a}{19.147} \left(\frac{20}{300 \times 320}\right)$$

$$E_a = \frac{2 \times 0.3010 \times 19.147 \times 300 \times 320}{20} = 55327 \text{J}$$

$$\textbf{E}_a = \textbf{55.327 kJ}$$

Example - 47

In a reaction $R \rightarrow P$ the concentration of R was observed. **Find the rate of the reaction**

Conc., Mol/L	50	25	15	10
Time (s)	0	10	20	30

Sol: In 1st time interval rate = –2.5 mol/Ls. In 2nd time interval rate = –1 mol/Ls. In 3rd time interval rate = – 0.5mol/Ls. The rate comes out as negative as the concentration of A is reducing with time.

Example - 48

In a reaction $H_2 + I_2 \rightarrow 2HI$ the rate of disappearance of I_2 is found to be 10^{-6} mole per litre per second. What would be the corresponding rate of appearane of HI ?

Sol. In the given reaction

rate = rate of disappearance of H_2 per mole

= rate of disappearance of I_2 per mole

= rate of appearance of HI per mole

$\therefore \quad -\dfrac{d[H_2]}{dt} = -\dfrac{d[I_2]}{dt} = +\dfrac{1}{2} \times \dfrac{d[HI]}{dt} = 10^{-6}$

$\therefore \quad \dfrac{d[HI]}{dt} = 2 \times 10^{-6}$ mole $L^{-1}s^{-1}$.

Example - 49

The reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl$ was studied at $-10\ ^\circ C$, and the following data were obtained :

Initial concentration, mol/L

R×n	NO	Cl_2	Initial rate of formation of NOCl, mol/L. min
1	0.10	0.10	0.18
2	0.10	0.20	0.35
3	0.20	0.20	1.45

What is the order of reaction with respect to NO and with respect to Cl_2 ?

Sol. When the Cl_2 concentration is doubled, holding the NO concentration constant (compare run 1 and 2), the initial rate doubles. Hence the reaction is first order with respect to Cl_2. When the NO concentration is doubled (compare runs 2 and 3), the initial rate quadruples. Hence the reaction is second order with respect to NO.

Example - 50

At $25^\circ C$, the second order rate constant for the reaction I^- + $ClO^- \rightarrow IO^- + Cl^-$ is $0.0606\ M^{-1}\cdot s^{-1}$. If solution is initially $3.50 \times 10^{-3}M$ with respect to each reactant, what will be the concentration of each species present after 300 s?

Sol. Since the concentrations of the two reactants are equal at the start and remain so throughout the entire reaction, the reaction can be treated as a simple second order reaction.

$k = 0.0606\ M^{-1}\cdot s^{-1}\ [B_0] = [A_0] = 3.50 \times 10^{-3}\ M$

$\dfrac{1}{[A]} - \dfrac{1}{[A_0]} = kt$

$\dfrac{1}{[A]} - \dfrac{1}{3.5 \times 10^{-3}} = (0.0606)\,(300) = 18.18$

$\dfrac{1}{[A]} = 18.18 + 285.7 = 303.9$

$[A] = 3.29 \times 10^{-3}\ M = [B]$

Example - 51

In the course of the reaction
$CH_3COOCH_3\,(g) \rightarrow C_2H_4\,(g) + H_2\,(g) + CO(g)$
the initial pressure was found to be 0.42 atm while after 6.5 minutes, it was 0.54 atm. If the reaction follows first order kinetics, find the rate constant.

Sol. Let the initial number of moles of CH_3COOCH_3 be a.

Initial moles :   a   0   0   0

$\qquad\qquad CH_3COOCH_3 \rightarrow C_2H_4 + H_2 + CO$

Moles after t :   (a – x)   x   x   x
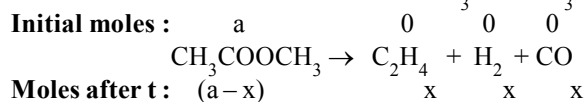
According to the given data,

a = 0.42 (initial moles corresponds to 0.42 atm)

and $\{(a-x)+x+x+x\} = 0.54$

(Mole after 6.5 min corresponds to 0.54 atm)

or a + 2x = 0.54

or $x = \dfrac{0.54-0.42}{2} = 0.06$.

Applying first-order rate equation,

$k = \dfrac{2.303}{6.5}\log\dfrac{0.42}{0.42-0.06} = 0.0237\ min^{-1}$

Example - 52

The decompositon of N_2O into N_2 and O in the presence of argon follows second-order kinetics with $k = (5.0 \times 10^{11})\ e^{-29000K/T}$. Calculate the energy of activation.

Sol. Comparing the given equation with Arrhenius's equation, we have,

$\dfrac{E}{RT} = \dfrac{29000K}{T}$ $E = 2900 \times 8.314 = 241\ kJ/mole$.

Example - 53

The optical rotation of cane sugar in 0.5 N lactic acid at 25ºC at various time intervals are given below :

Time (min)	0	1435	11360	∞
Rotation (º)	34.50º	31.10º	13.98º	−10.77º

Show that the reaction is of first order.

Sol. $C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Lactic acid}} C_6H_{12}O_6 + C_6H_{12}O_6$
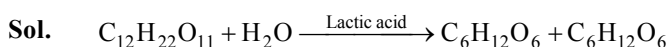
Sucrose (excess)   Glucose Fructose

Dextrorotatory   Dextro   Laevo

Laevorotatory

Since in this reaction dextro form changes to laevo form, the optical rotation decreases with the progress of the reaction. Thus change in rotation is proportional to the amount of sugar remained after different time intervals. We now have,

Time (min)	0	1435	11360	∞
Change in rotation (º)	34.50−(−10.77) =45.27 (a)	31.10−(−10.77) =41.87 (a−x)	13.98−(−10.77) =24.75 (a−x)	−10.77−(−10.77) =0

Substituting the data in Equation (5),

for t = 1435 min

$k_1 = \dfrac{2.303}{1435}\log\dfrac{45.27}{41.87} = 5.442\times10^{-5}$

and, for t = 11360 min

$k_1 = \dfrac{2.303}{11360}\log\dfrac{45.27}{24.75} = 5.311\times10^{-5}$

The values of k_1 are fairly constant and so the reaction is of first order.

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

Rate of Reaction

1. The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2}\frac{d[C]}{dt} = -\frac{1}{3}\frac{d[D]}{dt} = +\frac{1}{4}\frac{d[A]}{dt} = -\frac{d[B]}{dt}.$$

The reaction is

(a) $4\,A + B \rightarrow 2\,C + 3\,D$ (b) $B + 3\,D \rightarrow 4\,A + 2\,C$

(c) $A + B \rightarrow C + D$ (d) $B + D \rightarrow A + C.$

2. The rate of formation of ammonia by the reaction :

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

expressed as $\frac{d[NH_3]}{dt} = 2.5 \times 10^{-4}\,mol\,L^{-1}\,s^{-1}$. The rate of

consumption expressed in terms of H_2 as $\frac{-d[H_2]}{dt}$ will be

(a) double   (b) Three times

(c) same

(d) one and a half time of that expressed in terms of NH_3.

3. For the reaction. $2\,HI \rightarrow H_2 + I_2$, the expression $-\frac{1}{2}\frac{d[HI]}{dt}$

represents

(a) The rate of formation of HI

(b) The rate of disappearance of HI

(c) The instantaneous rate of the reaction

(d) The average rate of reaction.

4. The units of rate of reaction are

(a) litre mol $L^{-1}\,s^{-1}$ (b) mol $L^{-1}s^{-1}$

(c) mol s^{-1} (d) mol s^{-1}

5. Consider the reaction, $2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$. In the reaction NO_2 is being formed at the rate of $0.0125\,mol\,L^{-1}\,s^{-1}$. What is the rate of reaction at this time ?

(a) $0.0018\,mol\,L^{-1}\,s^{-1}$ (b) $0.0031\,mol\,L^{-1}\,s^{-1}$

(c) $0.0041\,mol\,L^{-1}\,s^{-1}$ (d) $0.050\,mol\,L^{-1}\,s^{-1}$

6. For a reaction $R \rightarrow P$, the concentration of a reactant changes from 0.05 M to 0.04 M in 30 minutes. What will be the average rate of reaction in minutes ?

(a) $4 \times 10^{-4}\,M\,min^{-1}$ (b) $8 \times 10^{-4}\,M\,min^{-1}$

(c) $3.3 \times 10^{-4}\,M\,min^{-1}$ (d) $2.2 \times 10^{-4}\,M\,min^{-1}$

7. In a reaction $2\,HI \rightarrow H_2 + I_2$, the concentration of HI decreases from $0.5\,mol\,L^{-1}$ to $0.4\,mol\,L^{-1}$ in 10 minutes. What is the rate of reaction during this interval ?

(a) $5 \times 10^{-3}\,M\,min^{-1}$ (b) $2.5 \times 10^{-3}\,M\,min^{-1}$

(c) $5 \times 10^{-2}\,M\,min^{-1}$ (d) $2.5 \times 10^{-2}\,M\,min^{-1}$

8. For the reaction $4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O,$ if the rate of disappearance of NH_3 is $3.6 \times 10^{-3}\,mol\,L^{-1}\,s^{-1}$, what is the rate of formation of H_2O ?

(a) $5.4 \times 10{-3}\,mol\,L^{-1}\,s^{-1}$ (b) $3.6 \times 10^{-3}\,mol\,L^{-1}\,s^{-1}$

(c) $4 \times 10^{-4}\,mol\,L^{-1}\,s^{-1}$ (d) $0.6 \times 10^{-4}\,mol\,L^{-1}\,s^{-1}$

9. Nitrogen dioxide (NO_2) dissociates into nitric oxide (NO) and oxygen (O_2) as follows :

$$2\,NO_2 \rightarrow 2\,NO + O_2$$
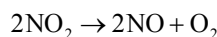
If the rate of decrease of concentration of NO_2 is $6.0 \times 10^{-12}\,mol\,L^{-1}\,s^{-1}$. What will be the rate of increase of concentration of O_2 ?

(a) $3 \times 10^{-12}\,mol\,L^{-1}\,s^{-1}$ (b) $6 \times 10^{-12}\,mol\,L^{-1}\,s^{-1}$

(c) $1 \times 10^{-12}\,mol\,L^{-1}\,s^{-1}$ (d) $1.5 \times 10^{-12}\,mol\,L^{-1}\,s^{-1}$

Rate law

10. For the gaseous reaction $2\,A + B \rightarrow C + D$, the rate is given by k [A] [B]. The volume of the container containing the reaction mixture is suddenly reduced to one fourth of its original volume. with respect to the original rate, now the rate would be
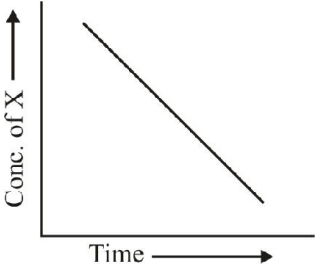
(a) $\frac{1}{16}$ (b) $\frac{1}{8}$

(c) 16 times   (d) 8 times

11. The rate of reaction $A + B + C \rightarrow$ Products is given by

Rate $= k\,[A]^{1/2}\,[B]^{1/3}\,[C]$

The order of the reaction is :

(a) 1   (b) 3

(c) $\dfrac{5}{6}$ (d) $\dfrac{11}{6}$

12. For the reaction $CH_3COCH_3 + I_2 \xrightarrow{H^+}$ Products, the rate is governed by the expression

$$\dfrac{dx}{dt} = k\,[Acetone]\,[H^+]$$

The order w.r.t. iodine is

(a) 0   (b) 1

(c) 2   (d) 3.

13. The rate of a reaction $2X + Y \rightarrow$ Products is given by

$$\dfrac{d[Y]}{dt} = k\,[X]^2\,[Y]$$

if X is present in large excess, the order of the reaction is :

(a) zero   (b) two

(c) one   (d) three

14. For a reaction $pA + qB \rightarrow$ products, the rate law expression is $r = k\,[A]^m\,[B]^n$ then

(a) $(p + q) \neq (m + n)$ (b) $(p + q) = (m + n\}$

(c) $(p + q)$ may or not be equal to $(m + n)$

(d) $(p + q) > (m + n)$

15. The rate constant of a reaction is 2.5×10^{-2} minutes^{-1}. The order of the reaction is

(a) one   (b) zero

(c) two   (d) three.

16. In the reaction $2A + B \rightarrow$ Products, the order w.r.t. A is found to be one and w.r.t. B equal to 2. Concentration of A is doubled and that of B is halved, the rate of reaction will be

(a) doubled   (b) halved

(c) remain unaffected   (d) four times.

17. For the reaction $A + B \rightarrow C + D$, doubling the concentration of both the reactants increases the reaction rate by 8 time and doubling the initial concentration of only B simply doubles the reaction rate. The rate law for the reaction is

(a) $r = k\,[A]\,[B]^2$ (b) $r = k\,[A]\,[B]$

(c) $r = k\,[A]^{1/2}\,[B]$ (d) $r = k\,[A]^2\,[B]$.

18. In the presence of acid, the initial concentration of cane-sugar was reduced from 0.2 M to 0.1 M in 5 hrs and to 0.05 M in 10 hrs. The reaction must be of

(a) zero order   (b) first order

(c) second order   (d) fractional order

19. The rate of formation of a dimer in a second order dimerisation reaction is $9.1 \times 10^6\,mol\,L^{-1}\,s^{-1}$ at $0.01\,mol\,L^{-1}$ monomer concentration. What will be the rate constant for the reaction ?

(a) $9.1 \times 10^{-2}\,L\,mol^{-1}\,s^{-1}$ (b) $9.1 \times 10^{-6}\,L\,mol^{-1}\,s^{-1}$

(c) $3 \times 10^{-4}\,L\,mol^{-1}\,s^{-1}$ (d) $27.3 \times 10^{-2}\,L\,mol^{-1}\,s^{-1}$

Integrated rate law

20. A reaction is of first order when

(a) The amount of product formed increases linearly with time

(b) The rate decreases linearly with time

(c) The rate is linearly related to the concentration of the reactant

(d) The concentration of the reactant decreases linearly with time.

21. For the first order reaction $A \rightarrow$ Products, which one of the following is the correct plot of log [A] versus time ?
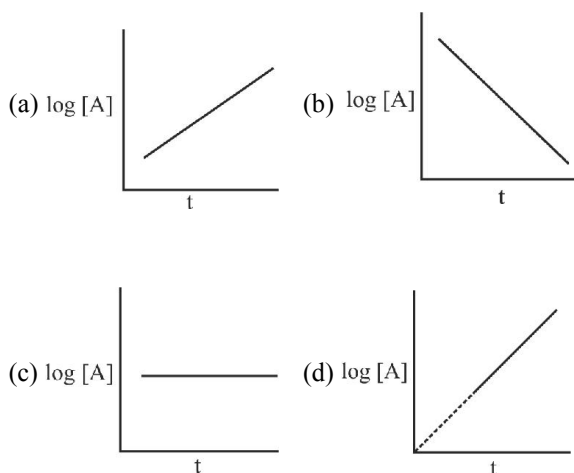
22. The half-life period of a first order reaction is

(a) directly proportional to the initial concentration 'a'

(b) inversely proportional to 'a'

(c) independent of 'a'

(d) independent of the rate constant of the reaction

23. Which of the following represents the expression for 3/4th life of a first order reaction

(a) $\dfrac{k}{2.303} \log 4/3$ (b) $\dfrac{2.303}{k} \log 3/4$

(c) $\dfrac{2.303}{k} \log 4$ (d) $\dfrac{2.303}{k} \log 3$.

24. The half-life of a radioactive isotope is three hours. If the initial mass of the isotope was 300 gm, the mass which remained undecayed in 18 hours would be

(a) 2.34 gm   (b) 1.17 gm

(c) 9.36 gm   (d) 4.68 gm

25. 1.386 hours are required for the disappearance of 75% of a reactant of first - order reaction. What is the rate constant of the reaction ?

(a) $3.6 \times 10^{-3} \, s^{-1}$ (b) $7.2 \times 10^{-3} \, s^{-1}$

(c) $2.7 \times 10^{-4} \, s^{-1}$ (d) $1.8 \times 10^{-3} \, s^{-1}$

26. The correct expression for the rate constant for reactions of zero order is

(a) $k = [A_0]/2t$

(b) $k = \dfrac{1}{t}\{[A_0] - [A]\}$

(c) $k = \dfrac{1}{t}\{[A] - [A_0]\}$

(d) $k = \dfrac{2.303}{t} \log \{[A_0] - [A]\}$

27. If 'a' is the initial concentration of the reactant, the time taken for completion of the reaction, if it is of zero order, will be

(a) a/k   (b) a/2k

(c) 2a/k   (d) k/a

28. Which one of the following formulae represents the first order reaction ?

(a) $k = \dfrac{2.303}{t} \log \dfrac{[A]}{[A]_0}$

(b) $k = \dfrac{2.303}{t} \log \dfrac{a - x}{a}$

(c) $[A] = [A_0] e^{-kt}$

(d) $k = \dfrac{2.303}{t} \log \dfrac{a}{a + x}$.

29. For a general reaction $X \longrightarrow Y$, the plot of conc. of X vs time is given in the figure. What is the order of the reaction and what are the units of rate constant ?

(a) Zero, $mol \, L^{-1} \, s^{-1}$ (b) First, $mol \, L^{-1} \, s^{-1}$

(c) First, s^{-1} (d) Zero, $L \, mol^{-1} \, s^{-1}$

30. The rate constant of a first order reaction is $15 \times 10^{-3} \, s^{-1}$. How long will 5.0 g of this reactant take to reduce to 3.0 g ?

(a) 34.07 s   (b) 7.57 s

(c) 10.10 s   (d) 15 s

31. Half-life period of a first order reaction is 10 min. What percentage of the reaction will be completed in 100 min ?

(a) 25%   (b) 50%

(c) 99.9%   (d) 75%

32. The half-life for radioactive decay of 14C is 5730 years. An archaeological artifact containing wood had only 80% of the 14 C found in a living tree. The age of the sample is

(a) 1485 years   (b) 1845 years

(c) 530 years   (d) 4767 years.

33. What will be the half-life of the first order reaction for which the value of rate constant is 200 s^{-1} ?

(a) 3.46×10^{-2} s

(b) 3.46×10^{-3} s

(c) 4.26×10^{-2} s

(d) 4.26×10^{-3} s

Practical Methods to Determine Order of Reaction

34. Half life of a chemical reaction at a particular concentration is 50 min. When the concentration of the reactant is doubled, the half life becomes 100 min, then the order of the reaction is :

(a) zero

(b) first

(c) second

(d) third

Practical Analaysis of First Order Reaction

35. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.

$$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$$
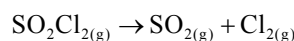
Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.5
2	100	0.6

What is the rate of reaction when total pressure is 0.65 atm ?

(a) 0.35 atm s^{-1}

(b) 2.235×10^{-3} atm s^{-1}

(c) 7.8×10^{-4} atm s^{-1}

(d) 1.55×10^{-4} atm s^{-1}

36. For the two gaseous reactions, following data are given

$$A \longrightarrow B; \; k_1 = 10^{10} \, e^{-20,000/T}$$

$$C \longrightarrow D; \; k_2 = 10^{12} \, e^{-24,606/T}$$
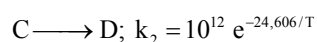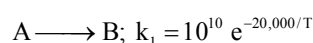
the temperature at which k_1 becomes equal to k_2 is

(a) 400 K

(b) 1000 K

(c) 800 K

(d) 1500 K

Reaction Mecanism

37. For the reaction $2A + B \rightarrow D + E$ the following mechanism has been proposed :

$A + B \rightarrow C + D$ (slow)

$A + C \rightarrow E$ (fast)
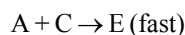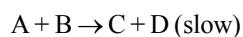
The rate law expression for the reaction is

(a) Rate $= k\,[A]^2\,[B]$

(b) Rate $= k\,[A]\,[B]$

(c) Rate $= k\,[A]\,[C]$

(d) Rate $= k\,[A]^2\,[B]\,[C]$

38. Which of the following statements is false ?

(a) For a first order reaction, the rate of reaction doubles as the concentration of reactant (s) doubles

(b) Active mass of 64g of HI present in a two-litre flask is 0.25

(c) For zero order reaction, the rate changes with temperature

(d) Both order and molecularity of a reaction are always the same.

39. Which one of the following statements is incorrect about the molecularity of a reaction ?

(a) Molecularity of a reaction is not the number of molecules of the reactants present in the balanced equation

(b) Molecularity of a reaction is the number of molecules in the slowest step

(c) Molecularity is always a whole number

(d) There is no difference between order and molecularity of a reaction.

40. For the reaction $2A + B \rightarrow D + E$ the following mechanism has been proposed :

$A + B \rightarrow C + D$ (slow)

$A + C \rightarrow E$ (fast)
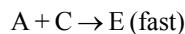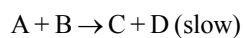
The rate law expression for the reaction is

(a) Rate $= k\,[A]^2\,[B]$

(b) Rate $= k\,[A]\,[B]$

(c) Rate $= k\,[A]\,[C]$

(d) Rate $= k\,[A]^2\,[B]\,[C]$

41. For a single step reaction ;

$A + 2B \rightarrow$ Products, the molecularity is
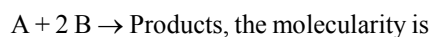
(a) zero

(b) 1

(c) 2

(d) 3

42. For a reaction $X + Y \rightarrow Z$, rate $\propto$ [X]. What is (i) molecularity and (ii) order of reaction ?

(a) (i) 2, (ii) 1   (b) (i) 2, (ii) 2

(c) (i) 1, (ii) 1   (d) (i) 1, (ii) 2

43. For a reaction, $2NO + 2H_2 \rightarrow N_2 + 2H_2O,$ the possible mechanism is

$2NO \rightleftharpoons N_2O_2$

$N_2O_2 + H_2 \xrightarrow{\text{slow}} N_2O + H_2O$

$N_2O + H_2O \xrightarrow{\text{fast}} N_2O + H_2O$

What is the rate law and order of the reaction ?

(a) Rate $= k\,[N_2O_2]$, order $= 1$

(b) Rate $= k\,[NO]^2\,[H_2]$, order $= 3$

(c) Rate $= k\,[NO]^2$, order $= 2$

(d) Rate $= k\,[N_2O_2]^2\,[H_2]$, order $= 3$

44. The chemical reaction, $2O_3 \rightarrow 3O_2$ proceeds as

$O_3 \rightleftharpoons O_2 + [O]$ (fast)

$[O] + O_3 \rightarrow 2O_2$ (slow)

The rate law expression will be

(a) Rate $= k\,[O]\,[O_3]$ (b) Rate $= k\,[O_3]^2\,[O_2]^{-1}$

(c) Rate $= k\,[O_3]^2$ (d) Rate $= k\,[O_2]\,[O]$

45. In a 1st order reaction the fraction of molecules at 450ºC having sufficient energy (or fraction of effective collisions) is 1.92×10^{-16}. What is activation energy value of this reaction ?

(a) $21.757 \times 10^2\,\text{J mole}^{-1}$ (b) $21.757 \times 10^3\,\text{J mole}^{-1}$

(c) $21.75 \times 10^4\,\text{J mole}^{-1}$ (d) None

Collision Theory

46. In a reaction $A \rightarrow B$ threshold energy of the reactant is $120\ \text{kJ mole}^{-1}$ and the normal energy of the reactant is $20\ \text{kJ mole}^{-1}$ what is the activation energy barrier of the reaction $A \rightarrow B$.

(a) $6\,\text{kJ mole}^{-1}$ (b) $100\,\text{kJ mole}^{-1}$

(c) $140\,\text{kJ mole}^{-1}$ (d) $2400\,\text{kJ mole}^{-1}$

47. The rates of reactions increase with increase of temperature because

(a) activating energy of the reacting molecules increases

(b) kinetic energy of the product molecules increases

(c) the fraction of the reacting molecules possessing an energy equal to the activation energy or more increases

(d) the collisions between molecules decrease.

48. Mark the correct statement.

(a) The catalyst catalyses the forward reaction

(b) the catalyst catalyses the backward reaction

(c) The catalyst influences the direct and the reverse reaction to the same extent

(d) The catalyst increases the rate of forward reaction and decreases the rate of backward reaction

49. The rate of reaction increases with increase of temperature because

(a) fraction of reactant molecules having sufficient energy increases

(b) the average energy of the products increases

(c) threshold energy changes

(d) activation energy is lowered.

50. The rate of reaction is doubled for every 10ºC rise in temperature. The increase in rate as result of increase in temperature from 10ºC to 100ºC is

(a) 112   (b) 512

(c) 400   (d) 256

51. The activation energy for a reaction is 9.0 Kcal/mol. The increase in the rate constant when temperature is increases from 298 to 308 K

(a) 10%   (b) 100%

(c) 50%   (d) 63%

52. Which of the following statement is/are correct ?

(a) A catalyst is used in the rate determining step of a mechanism, but then is formed again in some subsequent step so that there is no change in the concentration of the catalyst during the course of the reaction.

(b) Catalyst does not appear in the overall stoichiometric equation for the reaction.

(c) The role of the catalyst is to provide an alternate activated complex, one with a lower activation energy.

(d) All are correct.

53. The rate constant of a reaction is given by

$\ln K \ (\sec^{-1}) = 14.34 - (1.25 \times 10^4)/T$

What will be the energy of activation ?

(a) 24.83 Kcal mole

(b) 12.42 Kcal/mole

(c) 49.96 Kcal/mole

(d) None

54. The reactions of higher order are rare because

(a) many body collisions involved very high activation energy.

(b) many body collisions have a low probability energy

(c) many body collisions are not energetically favoured

(d) many body collisions can take place only in the gaseous phase.

55. According to collision theory of reaction rates, the rate of reaction depends

(a) only upon the total number of collisions per second

(b) upon the colliding molecules with energy greater than threshold energy

(c) upon the orientation of molecules at the time of collision

(d) both on (b) and (c)

56. The temperature dependence of the rate constant k is expressed as $k = Ae^{-E_a/RT}$. When a plot between logk and 1/T is plotted we get the graph as shown. What is the value of slope in the graph ?
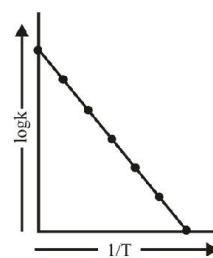
(a) $\dfrac{E_a}{RT}$

(b) $-\dfrac{E_a}{2.303R}$

(c) $-\dfrac{E_a}{2.303\,RT}\log A$

(d) $-\dfrac{E_a}{2.303}\dfrac{R}{T}$

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTION

1. The differential rate law for the reaction

   $H_2 + I_2 \rightleftharpoons 2HI$ is **(2002)**

   (a) $\dfrac{-d[H_2]}{dt} = \dfrac{-d[I_2]}{dt} = \dfrac{-d[HI]}{dt}$

   (b) $\dfrac{dH_2}{dt} = \dfrac{d[I_2]}{dt} = \dfrac{d[H]}{dt}$

   (c) $\dfrac{1}{2}\dfrac{d[H_2]}{dt} = \dfrac{1}{2}\dfrac{d[I_2]}{dt} = \dfrac{-d[HI]}{dt}$

   (d) $-2\dfrac{d[H_2]}{dt} = -2\dfrac{d[I_2]}{dt} = \dfrac{d[HI]}{dt}$

2. For a reaction, $A + 2B \rightarrow C$ rate is given by $R = K[A][B]^2$. The order of reaction is **(2002)**

   (a) 3 (b) 6

   (c) 5 (d) 7

3. The rate constant for the first and zero reaction in terms of molarity, M units respectively **(2002)**

   (a) sec^{-1}, $M\ sec^{-1}$ (b) sec^{-1}, M

   (c) $M\ sec^{-1}$, sec^{-1} (d) M, sec^{-1}

4. The rate law for a reaction between the substance A and B is given by rate = $k[A]^n[B]^m$. On doubling the concentration of A and halving the conc. of B, the ratio of the new rate of the earlier rate of reaction will be **(2003)**

   (a) $\dfrac{1}{2^{m+n}}$ (b) $m+n$

   (c) $n-m$ (d) $2^{(n-m)}$

5. Which one is correct for $K = Ae^{-E_a/RT}$? **(2003)**

   (a) E_a is energy of activation

   (b) R is Rydberg constant

   (c) K is equilibrium constant

   (d) A is adsorption factor

6. The rate equation for the reaction, $2A + B \rightarrow C$ is found to be : rate = k [A] [B]... The correct statement in relation to this reaction is that the **(2004)**

   (a) unit of k must be s^{-1}

   (b) value of k is independent of the initial concentrations of A and B

   (c) rate of formation of C is twice the rate of disappearance of A

   (d) $t_{1/2}$ is a constant.

7. In a first order reaction, the conc. of reactant decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is

   (2004)

   (a) 30 min (b) 60 min

   (c) 7.5 min (d) 15 min

8. A reaction involving the different reactants can never be

   (2005)

   (a) bi molecular reaction (b) second order reaction

   (c) first order reaction (d) Unimolecular reaction

9. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr,

   $NO_{(g)} + Br_{2(g)} \rightleftharpoons NOBr_{2(g)}$

   $NOBr_{2(g)} + NO_{(g)} \rightarrow 2NOBr_{(g)}$

   It the second step is the rate determining step, the order of the reaction with respect to $NO_{(g)}$ is **(2006)**

   (a) 2 (b) 1

   (c) 0 (d) 3

10. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will **(2006)**

    (a) Double (b) Remain unchanged

    (c) Triple (d) Increase by a factor of 4

11. Rate of a reaction can be expressed by Arrhenius equation as $k = A\,e^{-E/RT}$ In this equation, E represents **(2006)**

    (a) the energy above which all the colliding molecules will react

    (b) the energy below which colliding molecules will not react

    (c) the total energy of the reacting molecules at a temperature, T

    (d) the fraction of molecules with energy greater than the activation energy of the reation.

12. The energies of activation for forward and reverse reaction for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction $(A_2 + B_2 \rightarrow 2AB)$ in the presence of catalyst will be (in kJ mol^{-1}). **(2007)**

    (a) 300 (b) 120

    (c) 280 (d) 20

13. For a reaction $\frac{1}{2}A \rightarrow 2B$, rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression

    (2008)

    (a) $\dfrac{-d[A]}{dt} = \dfrac{1}{2}\dfrac{d[B]}{dt}$ (b) $-\dfrac{d[A]}{dt} = \dfrac{1}{4}\dfrac{d[B]}{dt}$

    (c) $-\dfrac{d[A]}{dt} = \dfrac{d[B]}{dt}$ (d) $-\dfrac{d[A]}{dt} = 4\dfrac{d[B]}{dt}$

14. The half life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301) **(2009)**

    (a) 230.3 minutes (b) 23.03 minutes

    (c) 46.06 minutes (d) 460.6 minutes

15. Consider the reaction,

    $Cl_2\,(aq) + H_2S\,(aq) \rightarrow$

    $\qquad\qquad S\,(s) + 2H^+\,(aq) + 2Cl^-\,(aq)$

    The rate equation for this reaction is,

    rate = $k\,[Cl_2]\,[H_2S]$

    Which of these mechanisms is/are consistent with this rate equation ? **(2010)**

    (A) $Cl_2 + H_2S \rightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)

    $\qquad Cl^+ + HS^- \rightarrow H^+ + Cl^- + S$ (fast)

    (B) $H_2S \rightleftharpoons H^+ + HS^-$ (fast equilibrium)

    $\qquad Cl_2 + HS^- \rightarrow 2Cl^- + H^+ + S$ (slow)

    (a) (B) only (b) Both (A) and (B)

    (c) Neither (A) nor (B) (d) (A) only

16. The time for half-like period of a certain reaction, A $\rightarrow$ products is 1 h. When the initial concentration of the reactant 'A', is 2.0 mol L^{-1}, how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1}, if it is a zero order reaction ? **(2010)**

    (a) 4 h (b) 0.5 h

    (c) 0.25 h (d) 1 h

17. A reactant (A) forms two products **(2011)**

    A $\xrightarrow{\ k_1\ }$ B, Activation energy E_{a_1}

    A $\xrightarrow{\ k_2\ }$ C, Activation energy E_{a_2}

    If $E_{a_2} = 2E_{a_1}$, then k_1 and k_2 are

    (a) $k_1 = 2k_2\,e^{E_{a_2}/RT}$ (b) $k_1 = k_2\,e^{E_{a_1}/RT}$

    (c) $k_2 = k_1 e^{E_{a_2}/RT}$ (d) $k_1 = A\,k_2\,e^{E_{a_1}/RT}$

18. The rate of a chemical reaction doubles for every 10ºC rise of temperature. If the temperature is raised by 50ºC, the rate of the reaction increases by about **(2011)**

    (a) 10 times (b) 24 times

    (c) 32 times (d) 64 times

19. For a first order reaction, (A) $\longrightarrow$ product the concentration of A changes from 0.1 M to 0.025 M in 40 min. The rat of reaction when the concentration of A is 0.01 M is **(2012)**

    (a) 1.73×10^{-5} M/min (b) 3.47×10^{-4} M/min

    (c) 3.47×10^{-5} M/min (d) 1.73×10^{-4} M/min

20. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be (R = 8.314 JK^{-1} mol^{-1} and log 2 = 0.301)

    (2013)

    (a) 53.6 kJ mol^{-1} (b) 48.6 kJ mol^{-1}

    (c) 58.5 kJ mol^{-1} (d) 60.5 kJ mol^{-1}

21. Higher order (>3) reactions are rare due to : **(2015)**

(a) shifting of equilibrium towards reactants due to elastic collisions

(b) loss of active species on collision

(c) low probability of simultaneous collision of all the reacting species

(d) increase in entropy and activation energy as more molecules are involved

22. Decomposition of H_2O_2 follows a first order reaction. In fifty minutes the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be: **(2016)**

(a) 6.93×10^{-4} mol min^{-1} (b) 2.66 L min^{-1} at STP

(c) 1.34×10^{-2} mol min^{-1} (d) 6.93×10^{-2} mol min^{-1}

23. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kj mol^{-1}. If k_1 and k_2 are rate constants for reactions R_1 and R_2, respectively at 300 K, then $\ln\left(\dfrac{k_2}{k_1}\right)$ is equal to ($R = 8.314$ J mol^{-1}K^{-1}) **(2017)**

(a) 8 (b) 12

(c) 6 (d) 4

24. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction ? **(2018)**
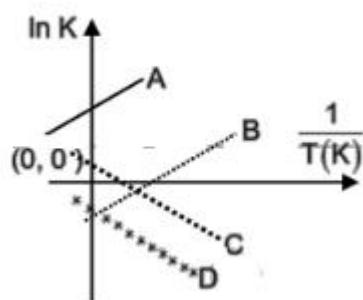
(a) C and D (b) A and D

(c) A and B (d) B and C

25. At 518°C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torrs s^{-1} when 5% had reacted and 0.5 Torr s^{-1} when 33% had reacted. The order of the reaction is **(2018)**

(a) 1 (b) 0

(c) 2 (d) 3

JEE MAINS ONLINE QUESTION

1. The half life period of a first order reaction is 15 minutes. The amount of substance left after one hour will be:

Online 2014 SET (1)

(a) $\dfrac{1}{4}$ of the original amount

(b) $\dfrac{1}{8}$ of the original amount

(c) $\dfrac{1}{16}$ of the original amount

(d) $\dfrac{1}{32}$ of the original amount

2. For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, the rate equation can be expressed in two ways $-\dfrac{d[N_2O_5]}{dt} = k$ $[N_2O_5]$ and $+\dfrac{d[NO_2]}{dt} = k'[N_2O_5]$ k and k' are related as:

Online 2014 SET (2)

(a) $2k = k'$ (b) $k = k'$

(c) $k = 2k'$ (d) $k = 4k'$

3. In the reaction of formation of sulphur trioxide by contact process $2SO_2 + O_2 \rightleftharpoons 2SO_3$ the rate of reaction was measured as $\dfrac{d[O_2]}{dt} = -2.5 \times 10^{-4}$ mol L^{-1} s^{-1}. The rate of reaction in terms of $[SO_2]$ in mol L^{-1} s^{-1} will be:

Online 2014 SET (2)

(a) -3.75×10^{-4} (b) -5.00×10^{-4}

(c) -1.25×10^{-4} (d) -2.50×10^{-4}

4. The rate coefficient (k) for a particular reactions is $1.3 \times 10^{-4} \, M^{-1} s^{-1}$ at $100^0 C$, and $1.3 \times 10^{-3} \, M^{-1} s^{-1}$ at $150^0 C$. What is the energy of activation (E_A) (in kJ) for this reaction? **Online 2014 SET (3)**

(R = molar gas constant = $8.314 \, JK^{-1} mol^{-1}$)

(a) 132   (b) 99

(c) 16   (d) 60

5. For the reaction,   **Online 2014 SET (4)**

$3A + 2B \rightarrow C + D$

The differential rate law can be written as :

(a) $+\dfrac{1}{3}\dfrac{d[A]}{dt} = -\dfrac{d[C]}{dt} = k[A]^n [B]^m$

(b) $-\dfrac{1}{3}\dfrac{d[A]}{dt} = \dfrac{d[C]}{dt} = k[A]^n [B]^m$

(c) $-\dfrac{d[A]}{dt} = \dfrac{d[C]}{dt} = k[A]^n [B]^m$

(d) $\dfrac{1}{3}\dfrac{d[A]}{dt} = \dfrac{d[C]}{dt} = k[A]^n [B]^m$

6. The reaction of ozone with oxygen atoms in the presence of chlorine atoms can occur by a two step process shown below   **Online 2016 SET (1)**

$$O_3(g) + Cl^\bullet(g) \rightarrow O_2(g) + ClO^\bullet(g) \text{—(i)}$$

$$k_i = 5.2 \times 10^9 \, L \, mol^{-1} s^{-1}$$

$$ClO^\bullet(g) + O^\bullet(g) \rightarrow O_2(g) + Cl^\bullet(g) \text{—(ii)}$$

$$k_{ii} = 2.6 \times 10^{10} \, L \, mol^{-1} s^{-1}$$

The closet rate constant for the overall reaction $O_3(g) + O^\bullet(g) \rightarrow 2O_2(g)$ is

(a) $5.2 \times 10^9 \, L \, mol^{-1} s^{-1}$ (b) $2.6 \times 10^{10} \, L \, mol^{-1} s^{-1}$

(c) $3.1 \times 10^{10} \, L \, mol^{-1} s^{-1}$ (d) $1.35 \times 10^{20} \, L \, mol^{-1} s^{-1}$

7. The rate law for the reaction below is given by the expression K [A] [B]

$A + B \rightarrow$ Product

If the concentration of B is increased from 0.1 to 0.3 mole, keeping the value of A at 0.1 mole, the rate constant will be :   **Online 2016 SET (2)**

(a) k   (b) k/3

(c) 3k   (d) 9k

8. The rate of a reaction A doubles on increasing the temperature from 300 to 310 K. By how much, the temperature of reaction B should be increased from 300 K so that rate doubles if activation energy of the reaction B is twice to that of reaction A.   **Online 2017 SET (1)**

(a) 9.84 K   (b) 4.92 K

(c) 2.45 K   (d) 19.67 K

9. The rate of a reaction quadruples when the temperature changes from 300 to 310 K. The activation energy of this reaction is :   **Online 2017 SET (2)**

(Assume activation energy and pre-exponential factor are independent of temperature; ln 2 = 0.693;

$R = 8.314 \, J \, mol^{-1} K^{-1}$)

(a) $107.2 \, kJ \, mol^{-1}$ (b) $53.6 \, kJ \, mol^{-1}$

(c) $26.8 \, kJ \, mol^{-1}$ (d) $214.4 \, kJ \, mol^{-1}$

10. N_2O_5 decomposes to NO_2 and O_2 and follows first order kinetics. After 50 minutes, the pressure inside the vessel increases from 50 mmHg to 87.5 mmHg. The pressure of the gaseous mixture after 100 minute at constant temperature will be: **Online 2018 SET (1)**

(1) 175.0 mmHg   (2) 116.25 mmHg

(3) 136.25 mmHg   (4) 106.25 mmHg

11. For a first order reaction, $A \rightarrow P, t_{1/2}$ (half- life) is 10 days.

The time required for $\dfrac{1}{4}^{th}$ conversion of A (in days) is :

(In 2 = 0.693, In 3 = 1.1)   **Online 2018 SET (2)**

(1) 5   (2) 3.2

(3) 4.1   (4) 2.5

12. If 50 percent of a reaction occurs in 100 second and 75 percent of the reaction occurs in 200 second, the order of this reaction is :   **Online 2018 SET (3)**

(1) Zero   (2) 1

(3) 2   (4) 3

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1.   All questions marked **"S"** are single choice questions
2.   All questions marked **"M"** are multiple choice questions
3.   All questions marked **"C"** are comprehension based questions
4.   All questions marked **"A"** are assertion–reason type questions
   (A) If both assertion and reason are correct and reason is the correct explanation of assertion.
   (B) If both assertion and reason are true but reason is not the correct explanation of assertion.
   (C) If assertion is true but reason is false.
   (D) If reason is true but assertion is false.
5.   All questions marked **"X"** are matrix–match type questions
6.   All questions marked **"I"** are integer type questions

Rate of reaction

1. (S) The rate of reaction is defined as
(a) decreases in the concentration of a reactant
(b) increase in the concentration of a product
(c) change in the concentration of any one of the reactants or products per unit time.
(d) all the above three are correct.

2. (S) For the reaction $A + 2B \rightarrow C$, the rate of reaction at a given instant can be represented by

(a) $+\dfrac{d[A]}{dt} = \dfrac{1}{2}\dfrac{d[B]}{dt} = +\dfrac{d[C]}{dt}$

(b) $\dfrac{d[A]}{dt} = +\dfrac{1}{2}\dfrac{d[B]}{dt} = -\dfrac{d[C]}{dt}$

(c) $-\dfrac{d[A]}{dt} = -\dfrac{1}{2}\dfrac{d[B]}{dt} = +\dfrac{d[C]}{dt}$

(d) $+\dfrac{d[A]}{dt} = +\dfrac{1}{2}\dfrac{d[B]}{dt} = +\dfrac{d[C]}{dt}$

3. (S) As the reaction progresses, the rate of reaction
(a) increases   (b) decreases
(c) remains constant
(d) first increases, then decreases.

4. (S) For the reaction $4A + B \rightarrow 2C + 2D$, which of the following statement is not correct ?
(a) the rate of disappearance of B is one fourth of the rate of disappearance of A
(b) the rate of formation of C is one-half of the rate of consumption of A
(c) the rate of appearance of D is half of the rate of disappearance of B
(d) the rates of formation of C and D are equal.

5. (A) **Asseration :** The rate of the reaction is the rate of change of concentration of a reactant or a product.

    Reason : Rate of reaction remains constant during the complete reaction.

(a) Both Assertion and Reason are true and Reason is the correct explanation of 'Assertion'

(b) Both Asseration and Reason are true and Reason is not the correct explanation of 'Assertion'

(c) Assertion is true but Reason is false

(d) Assertion is false but Reason is true

Comprehension

Concentrations measured as a function of time when gaseous N_2O_5 at initial concentration of 0.0200 M decomposes to gaseous NO_2 and O_2 at 55ºC. The change in concentration with time is given by the following graph.
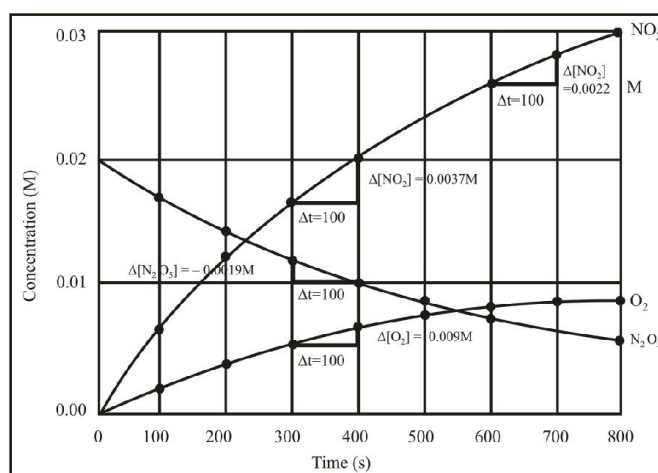
6. (C) The instantaneous rate of reaction at the beginning of the reaction is

(a) 2.2×10^{-5} M/s   (b) 1×10^{-5} M/s

(c) 6.3×10^{-5} M/s   (d) zero

7. (C) The rate of formation of NO_2 during the period $600 - 700$ s is

(a) 3.7×10^{-5} M/s   (b) 2.2×10^{-5} M/s

(c) 4.8×10^{-5} M/s   (d) 1.6×10^{-5} M/s

8. (C) The rate of decomposition of N_2O_5 during the period $300 - 400$ s is

(a) 3.7×10^{-4} M/s   (b) 2.6×10^{-5} M/s

(c) 1.9×10^{-5} M/s   (d) 3.6×10^{-8} M/s

Rate law

9. (S) Two gases A and B are filled in a container. The experimental rate law for the reaction between them, has been found to be

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

Predict the effect on the rate of the reaction when pressure is doubled :

(a) the rate is doubled

(b) the rate becomes four times

(c) the rate becomes six times

(d) the rate becomes eight times

10. (S) For the reaction $A + B \rightarrow C + D$, the variation of the concentration of the product with time is given by the curve.
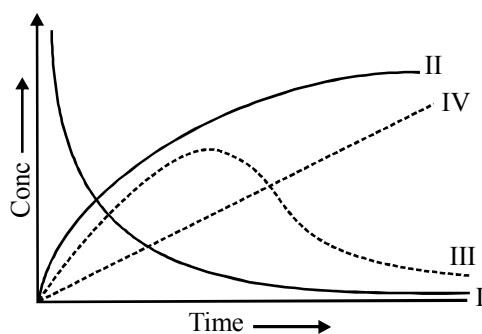
(a) I   (b) II

(c) III   (d) IV

11. (S) For a gaseous reaction, the units of rate of reaction are

(a) $L\ atm\ s^{-1}$ (b) $atm\ s^{-1}$

(c) $atm\ mol^{-1}\ s^{-1}$ (d) $mol\ s^{-1}$

12. (S) Under a given set of experimental conditions, with increase of concentration of the reactants, the rate of a chemical reaction

(a) Decreases   (b) increases

(c) Remains unaffected

(d) First decreases, then increases.

13. (S) The rate law expression for the hypothetical reaction

$$2\,A + 3\,B \rightarrow 2\,C \text{ is } \frac{dx}{dt} = k\,[A]\,[B]^2$$
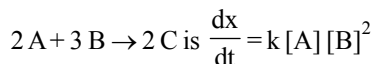
The order of reaction is

(a) 1   (b) 2

(c) 3   (d) 5

14. (S) What is the order of a reaction which has a rate expression rate $= k\,[A]^{3/2}\,[B]^{-1}$?

(a) 3/2   (b) 1/2

(c) zero   (d) none of these.

15. (S) A reaction involves two reactants. The rate of reaction is directly proportional to the concentration of one of them and inversely proportional to the concentration of the other. The overall order of reaction will be

(a) one   (b) two

(c) zero   (d) none of these.

16. (S) The rate of a reaction at different times $\left(-\dfrac{dx}{dt}\right)$ is found as follows :

Time (in minute)	Rate in $(mol\ L^{-1}\ s^{-1})$
0	2.80×10^{-2}
10	2.78×10^{-2}
20	2.81×10^{-2}
30	2.79×10^{-2}

The order of reaction is

(a) zero   (b) one

(c) two   (d) three.

17. (S) Order of a reaction can be

(a) fractional   (b) zero

(c) integer   (d) all the above.

18. (S) If order of reaction is zero. It means that

    (a) rate of reaction is independent of temperature

    (b) rate of reaction is independent of the concentration of the reacting species

    (c) the rate of formation of activated complex is zero

    (d) rate of decomposition of activated complex is zero

19. (S) Which one of the following statements is incorrect ?

    (a) Rate law expression cannot be written from the stoichiometric equation.

    (b) Law of mass action expression can be written from the balanced equation.

    (c) Specific reaction rate of a reaction is constant at constant temperature.

    (d) Rate of reaction and rate constant have same units.

20. (S) The unit of rate constant for a zero order reaction is

    (a) litre sec^{-1} (b) litre $mol^{-1} sec^{-1}$

    (c) mol $litre^{-1} sec^{-1}$ (d) mol sec^{-1}.

21. (S) The rate constant of a reaction has same units as the rate of reaction. The reaction is of

    (a) zero order   (b) first order

    (c) second order   (d) none of these.

22. (S) The rate constant of a reaction is $2.1 \times 10^{-2} mol^{-2} litre^2 min^{-1}$. The order of reaction is

    (a) zero   (b) 1

    (c) 2   (d) 3.

23. (S) When concentration of reactant in reaction $A \rightarrow B$ is increased by 8 times, the rate increases only 2 times. The order of the reaction would be

    (a) 2   (b) 1/3

    (c) 4   (d) 1/2

24. (S) The rate of reaction between A and B increases by a factor of 100, when the concentration of A is changed from $0.1 mol L^{-1}$ to $1 mol L^{-1}$. The order of reaction with respect to A is :

    (a) 10   (b) 1

    (c) 3   (d) 2

25. (S) For the reaction, $A \rightarrow B$, the rate of reaction is quadrupled when the concentration of A is doubled, the rate expression of the reaction is $r = k [A]^n$, when the value of n is

    (a) 1   (b) zero

    (c) 3   (d) 2

26. (S) The thermal decomposition of $A \rightarrow B + C$ has rate constant x $mole^{-1/2} lit^{1/2} min^{-1}$ at a given temperature. How would $-\dfrac{dA}{dt}$ will change if concentration of A is doubled keeping temperature constant

    (a) will increase by 2.828 times

    (b) will increase by 4 times

    (c) will increase by 11.313 times

    (d) will not change

27. (S) The equilibrium constant of reaction is 20.0 At equilibrium, the rate constant of forward reaction is 10.0. The rate constant for backward reaction is

    (a) 0.5   (b) 2.0

    (c) 10.0   (d) 200.0

28. (S) The thermal decomposition of acetaldehyde :
$CH_3CHO \rightarrow CH_4 + CO$, has rate constant of 1.8×10^{-3} $mole^{-1/2} L^{1/2} min^{-1}$ at a given temperature. How would $-\dfrac{d[CH_3CHO]}{dt}$ will change if concentration of acetaldehyde is doubled keeping the temperature constant ?

    (a) will increase by 2.828 times

    (b) will increase by 11.313 times

    (c) will not change   (d) will increase by 4 times

29. (M) Hydrolysis of an ester is catalysed by H^+ ion.

    Using equimolar concentrations of two acids HX and HY, both being strong acids, the rate constants of the reaction are found to be $3 \times 10^{-3} min^{-1}$ and $5 \times 10^{-3} min^{-1}$ respectively at a fixed temperature. It can be concluded that

    (a) Rate constant may be taken as the measure of degree of ionization of the acid used as catalyst

    (b) HX is a stronger acid than HY, their relative strength being 1.7

    (c) HX is a weaker acid than HY, their relative strength being 0.6

    (d) none is correct

30.(M) Estrification of acetic anhydride by ethanol takes place as

$(CH_3CO)_2 O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3COOH$
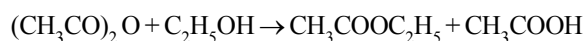
Select the correct statements of the following :

(a) When reaction is carried out in dilute hexane solution, the rate law is given by k [Anhydride] [Alcohol]

(b) When ethanol is the solvent, the rate law is given by k [Anhydride]

(c) The values of k in the two cases are the same

(d) Using ethanol as the solvent, its concentration changes significantly during the course of the reaction

Integrated rate law

31. (S) The rate law of gaseous reaction : $A_{(g)} + B_{(g)} \rightarrow$ Products

is given by $k[A]^2[B]$. If the volume of the reaction vessel is suddenly doubled, which of the following will happen ?

(a) The rate w.r.t. A will decrease two times

(b) The rate w.r.t. A will decrease four times

(c) The rate w.r.t. B will decrease two times

(d) The overall rate will decrease 8 times of the original value

32. (S) Half life period of 2nd order reaction is :

(a) proportional to initial conc. of reactants

(b) independent of initial concentration of reactants

(c) inversely proportional to initial concentration of reactants

(d) inversely proportional to square of initial concentration of reactants.

33. (S) The half-life period of a zero order reaction is

(a) directly proportional to initial concentration

(b) inversely proportional to initial concentration

(c) independent of initial concentration

(d) proportional to the square of initial concentration.

34. (S) Radioactive decay is a

(a) zero-order reaction   (b) first-order reaction

(c) second order reaction   (d) third order reaction

35. (S) The half-life period of a radio active element is 30 min. One sixteenth the original quantity of the element will remain unchanged after

(a) one hour   (b) sixteen hour

(c) four hour   (d) two hour

36. (S) The half-life period of a radioactive element is 120 days. Starting with 1 gm, the amount of element decayed in 600 days will be

(a) $\frac{1}{16}$ g   (b) $\frac{15}{16}$ g

(c) $\frac{1}{32}$ g   (d) $\frac{31}{32}$ g

37. (S) A sample of rock from the moon contains equal number of atoms of U and Pb ($t_{1/2}$ for uranium $= 4.5 \times 10^9$ years). The age of rock would be

(a) 4.5×10^9 years   (b) 90×10^9 years

(c) 13.5×10^9 years   (d) 2.25×10^9 years

38. (S) The rate constant for the reaction

$2N_2O_5 \rightarrow 4NO_2 + O_2$ is $3.0 \times 10^{-5} \sec^{-1}$
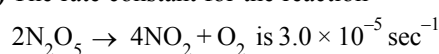
If the rate is 2.4×10^{-5} mol $Lt^{-1} \sec^{-1}$ the concentration of N_2O_5 (in mol litre^{-1}) is

(a) 1.4   (b) 1.2

(c) 0.04   (d) 0.8

39. (S) $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$ is the first order as gas reaction with $K = 2.2 \times 10^{-5} \sec^{-1}$ at $320ºC$. The percentage of SO_2Cl_2 decomposed on heating for 90 minutes is

(a) 1.118   (b) 0.1118

(c) 18.11   (d) 11.30

40. (S) Four vessels 1, 2, 3 and 4 contain respectively, 10 mol atom ($t_{1/2}$ = 10 hours), 1mol atom ($t_{1/2}$ = 5 hours), 5 mol atom ($t_{1/2}$ = 2 hour) and 2 mol atom ($t_{1/2}$ = 1 hour) of different radioactive nuclides. In the beginning, the maximum radioactivity would be exhibited by the vessel

(a) 4   (b) 3

(c) 2   (d) 1

41. (S) For a first order reaction : $A \rightleftharpoons B$, Whose concentration vs. time curve is as shown in the figure. The rate constant is equal to

(a) $41.58 \, h^{-1}$ (b) $4.158 \, s^{-1}$

(c) $1.155 \times 10^{-3} \, s^{-1}$ (d) $6.93 \, min^{-1}$
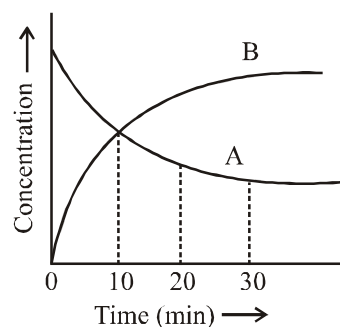
42. (S) The half-life a first order reaction is 24 hours. If we start with 10M initial concentration of the reactant then conc. after 96 hours will be

(a) 6.25 M   (b) 1.25 M

(c) 0.125 M   (d) 0.625 M

43. (S) The rate constant for a zero order reaction is 2×10^{-2} mol L^{-1} sec^{-1}. If the concentration of the reactant after 25 sec is 0.5 M, the initial concentration must have been

(a) 0.5 M   (b) 1.25 M

(c) 12.5 M   (d) 1.0 M

44. (M) Which of the following statements are correct ?

(a) Time required for 75% completion is 1.5 times of half-life for zero order reaction

(b) Time needed for a definite fraction of first order reaction does not vary with the initial concentration

(c) Time for 25% reaction is one-third of half-life in second order process

(d) Rate of zero order reaction gets doubled if the concentration of the reactant is increased to a two fold value

45. (A) Asseration : If in a zero order reaction, the concentration of the reactant is doubled, the half-life period is also doubled.

Reason : For a zero order reaction, the rate of reaction is independent of initial concentration.

(a) Both Assertion and Reason are true and Reason is the correct explanation of 'Assertion'

(b) Both Asseration and Reason are true and Reason is not the correct explanation of 'Assertion'

(c) Assertion is true but Reason is false

(d) Assertion is false but Reason is true

46. (X) C_0 = Initial concentration of reactant; C = Concentration of reactant at any time t; k = rate constant

Match the following :

Plots		Slopes
(A) C vs (abscissa) for zero order	(P)	Unity
(B) log C vs t (abscissa) for first order	(Q)	Zero

(C) $\left(-\dfrac{dc}{dt} \right)$ vs C for zero order   (R) – k

(D) ln (–dc/dt) vs ln C for first order   (S) -k/2.303

Practical methods to find order of reaction

47. (I) 4.0 kg of a radioactive drug is supplied from a reactor to a laboratory but laboratory receives only $\sqrt{2}$ kg of the radioactive substance due to its rapid decay during transportation. If 6.0 hrs are elapsed in transportation, then half-life of the radioactive drug is

48. (S) For a given reaction half life period was found to be directly proportional to the initial concentration of the reactant. The order is

(a) Zero   (b) 1

(c) 2   (d) 3

49. (S) For the reaction

$CH_3Cl_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3OH_{(aq)} + Cl^-_{(aq)}$
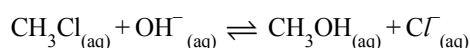
The kinetic data are as given below :

$[CH_3Cl]$	$[OH^-]$	$+d\,[CH_3OH]/dt\,(M\,min^{-1})$
0.2	0.1	2×10^{-3}
0.4	0.1	4×10^{-3}
0.4	0.2	8×10^{-3}

If K_c for the above reaction is 1×10^{14}, then the specific reaction rate $(M^{-1}\,min^{-1})$ for the replacement of –OH group of methanol by Cl atom is :

(a) 10^{-18} (b) 10^{-15}

(c) 10^{15} (d) 10

50. (S) The half-life period for a reaction at initial concentrations of 0.5 and 1.0 mol lit^{-1} are 200 sec and 100 sec respectively. The order of the reaction is

(a) zero   (b) 1

(c) 2   (d) 3

51. (S) In the presence of acid, the initial concentration of cane-sugar was reduced from 0.2 M to 0.1 M in 5 hrs and to 0.05 M in 10 hrs. The reaction must be of

(a) zero order   (b) first order

(c) second order   (d) fractional order

52. (M) Hydrolysis of a sugar is catalysed by H^+ ion. Half-life of the reaction is independent of initial concentration of sugar at a particular pH. At a constant concentration of sugar rate increases 10 times when pH is decreased by one unit. Pick out the correct statements of the following :

(a) Rate $\propto$ [sugar]   **(b) Rate** $\propto$ [H^+]

(c) Rate law : rate = k (sugar)

(d) Rate law : rate = k [sugar] [H^+]

53. (I) For the reaction : A + B $\rightarrow$ P, if concentration of B is doubled, maintaining concentration of A constant, rate of reaction is also doubled. If concentration of A is tripled. maintaining concentration of B constant, rate of reaction increases by a factor of nine. If concentrations both A and B are doubled simultaneously, the rate of reaction will increase by a factor of

Practical analysis of first order reaction

54. (I) For the reaction : A $\rightarrow$ P

when initial concentration of reactant is halved, the half-life increases by a factor of eight. Order of reaction is

55. (S) In the decomposition of Ammonia it was found that at 50 torr pressure $T_{1/2}$ was 3.64 hour while at 100 torr $T_{1/2}$ was 1.82 hours. Then order of reaction would be

(a) 0   (b) 1

(c) 2   (d) 3

56. (S) For a first order reaction $P_{(g)} \longrightarrow Q_{(g)} + R_{(g)}$. After 10 minutes the volume of R gas is 10 L and after complete reaction 50L. Hence rate constant will be (in min^{-1}).

(a) $\dfrac{1}{10} \ln 5$ (b) $\dfrac{1}{10} \ln \dfrac{1}{5}$

(c) $\dfrac{1}{10} \ln 4$ (d) $\dfrac{1}{10} \ln 1.25$

Reaction Mechamism

57. (S) When concentration of reactant in reaction A $\rightarrow$ B is increased by 8 times, the rate increases only 2 times. The order of the reaction would be

(a) 2   (b) 1/3

(c) 4   (d) 1/2

58. (S) For a single step reaction;

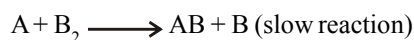A + 2B $\rightarrow$ Products, the molecularity is

(a) Zero   (b) 1

(c) 2   (d) 3

59. (S) A hypothetical reaction $A_2 + B_2 \rightarrow 2\,AB$ follows the mechanism as given below :

$A_2 \rightleftharpoons A + A$ (fast)

$A + B_2 \rightarrow AB + B$ (slow)

$A + B \rightarrow AB$ (fast)

The order of the over all reaction is :

(a) 2   (b) 1

(c) $1\dfrac{1}{2}$ (d) 0

60. (S) In the sequence of reaction

$A \xrightarrow{k_1} B \xrightarrow{k_2} \longrightarrow C \xrightarrow{k_3} D$

$k_3 > k_2 > k_1$, then the rate determining step of the reaction is :

(a) A $\rightarrow$ B   (b) B $\rightarrow$ C

(c) C $\rightarrow$ D   (d) A $\rightarrow$ D

61. (S) The chemical reaction, $2O_3 \longrightarrow 3O_2$ proceeds as follows

$O_3 \rightleftharpoons O_2 + O$ (Fast)

$O + O_3 \longrightarrow 2O_2$ (slow)

The rate law expression should be

(a) Rate = K $[O_3]^2$ (b) Rate = $K[O_3]^2 [O_2]^{-1}$

(c) Rate = K $[O_3][O_2]$ (d) None

62. (S) The decomposition of ozone is believed to occur by the mechanism :

$O_3 \rightleftharpoons O_2 + O$ (fast)

$O + O_3 \rightarrow O_2$ (slow)

When the concentration of O_2 is increased, then the rate

(a) increases   (b) decreases

(c) remains same   (d) cannot be predicted

63. (M) For the hypothetical reaction

$A_2 + B_2 \longrightarrow 2AB,$ the mechanism is given as below

$A_2 \rightleftharpoons A + A$ (fast reaction)

$A + B_2 \longrightarrow AB + B$ (slow reaction)

$A + B \longrightarrow AB$ (fast reaction)

then

(a) the rate determining step is $A + B_2 \longrightarrow AB + B$

(b) the order of the reaction is 3/2

(c) the overall molecularity is 4

(d) the rate expression is Rate $= k [A] [B_2]$

64. (A) Assertion : According to steady state hypothesis, in a multistep reaction, the change in concentration with time for reactive intermediates is zero.

Reason : The intermediates are so reactive that after a brief initial period their concentrations rise from zero to a small value and remains constant for most of the duration of the reaction.

(a) Both Assertion and Reason are true and Reason is the correct explanation of 'Assertion'

(b) Both Asseration and Reason are true and Reason is not the correct explanation of 'Assertion'

(c) Assertion is true but Reason is false

(d) Assertion is false but Reason is true

Collision Theory

65. (A) Assertion : For the $2N_2O_5 \rightarrow 4NO_2 + O_2$; Rate $= K[N_2O_5]$.

Reason : Rate of decomposition of N_2O_5 is determined by slow step.

(a) Both Assertion and Reason are true and Reason is the correct explanation of 'Assertion'

(b) Both Asseration and Reason are true and Reason is not the correct explanation of 'Assertion'

(c) Assertion is true but Reason is false

(d) Assertion is false but Reason is true

66. (S) Rate of a reaction

(a) increases with increase in temperature

(b) decreases with increase in temperature

(c) does not depend upon temperature

(d) does not depend upon concentration.

67. (S) In the accompanied diagram, E_R, E_P and E_X represent the energy of the reactants, products and activated complex respectively. Which of the following is the activation energy for the backward reaction ?
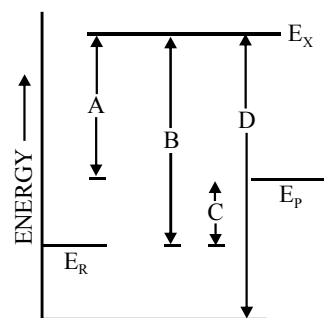
(a) A   (b) B

(c) C   (d) D

68. (S) If E_f and E_r are the activation energies of the forward and reverse reactions and the reaction is known to be exothermic, then

(a) $E_f < E_r$ (b) $E_f > E_r$

(c) $E_f = E_r$

(d) No relation can be given between E_f and E_r as data are not sufficient.

69. (S) An endothermic reaction $A \rightarrow B$ has an activation energy as x kJ mol^{-1} of A. If energy change of the reaction is y kJ, the activation energy of the reverse reactions is :

(a) $-x$ (b) $x - y$

(c) $x + y$ (d) $y - x$.

70. (S) Energy of activation of an exothermic reaction is

(a) zero   (b) negative

(c) positive   (d) can't be predicted

71. (M) An increase in the rate of reaction with rise in temperature is due to

(a) an increase in the number of collisions

(b) an increase in the number of activated molecules

(c) lowering of activation energy

(d) shortening of mean free path.

72. (S) Which one of the following statements is incorrect ?

(a) The temperature coefficient of a reaction is the ratio of the rate constant at any two temperatures

(b) The temperature coefficient of a reaction is the ratio of the rate constants at 298 K and 308 K

(c) The temperature coefficient of most of the reactions lies between 2 and 3

(d) In an endothermic reaction, activation energy of reactants is more than that of the products

73. (S) If a reaction A + B $\rightarrow$ C is exothermic to the extent of 30 kJ/mol and the forward reaction has an activation energy 70 kJ/mol, the activation energy for the reverse reaction is

(a) 30 kJ/mol (b) 40 kJ/mol

(c) 70 kJ/mol (d) 100 kJ/mol

74. (S) For an endothermic reaction, where ΔH represents the enthalpy of reaction in kJ mol, the minimum value for the energy of activation will be

(a) Less than ΔH (b) zero

(c) More than ΔH (d) Equal to ΔH

75. (S) E_a and ΔH values of reactions R_1, R_2, R_3 and R_4 carried out at the same temperature are as given below :

R_1 $\quad$ $E_a = 40\,kJ\,mol^{-1}$, $\quad$ $\Delta H = -80\,kJ\,mol^{-1}$

R_2 $\quad$ $E_a = 20\,kJ\,mol^{-1}$, $\quad$ $\Delta H = -30\,kJ\,mol^{-1}$

R_3 $\quad$ $E_a = 60\,kJ\,mol^{-1}$, $\quad$ $\Delta H = +40\,kJ\,mol^{-1}$

R_4 $\quad$ $E_a = 30\,kJ\,mol^{-1}$, $\quad$ $\Delta H = +20\,kJ\,mol^{-1}$

At a given temperature and assuming that the backward reactions of all these reactions have the same frequency factor, the rates of R_1, R_2, R_3 and R_4 in their respective backward reactions are in the increasing order of

(a) $R_2 < R_3 < R_4 < R_1$

(b) $R_4 < R_3 < R_2 < R_1$

(c) $R_1 < R_4 < R_3 < R_2$

(d) $R_1 < R_2 < R_3 < R_4$

76. (S) For the decomposition of N_2O_5 at a particular Temperature according to the equations

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$
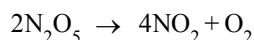
the activation energies are E_1 and E_2 respectively, then

(a) $E_1 > E_2$ (b) $E_1 < E_2$

(c) $E_1 = 2E_2$ (d) $E_1 = E_2$

77. (S) The activation energy of a reaction is zero. The rate constant of the reaction

(a) increases with increase of temperature

(b) decreases with increase of temperature

(c) decreases with decrease of temperature

(d) is nearly independent of temperature.

78. (S) Milk turns sour at 40ºC three times faster at 0ºC. Hence Ea in calories of turning of milk sour is

(a) $\dfrac{2.303 \times 2 \times 313 \times 273}{40} \log 3$

(b) $\dfrac{2.303 \times 2 \times 313 \times 273}{40} \log(1/3)$

(c) $\dfrac{2.303 \times 2 \times 40}{273 \times 313} \log 3$

(d) none

79. (S) The ratio of the rate constant of a reaction at any temperature T to the rate constant $T \rightarrow \infty$ is equal to

(a) Energy of activation of the reaction

(b) Fraction of molecules in the activated state

(c) Average life of the reaction

(d) Pre-exponential factor in the Arrhenius equation

80. (S) The rate constant of a reaction A $\rightarrow$ B + C at 27ºC is $3.0 \times 10^{-5}\,s^{-1}$ and at this temperature 1.5×10^{-4} percent of the reactant molecules are able to cross-over the P.E. barrier. The maximum rate constant of the reaction is

(a) $4.5 \times 10^{-9}\,s^{-1}$ (b) $4.5 \times 10^{-11}\,s^{-1}$

(c) $0.2\,s^{-1}$ (d) $20\,s^{-1}$

81. (S) According to the collision model of kinetics, certain activation energy must be overcome before a reaction can proceed. Based on the data given below, what is a reasonable estimate of the activation energy for the decomposition of NOCl ?

$$2\,NOCl(g) \rightarrow 2\,NO(g) + Cl_2(g)$$
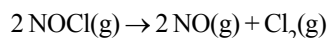
temperature (K)	rate constant, k (L/mol s)
400	6.6×10^{-4}
500	2.9×10^{-1}
600	1.63×10^{1}

(a) 1.00×10^{2} J/K mol   (b) 1.23×10^{3} J/K mol

(c) 1.05×10^{5} J/K mol   (d) 1.34×10^{6} J/K mol

82. (S) The rate constant of a reaction at 27ºC is 2.3×10^{-3} min^{-1} and at this temperature 0.002% of the reactant molecules are able to cross over the energy barrier existing between the reactants and products. By increasing the temperature, the rate constant of reaction will increase to a maximum of

(a) 2.3×10^{-2} min^{-1} (b) 4.6×10^{-2} min^{-1}

(c) 2.30 min^{-1} (d) 115 min^{-1}

83. (M) Which of the following statements about the Arrhenius equation is/are correct ?

(a) The pre-exponential factor becomes equal to the rate constant of the reaction at extremely high temperature

(b) When the activation energy of the reaction is zero, the rate becomes independent of temperature

(c) The term $e^{-Ea/RT}$ represents the fraction of the molecules having energy in excess of threshold value

(d) On raising temperature, rate constant of the reaction of greater activation energy increases less rapidly than that of the reaction of smaller activation energy.

84. (M) When the temperature of a reaction is changed from T_1 to T_2 half-life is found to decrease. Thus :
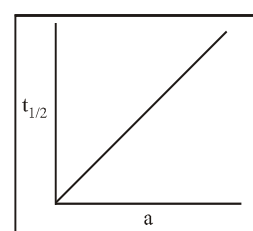
(a) $T_2 > T_1$

(b) The reaction is exothermic

(c) The reaction is endothermic

(d) The reaction can be exothermic or endothermic

85. (M) Which of the following graphs plotted are true ?

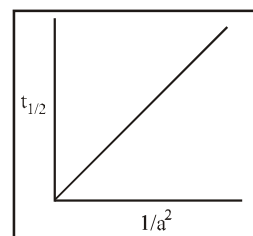(a) For a zero order reaction
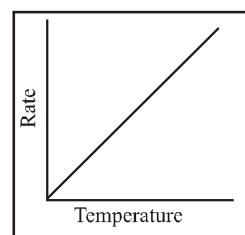
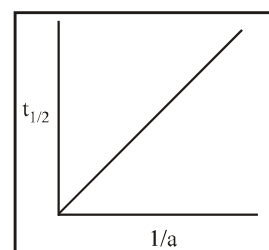(b) For a zero order reaction

where a is initial concentration
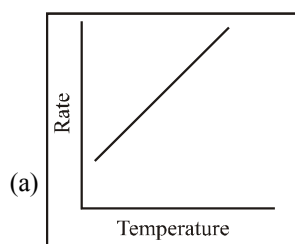
(c) For a 3rd order reaction

(d) For a 1st order reaction

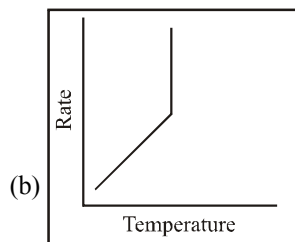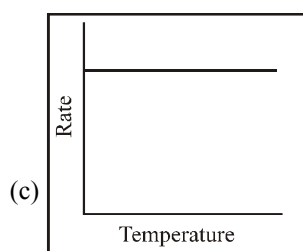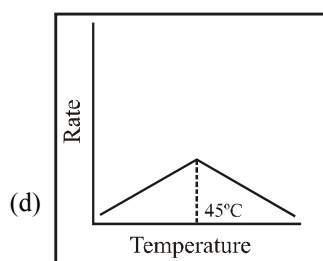**86. (M)** Which of the following graphs are properly represented

(a)

For normal reaction

(b)

For explosive reaction

(c)

For all normal reaction

(d)

For explosive reaction

87. **Asseration :** If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.

Reason : Lower the activation energy, faster is the reaction.

(a) A   (b) B

(c) C   (d) D

Comprehension

Measurement of rate of reactions provides as insight into the series of elementary steps by which a reaction takes place. In most cases, the rate depends on the concentrations of the reactants which decreases with the progress of the reaction. In consequence, the rate invariably decreases with time. In chemical kinetics, the rate at any instant of time i.e., instantaneous rate is

expressed as $\dfrac{-d[R]}{dt}$ or $\dfrac{d[P]}{dt}$, where R and P are the reactants and products respectively. For example, for the reaction

$$A + 2B \rightarrow 3C + D \qquad \text{.............. (i)}$$

The rate w.r.t. A, B, C and D would be $\dfrac{-d[A]}{dt}, \dfrac{-d[B]}{dt}, \dfrac{d[C]}{dt}$ and $\dfrac{d[D]}{dt}$ respectively. Obviously, these rates will be different .

However, the unique or rationalized rate of reaction is defined as the rate of change of extent of reaction as :

Rate (unique) of reaction

$$= \dfrac{-d[A]}{dt} = -\dfrac{1}{2}\dfrac{-d[B]}{dt} = \dfrac{1}{3}\dfrac{d[C]}{dt} = \dfrac{d[D]}{dt}$$

The dependence of rate on concentrations of reactants is expressed in terms of rate law, which is established experimentally.

$$\text{Rate} = k\,[A]^a\,[B]^b \qquad \text{(Rate law)} \text{...............(ii)}$$

The exponents a, b, etc. (determined experimentally) may or may not be equal to the respective stoichiometric coefficients. k is the velocity constant of the reaction.

The determination of rate law is simplified by the isolation method in which the concentration of all the reactants except one are in large excess. The concentrations of the reactants in large excess remain practically constant throughout the reaction. If B is in large excess. we can approximate [B] by $[B]_0$

Hence, $\text{Rate} = k\,[A]^a\,[B]^b = k\,[A]^a\,[B]_0^b = k'[A]^a$

$$(k' = k[B]_0^b)$$

or $\log(\text{initial rate}) = \log \upsilon_0 = \log k' + a \log[A]$ .... (iii)

A plot of log (rate) against log [A] values will be a straight line which enables to calculate both k' and a. Similarly orders with respect to other reactants. taken in much smaller concentrations turn by turn, can be determined. Consider the reaction :
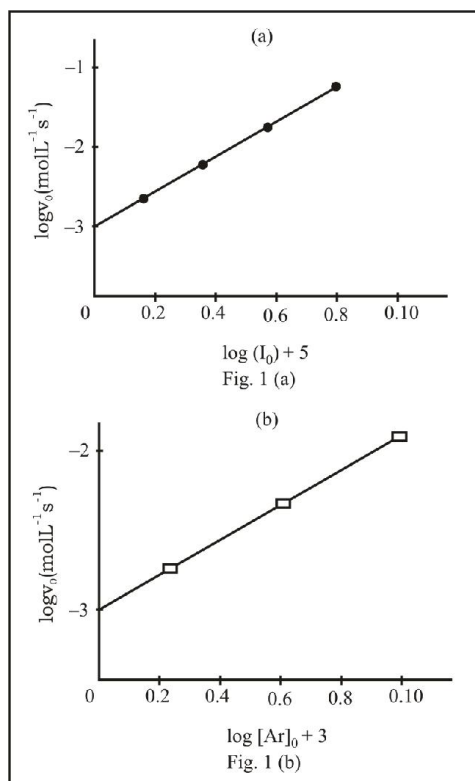
$$2I_{(g)} + Ar_{(g)} \longrightarrow I_{2(g)} + Ar_{(g)}$$
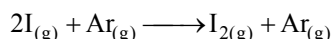
The following figures show the variation of $\log \upsilon_0$ against (a) $\log I_0$ for a given $[Ar]_0$ and (b) $\log [Ar]_0$ for a given $[I]_0$

The rate constants of most reactions increase as the temperature is increased. The rate constant increases by about 100-200% for a temperature rise of 10K. It is found experimentally for many reactions that a plot of ℓn k against 1/T gives a straight line. This behaviour is expressed in the form of equation.

$$\ell n \ k = \ell n \ A - \frac{E_a}{RT} \qquad \text{............. (iv)}$$

A and E_a are called pre-exponential factor and activation energy respectively. From the plot of ℓn k versus 1/T, the values of A and E_a can be calculated.

88. (C) The rate of change of molar concentration of C in Reaction – 1, is found to be 3.0×10^{-3} mol $L^{-1} s^{-1}$. The rate of reaction and rate of disappearance of the reactant B are respectively.

(a) 3.0×10^{-3} mol $L^{-1} s^{-1}$ each

(b) 1.0×10^{-3} mol $L^{-1} s^{-1}$ each

(c) 1.0×10^{-3} mol $L^{-1} s^{-1}$ and 2.0×10^{-3} mol $L^{-1} s^{-1}$

(d) None of these.

89. (C) According to the fig-1 (a) and 1 (b), the rate law for the reaction

$$2I_{(g)} + Ar_{(g)} \longrightarrow I_{2(g)} + Ar_{(g)} \text{ is given by}$$
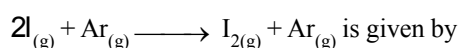
(a) Rate = k [I] [Ar]   (b) Rate = $k[I]^2$

(c) Rate = $k[I]^2 [Ar]^2$ (d) Rate = $k[I]^2 [Ar]$

90.(C) The greater slope of the plot of ℓn k against 1/T for a reaction shows the rate constant to be

(a) Independent of temperature

(b) Strongly dependent on temperature

(c) Poorly dependent on temperature

(d) Insufficient information to predict

91. (C) Which of the following statements is not correct ?

(a) Rate of effective collisions between reacting molecules is equal to A

(b) Rate of the effective collisions between reacting molecules is $Ae^{-E_a/RT}$

(c) Rate of total collisions between reacting molecules is equal to A

(d) Fraction of collisions between reacting molecules having energy in excess of activation energy $= e^{-E_a/RT}$

92. (I) Temperature coefficient is defined as the factor by which the rate of reaction increases on increasing the temperature by 10ºC at a given temperature. If activation energy of a reaction is 85 kJ, determine the temperature coefficient at 300 K (Rounded off to the nearest whole number).

# EXERCISE – 4 : PREVIOUS YEAR JEE ADVANCED QUESTION

1. For the elementary reaction M $\rightarrow$ N, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is **(2015)**

   (a) 4   (b) 3

   (c) 2   (d) 1

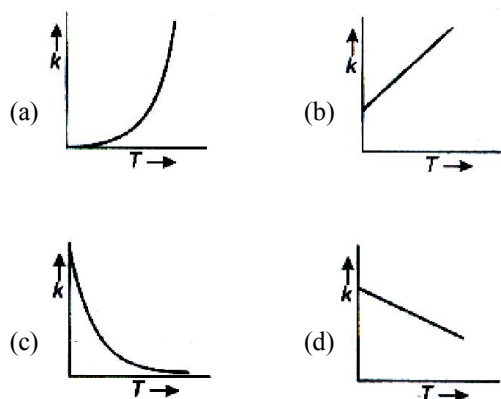2. In the reaction,

   $$P + Q \longrightarrow R + S$$
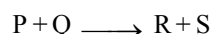
   the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is **(2013)**
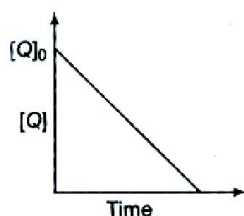
   (a) 2   (b) 3

   (c) 0   (d) 1

3. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is **(2010)**

4. For a first order reaction A $\rightarrow$ P, the temperature (T) dependent rate constant (k) was found to follow the equation :

   $$\log k = \frac{2000}{T} + 6.0$$

The pre-exponential factor A and the activation energy E_a, respectively, are **(2009)**

(a) $1.0 \times 10^6 \, s^{-1}$ and $9.2 \, kJ \, mol^{-1}$

(b) $6.0 \, s^{-1}$ and $16.6 \, kJ \, mol^{-1}$

(c) $1.0 \times 10^6 \, s^{-1}$ and $16.6 \, kJ \, mol^{-1}$

(d) $1.0 \times 10^6 \, s^{-1}$ and $38.3 \, kJ \, mol^{-1}$

5. Under the same reaction conditions, initial concentration of $1.386 \, mol \, dm^{-3}$ of a substance becomes half in 40 s and 20 s through first order and zero order kinetics respectively.

   Ratio $\left(\dfrac{k_0}{k_1} \right)$ of the rate constants for first order (k_1) and zero order (k_0) of the reaction is **(2008)**

   (a) $0.5 \, mol^{-1} \, dm^3$ (b) $1.0 \, mol \, dm^{-3}$

   (c) $1.5 \, mol \, dm^{-3}$ (d) $2.0 \, mol^{-1} \, dm^3$

6. T_{50} of first-order reaction is 10 min. Starting with $10 \, mol \, L^{-1}$, rate after 20 min is **(2008)**

   (a) $0.0693 \, mol \, L^{-1} \, min^{-1}$

   (b) $0.0693 \times 2.5 \, mol \, L^{-1} \, min^{-1}$

   (c) $0.0693 \times 5 \, mol \, L^{-2} \, min^{-1}$

   (d) $0.0693 \times 10 \, mol \, L^{-1} \, min^{-1}$
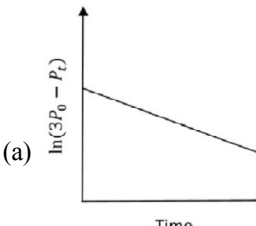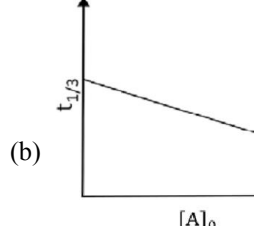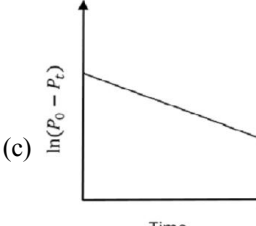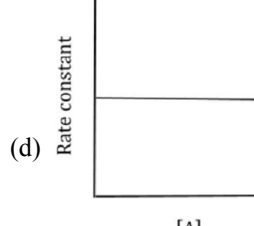
7. Consider a reaction aG + bH $\rightarrow$ Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is **(2007)**

   (a) 0   (b) 1

   (c) 2   (d) 3

8. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation $k = Ae^{-E_a / RT}$. Activation energy (E_a) of the reaction can be calculated by ploting **(2007)**

   (a) $\log k$ vs T   (b) $\log k$ vs $\dfrac{1}{T}$

   (c) k vs T   (d) k vs $\dfrac{1}{\log T}$

9. Consider the reaction, $2A + B \rightarrow$ products

   When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is   **(2007)**

   (a) $L\ mol^{-1}\ s^{-1}$ (b) no unit

   (c) $mol\ L^{-1}\ s^{-1}$ (d) s^{-1}

10. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial activity is ten times the permissible value, after how many days will it be safe to enter the room ?   **(2007)**

    (a) 1000 days   (b) 300 days

    (c) 10 days   (d) 100 days

11. $Ag^+ NH_3 \rightleftharpoons [Ag(NH_3)^+]\ ;\ k_1 = 6.8 \times 10^{-3}$

    $[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+\ ;\ k_2 = 1.6 \times 10^{-3}$

    then the formation constant of $[Ag(NH_3)_2]^+$ is   **(2006)**

    (a) 6.8×10^{-6} (b) 1.08×10^{-5}

    (c) 1.08×10^{-6} (d) 6.8×10^{-5}

12. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr

    $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$

    $NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$

    If the second step is the rate determining step, the order of the reaction with respect to NO (g) is   **(2006)**

    (a) 1   (b) 0

    (c) 3   (d) 2

13. For the reaction $A + B$ .... C, it found that doubling the concentration of A increases the rate by 4 times, and doubling the concentration of B doubles reaction rate. What is the overall order of the reaction ?   **(2006)**

    (a) 4   (b) 3/2

    (c) 3   (d) 1

14. $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to 3/4 of its initial value. If the rate constant for a first order reaction is k, the $t_{1/4}$ can be written as   **(2005)**

    (a) 0.75/k   (b) 0.69/k

    (c) 0.29/k   (d) 0.10/k

15. Consider an endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for the backward and forward reactions respectively. In general   **(2005)**

    (a) there is no definite relation between E_b and E_f

    (b) $E_b = E_f$

    (c) $E_b > E_f$ (d) $E_b < E_f$

16. Which one of the following statement for order of reaction is not correct ?   **(2005)**

    (a) Order can be determind experimentally

    (b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.

    (c) It is not affected with the stoichiometric coefficient of the reactants

    (d) Order cannot be fractional

17. The reaction, $X \rightarrow$ Product, follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 to 0.025 M. The rate of reaction, when concentration of X is 0.01 M is   **(2004)**

    (a) $1.73 \times 10^{-4} M\ min^{-1}$ (b) $3.47 \times 10^{-4}\ M\ min^{-1}$

    (c) $3.47 \times 10^{-4} M\ min^{-1}$ (d) $1.73 \times 10^{-5} M\ min^{-1}$

18. The rate constant of a reaction depends upon :   **(2004)**

    (a) extent of reaction

    (b) time of reaction

    (c) temperature of the system

    (d) concentration of the system

19. In a first order reaction the concentration of reactant decreases from $800\ mol/dm^3$ to $50\ mol/dm^3$ in 2×10^4 sec. The rate constant of reaction in sec^{-1} is :   **(2003)**

    (a) 2×10^4 (b) 3.45×10^{-5}

    (c) 1.386×10^{-4} (d) 2×10^{-4}

20. The rate constant of a reaction depends on :   **(2003)**

    (a) the temperature of a reaction

    (b) the time of a reaction   (c) the extent of reaction

    (d) the initial conc. of the reactant

21. Consider the chemical reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions. **(2002)**

(a) Rate $= -d[N_2]/dt = -1/3\,d[H_2]/dt = 1/2\,d[NH_3]/dt$

(b) Rate $= -d[N_2]/dt = -3\,d[H_2]/dt = 2\,d[NH_3]/dt$

(c) Rate $= -d[N_2]/dt = 1/3\,d[H_2]/dt = 1/2\,d[NH_3]/dt$

(d) Rate $= -d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$

22. If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process, $AB + h\nu \longrightarrow AB^*$, the rate of formation of AB^* is directly proportional to **(2001)**

(a) C   (b) I

(c) I^2 (d) C.I

23. The rate constant for the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, is 3.0×10^{-5} sec^{-1}. If the rate is 2.40×10^{-5} mol litre^{-1} sec^{-1}, then the concentration of N_2O_5 (in mol litre^{-1}) is **(2000)**

(a) 1.4   (b) 1.2

(c) 0.04   (d) 0.8

24. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25ºC are $3.0 \times 10^{-4}\,s^{-1}$, 104.4 kJ mol^{-1} and $6.0 \times 10^{14}\,s^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is, **(1996)**

(a) $2.0 \times 10^{18}\,s^{-1}$ (b) $6.0 \times 10^{14}\,s^{-1}$

(c) infinity   (d) $3.6 \times 10^{30}\,s^{-1}$

25. The half-life period of a radioactive element is 140 days. After 650 days, one gram of the element will reduce to : **(1986)**

(a) $\dfrac{1}{2}\,g$ (b) $\dfrac{1}{4}\,g$

(c) $\dfrac{1}{8}\,g$ (d) $\dfrac{1}{16}\,g$

26. A catalyst is a substance which **(1983)**

(a) increases the equilibrium concentration of the product

(b) changes the equilibrium constant of the reaction

(c) shortens the time to reach equilibrium

(d) supplies energy to the reaction

27. The specific rate constant of a first order reaction depends on the **(1983)**

(a) concentration of the reactant

(b) concentration of the product

(c) time

(d) temperature

Objective Questions (One or more than one correct option)

28. For a first order reaction $A(g) \rightarrow 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning (t - 0) and at time t are P_0 and P_t, respectively. Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach $1/3^{rd}$ of its initial value. The correct option(s) is (are) (Assume that all these gases behave as ideal gases) **(2018)**

29. In a bimolecular reaction, the steric factor P was experimentaly determined to be 4.5. the correct option(s) among the following is (are) **(2017)**

(a) The activation energy of the reaction is unaffected by the value of the steric factor

(b) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation

(c) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

(d) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used

30. According to the Arrhenius equation, **(2016)**

(a) a high activation energy usually implies a fast reaction.

(b) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy.

(c) higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant.

(d) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

31. The following statement (s) is (are) correct **(1999)**

(a) A plot of $\log K_p$ vs $\dfrac{1}{T}$ is linear

(b) A plot of $\log [X]$ vs time is linear for a first order reaction, $x \to p$

(c) A plot of $\log p$ vs $\dfrac{1}{T}$ is linear at constant volume

(d) A plot of p vs $\dfrac{1}{V}$ is linear at constant temperature

32. For the first order reaction **(1998)**

(a) the degree of dissociation is equal to $(1 - e^{-kt})$

(b) a plot of reciprocal concentration of the reactant vs time gives a straight line

(c) the time taken for the completion of 75% reaction is thrice the $\dfrac{1}{2}$ of the reaction

(d) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}

33. A catalyst **(1984)**

(a) increases the average kinetic energy of reacting molecules

(b) decreases the activation energy

(c) alters the reaction mechanism

(d) increase the frequency of collisions of reacting species.

Comprehension - I (Ques 34 to 36)

Carbon-14 is used to determine the age of organic material. The procedure is based on the formation of ^{14}C by neutron capture in the upper atmosphere.

$$^{14}_{7}N + {}_{0}n^{1} \longrightarrow {}^{14}_{6}C + {}_{1}p^{1}$$
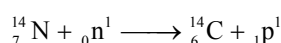
^{14}C is absorbed by living organisms during photosynthesis. The ^{14}C content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead being, falls due to the decay which C-14 underoges

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + \beta^{-}$$
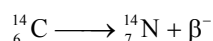
The half-life period of ^{14}C is 5770 yr.

The decay constant (λ) can be calculated by using the following formula $\lambda = \dfrac{0.693}{t_{1/2}}$

The comparison of the β^{-} activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 yr. The proportion of ^{14}C to ^{12}C in living matter is $1 : 10^{12}$. **(2006)**

34. Which of the following option is correct ?

(a) In living organisms, circulation of ^{14}C from atmosphere is high so the carbon content is constant in organism

(b) Carbon dating can be used to find out the age of earth crust and rocks

(c) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbons content remains constant in living organisms

(d) Carbon dating cannot be used to determine concentration of ^{14}C in dead beings.

35. What should be the age of fossil for meaningful determination of its age ?

(a) 6 yr   (b) 6000 yr

(c) 60,000 yr

(d) It can be used to calculate any age

36. A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the places respectively then

(a) the age of fossil will increase at the place where explosion has taken place and $T_1 - T_2 = \dfrac{1}{\lambda} \ln \dfrac{C_1}{C_2}$

(b) the age of fossil will decrease at the place where explosion has taken place and $T_1 - T_2 = \dfrac{1}{\lambda} \ln \dfrac{C_1}{C_2}$

(c) the age of fossil will be determined to be the same

(d) $\dfrac{T_1}{T_2} = \dfrac{C_1}{C_2}$

Fill in the Blanks

37. The rate of chemical change is directly proportional to .... **(1985)**

38. The hydrolysis of ethyl acetate in .... medium is a .... order reaction. **(1986)**

39. For the reaction : $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 0.001 kg/h^{-1}.

The rate of conversion of H_2 under the same condition is .... kg/h^{-1}. **(1994)**

40. In the Arrhenius equation, $k = A \exp^{(-E_a/RT)}$. A may be termed as the rate constant at .... **(1997)**

True/False

41. For a first order reaction, the rate of the reaction doubles as the concentration of the reaction (s) doubles. **(1986)**

Subjective Questions

42. An organic compound undergoes first order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$?

$(\log_{10} 2 = 0.3)$

43. $2X(g) \rightarrow 3Y(g) + 2Z(g)$

Time (in min)	0	100	200
Partial pressure of X			
(in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate

(a) Order of reaction

(b) Rate constant

(c) Time taken for 75% completion of reaction

(d) Total pressure when $p_x = 700$ mm **(2005)**

44. For the given reaction,

$$A + B \rightarrow \text{Products}$$
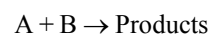
Following data are given

Initial conc. (m/L)	Initial conc. (m/L)	Initial rate ($\text{mL}^{-1}\text{s}^{-1}$)
$[A]_0$	$[B]_0$	
0.1	0.1	0.05
0.2	0.1	0.1
0.1	0.2	0.05

(a) Write the rate equation.

(b) Calculate the rate constant. **(2004)**

45. ^{64}Cu (half-life = 12.8 h) decays by β emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes. **(2002)**

46. The rate of first order reaction is $0.04 \text{ mol L}^{-1}\text{s}^{-1}$ at 10 min and $0.03 \text{ mol L}^{-1}\text{s}^{-1}$ at 20 min after initiation. Find the half-life of the reaction. **(2001)**

47. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1}. **(2000)**

48. The rate constant for an isomerization reaction, $A \rightarrow B$ is 4.5×10^{-3} min. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1h. **(1999)**

49. (a) The rate constant of a reaction is $1.5 \times 10^7 \text{ s}^{-1}$ at 50ºC and $4.5 \times 10^7 \text{ s}^{-1}$ at 100ºC. Evaluate the Arrhenius parameters A and E_a. **(1998)**

(b) For the reaction, $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2} O_2(g)$, calculate the mole fraction $N_2O_5(g)$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

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

$$\log k \; (s^{-1}) = 14.34 - \frac{1.25 \times 10^4 \, K}{T}$$

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

(ii) At what temperature will its half-life period be 256 min ?

(1997)

51. At 380° C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450° C. **(1995)**

52. One of the hazards of nuclear explosion is the generation of Sr^{90} and its subsequent incorporation in bones. This nucleide has a half-life of 28.1 yr. Suppose one microgram was absorbed by a new-born child, how much Sr^{90} will remain in his bones after 20 yr. **(1995)**

53. From the following data for the reaction between A and B

[A], (mol/L)	[B] (mol/L)	Initial rate (mol L^{-1} s^{-1} at) 300 K	320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	—
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	—

Calculate

(i) the order of the reaction with respect to A and with respect to B.

(ii) the rate constant at 300 K.

(iii) the pre-exponential factor. **(1994)**

54. The gas phase decomposition of dimethyl ether follows first order kinetics

$$CH_3 - O - CH_3 \, (g) \rightarrow CH_4 \, (g) + H_2 \, (g) + CO \, (g)$$
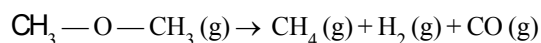
The reaction is carried out in a constant volume container at 500°C and has a half-life of 14.5 min. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min ? Assume ideal gas behaviour. **(1993)**

55. A first order reaction A → B, requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 min, 25% decomposition took place. What will be the percentage decomposition in the same time in a 30%

solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature.

(1993)

56. Two reactions (i) A → products (ii) B → products, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 min. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i) calculate in this range of temperature. **(1992)**

57. The nuclidic ratio, $_1^3 H$ to $_1^1 H$ in a sample of water is 8.0×10^{-18} : 1. Tritium undergoes decay with a half-life period of 12.3 yr. How many tritium atoms would 10.0 g of such a sample contain 40 yr after the original sample is collected. **(1992)**

58. The decomposition of N_2O_5 according to the equation,

$$2N_2O_5 \, (g) \rightarrow 4NO_2 \, (g) + O_2 \, (g)$$
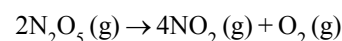
is a first order reaction. After 30 min from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg. On complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction. **(1991)**

59. In the Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are 4×10^{13} s^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period be 10 min ?

(1990)

60. An experiment requires minimum beta activity produced at the rate of 346 beta particles per minute. The half-life period of $_{42}Mo^{99}$ which is a beta emitter is 66.6 h. Find the minimum amount of $_{42}Mo^{99}$ required to carry out the experiment in 6.909 h. **(1989)**

61. A first order gas reaction has k = 1.5×10^{-6} per second at 200°C. If the reaction is allowed to run for 10 h, what percentage of the initial concentration would have change in the product ? What is the half-life of this reaction ?

(1987)

62. While studying the decomposition of gaseous N_2O_5, it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameters can be obtained from this observation ? **(1985)**

63. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 yr. What is the rate constant (in yr^{-1}) for the decay ? What fraction would remain after 11540 yr ? **(1984)**

64. A first order reaction is 20% complete in 10 min. Calculate

(i) the specific rate constant of the reaction, and

(ii) the time taken for the reaction to go to 75% completion.

(1983)

65. Rate of reaction A + B → products is given below as a function of different initial concentration of A and B

[A] mol/L	[B] (mol/L)	Initial rate $(mol\ L^{-1}\ min^{-1})$
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and B. What is the half-life of A in the reaction ? **(1982)**

66. Consider the following reversible reaction,

$A(g) + B(g) \rightleftharpoons AB(g).$ **(2018)**

The activation energy of the backward reaction exceeds that of the forward reaction by 2RT (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^- (in J mol^{-1}) for the reaction at 300 K is ....

(Given; ln(2) = 0.7, RT = 2500 J mol^{-1} at 300 K and G is the Gibbs energy)

ANSWER KEY

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

1. (b)	**2.** (d)	**3.** (c)	**4.** (b)	**5.** (b)	**6.** (c)	**7.** (a)	**8.** (a)	**9.** (a)	**10.** (c)
11. (d)	**12.** (a)	**13.** (c)	**14.** (c)	**15.** (a)	**16.** (b)	**17.** (d)	**18.** (b)	**19.** (a)	**20.** (c)
21. (b)	**22.** (c)	**23.** (c)	**24.** (d)	**25.** (c)	**26.** (b)	**27.** (a)	**28.** (c)	**29.** (a)	**30.** (a)
31. (c)	**32.** (b)	**33.** (b)	**34.** (a)	**35.** (c)	**36.** (b)	**37.** (b)	**38.** (d)	**39.** (d)	**40.** (b)
41. (d)	**42.** (a)	**43.** (b)	**44.** (b)	**45.** (c)	**46.** (b)	**47.** (c)	**48.** (c)	**49.** (a)	**50.** (b)
51. (d)	**52.** (d)	**53.** (a)	**54.** (b)	**55.** (d)	**56.** (b)				

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTIONS

1. (d)	**2.** (a)	**3.** (a)	**4.** (d)	**5.** (a)	**6.** (b)	**7.** (a)	**8.** (d)	**9.** (a)	**10.** (d)
11. (b)	**12.** (d)	**13.** (b)	**14.** (c)	**15.** (d)	**16.** (c)	**17.** (b)	**18.** (c)	**19.** (b)	**20.** (a)
21. (c)	**22.** (a)	**23.** (d)	**24.** (c)	**25.** (c)					

JEE Mains Online

1. (c)	**2.** (a)	**3.** (b)	**4.** (d)	**5.** (b)	**6.** (a)	**7.** (a)	**8.** (b)	**9.** (a)	**10.** (d)
11. (c)	**12.** (b)								

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. (c)	**2.** (c)	**3.** (b)	**4.** (c)	**5.** (c)	**6.** (d)	**7.** (b)	**8.** (c)	**9.** (d)	**10.** (b)
11. (b)	**12.** (b)	**13.** (c)	**14.** (b)	**15.** (c)	**16.** (a)	**17.** (d)	**18.** (b)	**19.** (d)	**20.** (c)
21. (a)	**22.** (d)	**23.** (b)	**24.** (d)	**25.** (d)	**26.** (a)	**27.** (a)	**28.** (a)	**29.** (ac)	**30.** (a,b)
31. (d)	**32.** (c)	**33.** (a)	**34.** (b)	**35.** (d)	**36.** (d)	**37.** (a)	**38.** (d)	**39.** (d)	**40.** (b)
41. (c)	**42.** (d)	**43.** (d)	**44.** (abc)	**45.** (b)	**46.** (A – R; B – S; C – Q; D – P)		**47.** (0004)		
48. (a)	**49.** (b)	**50.** (c)	**51.** (b)	**52.** (abc)	**53.** (0008)	**54.** (0004)	**55.** (c)	**56.** (d)	**57.** (b)
58. (d)	**59.** (c)	**60.** (a)	**61.** (b)	**62.** (b)	**63.** (ab)	**64.** (a)	**65.** (a)	**66.** (a)	**67.** (a)
68. (a)	**69.** (b)	**70.** (c)	**71.** (abc)	**72.** (a)	**73.** (d)	**74.** (c)	**75.** (d)	**76.** (d)	**77.** (d)
78. (a)	**79.** (b)	**80.** (d)	**81.** (c)	**82.** (d)	**83.** (abc)	**84.** (ad)	**85.** (bc)	**86.** (ab)	**87.** (b)
88. (c)	**89.** (d)	**90.** (b)	**91.** (a)	**92.** (0003)					

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTIONS

1. (b)	**2. (d)**	**3. (a)**	**4.** (d)	**5.** (d)	**6.** (b)	**7.** (d)	**8.** (b)	**9.** (a)	**10.** (d)
11. (b)	**12.** (d)	**13.** (c)	**14.** (c)	**15.** (d)	**16.** (d)	**17.** (c)	**18.** (c)	**19.** (c)	**20.** (a)
21. (a)	**22.** (b)	**23.** (d)	**24.** (b)	**25.** (d)	**26.** (c)	**27.** (d)	**28.** (a,d)	**29.** (a,c)	**30.** (a,b,d)

31. (b,c,d)

32. (ad)   **33.** (bc)   **34.** (c)   **35.** (b)   **36.** (b)   **37.** concentration of reactant(s) at that instant

38. acidic, first or basic, second   **39.** $0.0015 \, kg \, h^{-1}$ **40.** At $T = \infty$, $k = A$ **41.** (T)   **42.** (0009)

43. (a) 1, **(b)** $6.93 \times 10^{-3} \, min^{-1}$, **(c)** 200 min, **(d)** 950 mm   **44. (a)** Rate = k [A], **(b)** $0.5 \, s^{-1}$

45. $T_1 = 33.68h$, $T_2 = 67.36 \, h$, $T_3 = 29.76h$ **46.** 25 min   **47.** 100 kJ   **48.** $3.42 \times 10^{-3} \, mol \, L^{-1} \, min^{-1}$

49. (a) $A = 4.15 \times 10^3 \, s^{-1}$, $E_a = 22kJ$, **(b)** 0.375   **50. (i)** 239.33 kJ, **(ii)** 669 K   **51.** 20.74 min   **52.** $6.1 \times 10^{-7} \, g$

53. (i) order wrt. A = 2, order wrt. B = 1 **(ii)** $2.66 \times 10^8 \, s^{-1} \, L^2 \, mol^{-2}$ **(iii)** 1.2×10^{18} **54.** 0.75 atm   **55.** 67%

56. $3.26 \times 10^{-2} \, min^{-1}$ **57.** 5.6×10^5 **58.** $5.2 \times 10^{-3} \, min^{-1}$ **59.** 311.34 K   **60.** $3.56 \times 10^{-16} \, g$

61. 128.33 h   **63.** $1.2 \times 10^{-4} \, yr^{-1}$, 0.25   **64. (i)** $0.023 \, min^{-1}$, **(ii)** 60 min   **65.** 1.386 min.

66. 8500

Dream on !!

卐卐卐卐卐卐卐卐