

CHAPTER 8

CHEMICAL KINETICS

8.1 INTRODUCTION

Thermodynamics deals with the feasibility of a chemical change. The free energy change, ΔG , of a reaction helps us to understand whether the reaction will occur or not. Even though there may be decrease in free energy but reactants do not always form the products instantaneously and actual rate of the reaction may vary from extremely slow to very fast. Thermodynamics is concerned only with initial and final states of reacting systems but offers no explanation about the various stages through which the reactants pass to reach the final state. This leads to following questions concerning chemical changes.

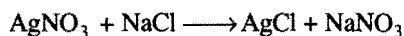
- How fast do the chemical reactions go?
- How can the speed of the reaction change?
- What intermediate steps, the reactants follow to reach the final state of products, i.e., the mechanism of the reaction.

The branch of physical chemistry which deals with the rate at which the chemical reactions occur, the mechanism by which the chemical reactions take place and the influence of various factors such as concentration, temperature, pressure, catalyst, etc., on the reaction rates, is called the **chemical kinetics**.

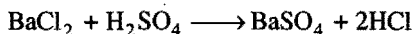
Different chemical reactions occur at different rates. On the basis of rates, the chemical reactions are broadly divided into three categories:

(a) Very fast or instantaneous reactions: These reactions are so fast that they occur as soon as the reactants are brought together. Generally, these reactions involve ionic species and thus known as ionic reactions. These reactions take about 10^{-14} to 10^{-16} seconds for completion. It is almost impossible to determine the rates of these reactions. Some such examples are:

(i) Precipitation of AgCl when solutions of silver nitrate and sodium chloride are mixed.



(ii) Precipitation of BaSO_4 when solutions of barium chloride and sulphuric acid are mixed.



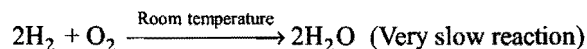
(iii) Neutralisation of an acid with a base when their aqueous solutions are mixed.



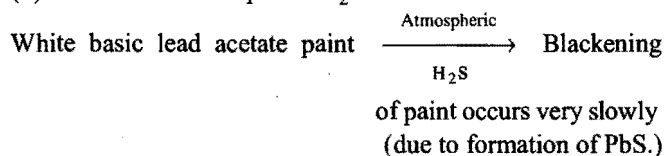
(b) Very slow reactions: There are certain reactions which are extremely slow. They may take months together to show any measurable change at room temperature. It is also difficult to study the kinetics of such reactions.

Some examples are:

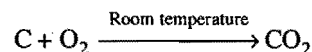
(i) Reaction between hydrogen and oxygen at room temperature.



(ii) Reaction of atmospheric H_2S on basic lead acetate.

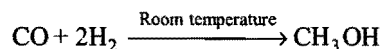


(iii) Reaction between carbon and oxygen.



Carbon and oxygen are thermodynamically less stable than CO_2 at 298 K, yet coke does not spontaneously catch fire in air and remains unreacted even for years.

(iv) Reaction between carbon monoxide and hydrogen.



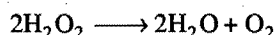
The reaction is thermodynamically feasible at 298 K but in actual practice the reaction proceeds infinitesimally slowly.

(v) Rusting of iron occurs very slowly.

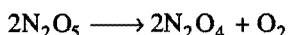
(c) Moderate reactions: Between the above two extremes, there are a number of reactions which take place at moderate and measurable rates at room temperature and it is these reactions which are studied in chemical kinetics. Mostly these reactions are

molecular in nature. Some common examples of such type are given below:

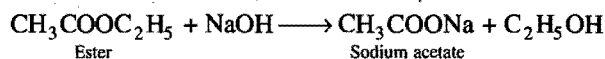
- (i) Decomposition of hydrogen peroxide.



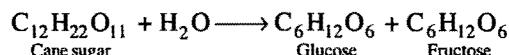
- (ii) Decomposition of nitrogen pentoxide.



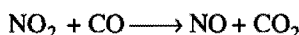
- (iii) Hydrolysis of an ester.



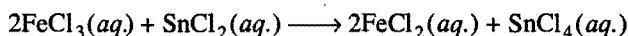
- (iv) Inversion of cane sugar in aqueous solution.



- (v) Reaction between nitrogen dioxide and carbon monoxide.

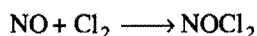


- (vi) Reaction between ferric chloride and stannous chloride.



- (vii) Decolourisation of acidified potassium permanganate with sodium oxalate.

- (viii) Reaction between nitric oxide and chlorine.



The chemical reactions can be slowed down or speeded up by changing conditions under which they occur. For example, very slow reaction, $\text{CO} + 2\text{H}_2 \longrightarrow \text{CH}_3\text{OH}$, can be speeded up by maintaining temperature around 400°C , pressure about 300 atmospheres and using a catalyst containing ZnO and Cr_2O_3 . The decay of food articles can be slowed down by preserving them in refrigerators. There are two principal reasons for studying chemical kinetics.

(i) **To predict the rate of a particular reaction under specified conditions:** The conditions can be adjusted to make the reaction to go at a desired rate, either rapidly or slowly or moderately. The field of chemical kinetics is useful in industry as the conditions for maximum yields of industrial products can be ascertained.

(ii) **To predict the mechanism of the reaction:** The intelligent guess regarding various elementary processes responsible for the formation of products can be made which should be consistent with experimental data.

8.2 RATE OF REACTION (Average and Instantaneous Rate)

We are all familiar with processes in which something changes with time. Rate is usually expressed as the ratio of the amount of change in some quantity to the time required to produce that change.

$$\text{Rate} = \frac{\text{Change in some quantity}}{\text{Time taken for the change}} = \frac{\Delta X}{\Delta t}$$

The term ΔX means $X_{\text{final}} - X_{\text{initial}}$ and Δt is the amount of time elapsed. For example, a car driver starts his journey at 9.0 a.m. with odometer reading x miles. At 11.0 a.m. he reaches his

destination. The odometer reading at destination is y miles. The rate of his travel can be calculated as:

$$\begin{aligned} \text{Rate} &= \frac{\Delta(\text{distance})}{\Delta(\text{time})} = \frac{\text{distance}_{(f)} - \text{distance}_{(in)}}{\text{time}_{(f)} - \text{time}_{(in)}} \\ &= \frac{y - x}{11.0 - 9.0} = \frac{y - x}{2} \text{ miles hr}^{-1} \end{aligned}$$

The above example indicates that the car has been driven with uniform rate but actually it has been driven sometimes faster and sometimes slower depending upon the conditions of the road. Thus, the overall rate is an average rate and the rate at which the car was moving at any instant, *i.e.*, instantaneous rate was changeable.

The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate.

In a chemical change, reactants and products are involved. As the chemical reaction proceeds, the concentration of the reactants decreases, *i.e.*, reactants are consumed and the concentration of products increases, *i.e.*, products are produced. **The rate of reaction (average rate) is defined as the change of concentration of any one of its reactants (or products) per unit time.**

Average rate of reaction,

$$r_{\text{av}} = \frac{\text{Change of concentration of one of the reactants or products}}{\text{Time taken for the change}}$$

Consider a common hypothetical reaction,



The average rate of reaction may be expressed either in terms of decrease in concentration of A (reactants) or in terms of increase in concentration of B (product).

$$\text{Average rate of reaction} = \frac{\text{Decrease in concentration of } A}{\text{Time taken}}$$

$$\text{or Average rate of reaction} = \frac{\text{Increase in concentration of } B}{\text{Time taken}}$$

The concentrations of reactants or products are expressed as number of moles per litre. The symbol for the molar concentration consists of the formula of the substance enclosed in bracket. The symbol $[A]$ stands for the molar concentration of A . The symbol $\Delta[A]$, therefore, stands for the change in molar concentration of A .

The rate of decrease or increase in the concentration of reactants or products may also be expressed in terms of change in their concentration during the time interval, Δt , as:

$$\text{Average rate of reaction} = - \frac{\Delta[A]}{\Delta t}$$

$$\text{or Average rate of reaction} = + \frac{\Delta[B]}{\Delta t}$$

(A negative sign placed before a reaction rate symbol signifies a decrease in concentration of the reactant with increase of time and a positive sign before the rate symbol signifies that the concentration of the product increases with increase in time. The

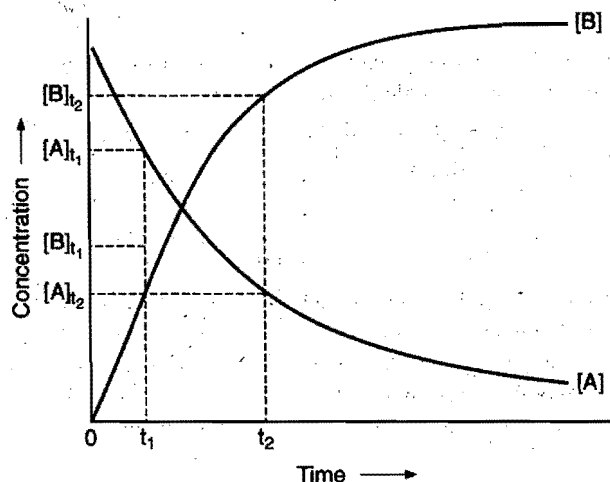


Fig. 8.1

concentration change may be positive or negative but the rate of reaction is always positive. The minus sign is always written when required, but the plus sign is usually not mentioned.)

Figure 8.1 shows the change of concentrations of reactant (A) and product (B) as the chemical reaction $A \rightarrow B$ progresses with time. Let $[A]_{t_1}$ and $[A]_{t_2}$ be the concentrations of A at time t_1 and t_2 , respectively.

$$\Delta[A] = [A]_{t_2} - [A]_{t_1}$$

and

$$\Delta t = t_2 - t_1$$

$$r_{av} = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1}$$

Over the same time interval t_1 to t_2 , the concentration of B changes from $[B]_{t_1}$ to $[B]_{t_2}$.

$$r'_{av} = \frac{\Delta[B]}{\Delta t} = \frac{[B]_{t_2} - [B]_{t_1}}{t_2 - t_1}$$

Since, one mole of A produces one mole of B , the rate of decrease in concentration of A should be equal to the rate of increase in concentration of B . Thus,

$$r_{av} = r'_{av}$$

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

Reaction rate has the units of concentration or molarity divided by time. Therefore, the units of rate of reaction may be expressed as:

$$\text{mole/litre sec (mol L}^{-1} \text{ s}^{-1}\text{)}$$

$$\text{or mole/litre min (mol L}^{-1} \text{ min}^{-1}\text{)}$$

$$\text{or mole/litre hour (mol L}^{-1} \text{ h}^{-1}\text{)}$$

$$\text{or mole/litre day (mol L}^{-1} \text{ d}^{-1}\text{)}$$

$$\text{or mole/litre year (mol L}^{-1} \text{ y}^{-1}\text{)}$$

Note : In case of gaseous reaction, pressure may be taken in place of concentration. Thus, rate will have the unit of atm sec⁻¹ or atm min⁻¹.

$$PV = nRT \quad \text{or} \quad P = \left[\frac{n}{V} \right] RT \quad \text{or} \quad P = CRT$$

$$\frac{\Delta[P]}{\Delta t} = \frac{\Delta[C]}{\Delta t} \cdot RT \quad \text{or} \quad \text{Rate in [atm/sec]} = \text{Rate in [molarity/sec]} \times RT$$

SOME SOLVED EXAMPLES

Example 1. In a reaction, the concentration of a reactant (A) changes from 0.200 mol litre⁻¹ to 0.150 mol litre⁻¹ in 10 minutes. What is the average rate of reaction during this interval?

$$\text{Solution:} \quad \Delta[A] = [A]_{\text{final}} - [A]_{\text{initial}}$$

$$= [0.150 - 0.200] = -0.050 \text{ mol litre}^{-1}$$

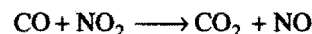
$$\Delta t = 10 \text{ minutes}$$

$$\text{Average rate of reaction} = \frac{-\Delta[A]}{\Delta t} = \frac{-[-0.050]}{10}$$

$$= \frac{0.050}{10} = 0.005 \text{ mol litre}^{-1} \text{ min}^{-1}$$

Expression of Rate

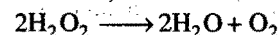
Consider the following reaction between CO and NO₂:



The equation shows that when one mole of CO reacts with one mole of NO₂, one mole each of CO₂ and NO are formed. The average rate of reaction can be expressed either by decrease of concentration of any one of the reactants (CO or NO₂) or by the increase in concentration of any one of the products (CO₂ or NO).

$$\text{Thus,} \quad -\frac{\Delta[\text{CO}]}{\Delta t} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t}$$

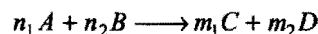
However, for the reaction,



it is observed that when 2 moles of H₂O₂ decompose, one mole of O₂ is formed in the same time interval. The rate of increase in the concentration of O₂, therefore, is half that of the disappearance of the concentration of H₂O₂ in the same time interval;

$$\text{So,} \quad \frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}$$

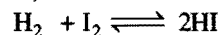
In general, for a reaction,



the rate expression may be expressed as:

$$-\frac{1}{n_1} \frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2} \frac{\Delta[B]}{\Delta t} = \frac{1}{m_1} \frac{\Delta[C]}{\Delta t} = \frac{1}{m_2} \frac{\Delta[D]}{\Delta t}$$

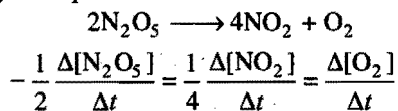
Thus, for the reaction,



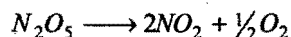
the rate may be expressed as:

$$-\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

Similarly, for the decomposition of N_2O_5 in CCl_4 medium, the rate may be expressed as:



Example 2. Decomposition of N_2O_5 is expressed by the equation,



If during a certain time interval, the rate of decomposition of N_2O_5 is $1.8 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$, what will be the rates of formation of NO_2 and O_2 during the same interval?

Solution: The rate expression for the decomposition of N_2O_5 is:

$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[NO_2]}{\Delta t} = 2 \cdot \frac{\Delta[O_2]}{\Delta t}$$

$$\text{So, } \frac{\Delta[NO_2]}{\Delta t} = 2 \frac{\Delta[N_2O_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3}$$

$$= 3.6 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

$$\text{and } \frac{\Delta[O_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3}$$

$$= 0.9 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

(Rate is always positive and hence $-\frac{\Delta[N_2O_5]}{\Delta t}$ is taken positive.)

Instantaneous Rate

In chemical kinetics, the rate at any particular instant, i.e., instantaneous rate rather than the average rate over a time interval has much more practical application and importance. It is defined as the rate of change of concentration of any one of the reactants or products over a very small interval of time.

If we take infinitesimal small interval of time dt , it may be assumed that the rate is uniform through this interval; then if dx is amount of substance A transformed to B during this interval, the rate of reaction at that instant is given as $-\frac{dx}{dt}$.

[In differential calculus, when Δt becomes very small and approaches zero, the ratio $\frac{\Delta[A]}{\Delta t}$ may be replaced by the derivative, $\frac{d[A]}{dt}$, i.e.,

$$r_{\text{inst}} = \lim_{\Delta t \rightarrow 0} -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}]$$

On the other hand, if the rate of reaction is expressed in terms of the concentration of any of the products which goes on increasing, then rate of reaction at particular instant $= \frac{dx}{dt}$.

In general, for a reaction,



The instantaneous rate may be expressed as:

$$r_{\text{inst}} = -\frac{1}{n_1} \frac{d[A]}{dt} = -\frac{1}{n_2} \frac{d[B]}{dt} = \frac{1}{m_1} \frac{d[C]}{dt} = \frac{1}{m_2} \frac{d[D]}{dt}$$

Experimental Determination of Instantaneous Rate of Reaction

In order to determine changes in concentration of reactants or products, it is customary to take small portions of the reaction mixture at suitable intervals of time and freeze them rapidly to about 0°C as to stop the reaction. The concentration is then measured with the help of a suitable method. In several cases, concentration changes are measured by observing changes in certain physical properties which are proportional to it such as optical densities, electrical conductivity, optical rotation, etc. A curve is plotted between concentration and time. A tangent is drawn to the curve at the point corresponding to time interval ' t '. The slope of this tangent gives the instantaneous rate of reaction. This is shown in Fig. 8.2 (a).

Instantaneous rate of reaction = Slope of curve

$$= \frac{\text{Intercept along ordinate}}{\text{Intercept along abscissa}} = \frac{\Delta x}{\Delta t}$$

Since, the concentrations of the reactants keep on decreasing with time, the rate of reaction correspondingly decreases with time. Thus, the rate of reaction will depend on the stage considered during progress of the reaction. The rate of reaction is maximum at the initial stage and decreases with time. Theoretically, infinite time would be required for a reaction to complete. But the reaction rate becomes so slow after a certain time that for all practical purposes, the reaction can be considered to be completed. It is evident from Fig. 8.2 (b) that the rate of reaction is varying from moment to moment.

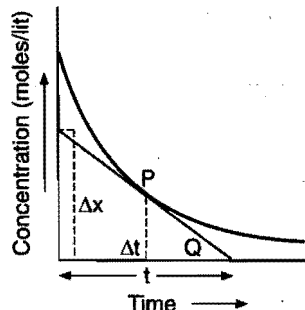


Fig. 8.2(a) Determination of rate of reaction

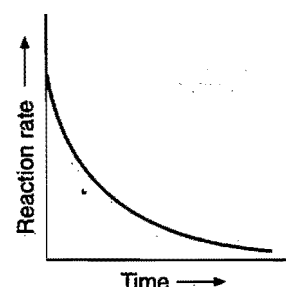
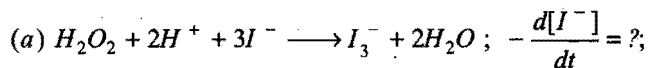


Fig. 8.2(b) Variation of rate of reaction

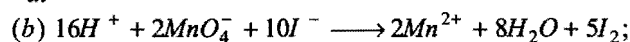
Reaction Life Time

It is defined as the time taken by a reaction to proceed to 98% of completion. The shorter the life time, the faster the reaction. Reaction life times are used to compare the various reactions. Reactions are also compared with half life periods. The half life period is defined as the time during which the concentration of a reactant is reduced to one-half of its initial value or the time in which half of the reaction is completed. It is generally denoted by $t_{1/2}$. The shorter the half life period, the faster is the reaction.

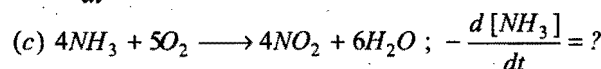
Example 3. For each of the following reactions express the given rate of change of concentration of the reactant or product in terms of the rate of change of concentration of other reactants or products in that reaction :



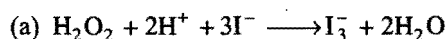
$$-\frac{d[H^+]}{dt} = ?$$



$$-\frac{d[MnO_4^-]}{dt} = ?$$



Solution: We have,

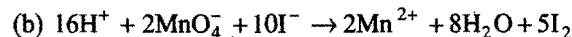


The equality in this case is:

$$-\frac{d[H_2O_2]}{dt} = -\frac{1}{2} \frac{d[H^+]}{dt} = -\frac{1}{3} \frac{d[I^-]}{dt} = \frac{d[I_3^-]}{dt} = \frac{1}{2} \frac{d[H_2O]}{dt}$$

$$\text{So, } -\frac{d[I^-]}{dt} = -3 \frac{d[H_2O_2]}{dt} = -\frac{3}{2} \frac{d[H^+]}{dt} = 3 \frac{d[I_3^-]}{dt} = \frac{3}{2} \frac{d[H_2O]}{dt}$$

$$\text{and } -\frac{d[H^+]}{dt} = -2 \frac{d[H_2O_2]}{dt} = -\frac{2}{3} \frac{d[I^-]}{dt} = 2 \frac{d[I_3^-]}{dt} = \frac{d[H_2O]}{dt}$$



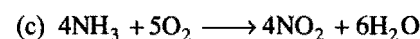
The equality in this case is:

$$-\frac{1}{16} \frac{d[H^+]}{dt} = -\frac{1}{2} \frac{d[MnO_4^-]}{dt} = -\frac{1}{10} \frac{d[I^-]}{dt}$$

$$= \frac{1}{2} \frac{d[Mn^{2+}]}{dt} = \frac{1}{8} \frac{d[H_2O]}{dt} = \frac{1}{5} \frac{d[I_2]}{dt}$$

$$\text{So, } -\frac{d[MnO_4^-]}{dt} = -\frac{1}{8} \frac{d[H^+]}{dt} = -\frac{1}{5} \frac{d[I^-]}{dt}$$

$$= \frac{d[Mn^{2+}]}{dt} = \frac{1}{4} \frac{d[H_2O]}{dt} = \frac{2}{5} \frac{d[I_2]}{dt}$$

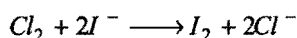


The equality in this case is:

$$-\frac{1}{4} \frac{d[NH_3]}{dt} = -\frac{1}{5} \frac{d[O_2]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{1}{6} \frac{d[H_2O]}{dt}$$

$$\text{So, } -\frac{d[NH_3]}{dt} = -\frac{4}{5} \frac{d[O_2]}{dt} = \frac{d[NO_2]}{dt} = \frac{2}{3} \frac{d[H_2O]}{dt}$$

Example 4. The following reaction was carried out in water:



The initial concentration of I^- was 0.25 mol L^{-1} and the concentration after 10 minutes 0.23 mol L^{-1} . Calculate the rate of disappearance of I^- and appearance of I_2 .

Solution: $\Delta[I^-] = [I^-]_{\text{final}} - [I^-]_{\text{initial}}$

$$= 0.23 - 0.25 = -0.02 \text{ mol L}^{-1}$$

$$\Delta t = 10 - 0 = 10 \text{ min}$$

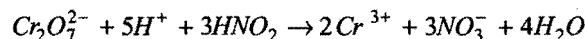
$$-\frac{\Delta[I^-]}{\Delta t} = -\frac{(-0.02)}{10} = 0.002 \text{ mol L}^{-1} \text{ min}^{-1}$$

$$\text{Rate of appearance of } I_2 = -\frac{1}{2} \frac{\Delta[I^-]}{\Delta t} = \frac{0.002}{2}$$

$$= 0.001 \text{ mol L}^{-1} \text{ min}^{-1}$$

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

Example 5. The reaction between $Cr_2O_7^{2-}$ and HNO_2 in an acidic medium is:



The rate of disappearance of $Cr_2O_7^{2-}$ is found to be $2.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ during a measured time interval. Find the rate of disappearance of HNO_2 and the rate of appearance of Cr^{3+} during this time interval.

Solution: The equality in this case is:

$$-\frac{\Delta[Cr_2O_7^{2-}]}{\Delta t} = -\frac{1}{3} \frac{\Delta[HNO_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[Cr^{3+}]}{\Delta t}$$

It is given that,

$$-\frac{\Delta[Cr_2O_7^{2-}]}{\Delta t} = 2.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{So, } -\frac{\Delta[HNO_2]}{\Delta t} = 3 \times 2.4 \times 10^{-4} = 7.2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{and } \frac{\Delta[Cr^{3+}]}{\Delta t} = 2 \times 2.4 \times 10^{-4} = 4.8 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. For the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$ rate of reaction is:

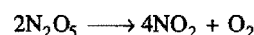
(AIIMS 2006)

$$(a) \frac{1}{2} \frac{d}{dt} [N_2O_5] \quad (b) 2 \frac{d}{dt} [N_2O_5]$$

$$(c) \frac{1}{4} \frac{d}{dt} [NO_2] \quad (d) 4 \frac{d}{dt} [NO_2]$$

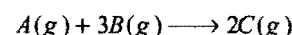
[Ans. (c)]

[Hint: For the reaction:



$$-\frac{1}{2} \frac{d[N_2O_5]}{dt} = +\frac{1}{4} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt} = \text{Rate}]$$

2. Observe the following reaction:



The rate of this reaction $\left\{ \frac{-d[A]}{dt} \right\}$ is $3 \times 10^{-3} \text{ mol litre}^{-1}$

min^{-1} . What is the value of $\frac{-d[B]}{dt}$ in $\text{mol litre}^{-1} \text{ min}^{-1}$?

(EAMCET 2006)

$$(a) 3 \times 10^{-3} \quad (b) 9 \times 10^{-3} \quad (c) 10^{-3} \quad (d) 1.5 \times 10^{-3}$$

[Ans. (b)]

$$[\text{Hint: } \frac{-d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt}]$$

$$\therefore \frac{-d[B]}{dt} = 3 \left\{ \frac{-d[A]}{dt} \right\} = 3 \times 3 \times 10^{-3}$$

$$= 9 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}]$$

3. For the reaction, $2A + B \longrightarrow 3C + D$, which of the following does not express the reaction rate?

[CBSE (Med.) 2006]

- (a) $\frac{-d[C]}{3 dt}$ (b) $\frac{-d[B]}{dt}$ (c) $\frac{d[D]}{dt}$ (d) $\frac{-d[A]}{2 dt}$

[Ans. (a)]

[Hint: $-\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{1}{3} \frac{d[C]}{dt} = +\frac{d[D]}{dt} = \text{Rate}$]

4. Consider the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is:

[CBSE (Med.) 2006]

- (a) $\frac{d[NH_3]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt}$ (b) $+\frac{d[NH_3]}{dt} = -\frac{2}{3} \frac{d[H_2]}{dt}$
(c) $+\frac{d[NH_3]}{dt} = -\frac{3}{2} \frac{d[H_2]}{dt}$ (d) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$

[Ans. (b)]

[Hint: $-\frac{1}{3} \frac{d[H_2]}{dt} = +\frac{1}{2} \frac{d[NH_3]}{dt}$]

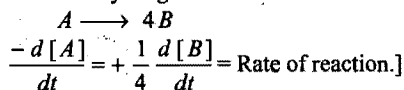
5. For a reaction $\frac{1}{2}A \longrightarrow 2B$ rate of disappearance of A is related to the rate of appearance of B by the expression:

(AIEEE 2008)

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

[Ans. (c)]

[Hint: The reaction may be given as



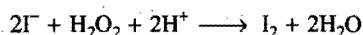
6. In a reaction of acidified hydrogen peroxide with potassium iodide, the concentration of iodine formed rises from 0 to $10^{-5} \text{ mol dm}^{-3}$ in 10 seconds. What is the rate of reaction?

[PET (Raj.) 2008]

- (a) $10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ (b) $10^6 \text{ mol dm}^{-3} \text{ s}^{-1}$
(c) $10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ (d) $10^4 \text{ mol dm}^{-3} \text{ s}^{-1}$

[Ans. (a)]

[Hint: The reaction is



$$\text{Rate} = +\frac{d[I_2]}{dt} = \frac{10^{-5}}{10} = 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}]$$

8.3 LAW OF MASS ACTION (Guldberg and Waage, 1864)

This law relates rate of reaction with active mass or molar concentration of reactants.

“At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the active masses of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction.”

Active mass = molar concentration of the substance

$$= \frac{\text{number of gram moles of the substance}}{\text{volume in litres}}$$

$$= \frac{w/M}{V} = \frac{n}{V}$$

where, w = mass of substance and ‘ M ’ is the molecular mass in gram, ‘ n ’ is the number of gram moles and V is volume in litre.

Example 6. 4 g of hydrogen and 128 g of hydrogen iodide are present in a 2 litre flask. What are their active masses?

Solution: Mass of hydrogen = 4 g

Mol. mass of hydrogen = 2

Volume of the flask = 2 litre

$$\text{Active mass of hydrogen} = \frac{4}{2 \times 2} = 1 \text{ mol L}^{-1}$$

Mass of HI = 128 g

Mol. mass of HI = 128

Volume of the flask = 2 litre

$$\text{Active mass of hydrogen iodide} = \frac{128}{128 \times 2} = 0.5 \text{ mol L}^{-1}$$

8.4 RATE CONSTANT

Consider a simple reaction $A \rightarrow B$.

If C_A is the molar concentration or active mass of A at a particular instant, then

$$\frac{dx}{dt} \propto C_A \text{ or } \frac{dx}{dt} = k C_A$$

where, k is a proportionality constant, called velocity constant or rate constant or specific reaction rate.

At a fixed temperature, if $C_A = 1$, then

$$\text{Rate} = \frac{dx}{dt} = k \quad \dots (i)$$

Let us consider a general reaction.



$$\text{Rate} = \left(\frac{dx}{dt} \right) \propto [A]^a [B]^b$$

$$\text{Rate} = k [A]^a [B]^b \quad \dots (ii)$$

When $[A] = [B] = 1 \text{ mol/litre}$, then

$$\text{Rate} = k$$

Rate of a reaction at unit concentration of reactants is called rate constant.

The value of rate constant depends on:

- Nature of reactant
- Temperature
- Catalyst

Unit of Rate Constant

Rate constant has different units for reactions of different order. General rule for rate of reaction may be given as:

$$\begin{aligned}\text{Unit of rate constant} &= \left[\frac{1}{\text{unit of concentration}} \right]^{n-1} \times \text{time}^{-1} \\ &= \left[\frac{1}{\text{mol/litre}} \right]^{n-1} \times \text{sec}^{-1} \\ &= \left[\frac{\text{litre}}{\text{mol}} \right]^{n-1} \times \text{sec}^{-1}\end{aligned}$$

where, n = order of reaction.

S. No.	Rate of reaction	Reaction rate constant
1.	It is the speed with which reactants are converted into products.	It is proportionality constant.
2.	It is measured as the rate of decrease of concentration of reactants or the rate of increase of concentration of products with time.	It is equal to the rate of reaction when the concentration of each of the reactants is unity.
3.	It depends upon the initial concentration of reactants.	It is independent of the initial concentration of the reactants. It has a constant value at fixed temperature.

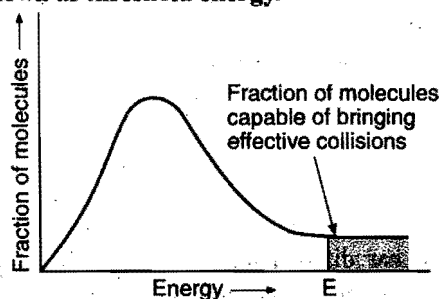
8.5 COLLISION THEORY OF REACTION RATE (Arrhenius Theory of Reaction Rate)

(1) A chemical reaction takes place due to collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as **collision frequency (Z)**. The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.

(2) Every collision does not bring a chemical change. The collisions that actually produce the products are **effective collisions**. The effective collisions which bring chemical change are few in comparison to the total number of collisions. The collisions that do not form a product are **ineffective elastic collisions**, i.e., molecules just collide and disperse in different directions with different velocities. For a collision to be effective, the following two barriers are to be cleared:

Energy Barrier

The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as **threshold energy**.



In the graph (Fig. 8.3), ' E ' corresponds to minimum or threshold energy for effective collision in a hypothetical reaction.

There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy as to cross the energy barrier.

The minimum amount of energy required by reactant molecules to participate in a reaction is called **activation energy**.

Activation energy = threshold energy – average kinetic energy of reacting molecules
Threshold energy = initial potential energy of reactant molecules + activation energy.

A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the **activated complex**. The life span of an activated complex is very small. Thus, the activated complex breaks either into reactants again or new substances, i.e., products. The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products. The energy changes during exothermic and endothermic reactions *versus* the progress of the reaction are shown in Fig. 8.4.

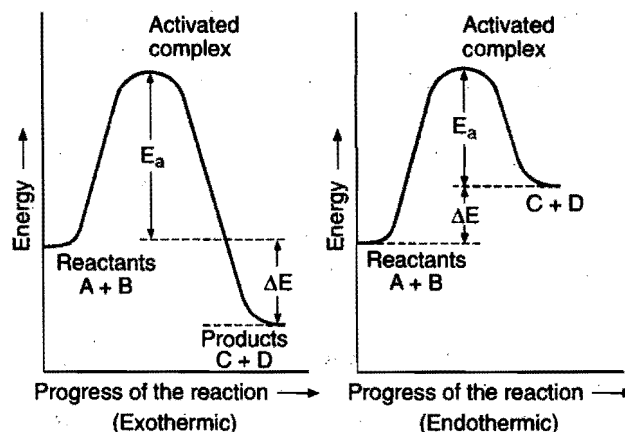


Fig. 8.4 Activation energy of exothermic and endothermic reaction

Thus, every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after collision and then they can go to the right side of the slope and consequently change into products. If the activation energy for a reaction is low, the fraction of effective collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of active molecules increases, i.e., the number of effective collisions will increase and the rate of reaction will increase.

$$\text{Activation energy } E_a = E_{(\text{activated complex})} - E_{(\text{ground state})}$$

$$\Delta H = \text{activation energy of forward reaction}$$

$$- \text{activation energy of backward reaction.}$$

Orientation Barrier

Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper manner if the reaction is to occur. This has been shown in Fig. 8.5.

Rate of reaction is directly proportional to the number of effective collisions.

$$\text{Rate} = -\frac{dx}{dt} = \text{collision frequency} \times \text{fraction of effective collisions} \\ = Z \times f$$

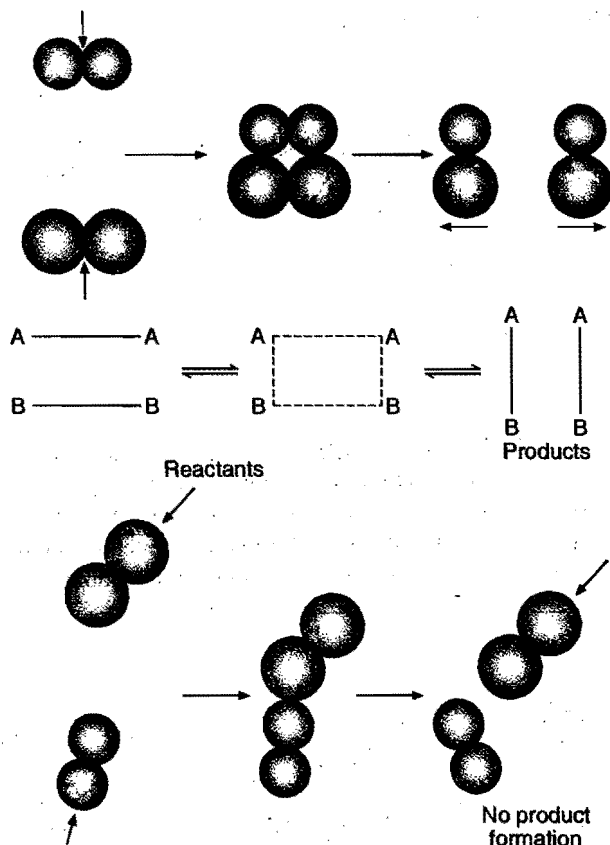


Fig. 8.5 Orientation of collisions

Factors Affecting Rate of Reaction

(i) Nature of the reactants

(a) Physical state of reactants: This has considerable effect over rate of reaction.

Gaseous state > Liquid state > Solid state

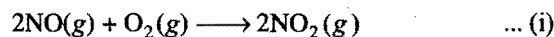
Decreasing rate of reaction

Similarly, in a heterogeneous system, collision is not so effective as in homogeneous system. Thus, reactions in liquid phase or solution phase will be faster in comparison to heterogeneous conditions when same concentrations of the reactants are taken.

(b) Physical size of the reactants: Among the solids, rate increases with decrease in particle size. In powdered state rate of

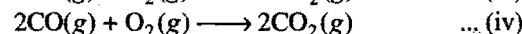
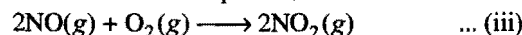
reaction is maximum because in powdered state, surface area is maximum.

(c) Chemical nature of reactants: Consider the following two reactions:



The first reaction is faster than the second because in the first reaction only N≡O bond is to be broken whereas in the second reaction four (C—H) bonds are to be broken.

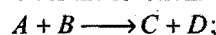
Similarly, consider another example of two similar reactions:



NO bond is weaker than CO bond, hence broken easily. Thus, reaction (iii) is faster than (iv).

(ii) Concentration of reactants

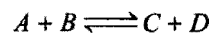
Let us consider the reaction:



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

Rate of the above reaction decreases with the passage of time because the concentration of reactants A and B will decrease as time passes on.

Let us consider the following reversible reaction:



$$\text{Rate of forward reaction} = k_f[A][B]$$

$$\text{Rate of backward reaction} = k_b[C][D]$$

Rate of forward reaction decreases and that of backward reaction increases with passage of time. At equilibrium both the rates become equal.

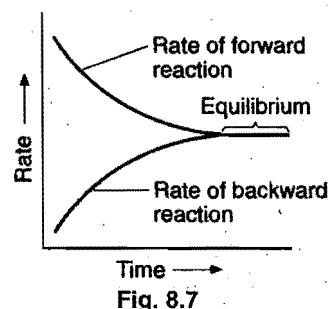


Fig. 8.6

Fig. 8.7

(iii) Effect of temperature

The rate of reaction increases considerably with an increase in temperature. The rates of many reactions are approximately doubled or tripled for every 10°C rise in temperature. The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperatures differing by 10°C.

$$\mu = \text{Temperature coefficient} = \frac{k_{t+10}}{k_t}$$

Let temperature coefficient of a reaction be ' μ ' when temperature is raised from T_1 to T_2 ; then the ratio of rate constants or rate may be calculated as:

$$\frac{k_{T_2}}{k_{T_1}} = (\mu)^{(T_2 - T_1)/10} = \mu^{\Delta T/10}$$

$$\log_{10} \left(\frac{k_{T_2}}{k_{T_1}} \right) = \frac{\Delta T}{10} \log_{10} \mu$$

$$\frac{k_{T_2}}{k_{T_1}} = \text{antilog} \left[\frac{\Delta T}{10} \log_{10} \mu \right]$$

Its value lies generally between 2 and 3.

When the temperature is increased, heat energy is supplied which increases the kinetic energy of the reacting molecules. This will increase the number of collisions and ultimately the rate of reaction will be enhanced. Arrhenius suggested an equation which describes k as a function of temperature, i.e.,

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

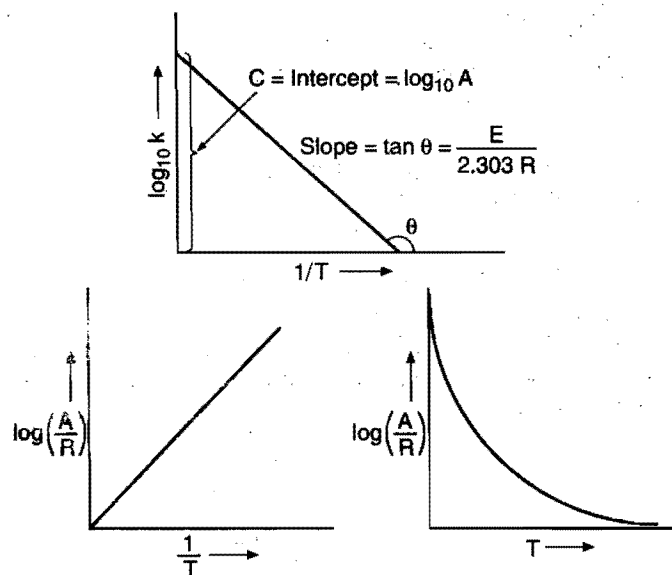


Fig. 8.8

where, $k \rightarrow$ rate constant

$A \rightarrow$ a constant (frequency factor)

$E_a \rightarrow$ energy of activation

At two temperatures T_1 and T_2 , taking log of Arrhenius equation, we get

$$\log_e k_1 = \log A - \frac{E_a}{RT_1} \log_e e \quad \dots (i)$$

and

$$\log_e k_2 = \log A - \frac{E_a}{RT_2} \log_e e \quad \dots (ii)$$

Subtracting eq. (ii) from eq. (i) and converting the log to the base 10, we get

$$\log_{10} \frac{k_1}{k_2} = -\frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \text{ or } \log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

This equation can be used for calculation of energy of activation.

Logarithmic Arrhenius equation is:

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303R} \left[\frac{1}{T} \right]$$

$$Y = C + MX$$

It is the equation of straight line with negative slope. On plotting $\log_{10} k$ against $[1/T]$ we get a straight line as shown in Fig. 8.8. The graph gives two kinetic parameters.

The slope gives **activation energy** and intercept gives **frequency factor**.

The dependence of rate constant on temperature for two reactions is shown in the Fig. 8.9.

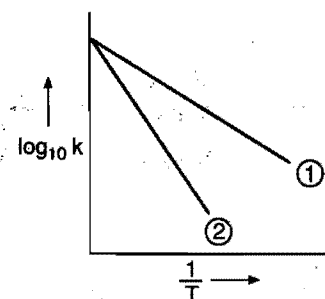


Fig. 8.9

In the reaction (2), the modulus of slope is greater than that of reaction (1), hence reaction (2) has higher activation energy. The reaction (2) will be more sensitive to temperature change.

Reactions on the basis of influence of temperature are classified into five types. These are shown in the graphs.

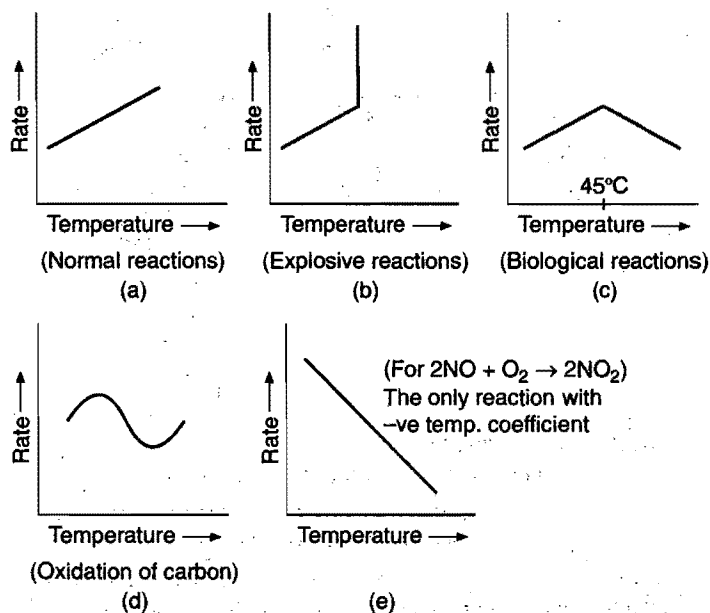


Fig. 8.10

(iv) Presence of a positive catalyst

The function of a positive catalyst is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate. In

the presence of a catalyst, the reaction follows a path of lower activation energy. Under this condition, a large number of reacting molecules are able to cross over the energy barrier and thus the rate of reaction increases. Fig. 8.11 shows how the activation energy is lowered in presence of a catalyst.

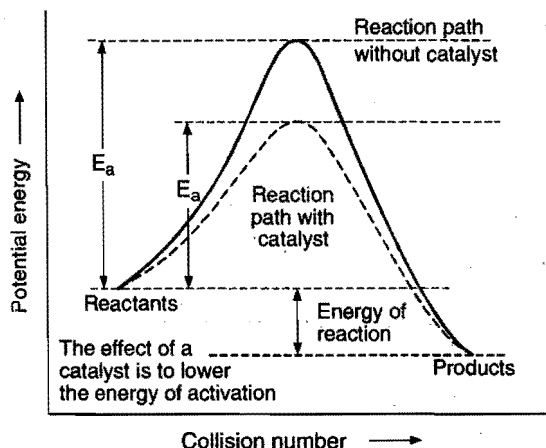


Fig. 8.11 A catalyst changes the reaction path (Positive catalyst)

(v) Presence of negative catalyst

A negative catalyst increases the activation energy of reaction by forming a new intermediate of high energy, i.e., by changing the reaction mechanism.

Due to increased activation energy, some active molecules become inactive, therefore, rate of reaction decreases.

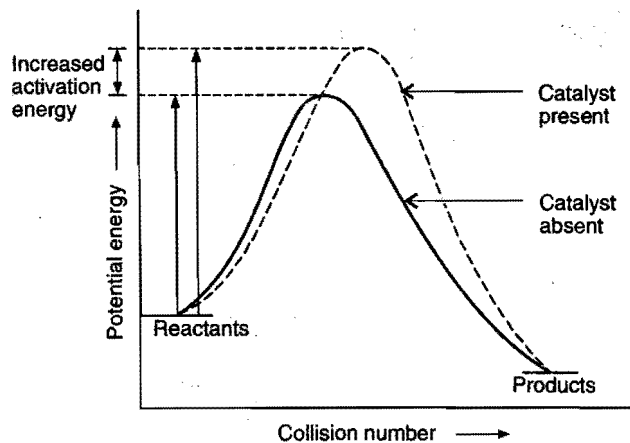


Fig. 8.12 Negative catalyst

Let 'p' denote presence of catalyst and 'a' denote absence of catalyst.

$$k_p = Ae^{-E_p/RT} \quad \dots (i)$$

$$k_a = Ae^{-E_a/RT} \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii), we get

$$\frac{k_p}{k_a} = e^{(E_a - E_p)/RT} = e^{\Delta E/RT}$$

$$\frac{k_p}{k_a} = \text{antilog} \left[\frac{\Delta E}{2.303RT} \right]$$

SOME SOLVED EXAMPLES

Example 7. The rate of a reaction triples when temperature changes from 20°C to 50°C. Calculate energy of activation for the reaction. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

Solution: The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{R \times 2.303} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Given: $\frac{k_2}{k_1} = 3$; $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$; $T_1 = 20 + 273 = 293 \text{ K}$

and

$$T_2 = 50 + 273 = 323 \text{ K}$$

Substituting the given values in the Arrhenius equation,

$$\log_{10} 3 = \frac{E_a}{8.314 \times 2.303} \left[\frac{323 - 293}{323 \times 293} \right]$$

$$E_a = \frac{2.303 \times 8.314 \times 323 \times 293 \times 0.477}{30}$$

$$= 28811.8 \text{ J mol}^{-1}$$

$$= 28.8118 \text{ kJ mol}^{-1}$$

Example 8. In Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ mol^{-1} respectively. At what temperature, the reaction will have specific rate constant $1.1 \times 10^{-3} \text{ sec}^{-1}$?

Solution: According to Arrhenius equation,

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

$$\text{or} \quad \log_e k = \log_e A - \frac{E_a}{RT} \log_e e$$

$$\text{or} \quad 2.303 \log_{10} k = 2.303 \log_{10} A - \frac{E_a}{RT}$$

$$\text{or } 2.303 \log (1.1 \times 10^{-3}) = 2.303 \log (4 \times 10^{13}) - \frac{98.6 \times 10^3}{8.314 \times T}$$

$$T = \frac{98.6 \times 10^3}{8.314 \times 2.303 \times 16.56} \text{ K}$$

$$= 310.96 \text{ K}$$

Example 9. The rate constant is given by Arrhenius equation,

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

Calculate the ratio of the catalysed and uncatalysed rate constants at 25°C if the energy of activation of a catalysed reaction is 162 kJ and for the uncatalysed reaction the value is 350 kJ.

Solution: Let k_{ca} and k_{un} be the rate constants for catalysed and uncatalysed reactions.

$$2.303 \log_{10} k_{ca} = 2.303 \log_{10} A - \frac{162 \times 10^3}{RT} \quad \dots (i)$$

and $2.303 \log_{10} k_{\text{un}} = 2.303 \log_{10} A - \frac{350 \times 10^3}{RT}$... (ii) or

Subtracting eq. (ii) from eq. (i)

$$\begin{aligned} \log_{10} \frac{k_{\text{ca}}}{k_{\text{un}}} &= \frac{10^3}{2.303RT} (350 - 162) \\ &= \frac{188 \times 10^3}{2.303 \times 8.314 \times 298} = 32.95 \\ \frac{k_{\text{ca}}}{k_{\text{un}}} &= 8.88 \times 10^{32} \end{aligned}$$

Example 10. Calculate the rate constant of a reaction at 293 K when the energy of activation is 103 kJ mol^{-1} and the rate constant at 273 K is $7.87 \times 10^{-7} \text{ s}^{-1}$.
($R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$)

Solution: The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Given: $k_1 = 7.87 \times 10^{-7} \text{ s}^{-1}$; $E_a = 103 \text{ kJ mol}^{-1}$;
 $R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$;

$T_1 = 273 \text{ K}$ and $T_2 = 293 \text{ K}$

Substituting the values in Arrhenius equation,

$$\begin{aligned} \log_{10} \frac{k_2}{7.87 \times 10^{-7}} &= \frac{103 \times 20}{2.303 \times 8.314 \times 10^{-3} \times 293 \times 273} \\ &= 1.345 \\ k_2 &= 1.74 \times 10^{-5} \text{ s}^{-1} \end{aligned}$$

Example 11. At 407 K, the rate constant of a chemical reaction is $9.5 \times 10^{-5} \text{ s}^{-1}$ and at 420 K, the rate constant is $1.9 \times 10^{-4} \text{ s}^{-1}$. Calculate the frequency factor of the reaction.

Solution: The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Given: $k_1 = 9.5 \times 10^{-5} \text{ s}^{-1}$; $k_2 = 1.9 \times 10^{-4} \text{ s}^{-1}$;

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$;

$T_1 = 407 \text{ K}$ and $T_2 = 420 \text{ K}$

Substituting the values in Arrhenius equation

$$\begin{aligned} \log_{10} \frac{1.9 \times 10^{-4}}{9.5 \times 10^{-5}} &= \frac{E_a}{2.303 \times 8.314} \left[\frac{420 - 407}{420 \times 407} \right] \\ E_a &= 75782.3 \text{ J mol}^{-1} \end{aligned}$$

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

$$\log 9.5 \times 10^{-5} = \log A - \frac{75782.3}{2.303 \times 8.314 \times 407}$$

$$\log \frac{A}{9.5 \times 10^{-5}} = \frac{75782.3}{2.303 \times 8.314 \times 407} = 9.7246$$

$$A = 5.04 \times 10^5 \text{ s}^{-1}$$

Example 12. The energy of activation for a reaction is 100 kJ mol^{-1} . Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C , other things being equal?

Solution: The Arrhenius equation is,

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

In absence of catalyst, $k_1 = Ae^{-100/RT}$

In presence of catalyst, $k_2 = Ae^{-25/RT}$

So, $\frac{k_2}{k_1} = e^{75/RT}$ or $2.303 \log \frac{k_2}{k_1} = \frac{75}{RT}$

or $2.303 \log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293}$

or $\log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293 \times 2.303}$

or $\frac{k_2}{k_1} = 2.34 \times 10^{13}$

As the things being equal in presence or absence of a catalyst,

$$\frac{k_2}{k_1} \text{ must be } = \frac{\text{rate in presence of catalyst}}{\text{rate in absence of catalyst}}$$

i.e., $\frac{r_2}{r_1} = \frac{k_2}{k_1} = 2.34 \times 10^{13}$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

7. For a reaction $E_a = 0$ and $k = 3.2 \times 10^4 \text{ s}^{-1}$ at 300 K. The value of k at 310 K would be:

- (a) $6.4 \times 10^4 \text{ s}^{-1}$ (b) $3.2 \times 10^4 \text{ s}^{-1}$
(c) $3.2 \times 10^8 \text{ s}^{-1}$ (d) $3.2 \times 10^5 \text{ s}^{-1}$

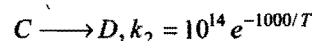
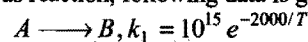
[Ans. (b)]

[Hint: $k = Ae^{-E_a/RT}$

When $E_a = 0$, $k = A = \text{constant}$

$$\therefore k_{310} = k_{300} = 3.2 \times 10^4 \text{ s}^{-1}]$$

8. For a gaseous reaction, following data is given:



The temperature at which $k_1 = k_2$ is:

- (a) 1000 K (b) 2000 K (c) 868.82 K (d) 434.2 K

[Ans. (d)]

[Hint: When $k_1 = k_2$,

$$10^{15} e^{-2000/T} = 10^{14} e^{-1000/T}$$

$$10 = e^{1000/T}$$

$$2.303 \log 10 = \frac{1000}{T}$$

$$T = 434.2 \text{ K}]$$

9. For $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g}) + 22 \text{ kcal}$, E_a for the reaction is 70 kcal. Hence, the activation energy for $2\text{NH}_3(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ is:

(a) 92 kcal (b) 70 kcal (c) 48 kcal (d) 22 kcal

[Ans. (a)]

[Hint:

$$\Delta H = E_f - E_b$$

$$-22 = 70 - E_b$$

$$E_b = 92 \text{ kcal}]$$

10. On introducing a catalyst at 500 K, the rate of a first order reaction increases by 1.718 times. The activation energy in the presence of a catalyst is 6.05 kJ mol^{-1} . The slope of the plot of $\ln k$ (sec^{-1}) against $1/T$ in the absence of catalyst is:

(a) +1 (b) -1 (c) +1000 (d) -1000

[Ans. (d)]

[Hint: $\frac{\text{Rate in presence of catalyst}}{\text{Rate in absence of catalyst}} = \text{Antilog} \left[\frac{+ \Delta E}{2.303RT} \right]$

$$1.718 = \text{Antilog} \frac{E_a - E_p}{2.303 \times 8.314 \times 500}$$

$$E_a - E_p = 2.25 \text{ kJ}$$

$$E_a = E_p + 2.25 = 6.05 + 2.25 = 8.30 \text{ kJ mol}^{-1}$$

$$= 8.3 \text{ kJ mol}^{-1}$$

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

$$\text{Slope} = \frac{-E_a}{R} = \frac{-8.3 \times 1000}{8.3} = -1000]$$

11. For which of the following reactions k_{310}/k_{300} would be maximum?

(a) $A + B \longrightarrow C$; $E_a = 50 \text{ kJ}$

(b) $X + Y \longrightarrow Z$; $E_a = 40 \text{ kJ}$

(c) $P + Q \longrightarrow R$; $E_a = 60 \text{ kJ}$

(d) $E + F \longrightarrow G$; $E_a = 100 \text{ kJ}$

[Ans. (d)]

[Hint: Increase in rate constant is maximum for the reaction having maximum activation energy.]

12. The activation energy of exothermic reaction $A \longrightarrow B$ is 80 kJ mol^{-1} . The heat of reaction is 200 kJ mol^{-1} . The activation energy for the reaction $B \longrightarrow A$ (in kJ/mol) will be:

(a) 80 (b) 120 (c) 40 (d) 200

(e) 280

[Ans. (e)]

[Hint:

$$\Delta H = E_f - E_b$$

$$-200 = 80 - E_b$$

$$E_b = 280 \text{ kJ/mol}]$$

13. Which equation is true to calculate the energy of activation, if the rate of reaction is doubled by increasing temperature from $T_1 \text{ K}$ to $T_2 \text{ K}$?

[CET (Gujarat) 2008]

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

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

(c) $\log_{10} \frac{1}{2} = \frac{E_a}{2.303 R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$

(d) $\log_{10} 2 = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

[Ans. (d)]

[Hint: We know, $\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

When reaction rate becomes double then $\frac{k_2}{k_1}$ will be equal to 2.

Then, $\log_{10} 2 = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

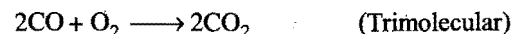
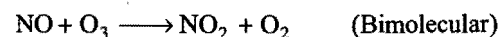
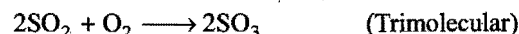
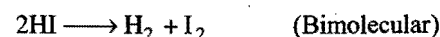
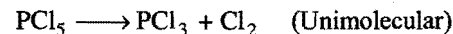
8.6 MOLECULARITY OF REACTION

In general, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation.

OR

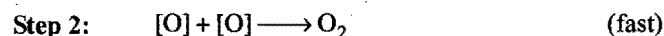
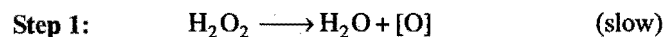
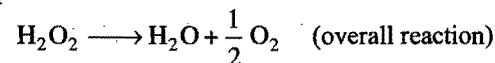
The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

e.g.,



The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of a reaction.

For example, decomposition of H_2O_2 takes place in the following two steps:



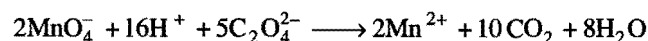
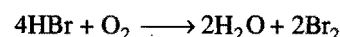
The slowest step is rate-determining. Thus, from step 1, reaction appears to be unimolecular.

Note: (i) Molecularity is a theoretical concept.

(ii) Molecularity cannot be zero, -ve, fractional, infinite and imaginary.

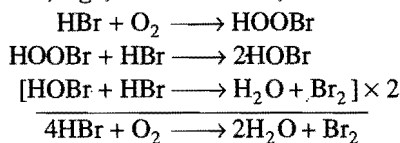
(iii) Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, e.g., in



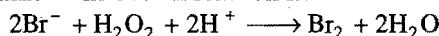
In the first reaction, molecularity seems to be '5' and in the second reaction molecularity seems to be '23'. Such reactions

involve two or more steps; each step has its own molecularity not greater than three, e.g., in first reaction,

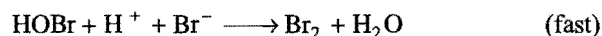
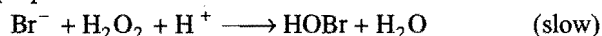


Molecularity of each of the above steps is 2.

(a) Reaction between Br^- and H_2O_2 in acidic medium: The overall reaction is:



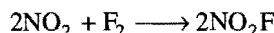
The proposed mechanism is:



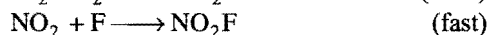
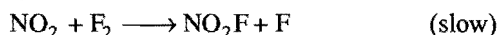
$$\text{Rate} = k [\text{Br}^-][\text{H}_2\text{O}_2][\text{H}^+]$$

The reaction is trimolecular.

(b) Reaction between NO_2 and F_2 : The overall reaction is:



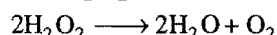
The proposed mechanism is:



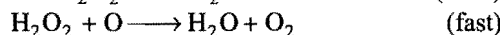
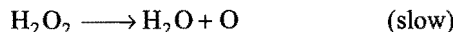
$$\text{Rate} = k [\text{NO}_2][\text{F}_2]$$

The reaction is bimolecular.

(c) Decomposition of H_2O_2 : The overall reaction is:



The proposed mechanism is:



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

The reaction is unimolecular.

8.7 ORDER OF REACTION

Let us consider a general reaction:



Let active moles of 'A', 'B' and 'C' be ' α ', ' β ' and ' γ ' respectively. Then, rate of reaction may be given as:

$$\text{Rate} = k[A]^\alpha[B]^\beta[C]^\gamma$$

Sum of powers of concentration terms involved in rate law expression is called order of reaction.

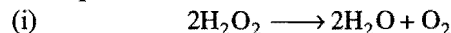
$$\alpha + \beta + \gamma = \text{order}$$

When $\alpha + \beta + \gamma = m_1 + m_2 + m_3$, then

Order of reaction = molecularity of reaction.

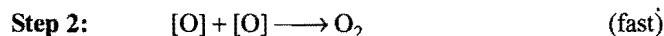
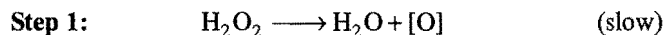
Order is an experimentally determined quantity. It may be equal to zero, positive, negative, fractional and greater than three. Infinite and imaginary values are not possible.

Examples:



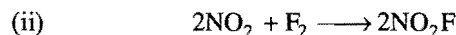
$$-\frac{dx}{dt} = k [\text{H}_2\text{O}_2]^2$$

(observed from law of mass action)



Actual rate $-\frac{dx}{dt} = k [\text{H}_2\text{O}_2]$

Thus, order of reaction is unity.

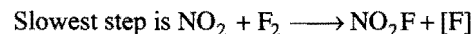


Rate law from law of mass action:

$$-\frac{dx}{dt} = k [\text{NO}_2]^2 [\text{F}_2]$$

Experimentally observed rate law:

$$-\frac{dx}{dt} = k [\text{NO}_2][\text{F}_2]$$



Thus, order of reaction = $1 + 1 = 2$



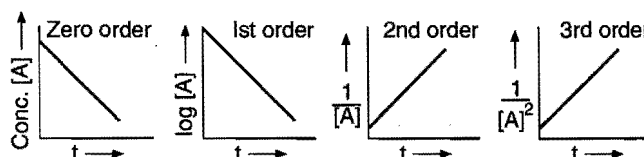
The rate equation derived from experimental data is found to be

$$-\frac{dx}{dt} = k [\text{CH}_3\text{CHO}]^{1.5}$$

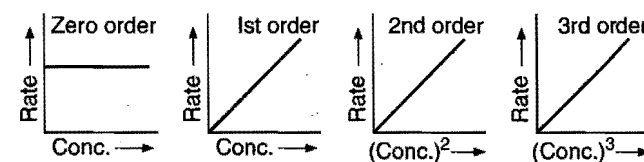
The order of reaction is 1.5.

Some typical linear plots for the reactions of different orders:

(a) Plots of rate vs concentrations [$\text{Rate} = k(\text{conc.})^n$]

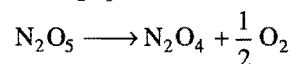


(b) Plots from integrated rate equations:



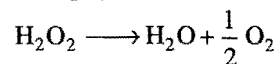
From the study of the kinetics of many simple reactions, it is observed that for a large number of reactions, the molecularity and order are the same. Some examples are given below to justify this point.

1. Dissociation of N_2O_5 ,



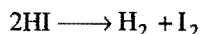
Order = 1, Molecularity = 1

2. Dissociation of H_2O_2 ,



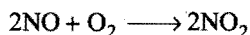
Order = 1, Molecularity = 1

3. Dissociation of HI,



Order = 2, Molecularity = 2

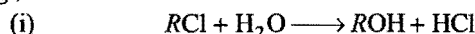
4. Formation of NO_2 ,



Order = 3, Molecularity = 3

8.8 PSEUDO-ORDER REACTION

Reactions whose actual order is different from that expected using rate law expression are called **pseudo-order reactions**, e.g.,



Expected rate law:

$$\text{Rate} = k [\text{RCI}][\text{H}_2\text{O}]$$

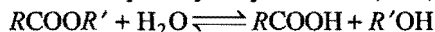
Expected order = 1 + 1 = 2

Actual rate law:

$$\text{Rate} = k' [\text{RCI}];$$

Actual order = 1

Water is taken in excess; therefore, its concentration may be taken constant. The reaction is, therefore, **pseudo first order**. Similarly, the acid catalysed hydrolysis of ester, viz.,



follow first order kinetics:

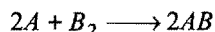
$$\text{Rate} = k [\text{RCOOR}']$$

It is also a pseudo first order reaction.

The main differences between molecularity and order of reaction are given below:

Molecularity	Order of reaction
1. It is the total number of reacting species (molecules, atoms or ions) which bring the chemical change.	It is the sum of powers of molar concentrations of the reacting species in the rate equation of the reaction.
2. It is always a whole number.	It may be a whole number, zero, fractional, positive or negative.
3. It is a theoretical concept.	It is experimentally determined.
4. It is meaningful only for simple reactions or individual steps of a complex reaction. It is meaningless for overall complex reaction.	It is meant for the reaction and not for its individual steps.

Example 13. The experimental data for the reaction,



is as follows:

Expt. No.	[A] (mol L ⁻¹)	[B ₂] (mol L ⁻¹)	Rate (mol L ⁻¹ s ⁻¹)
1.	0.50	0.50	1.6×10^{-4}
2.	0.50	1.00	3.2×10^{-4}
3.	1.00	1.00	3.2×10^{-4}

Write the most probable equation for the rate of reaction giving reason for your answer.

Solution: From an examination of above data, it is clear that when the concentration of B_2 is doubled, the rate is doubled. Hence, the order of reaction with respect to B_2 is one.

Further, when concentration of A is doubled, the rate remains unaltered. So, order of reaction with respect to A is zero.

The probable rate law for the reaction will be

$$-\frac{dx}{dt} = k[\text{B}_2][\text{A}]^0 = k[\text{B}_2]$$

Alternatively, $\text{Rate} = k[\text{B}_2]^\alpha$

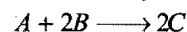
$$1.6 \times 10^{-4} = k[0.5]^\alpha$$

$$3.2 \times 10^{-4} = k[1]^\alpha$$

On dividing we get, $\alpha = 1$

$$\therefore \text{Rate} = k[\text{A}]^0[\text{B}_2]^1 = k[\text{B}_2]$$

Example 14. For the reaction,



the following data were obtained:

Expt. No.	Initial concentrations (mol L ⁻¹)		Initial reaction rates (mol L ⁻¹ min ⁻¹)
	[A]	[B]	
1.	1.0	1.0	0.15
2.	2.0	1.0	0.30
3.	3.0	1.0	0.45
4.	1.0	2.0	0.15
5.	1.0	3.0	0.15

Write down the rate law for the reaction.

Solution: Let the rate law be

$$-\frac{dx}{dt} = k[\text{A}]^x[\text{B}]^y$$

By keeping the concentration of B constant in experiments (1), (2) and (3) and increasing the concentration uniformly, the rate also increases uniformly. Thus,

$$\text{Rate} \propto [\text{A}], \text{ i.e., } x = 1$$

By keeping the concentration of A constant in experiments (1), (4) and (5) and increasing the concentration of B, the rate remains the same.

Hence,

$$y = 0$$

The rate law is

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

Alternative method:

From expt. (1), $k[1.0]^x[1.0]^y = 0.15$... (i)

From expt. (2), $k[2.0]^x[1.0]^y = 0.30$... (ii)

Dividing eq. (ii) by eq. (i),

$$\frac{[2.0]^x}{[1.0]^x} = \frac{0.30}{0.15} = 2$$

So,

$$x = 1$$

From expt. (1), $k[1.0]^x[1.0]^y = 0.15$... (i)

From expt. (4), $k[1.0]^x[2.0]^y = 0.15$... (iii)

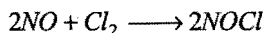
Dividing eq. (iii) by eq. (i),

$$\frac{[2.0]^y}{[1.0]^y} = 1$$

So, $y = 0$

Hence, the rate law is $-\frac{dx}{dt} = k[A]$

Example 15. For the reaction,



at 300 K, following data are obtained:

Expt. No.	Initial Concentration		Initial rate
	[NO]	[Cl ₂]	
1.	0.010	0.010	1.2×10^{-4}
2.	0.010	0.020	2.4×10^{-4}
3.	0.020	0.020	9.6×10^{-4}

Write rate law for the reaction. What is the order of the reaction? Also calculate the specific rate constant.

Solution: Let the rate law for the reaction be

$$\text{Rate} = k[NO]^x[Cl_2]^y$$

From expt. (1), $1.2 \times 10^{-4} = k[0.010]^x[0.010]^y$... (i)

From expt. (2), $2.4 \times 10^{-4} = k[0.010]^x[0.020]^y$... (ii)

Dividing eq. (ii) by eq. (i),

$$\frac{2.4 \times 10^{-4}}{1.2 \times 10^{-4}} = \frac{[0.020]^y}{[0.010]^y}$$

$$\text{or } 2 = (2)^y$$

$$y = 1$$

From expt. (2), $2.4 \times 10^{-4} = k[0.010]^x[0.020]^y$... (ii)

From expt. (3), $9.6 \times 10^{-4} = k[0.020]^x[0.020]^y$... (iii)

Dividing eq. (iii) by eq. (ii),

$$\frac{9.6 \times 10^{-4}}{2.4 \times 10^{-4}} = \frac{[0.020]^x}{[0.010]^x}$$

$$\text{or } 4 = 2^x$$

$$x = 2$$

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

Rate law for the reaction is

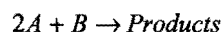
$$\text{Rate} = k[NO]^2[Cl_2]$$

Considering eq. (i) again,

$$1.2 \times 10^{-4} = k[0.010]^2[0.010]$$

$$k = \frac{1.2 \times 10^{-4}}{[0.010]^3} = 1.2 \times 10^2 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Example 16. For the hypothetical reaction



the following data are obtained:

Expt. No.	Initial conc. of (A) (mol L ⁻¹)	Initial conc. of (B) (mol L ⁻¹)	Initial rate mol L ⁻¹ s ⁻¹
1.	0.10	0.20	3×10^2
2.	0.30	0.40	3.6×10^3
3.	0.30	0.80	1.44×10^4
4.	0.10	0.40	...
5.	0.20	0.60	...
6.	0.30	1.20	...

Find out how the rate of the reaction depends upon the concentration of A and B and fill in the blanks.

Solution: From expt. (2) and (3), it is clear that when concentration of A is kept constant and that of B is doubled, the rate increases four times. This shows that the reaction is of second order with respect to B.

Similarly, from expt. (1) and (2), it is observed that when concentration of A is increased three times and that of B two times, the rate becomes twelve times. Hence, the reaction is first order with respect to A.

Thus, the rate law for the reaction is:

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

Fill in the blanks: Substituting the values of expt. (1) in the rate equation,

$$3 \times 10^2 = k[0.10][0.20]^2$$

$$\text{or } k = \frac{3 \times 10^2}{[0.10][0.20]^2} = 7.5 \times 10^4 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

$$\text{Expt. (4): Rate} = k[0.10][0.40]^2$$

$$= 7.5 \times 10^4 \times 0.10 \times 0.40 \times 0.40$$

$$= 1.2 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Expt. (5): Rate} = k[0.20][0.60]^2$$

$$= 7.5 \times 10^4 \times 0.20 \times 0.60 \times 0.60$$

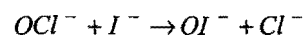
$$= 5.4 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Expt. (6): Rate} = k[0.30][1.20]^2$$

$$= 7.5 \times 10^4 \times 0.30 \times 1.20 \times 1.20$$

$$= 3.24 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$$

Example 17. The table given below gives kinetic data for the following reaction at 298 K:



Expt. No.	$[OCl^-]$ mol dm ⁻³	$[I^-]$ mol dm ⁻³	$[OH^-]$ mol dm ⁻³	$10^{-4} \times d[IO^-]/dt$ mol dm ⁻³ s ⁻¹
1.	0.0017	0.0017	1.0	1.75
2.	0.0034	0.0017	1.0	3.50
3.	0.0017	0.0034	1.0	3.50
4.	0.0017	0.0017	0.5	3.50

What is the rate law and what is the value of rate constant?

Solution: Let the rate law be $= k[OCl^-]^x [I^-]^y [OH^-]^z$

From expt. (1), $1.75 \times 10^{-4} = k[0.0017]^x [0.0017]^y [1.0]^z$... (i)

From expt. (2), $3.50 \times 10^{-4} = k[0.0034]^x [0.0017]^y [1.0]^z$... (ii)

Dividing eq. (ii) by eq. (i),

$$\frac{3.50 \times 10^{-4}}{1.75 \times 10^{-4}} = \frac{[0.0034]^x}{[0.0017]^x}$$

or $2 = 2^x$

or $x = 1$, i.e., first order w.r.t. OCl^-

From expt. (1), $1.75 \times 10^{-4} = k[0.0017]^x [0.0017]^y [1.0]^z$... (i)

From expt. (3),

$$3.50 \times 10^{-4} = k[0.0017]^x [0.0034]^y [1.0]^z$$
 ... (iii)

Dividing eq. (iii) by eq. (i),

$$\frac{3.50 \times 10^{-4}}{1.75 \times 10^{-4}} = \frac{[0.0034]^y}{[0.0017]^y}$$

or $2 = 2^y$

or $y = 1$, i.e., first order w.r.t. I^-

From expt. (1), $1.75 \times 10^{-4} = k[0.0017]^x [0.0017]^y [1.0]^z$... (i)

From expt. (4),

$$3.50 \times 10^{-4} = k[0.0017]^x [0.0017]^y [0.5]^z$$
 ... (iv)

Dividing eq. (i) by eq. (iv),

$$\frac{1.75 \times 10^{-4}}{3.50 \times 10^{-4}} = \frac{[1.0]^z}{[0.5]^z}$$

or $\frac{1}{2} = 2^z$

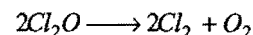
or $2^{-1} = 2^z$

$z = -1$, i.e., order w.r.t. OH^- is -1 .

$$\text{Rate law} = \frac{k[OCl^-][I^-]}{[OH^-]}$$

$$\begin{aligned} \text{From expt. (1)} \quad k &= \frac{1.75 \times 10^{-4} [OH^-]}{[OCl^-][I^-]} = \frac{1.75 \times 10^{-4} \times 1.0}{0.0017 \times 0.0017} \\ &= 60.55 \text{ s}^{-1} \end{aligned}$$

Example 18. The rate law for the reaction,



at 200°C is found to be: $\text{rate} = k[Cl_2O]^2$.

(a) How would the rate change if $[Cl_2O]$ is reduced to one-third of its original value?

(b) How should the $[Cl_2O]$ be changed in order to double the rate?

(c) How would the rate change if $[Cl_2O]$ is raised to threefold of its original value?

Solution: (a) Rate equation for the reaction,

$$r = k[Cl_2O]^2$$

Let the new rate be r' ; so, $r' = k \left[\frac{Cl_2O}{3} \right]^2 = \frac{1}{9} r$

(b) In order to have the rate $= 2r$, let the concentration of Cl_2O be x .

$$\text{So,} \quad 2r = kx^2 \quad \dots (i)$$

$$\text{We know that,} \quad r = k[Cl_2O]^2 \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii),

$$\frac{2r}{r} = \frac{kx^2}{k[Cl_2O]^2}$$

$$\text{or} \quad 2 = \frac{x^2}{[Cl_2O]^2}$$

$$\text{or} \quad x^2 = 2[Cl_2O]^2$$

$$\text{or} \quad x = \sqrt{2}[Cl_2O]$$

(c) New rate $= k[3Cl_2O]^2 = 9k[Cl_2O]^2 = 9r$
i.e., nine times of the original rate.

Example 19. For a reaction in which A and B form C, the following data were obtained from three experiments:

Expt. No.	Initial conc. (mol L ⁻¹)		Initial rate (mol L ⁻¹ s ⁻¹)
	[A]	[B]	
1.	0.03	0.03	0.3×10^{-4}
2.	0.06	0.06	1.2×10^{-4}
3.	0.06	0.09	2.7×10^{-4}

What is the rate equation of the reaction and what is the value of rate constant?

Solution: Let the rate equation be $k[A]^x[B]^y$.

$$\text{From expt. (1),} \quad 0.3 \times 10^{-4} = k[0.03]^x [0.03]^y \quad \dots (i)$$

$$\text{From expt. (2),} \quad 1.2 \times 10^{-4} = k[0.06]^x [0.06]^y \quad \dots (ii)$$

$$\frac{1.2 \times 10^{-4}}{0.3 \times 10^{-4}} = \frac{[0.06]^x [0.06]^y}{[0.03]^x [0.03]^y}$$

$$= 2^x \times 2^y = 4 \quad \dots (iii)$$

Similarly, from expt. (1) and expt. (3),

$$2^x \times 3^y = 9 \quad \dots (iv)$$

Solving eqs. (iii) and (iv),

$$x = 0, y = 2$$

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

Considering eq. (i) again,

$$k = \frac{0.3 \times 10^{-4}}{[0.03]^2} = 3.33 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

14. For the decomposition of HI at 1000 K ($2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$), the following data were obtained:

[HI], M	Rate of decomposition of HI ($\text{mol L}^{-1} \text{s}^{-1}$)
0.1	2.75×10^{-8}
0.2	11×10^{-8}
0.3	24.75×10^{-8}

The order of reaction is:

- (a) 1 (b) 2 (c) 0 (d) 1.5

[Ans. (b)]

[Hint: $\text{Rate} = k[\text{HI}]^n$

$$11 \times 10^{-8} = k[0.2]^n \quad \dots (i)$$

$$2.75 \times 10^{-8} = k[0.1]^n \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii),

$$4 = 2^n, n = 2]$$

15. Consider a reaction, $A \longrightarrow B + C$. If the initial concentration of A was reduced from 2 M to 1 M in 1 hour and from 1 M to 0.25 M in 2 hours, the order of the reaction is:

- (a) 1 (b) 0 (c) 2 (d) 3

[Ans. (a)]

[Hint: Half life of the given reaction is independent of initial concentration, hence, it is a first order reaction.

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

16. The rate of a gaseous reaction is given by the expression $k[A]^2[B]^3$. The volume of the reaction vessel is suddenly reduced to one half of the initial volume. The reaction rate relative to the original rate will be:

- (a) 1/24 (b) 1/32 (c) 32 (d) 24

[Ans. (c)]

[Hint: $\text{Rate} = k[A]^2[B]^3$... (i)

When volume is halved, the concentration will become double.

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

$$= 32k[A]^2[B]^3$$

$$= 32 \times \text{Original rate from (i)]}$$

17. For a chemical reaction, $A \longrightarrow B$, the rate of reaction increases by a factor of 1.837 when the concentration of A is

increased by 1.5 times. The order of reaction with respect to A is:

- (a) 1 (b) 1.5 (c) 2 (d) -1

[Ans. (b)]

[Hint: $\text{Rate} = k[A]^n$... (i)

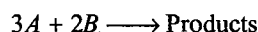
$$1.837 \times \text{Rate} = k[1.5A]^n \quad \dots (ii)$$

Dividing eq. (ii) by eq. (i),

$$1.837 = 1.5^n$$

$$\therefore n = 3/2 \quad (\text{solving by logarithmic method})]$$

18. The rate of the reaction,



is given by the rate expression:

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

If A is taken in excess, the order of the reaction would be:

- (a) 3 (b) 2 (c) 1 (d) 5

[Ans. (b)]

[Hint: When A is taken in excess, its concentration will become constant; the rate law may, therefore, be given as:

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

19. For a reaction $A + B \longrightarrow C + D$, if the concentration of A is doubled without altering the concentration of B, the rate gets doubled. If the concentration of B is increased by nine times without altering the concentration of A, the rate gets tripled. The order of the reaction is: (KCET 2006)

- (a) 2 (b) 1 (c) 3/2 (d) 4/3

[Ans. (c)]

[Hint: $\text{Rate} = k[A]^\alpha[B]^\beta$... (i)

$$2 \times \text{rate} = k[2A]^\alpha[B]^\beta \quad \dots (ii)$$

$$3 \times \text{rate} = k[A]^\alpha[9B]^\beta \quad \dots (iii)$$

$$\text{From eqs. (i) and (ii), } \alpha = 1$$

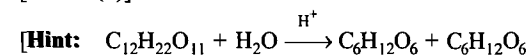
$$\text{From eqs. (i) and (iii), } \beta = 1/2$$

$$\text{Order} = \alpha + \beta = 1 + \frac{1}{2} = \frac{3}{2}]$$

20. Inversion of cane sugar in dilute acid is: [CET (J&K) 2007]

- (a) bimolecular reaction
(b) pseudo-unimolecular reaction
(c) unimolecular reaction
(d) trimolecular reaction

[Ans. (b)]



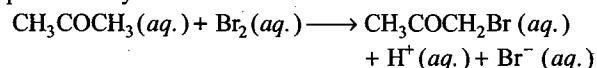
$$\text{Rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}_2\text{O}]$$

When water is in excess, its concentration will be constant.

$$\therefore \text{Rate} = k'[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

The reaction is, therefore, pseudo first order or pseudo unimolecular reaction.]

21. The bromination of acetone that occurs in acid solution is represented by



These kinetic data were obtained for given reaction concentrations:

Initial concentrations (M)			Initial rate of disappearance of Br ₂ , M s ⁻¹
[CH ₃ COCH ₃]	[Br ₂]	[H ⁺]	
0.30	0.05	0.05	5.7 × 10 ⁻⁵
0.30	0.10	0.05	5.7 × 10 ⁻⁵
0.30	0.10	0.10	1.2 × 10 ⁻⁴
0.40	0.05	0.20	3.1 × 10 ⁻⁴

[CBSE (PMT) 2008]

Based on these data, rate equation is :

(a) Rate = $k [\text{CH}_3\text{COCH}_3] [\text{Br}_2] [\text{H}^+]^2$

(b) Rate = $k [\text{CH}_3\text{COCH}_3] [\text{Br}_2] [\text{H}^+]$

(c) Rate = $k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$

(d) Rate = $k [\text{CH}_3\text{COCH}_3] [\text{Br}_2]$

[Ans. (c)]

[Hint : Rate = $k [\text{CH}_3\text{COCH}_3]^\alpha [\text{Br}_2]^\beta [\text{H}^+]^\gamma$

$$5.7 \times 10^{-5} = k [0.30]^\alpha [0.05]^\beta [0.05]^\gamma \quad \dots(i)$$

$$5.7 \times 10^{-5} = k [0.30]^\alpha [0.10]^\beta [0.05]^\gamma \quad \dots(ii)$$

$$1.2 \times 10^{-4} = k [0.30]^\alpha [0.10]^\beta [0.10]^\gamma \quad \dots(iii)$$

$$3.1 \times 10^{-4} = k [0.40]^\alpha [0.05]^\beta [0.20]^\gamma \quad \dots(iv)$$

Dividing eq. (i) by eq. (ii),

$$1 = \left[\frac{1}{2} \right]^\beta, \text{ i.e., } \beta = 0$$

Dividing eq. (ii) by eq. (iii),

$$\frac{1}{2} = \left[\frac{1}{2} \right]^\gamma, \text{ i.e., } \gamma = 1$$

Dividing eq. (i) by eq. (iv),

$$\frac{5.7 \times 10^{-5}}{3.1 \times 10^{-4}} = \left[\frac{3}{4} \right]^\alpha \times \left[\frac{1}{4} \right]^\gamma$$
$$\alpha \approx 1$$

Thus, rate law will be

rate = $k [\text{CH}_3\text{COCH}_3]^1 [\text{H}^+]^1$

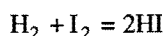
8.9 REACTION MECHANISM

Knowledge about involved steps in a reaction, and to determine which step is slowest or rate determining, is called mechanism.

The intelligent guess depending on the observed rates of reactions about the series of steps (known as elementary processes) leading to the formation of products is called the reaction mechanism.

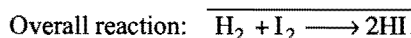
For illustration a few examples of reaction mechanisms are given below:

1. The reaction between H₂ and I₂ to form hydrogen iodide was originally postulated as a simple one step reaction.

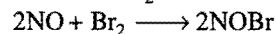


Rate = $k[\text{H}_2][\text{I}_2]$

But, the formation of HI has been explained on the basis of the following mechanism:



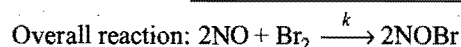
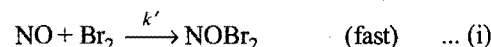
2. The reaction of NO and Br₂ is known to be of second order in NO and first order in Br₂.



Rate = $k [\text{NO}]^2 [\text{Br}_2]$

The likelihood of three molecules (2 molecules of NO and 1 molecule of Br₂) colliding simultaneously is far less than the likelihood that two molecules will collide.

The mechanism is believed to be as under:



The rate determining step involves 1 molecule of NO and 1 molecule of NOBr₂. Thus, the expected rate expression should be

Rate = $k'' [\text{NOBr}_2] [\text{NO}]$

However, NOBr₂ is a reaction intermediate and its concentration at the beginning of second step cannot be directly measured.

Concentration of NOBr₂ will be equal to

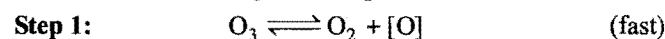
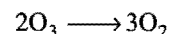
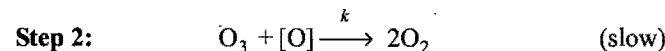
$$[\text{NOBr}_2] = k' [\text{NO}] [\text{Br}_2]$$

If this is substituted in the above equation, we get

$$\begin{aligned} \text{Rate} &= k' k'' [\text{NO}]^2 [\text{Br}_2] \\ &= k [\text{NO}]^2 [\text{Br}_2] \end{aligned}$$

3. Depletion of ozone takes place in the following steps:

Overall reaction:

(Equilibrium constant K_c)

Rate = $k[\text{O}_3][\text{O}] \quad \dots (i)$

Nascent oxygen [O] is not present in overall reaction; thus it should be eliminated.

$$K_c = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]}; [\text{O}] = K_c \frac{[\text{O}_3]}{[\text{O}_2]} \quad \dots (ii)$$

From eqs. (i) and (ii),

$$\text{Rate} = k[\text{O}_3] \cdot K_c \frac{[\text{O}_3]}{[\text{O}_2]}$$

$$= k K_c [\text{O}_3]^2 [\text{O}_2]^{-1}$$

$$= K [\text{O}_3]^2 [\text{O}_2]^{-1}$$

$$K = k \times K_c$$

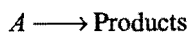
Order = $2 - 1 = 1$

8.10 REACTIONS OF VARIOUS ORDERS

(i) Zero order reactions

A reaction is said to be of zero order if its rate is independent of the concentration of the reactants, i.e., the rate is proportional to the zeroth power of the concentration of the reactants.

For the reaction



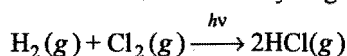
to be of zero order,

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

Some photochemical reactions and a few heterogeneous reactions are zero order reactions. Such reactions are not common.

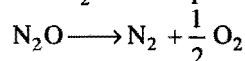
Examples:

1. Photochemical reaction between hydrogen and chlorine:



This photochemical reaction is zero order reaction. The reaction is studied by placing H_2 and Cl_2 gases over water. The rate of reaction is studied by noting the rate at which water rises in the vessel due to dissolution of HCl formed. The rate of rise of water is the same as the rate of disappearance of H_2 and Cl_2 , i.e., the concentration of the gases per unit volume in the gaseous phase will not change with time, although the quantities will change.

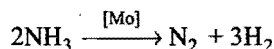
2. Decomposition of N_2O on hot platinum surface:



$$\text{Rate} \propto [\text{N}_2\text{O}]^0 = k[\text{N}_2\text{O}]^0 = k$$

$$\text{or} \quad \frac{d[\text{N}_2\text{O}]}{dt} = k$$

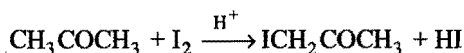
3. Decomposition of NH_3 in presence of molybdenum or tungsten is a zero order reaction.



The surface of the catalyst is almost completely covered by NH_3 molecules. The adsorption of gas on the surface cannot change by increasing the pressure or concentration of NH_3 . Thus, the concentration of gas phase remains constant although the product is formed. Therefore, this reaction shows zero order kinetics.

Other examples of zero order are:

4. Decomposition of HI on the gold surface.
5. Iodination of acetone in presence of H^+ ions,



The rate equation of this reaction does not include $[\text{I}_2]$ factor, i.e.,

$$-\frac{dx}{dt} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

Characteristics of zero order reaction

- (a) The concentration of reactant decreases linearly with time.

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

- (b) The time required for the reaction to be complete, i.e., time at which $[A]$ is zero.

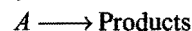
$$t_{\text{Completion}} = \frac{[A]_0}{k} = \frac{\text{Initial concentration}}{\text{Rate constant}}$$

- (c) The units of k are $\text{mol L}^{-1} \text{time}^{-1}$.

(ii) First order reactions

A reaction is said to be of first order if its rate is determined by the change of one concentration term only.

Consider the reaction,



Let a be the concentration of A at the start and after time t , the concentration becomes $(a - x)$, i.e., x has been changed into products. The rate of reaction after time ' t ' is given by the expression

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

or

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

upon integration of above equation,

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

or

$$-\log_e (a - x) = kt + c$$

where c is integration constant.

$$\text{When } t = 0, \quad x = 0,$$

$\therefore$

$$c = -\log_e a$$

Putting the value of ' c ',

$$-\log_e (a - x) = kt - \log_e a$$

or

$$\log_e a - \log_e (a - x) = kt$$

or

$$\log_e \frac{a}{(a - x)} = kt$$

or

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a - x)}$$

This is known as the kinetic equation for a reaction of the first order. The following two important conclusions are drawn from this equation:

- (a) A change in concentration unit will not change the numerical value of k . Let the new unit be n times the first one.

$$\text{So,} \quad k = \frac{2.303}{t} \log_{10} \frac{na}{n(a - x)}$$

or

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a - x)}$$

Thus, for first order reactions, any quantity which is proportional to concentration can be used in place of concentration for evaluation of ' k '.

- (b) The time taken for the completion of same fraction of change is independent of initial concentration. For example, for half change,

$$x = 0.5a \quad \text{and} \quad t = t_{1/2}$$

$$\text{So,} \quad k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{0.5a} = \frac{2.303}{t_{1/2}} \log_{10} 2$$

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

or

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

Thus, $t_{1/2}$ is independent of initial concentration 'a'.

This time 't' in which the initial concentration becomes half is termed as **half life period**. Half life period of a first order reaction is independent of the initial concentration of the reactant.

Since, the velocity constant is independent of concentration and depends inversely on the time, the unit of k will be time^{-1} , i.e., sec^{-1} or min^{-1} or hour^{-1} . The equation of the first order can also be written in the following form when initial concentration is not known:

$$k = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{(a - x_1)}{(a - x_2)}$$

$(a - x_1)$ is the concentration after time t_1 and $(a - x_2)$ the concentration after time t_2 when $t_2 > t_1$.

When the log of the concentration of the reactant at various intervals of time is plotted against the time intervals, a straight line is obtained (Fig. 8.13). The slope of this line gives the value $2.303/k$, from which k can be evaluated.

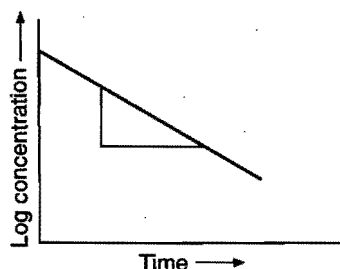
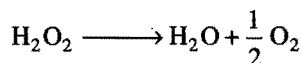


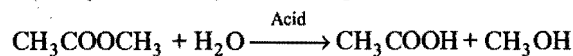
Fig. 8.13

Examples of first order reactions

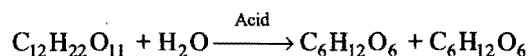
1. Decomposition of H_2O_2 in aqueous solution.



2. Hydrolysis of methyl acetate in presence of mineral acids.



3. Inversion of cane sugar in presence of mineral acids.



4. Decomposition of ammonium nitrite in aqueous solution.



5. Hydrolysis of diazo derivatives.



Note: In case of gases, pressure can be used in place of concentration.

First order growth kinetics

It is used for population growth and bacteria multiplication, e.g.,

Time	Population
0	a
dt	(a + x)

Growth rate is directly proportional to present population.

$$\begin{aligned} \frac{dx}{dt} &\propto (a + x) \\ &= k(a + x) \\ \frac{dx}{(a + x)} &= k dt \end{aligned} \quad \dots (i)$$

It is a differential equation of first order and first degree in variable separable form. It may be solved on integration.

$$\begin{aligned} \int \frac{dx}{(a + x)} &= k \int dt + c \\ \log_e (a + x) &= kt + c \end{aligned} \quad \dots (ii)$$

Here, c = integration constant

$$\begin{aligned} \text{At } t = 0, \quad x &= 0 \\ \therefore \log_e a &= k \times 0 + c \\ c &= \log_e a \end{aligned} \quad \dots (iii)$$

Substituting the value of 'c' in eq. (ii), we get

$$\begin{aligned} \log_e (a + x) &= kt + \log_e a \\ kt &= -\log_e \frac{a}{(a + x)} \\ k &= -\frac{2.303}{t} \log_{10} \left(\frac{a}{a + x} \right) \end{aligned}$$

This is the kinetics for first order growth kinetics.

Note: (1) If volumes of reagents are given in volumetric analysis then we use the following equation to determine rate constant:

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$$

where, V_0 = volume used at zero time,
 V_t = volume used at time 't',
 V_∞ = volume used at infinite time

Case I: When V_0 is not given, we use

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

Case II: When V_∞ is not given, then

$$k = \frac{2.303}{t} \log_{10} \left(\frac{V_0}{V_t} \right)$$

(2) If information is given in terms of angle of rotation of optically active compounds, measured by polarimeter with respect to time, then

$$k = \frac{2.303}{t} \log_{10} \left\{ \frac{r_\infty - r_0}{r_\infty - r_t} \right\}$$

where, r_0 = angle of rotation at zero time,
 r_t = angle of rotation at time 't',
 r_∞ = angle of rotation at infinite time

Case I: If r_0 is not given, then

$$k = \frac{2.303}{t} \log_{10} \left\{ \frac{r_{\infty}}{r_{\infty} - r_t} \right\}$$

Case II: If r_{∞} is not given, then

$$k = \frac{2.303}{t} \log_{10} \left\{ \frac{r_0}{r_t} \right\}$$

(3) If pressure is given in gaseous reactions, then we use the following kinetic equation:

$$k = \frac{2.303}{t} \log_{10} \left\{ \frac{p_0}{p_0 - x} \right\}$$

where, p_0 = pressure of reactant at initial stage,
 $(p_0 - x)$ = pressure of such a reactant at 't' time.

Values of ' p_0 ' and ' x ' can be calculated using the following examples:

	$A(g) \longrightarrow B(g) + C(g) + D(g)$			
At $t = 0$	p_0	0	0	0
Pressure after time 't'	$(p_0 - x)$	x	x	x
Pressure after a long time or infinite time	0	p_0	p_0	p_0

Case I: If total pressure of reaction mixture is given in place of pressure of reactant, then

$$p_t = (p_0 - x + x + x + x)$$

where, p_t = pressure of vessel at time 't'.

Case II: If pressure of vessel after a long time or infinite time is given, then

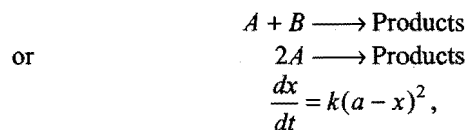
$$p_{\infty} = p_0 + p_0 + p_0$$

(iii) Second order reactions

A reaction is said to be of second order if its reaction rate is determined by the variation of two concentration terms.

The kinetics of second order reactions are given as follows:

(a) When concentrations of both reactants are equal or two molecules of the same reactant are involved in the change, i.e.,

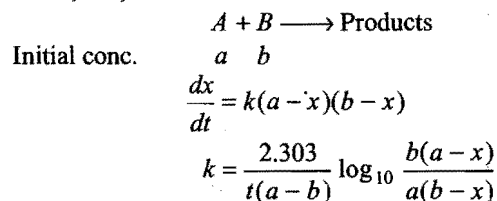


On solving this equation,

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

where, a = initial concentration of the reactant or reactants and
 x = concentration of the reactant changed in time t .

(b) When the initial concentrations of the two reactants are different, i.e.,



$(a-x)$ and $(b-x)$ are the concentrations of A and B after time interval, t .

Characteristics of the second order reactions

(i) The value of k (velocity constant) depends on the unit of concentration. The unit of k is expressed as $(\text{mol/litre})^{-1} \text{ time}^{-1}$ or $\text{litre mol}^{-1} \text{ time}^{-1}$.

$$(ii) \text{ Half life period } (t_{1/2}) = \frac{1}{k} \cdot \frac{0.5a}{a \times 0.5a} = \frac{1}{ka}$$

Thus, half life is inversely proportional to initial concentration.

(iii) Second order reaction conforms to the first order when one of the reactants is present in large excess.

$$\text{Taking, } k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}, \text{ if } a \gg b \text{ then}$$

$$(a-x) \approx a \text{ and } (a-b) \approx a$$

$$\text{Hence, } k = \frac{2.303}{ta} \log_{10} \frac{ba}{a(b-x)}$$

$$\text{or } ka = k' = \frac{2.303}{t} \log_{10} \frac{b}{(b-x)}$$

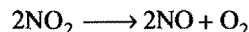
(since, ' a ' being very large, may be treated as constant after the change). Thus, the reaction follows first order kinetics with respect to the reactant taken relatively in small amount.

Examples of second order reactions

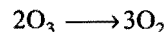
1. Hydrolysis of ester by an alkali (saponification).



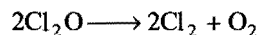
2. The decomposition of NO_2 into NO and O_2 .



3. Conversion of ozone into oxygen at 100°C .



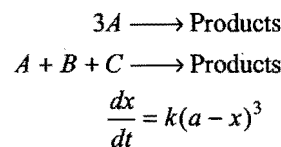
4. Thermal decomposition of chlorine monoxide.



(iv) Third order reactions

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms.

When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as:



On solving this equation,

$$k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$$

Characteristics of third order reactions

1. Half life period

$$= \frac{1}{k} \cdot \frac{0.5a(2a-0.5a)}{2a^2(0.5a)^2} = \frac{1}{k} \cdot \frac{0.5a \times 1.5a}{2a^2 \times 0.5a \times 0.5a}$$

$$= \frac{3}{2a^2k}$$

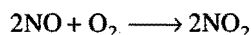
Thus, half life is inversely proportional to the square of initial concentration.

2. The change in the unit of concentration changes the numerical value of k .

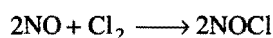
3. The unit of k is expressed as $(\text{mol/litre})^{-2} \text{ time}^{-1}$ or $\text{litre}^2 \text{ mol}^{-2} \text{ time}^{-1}$.

Examples of third order reactions

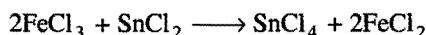
1. Reaction between nitric oxide and oxygen.



2. Reaction between nitric oxide and chlorine.



3. Reduction of FeCl_3 by SnCl_2 .

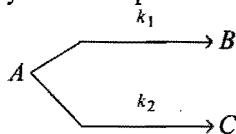


Expressions for rate constant for reactions of different orders:

Reaction	Order	Rate law eqn.	Expression for rate const.
$A \rightarrow \text{Products}$	0	$\text{Rate} = k$	$k = \frac{1}{t} [[A]_0 - [A]]$
$A \rightarrow \text{Products}$	1	$\text{Rate} = k[A]$	$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$
$2A \rightarrow \text{Products}$	2	$\text{Rate} = k[A]^2$	$k = \frac{1}{t} \left[\frac{1}{[A]} - \frac{1}{[A]_0} \right]$
$A + B \rightarrow \text{Products}$	2	$\text{Rate} = k[A][B]$	$k = \frac{2.303}{t([A]_0 - [B]_0)} \log \frac{[B]_0[A]}{[A]_0[B]}$
$3A \rightarrow \text{Products}$	3	$\text{Rate} = k[A]^3$	$k = \frac{1}{2t} \left[\frac{1}{[A]^2} - \frac{1}{[A]_0^2} \right]$

Parallel or Competing reaction

The reaction in which a substance reacts or decomposes in more than one way are called parallel or side reactions,

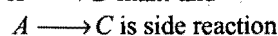
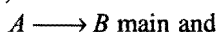


$$\frac{-d[A]}{dt} = (k_1 + k_2)[A] = k_{av}[A]$$

$$k_1 = \text{fractional yield of } B \times k_{av}$$

$$k_2 = \text{fractional yield of } C \times k_{av}$$

If $k_1 \gg k_2$ then,



Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

$$\begin{aligned}
 \frac{x}{y} &= \frac{k_1}{k_2} \\
 \text{i.e., } \frac{d[B]}{dt} / \frac{d[C]}{dt} &= \frac{k_1}{k_2}
 \end{aligned}$$

Variation of concentration A , B and C with time may be graphically represented as,

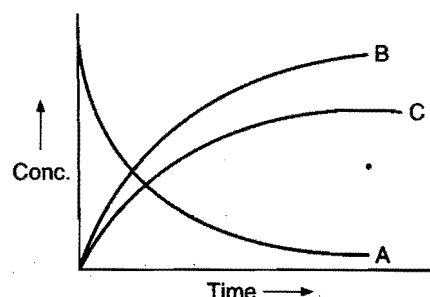
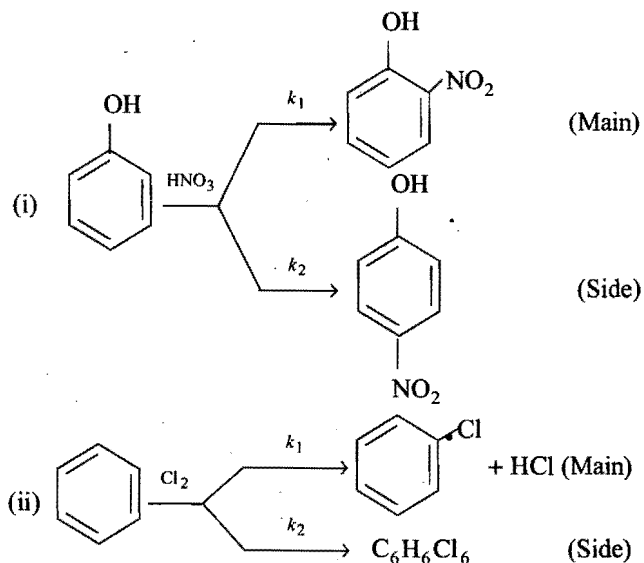


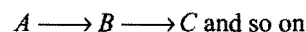
Fig. 8.14

Examples:

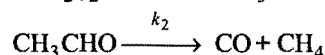
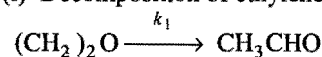


Consecutive reaction

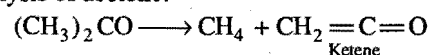
This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.



Examples: (i) Decomposition of ethylene oxide:



(ii) The pyrolysis of acetone:



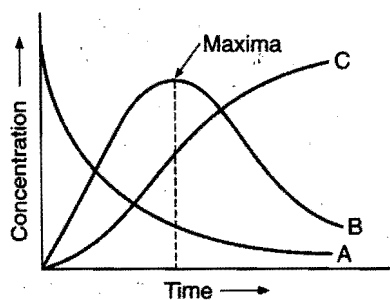
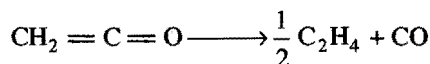
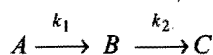


Fig. 8.15

Variation of concentration of various substances during the progress of reaction ($A \rightarrow B \rightarrow C$)



Let initially ($t = 0$), $[B] = 0$ and $k_1 < k_2$ then maximum concentration of $[B]$ may be calculated as,

$$[B]_{\max} = [A]_0 \left[\frac{k_1}{k_2} \right]^{k_2/k_1 - k_2}$$

where, $[A]_0$ = initial concentration of A

Time in which B attains maximum concentration may be given as,

$$t_{\max} = \frac{2.303}{k_2 - k_1} \log \left(\frac{k_2}{k_1} \right)$$

Concentration of $[B]$ after time ' t ' may be calculated as,

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

Activation energy diagram of a composite reaction involves more than one peaks and number of peaks indicate the number of different types of activated complexes involved. The number of valleys in the activation energy diagram indicates the number of different types of reactive intermediates involved.

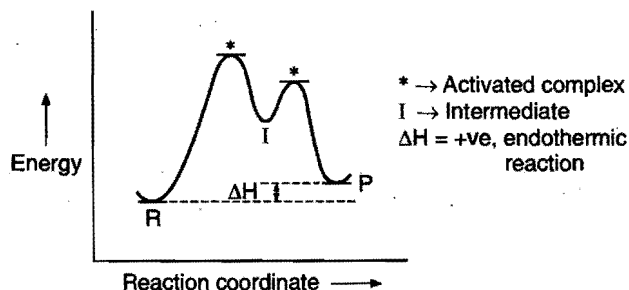
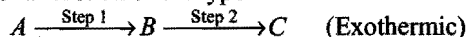


Fig. 8.16 Activation energy diagram of a two steps composite reaction

Energy Diagram of two Steps Reaction

Let us consider a reaction of the type :



These are two possibilities in this reaction

First possibility :

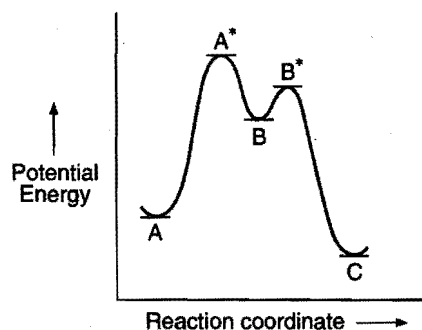
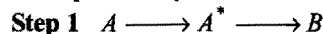


Fig. 8.17

Activation energy of **step 1** is greater than that of **step 2** thus **step 1** will be slow and rate determining.

Second possibility :

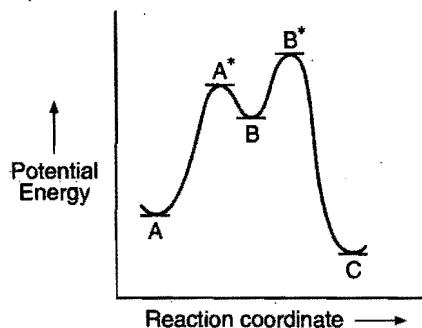


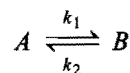
Fig. 8.18

Activation energy of **step 2** is greater than that of **step 1** hence **step 2** will be slow and rate determining

Reversible Reactions

The reactions in which the products of chemical change react together to form the original reactants, are called reversible reactions. These are also called opposing or counter reactions.

Let us consider a reversible reaction in which both forward and backward reactions are of first order.



Initial state ($t = 0$) a 0

Conc. at time (t) $a - x$ x

Equilibrium conc. $(a - x_e)$ x_e

$$k_1 + k_2 = \frac{2.303}{t} \log_{10} \left\{ \frac{x_e}{x_e - x} \right\}$$

8.11 METHODS FOR DETERMINATION OF ORDER OF A REACTION

The important methods used are the following:

1. Method of integration (Hit and trial method)

The most simple method is the one in which the quantities a , x and t are determined and substituted in the kinetic equations of various orders. The equation which gives the most constant value for the specific rate constant (k) for a series of time intervals is the one corresponding to the order of reaction. If all the reactants are at the same molar concentrations, the kinetic equations are:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}, \text{ for first order reactions;}$$

$$k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right], \text{ for second order reactions;}$$

$$k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right], \text{ for third order reactions.}$$

2. Graphical method

A graphical method based on the respective rate laws can also be used.

If the plot of $\log(a-x)$ versus ' t ' is a straight line, the reaction follows first order.

If the plot of $\frac{1}{(a-x)}$ versus ' t ' is a straight line, the reaction follows second order.

If the plot of $\frac{1}{(a-x)^2}$ versus ' t ' is a straight line, the reaction follows third order.

In general, for a reaction of n th order, a graph of $\frac{1}{(a-x)^{n-1}}$ versus ' t ' must be a straight line.

3. Half life method

A general expression for the half life, $(t_{1/2})$, is given by

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

where, ' n ' is the order of the reaction.

Starting with two different initial concentrations a_1 and a_2 for the same reaction, the half lives are $(t_{1/2})_1$ and $(t_{1/2})_2$ respectively are determined. As we know that,

$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}} \quad \dots (i)$$

$$\text{and} \quad (t_{1/2})_2 \propto \frac{1}{a_2^{n-1}} \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii),

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1} \right)^{n-1} \quad \dots (iii)$$

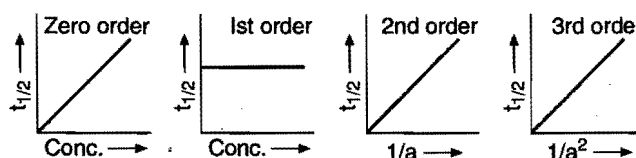
Taking logarithms on both sides,

$$\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2 = (n-1) [\log_{10} a_2 - \log_{10} a_1]$$

$$(n-1) = \frac{\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2}{\log_{10} a_2 - \log_{10} a_1}$$

$$\text{or} \quad n = 1 + \frac{\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2}{\log_{10} a_2 - \log_{10} a_1} \quad \dots (iv)$$

Plots of half lives vs. concentration ($t_{1/2} \propto a^{1-n}$):



This relation can be used to determine order of reaction ' n '.

4. van't Hoff differential method

As we know that, the rate of a reaction varies as the n th power of the concentration of the reactant where ' n ' is the order of the reaction. Thus, for two different initial concentrations C_1 and C_2 , equations can be written in the form

$$-\frac{dC_1}{dt} = kC_1^n \text{ and } -\frac{dC_2}{dt} = kC_2^n$$

Taking logarithms,

$$\log_{10} \left(-\frac{dC_1}{dt} \right) = \log_{10} k + n \log_{10} C_1 \quad \dots (i)$$

$$\text{and} \quad \log_{10} \left(-\frac{dC_2}{dt} \right) = \log_{10} k + n \log_{10} C_2 \quad \dots (ii)$$

Subtracting eq. (ii) from eq. (i),

$$\log_{10} \left(-\frac{dC_1}{dt} \right) - \log_{10} \left(-\frac{dC_2}{dt} \right) = n (\log_{10} C_1 - \log_{10} C_2)$$

$$\text{or} \quad n = \frac{\log_{10} \left(-\frac{dC_1}{dt} \right) - \log_{10} \left(-\frac{dC_2}{dt} \right)}{\log_{10} C_1 - \log_{10} C_2} \quad \dots (iii)$$

$-\frac{dC_1}{dt}$ and $-\frac{dC_2}{dt}$ are determined from concentration vs. time graphs and the value of ' n ' can be determined.

SOME SOLVED EXAMPLES

Example 20. Rate of a reaction $A + B \longrightarrow \text{product}$, is given as a function of different initial concentrations of A and B.

[A] (mol L ⁻¹)	[B] (mol L ⁻¹)	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 w.r.t. B. What is the half life of A in the reaction?

Solution: Let the rate of reaction be

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

From the data given, it is clear that by doubling the concentration of A, the rate also becomes double when B is kept constant. Thus, the rate is directly proportional to concentration of A.

$$\text{Rate} \propto [A], \text{ i.e., } x = 1$$

Or the order of reaction w.r.t. A is 1.

When the concentration of A is kept constant and the concentration of B is doubled, the rate does not change, i.e., $y = 0$; or the order of reaction w.r.t. B is zero.

$$\text{Thus, reaction rate, } -\frac{dx}{dt} = k[A]$$

$$\text{Again } k = \frac{0.005}{0.01} = 0.5 \text{ min}^{-1}$$

$$\text{Half life of A} = \frac{0.693}{k} = \frac{0.693}{0.5} = 1.386 \text{ min}$$

Example 21. Thermal decomposition of a compound is of the first order. If 50% of a sample of the compound is decomposed in 120 minutes, how long will it take for 90% of the compound to decompose?

Solution: Half life of reaction = 120 min

We know that,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{120} = 5.77 \times 10^{-3} \text{ min}^{-1}$$

Applying first order reaction equation,

$$t = \frac{2.303}{k} \log_{10} \frac{a}{a-x}$$

If $a = 100$, $x = 90$ or $(a-x) = 10$,

$$\text{So, } t = \frac{2.303}{5.77 \times 10^{-3}} \cdot \log_{10} 10 = \frac{2.303}{5.77 \times 10^{-3}} = 399 \text{ min}$$

Example 22. The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is a first order reaction.

(i) After 55 seconds at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

(ii) Calculate the pressure of Cl_2O_7 after 100 seconds of decomposition at this temperature.

Solution: (i) As pressure $\propto$ concentration,

$$\begin{aligned} k &= \frac{2.303}{t} \log_{10} \frac{P_i \text{ (initial pressure)}}{P_t \text{ (pressure after time } t)}} \\ &= \frac{2.303}{55} \log_{10} \frac{0.062}{0.044} = 6.2 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

(ii) Again applying the first order kinetic equation,

$$k = \frac{2.303}{t} \log_{10} \frac{P_i \text{ (initial pressure)}}{P_t \text{ (pressure after time } t)}}$$

$$6.2 \times 10^{-3} = \frac{2.303}{100} \log_{10} \frac{0.062}{P_t}$$

$$\text{or } \frac{6.2 \times 10^{-3} \times 100}{2.303} = \log_{10} 0.062 - \log_{10} (P_t)$$

$$\text{or } 0.2692 = \log_{10} 0.062 - \log_{10} (P_t)$$

$$\begin{aligned} \text{or } \log_{10} (P_t) &= \log_{10} 0.062 - 0.2692 \\ &= (2.7924 - 0.2692) \end{aligned}$$

$$P_t = 0.033 \text{ atmosphere}$$

Pressure after 100 sec = 0.033 atm

Example 23. The half life of a first order reaction is 60 min. How long will it take to consume 90% of the reactant?

Solution: For the first order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60} = 11.55 \times 10^{-3} \text{ min}^{-1}$$

Applying first order kinetic equation,

$$t = \frac{2.303}{k} \log_{10} \frac{a}{(a-x)}$$

Given: $a = 100$, $x = 90$, i.e., $(a-x) = (100-90) = 10$

$$\begin{aligned} \text{Hence, } t &= \frac{2.303}{11.55 \times 10^{-3}} \cdot \log_{10} 10 \\ &= 199 \text{ min} \end{aligned}$$

Example 24. A first order reaction has a rate constant of $15 \times 10^{-3} \text{ s}^{-1}$. How long will 5.0 g of this reactant take to reduce to 3.0 g?

Solution: Applying first order kinetic equation,

$$t = \frac{2.303}{k} \log_{10} \frac{a}{(a-x)}$$

Given: $k = 15 \times 10^{-3} \text{ sec}^{-1}$, $a = 5 \text{ g}$, $(a-x) = 3 \text{ g}$

$$\text{So, } t = \frac{2.303}{15 \times 10^{-3}} \log_{10} \frac{5}{3} = 34.07 \text{ sec}$$

Example 25. Catalytic decomposition of nitrous oxide by gold at 900°C at an initial pressure of 200 mm was 50% in 53 minutes and 73% in 100 minutes.

(a) What is the order of reaction?

(b) How much it will decompose in 100 minutes at the same temperature but at an initial pressure of 600 mm? (IIT 1990)

Solution: (a) Using first order kinetic equation and substituting given values,

$$\text{In first case: } k = \frac{2.303}{53} \log_{10} \frac{200}{200-100} = 0.0131 \text{ min}^{-1}$$

$$\text{In second case: } k = \frac{2.303}{100} \log_{10} \frac{200}{200-146} = 0.0131 \text{ min}^{-1}$$

As the values of k come out to be the same in both cases, the reaction is of first order.

(b) As in the first order reaction, the time required for the completion of same fraction is independent of initial concentration; the percentage decomposition in 100 minutes when the initial pressure is 600 mm will also be 73%.

Example 26. A substance reacts according to the first order rate law and the specific reaction rate for the reaction is $1 \times 10^{-2} \text{ s}^{-1}$. If the initial concentration is 1.0 M.

(a) What is the initial rate?

(b) What is the reaction rate after 1 minute?

Solution: (a) Initial rate of a first order reaction = kC

$$= 1 \times 10^{-2} \times 1.0 = 1 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

(b) Concentration after 60 seconds is calculated by applying first order kinetic equation,

$$k = \frac{2.303}{60} \log_{10} \frac{1}{(1-x)}$$

$$\text{or } 1 \times 10^{-2} = \frac{2.303}{60} [-\log(1-x)]$$

$$\text{or } \frac{60 \times 10^{-2}}{2.303} = -\log(1-x) = 0.2605$$

$$\log(1-x) = -0.2605$$

$$= \bar{1}.7395$$

$$(1-x) = \text{antilog of } (\bar{1}.7395) = 0.5489 \text{ mol L}^{-1}$$

Rate of reaction after 1 minute = $k \times C$

$$= 1 \times 10^{-2} \times 0.5489$$

$$= 5.489 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

Example 27. A first order reaction is 50% completed in 30 minutes at 27°C and in 10 minutes at 47°C . Calculate the reaction rate constant at 27°C and the energy of activation of the reaction in kJ mol^{-1} .

Solution: For first order reaction $k = \frac{0.693}{t_{1/2}}$

$$\text{At } 27^\circ\text{C}, \quad k_{27^\circ\text{C}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

$$\text{At } 47^\circ\text{C}, \quad k_{47^\circ\text{C}} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$$

Now applying the following equation:

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

$$\text{or } \log_{10} \frac{0.0231}{0.0693} = \frac{-E_a}{2.303 \times 8.314} \cdot \left(\frac{320 - 300}{320 \times 300} \right)$$

$$\begin{aligned} \text{or } -\log_{10} 0.3333 &= \frac{E_a}{19.1471} \times \frac{20}{96000} \\ E_a &= -\frac{19.1471 \times 96000}{20} \times \log 0.3333 \\ &= -91906 \times (-0.4772) \\ &= 43857 \text{ J mol}^{-1} = 43.857 \text{ kJ mol}^{-1} \end{aligned}$$

Example 28. In Arrhenius equation for a certain reaction, the values of A and E_a (activation energy) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half life period be 10 minutes?

(IIT 1990)

Solution: According to Arrhenius equation,

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

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

$$\text{or } 2.303 \log_{10} k = 2.303 \log_{10} A - \frac{E_a}{RT}$$

$$\text{For a first order reaction } t_{1/2} = \frac{0.693}{k}$$

$$\begin{aligned} \text{So, } k &= \frac{0.693}{600} \text{ sec}^{-1} \quad (t_{1/2} = 10 \text{ min} = 600 \text{ sec}) \\ &= 1.1 \times 10^{-3} \text{ sec}^{-1} \end{aligned}$$

$$\text{Hence, } \log(1.1 \times 10^{-3}) = \log(4 \times 10^{13}) - \frac{98.6 \times 10^3}{2.303 \times 8.314 \times T}$$

$$T = 310.95 \text{ K}$$

Example 29. A second order reaction, in which both the reactants have same concentration, is 20% completed in 500 seconds. How much time it will take for 60% completion?

Solution: The second order equation when both the reactants have same concentration is

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

If $a = 100$, $x = 20$, $t = 500$ seconds.

$$\text{So, } k = \frac{1}{500} \times \frac{20}{100 \times (100 - 20)}$$

When $a = 100$, $x = 60$, $t = ?$

$$t = \frac{1}{k} \cdot \frac{60}{100 \times 40}$$

Substituting the value of k ,

$$t = \frac{500 \times 100 \times 80}{20} \times \frac{60}{100 \times 40}$$

or $t = 3000$ seconds

Example 30. A first order reaction is 20% complete in 10 minutes. Calculate the time taken for the reaction to go to 80% completion.

Solution: Applying first order equation,

$$k = \frac{2.303}{t} \log_{10} \frac{100}{(100 - 20)}$$

$$= \frac{2.303}{10} \log_{10} \frac{100}{80} = 0.0223 \text{ min}^{-1}$$

Again applying first order equation,

$$\begin{aligned} t &= \frac{2.303}{k} \log_{10} \frac{100}{(100 - 80)} \\ &= \frac{2.303}{0.0223} \log_{10} \frac{100}{20} \\ &= 72.18 \text{ min} \end{aligned}$$

Example 31. The decomposition of dinitrogen pentoxide (N_2O_5) follows first order rate law. Calculate the rate constant from the given data:

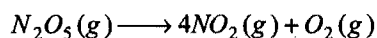
$$t = 800 \text{ sec} \quad [N_2O_5] = 1.45 \text{ mol L}^{-1} = [A_1]$$

$$t = 1600 \text{ sec} \quad [N_2O_5] = 0.88 \text{ mol L}^{-1} = [A_2]$$

Solution: Applying the formula,

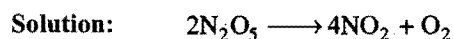
$$\begin{aligned} k &= \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{[A_1]}{[A_2]} \\ &= \frac{2.303}{(1600 - 800)} \log_{10} \frac{1.45}{0.88} \\ &= \frac{2.303}{800} \times 0.2169 = 6.24 \times 10^{-4} \text{ sec}^{-1} \end{aligned}$$

Example 32. The decomposition of N_2O_5 according to the equation,



is a first order reaction. After 30 minutes from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.4 mm Hg and on completion, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

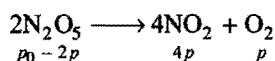
(IIT 1991)



On decomposition of 2 moles of N_2O_5 , 4 moles of NO_2 and 1 mole of O_2 are produced. Thus, the total pressure after completion corresponds to 5 moles and initial pressure to 2 moles.

$$\text{Initial pressure of } N_2O_5, p_0 = \frac{2}{5} \times 584.5 = 233.8 \text{ mm Hg}$$

$$\text{After 30 minutes, the total pressure} = 284.5 \text{ mm Hg}$$



$$\text{or} \quad p_0 + 3p = 284.5$$

$$\text{or} \quad 3p = 284.5 - 233.8 = 50.7 \text{ mm Hg}$$

$$\text{or} \quad p = \frac{50.7}{3} = 16.9 \text{ mm Hg}$$

$$\begin{aligned} \text{Pressure of } N_2O_5 \text{ after 30 minutes} &= 233.8 - (2 \times 16.9) \\ &= 200 \text{ mm Hg} \end{aligned}$$

$$k = \frac{2.303}{30} \log_{10} \frac{233.8}{200.0} = 5.2 \times 10^{-3} \text{ min}^{-1}$$

Example 33. The gas phase decomposition of dimethyl ether follows first order kinetics.



The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure after 12 minutes? Assume ideal gas behaviour.

(IIT 1993)

Solution: $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.5} = 0.047793 \text{ min}^{-1}$

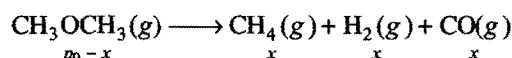
Let the pressure of dimethyl ether after 12 minutes be p atm. Applying first order equation,

$$\begin{aligned} k &= \frac{2.303}{t} \log_{10} \frac{p_0}{p} \\ \log_{10} \frac{0.4}{p} &= \frac{0.047793 \times 12}{2.303} = 0.2490 \end{aligned}$$

$$\text{or} \quad \frac{0.4}{p} = 1.7743$$

$$\text{or} \quad p = \frac{0.4}{1.7743} = 0.2254 \text{ atm}$$

$$\text{Decrease in pressure, } x = 0.4 - 0.2254 = 0.1746 \text{ atm}$$

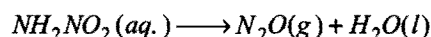


$$\text{Total pressure} = p_0 + 2x$$

$$= 0.4 + 2 \times 0.1746$$

$$= 0.7492 \text{ atm}$$

Example 34. The half life of first order decomposition of nitramide is 2.1 hours at 15°C .



If 6.2 g of NH_2NO_2 is allowed to decompose calculate (i) time taken for NH_2NO_2 to decompose 99% and (ii) the volume of dry N_2O produced at this point, measured at STP. (IIT 1994)

Solution: (i) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1} = 0.33 \text{ hr}^{-1}$

Applying kinetic equation of first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a - x)}$$

$$\begin{aligned} \text{or} \quad t &= \frac{2.303}{0.33} \log_{10} \frac{100}{(100 - 99)} \\ &= 13.96 \text{ hrs} \end{aligned}$$

(ii) No. of moles of NH_2NO_2 decomposed

$$= 0.99 \times \frac{6.2}{62}$$

$$= 0.099$$

$$\text{No. of moles of } N_2O \text{ formed} = 0.099$$

$$\text{Volume of } N_2O \text{ at STP} = 0.099 \times 22400 \text{ mL}$$

$$= 2217.6 \text{ mL}$$

Example 35. From the following data for the reaction between A and B:

Expt. No.	[A] (mol L ⁻¹)	[B] (mol L ⁻¹)	Initial rate (mol L ⁻¹ s ⁻¹)	
			300 K	320 K
(1)	2.5 × 10 ⁻⁴	3.0 × 10 ⁻⁵	5.0 × 10 ⁻⁴	2.0 × 10 ⁻³
(2)	5.0 × 10 ⁻⁴	6.0 × 10 ⁻⁵	4.0 × 10 ⁻³	...
(3)	1.0 × 10 ⁻³	6.0 × 10 ⁻⁵	1.6 × 10 ⁻²	...

Calculate the following:

- The order of the reaction with respect to A and with respect to B,
- The rate constant at 300 K,
- The energy of activation and
- The pre-exponential factor.

(IIT 1994)

Solution: (i) Let the rate law be:

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

From expt. (1), $5.0 \times 10^{-4} = k[2.5 \times 10^{-4}]^x [3.0 \times 10^{-5}]^y$... (i)

From expt. (2), $4.0 \times 10^{-3} = k[5.0 \times 10^{-4}]^x [6.0 \times 10^{-5}]^y$... (ii)

Dividing eq. (ii) by eq. (i), $\frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}} = 2^x \cdot 2^y = 8$

From expt. (3), $1.6 \times 10^{-2} = k[1.0 \times 10^{-3}]^x [6.0 \times 10^{-5}]^y$... (iii)

Dividing eq. (iii) by eq. (ii), $\frac{1.6 \times 10^{-2}}{4.0 \times 10^{-3}} = 2^x = 4$

or $x = 2$ and $y = 1$

Hence, order w.r.t. A is 2nd and order w.r.t. B is 1st.

(ii) $\text{Rate} = k \cdot [A]^2[B]$

From expt. (1), $5 \times 10^{-4} = k[2.5 \times 10^{-4}]^2 [3.0 \times 10^{-5}]$

or $k = \frac{5 \times 10^{-4}}{[2.5 \times 10^{-4}]^2 [3.0 \times 10^{-5}]} = 2.67 \times 10^8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$

(iii) From Arrhenius equation,

$$\log_{10} \frac{2.0 \times 10^{-3}}{5.0 \times 10^{-4}} = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{300 \times 320}$$

$$E_a = \frac{2.303 \times 8.314 \times 300 \times 320}{20} \times \log_{10} 4$$

$$= 55.333 \text{ kJ mol}^{-1}$$

(iv) Applying $\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$

$$\log_{10} \frac{A}{k} = \frac{55.333}{2.303 \times 8.314 \times 300} = 9.633$$

or $\frac{A}{k} = 4.29 \times 10^9$

or $A = 4.29 \times 10^9 \times 2.67 \times 10^8$
 $= 1.145 \times 10^{18}$

Example 36. At a certain temperature, the half change period for the catalytic decomposition of ammonia were found as follows:

Pressure (Pascals):	6667	13333	26666
Half life period in hours:	3.52	1.92	1.0

Calculate the order of reaction.

Solution: $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$ where, n is order of reaction

From the given data,

$$\frac{3.52}{1.92} = \left(\frac{13333}{6667}\right)^{n-1} \quad (a \propto \text{initial pressure})$$

$$= (2)^{n-1}$$

$$\log \frac{3.52}{1.92} = (n-1) \log 2$$

$$= 0.3010 \times (n-1)$$

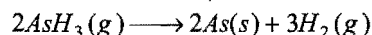
$$0.2632 = 0.3010 \times (n-1)$$

$$n = 1.87 \approx 2$$

Similar calculations are made between first and third observations. n comes equal to 1.908 (≈ 2).

Thus, the reaction is of second order.

Example 37. On heating, arsine (AsH_3) decomposes as:



The total pressure measured at constant temperature and constant volume varies with time as follows:

t (min)	0	5	7.5	10
p / mm Hg	760	836	866.4	896.8

Calculate the rate constant assuming the reaction to follow the first order rate law.

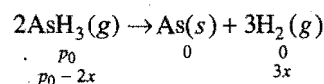
Solution: For first order, the rate equation is

Initially after time t

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{t} \log \frac{p_0}{p}$$

given, $p_0 = 760 \text{ mm Hg}$.

The decomposition reaction is:



Total pressure, $p_t = p_0 - 2x + 3x = p_0 + x$

$$x = p_t - p_0$$

$$p_{\text{AsH}_3} = (p_0 - 2x) = p_0 - 2p_t + 2p_0 = 3p_0 - 2p_t$$

After 5 minutes, $p_{\text{AsH}_3} = (3 \times 760) - (2 \times 836)$

$$= 608 \text{ mm Hg}$$

$$k = \frac{2.303}{5} \log_{10} \frac{760}{608} = 0.0446 \text{ min}^{-1}$$

After 7.5 minutes, $p_{\text{AsH}_3} = (3 \times 760) - (2 \times 866.4)$

$$= 547.2 \text{ mm Hg}$$

$$k = \frac{2.303}{7.5} \log_{10} \frac{760}{547.2} = 0.0438 \text{ min}^{-1}$$

After 10 minutes, $p_{\text{AsH}_3} = (3 \times 760) - (2 \times 896.8)$

$$= 486.4 \text{ mm Hg}$$

$$k = \frac{2.303}{10} \log_{10} \frac{760}{486.4} = 0.0446 \text{ min}^{-1}$$

Example 38. Cane sugar is gradually converted into dextrose and laevulose by dilute acid. The rate of inversion is observed by measuring the polarisation angle, at various times, when the following results are obtained:

Time (min)	0	10	20	30	40	100	∞
Angle	32.4	28.8	25.5	22.4	19.6	-6.1	-14.1

Show that the reaction is of first order. Calculate the value of t , when the solution is optically inactive.

Solution: In case, the inversion of cane sugar is a first order change, then

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]} = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

When, $t = 10$, $r_0 = 32.4$, $r_t = 28.8$, $r_\infty = -14.1$

$$k = \frac{2.303}{10} \log_{10} \frac{32.4 - (-14.1)}{28.8 - (-14.1)}$$

$$= \frac{2.303}{10} \log_{10} \frac{46.5}{42.9} = 0.008 \text{ min}^{-1}$$

When, $t = 20$, $r_0 = 32.4$, $r_t = 25.5$, $r_\infty = -14.1$

$$k = \frac{2.303}{20} \log_{10} \frac{32.4 - (-14.1)}{25.5 - (-14.1)} = \frac{2.303}{20} \log_{10} \frac{46.5}{39.6}$$

$$= 0.008 \text{ min}^{-1}$$

When, $t = 30$, $r_0 = 32.4$, $r_t = 22.4$, $r_\infty = -14.1$

$$k = \frac{2.303}{30} \log_{10} \frac{32.4 - (-14.1)}{22.4 - (-14.1)} = \frac{2.303}{30} \log_{10} \frac{46.5}{36.5}$$

$$= 0.008 \text{ min}^{-1}$$

Thus, the reaction is of first order as the value of k is constant.

The solution will be optically inactive when half of the cane sugar is inverted.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.008} = 86.6 \text{ min}$$

Example 39. 1 mL of methyl acetate was added to a flask containing 20 mL of N/20 HCl maintained at 25°C. 2 mL of the reaction mixture were withdrawn at different intervals and

titrated with a standard alkali solution. The following results were obtained:

Time (min)	0	75	119	183	∞
Alkali used (mL)	19.24	24.20	26.60	29.32	42.03

Show that the reaction follows first order kinetics.

Solution: In case the hydrolysis follows first order kinetics, then

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]} = \frac{2.303}{t} \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$$

When, $t = 75$ min, $V_\infty = 42.03$, $V_0 = 19.24$, $V_t = 24.20$

$$k = \frac{2.303}{75} \log_{10} \frac{(42.03 - 19.24)}{(42.03 - 24.20)} = \frac{2.303}{75} \log_{10} \frac{22.79}{17.83}$$

$$= 0.00327 \text{ min}^{-1}$$

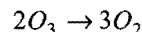
$t = 119$ min, $V_\infty = 42.03$, $V_0 = 19.24$, $V_t = 26.60$

$$k = \frac{2.303}{119} \log_{10} \frac{(42.03 - 19.24)}{(42.03 - 26.60)} = \frac{2.303}{119} \log_{10} \frac{22.79}{15.43}$$

$$= 0.00327 \text{ min}^{-1}$$

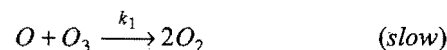
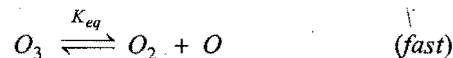
Since, the values of k are constant, hence, it follows first order kinetics.

Example 40. The gaseous decomposition of ozone



obeys the rate law $r = -\frac{d[\text{O}_3]}{dt} = \frac{k[\text{O}_3]^2}{[\text{O}_2]}$

Show that the following mechanism is consistent with the above rate law:



Solution: From the slow rate determining step

$$r = -\frac{d[\text{O}_3]}{dt} = k [\text{O}][\text{O}_3]$$

From the fast reaction,

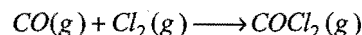
$$K_{\text{eq}} = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]}$$

or
$$[\text{O}] = \frac{K_{\text{eq}}[\text{O}_3]}{[\text{O}_2]}$$

Substituting the value of $[\text{O}]$ in the above expression

$$r = -\frac{d[\text{O}_3]}{dt} = \frac{k_1 K_{\text{eq}} [\text{O}_3]^2}{[\text{O}_2]} = \frac{k[\text{O}_3]^2}{[\text{O}_2]}$$

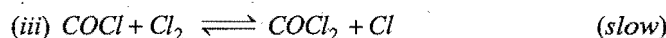
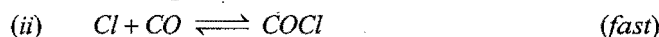
Example 41. For the formation of phosgene from $\text{CO}(\text{g})$ and chlorine,



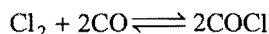
the experimentally determined rate equation is,

$$\frac{d[\text{COCl}_2]}{dt} = k[\text{CO}][\text{Cl}_2]^{3/2}$$

Is the following mechanism consistent with the rate equation?



Solution: Multiplying equation (ii) by 2 and adding (i), we get:



$$K = \frac{[\text{COCl}]^2}{[\text{Cl}_2][\text{CO}]^2}$$

$$[\text{COCl}] = (K)^{1/2} [\text{Cl}_2]^{1/2} [\text{CO}] \quad \dots(i)$$

Slowest step is rate determining, hence,

$$\text{Rate} = k[\text{COCl}][\text{Cl}_2] \quad \dots(ii)$$

From eqs. (i) and (ii), we get

$$\text{Rate} = kK^{1/2} [\text{Cl}_2]^{1/2} [\text{Cl}_2][\text{CO}]$$

$$\text{Rate} = k' [\text{Cl}_2]^{3/2} [\text{CO}]$$

Thus, rate law is in accordance with the mechanism.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

22. A first order reaction has half life of 14.5 hrs. What percentage of the reactant will remain after 24 hrs?

(a) 18.3% (b) 31.8% (c) 45.5% (d) 68.2%

[Ans. (b)]

[Hint: $k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$

$$\frac{0.693}{14.5} = \frac{2.303}{24} \log \frac{100}{(a-x)}$$

On solving, $(a-x) = 31.8\%$

23. Half life of a first order reaction is 10 min. What % of reaction will be completed in 100 min?

(a) 25% (b) 99.9% (c) 75% (d) 80%

[Ans. (b)]

[Hint: $\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$

$$\frac{0.693}{10} = \frac{2.303}{100} \log \left(\frac{100}{100-x} \right)$$

$$x = 99.9\%$$

24. A certain zero order reaction has $k = 0.025 \text{ M s}^{-1}$ for the disappearance of A. What will be the concentration of A after 15 seconds if the initial concentration is 0.5 M ?

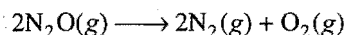
(a) 0.5 M (b) 0.32 M (c) 0.12 M (d) 0.06 M

[Ans. (c)]

[Hint: $x = kt = 0.025 \times 15 = 0.375 \text{ M}$

$$\text{Remaining conc.} = 0.5 - 0.375 = 0.125 \text{ M}$$

25. A first order reaction:



has a rate constant of $1.3 \times 10^{-11} \text{ s}^{-1}$ at 270°C and $4.5 \times 10^{-10} \text{ s}^{-1}$ at 350°C . What is the activation energy for this reaction?

(a) 15 kJ (b) 30 kJ (c) 68 kJ (d) 120 kJ

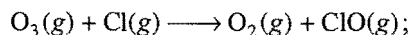
[Ans. (d)]

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

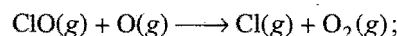
$$\log \left(\frac{4.5 \times 10^{-10}}{1.3 \times 10^{-11}} \right) = \frac{E_a}{2.303 \times 8.314 \times 10^{-3}} \left[\frac{1}{543} - \frac{1}{623} \right]$$

$$E_a = 120 \text{ kJ}$$

26. The reaction of O_3 with chlorine atom is given as:

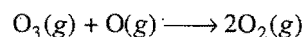


$$k_1 = 5.2 \times 10^9 \text{ L mol}^{-1} \text{ sec}^{-1}$$



$$k_2 = 2.6 \times 10^{10} \text{ L mol}^{-1} \text{ sec}^{-1}$$

Which of these values is closest to the rate constant of the overall reaction?



(a) 5.2×10^9 (b) 2.6×10^{10}

(c) 3.1×10^{10} (d) 1.4×10^{20}

[Ans. (a)]

[Hint: Lowest value of k shows that the step is rate determining.]

27. If a first order reaction takes 32 minutes for 75% completion, then time required for 50% completion is:

[AMU (Medical)]

(a) 32 min (b) 16 min (c) 8 min (d) 4 min

[Ans. (b)]

[Hint: $k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$

When, $a = 100$, $x = 75$, $t = 32$

$$k = \frac{2.303}{32} \log_{10} \left(\frac{100}{25} \right) = 0.0433 \text{ min}^{-1}$$

$$\text{Time for 50\% completion } (t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{0.0433} \approx 16 \text{ min}$$

28. Rate constant of a reaction is $175 \text{ litre}^{-2} \text{ mol}^{-2} \text{ sec}^{-1}$. What is the order of reaction? [CET (Gujarat) 1996]

(a) First (b) Second (c) Third (d) Zero

[Ans. (c)]

[Hint: Unit of $k = \left[\frac{\text{litre}}{\text{mol}} \right]^{n-1} \times \text{sec}^{-1}$... (i)

Given unit of $k = \text{litre}^2 \text{ mol}^{-2} \text{ sec}^{-1}$... (ii)

Comparing the unit of litre,

$$n - 1 = 2$$

$$n = 3$$

29. The half life of a first order reaction having rate constant $k = 1.7 \times 10^{-5} \text{ sec}^{-1}$ is: [JIPMER 2006]

(a) 12.1 hrs (b) 9.7 hrs (c) 11.3 hrs (d) 1.8 hrs

[Ans. (c)]

[Hint: $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.7 \times 10^{-5}} = 40764 \text{ sec} = 11.3 \text{ hrs}$

30. At 500 K, the half life period of a gaseous reaction at an initial pressure of 80 kPa is 350 sec. When the pressure is 40 kPa, the half life period is 175 sec; the order of the reaction is:

[PET (Kerala) 2097]

(a) zero (b) one (c) two (d) three

(e) half

[Ans. (a)]

[Hint: $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{p_2}{p_1}\right)^{n-1}$

$$\frac{350}{175} = \left(\frac{40}{80}\right)^{n-1}$$

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

$$n - 1 = -1$$

$$n = 0 \text{ (zero order reaction)}$$

31. 90% of the first order reaction is completed in 70 minutes. The velocity constant of the reaction is: [Comed (Karnataka) 2008]
- (a) 0.0329 (b) 0.329 (c) 3.29 (d) 0.0293

[Ans. (a)]

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

$$= \frac{2.303}{70} \log \frac{100}{100-90}$$

$$= 0.0329 \text{ min}^{-1}]$$

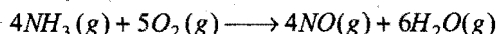
32. The half life period of a first order reaction is 1 min 40 seconds. Calculate its rate constant. (VITEEE 2008)
- (a) $6.93 \times 10^{-3} \text{ min}^{-1}$ (b) $6.93 \times 10^{-3} \text{ sec}^{-1}$
- (c) $6.93 \times 10^{-3} \text{ sec}$ (d) $6.93 \times 10^3 \text{ sec}$

[Ans. (b)]

[Hint: $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ sec}^{-1}$]

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. Ammonia and oxygen react at higher temperature as,



in an experiment, the concentration of NO increases by $1.08 \times 10^{-2} \text{ mol litre}^{-1}$ in 3 seconds. Calculate:

- (i) rate of reaction, (ii) rate of disappearance of ammonia, (iii) rate of formation of water.

Solution:

(i) Rate = $-\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{5} \frac{d[\text{O}_2]}{dt} = \frac{1}{4} \frac{d[\text{NO}]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$

$$\text{Rate} = \frac{1}{4} \times \frac{1.08 \times 10^{-2}}{3} = 9 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

(ii) $-\frac{d[\text{NH}_3]}{dt} = 4 \times \text{rate} = 4 \times 9 \times 10^{-4}$

$$= 36 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

(iii) $\frac{d[\text{H}_2\text{O}]}{dt} = 6 \times \text{rate} = 6 \times 9 \times 10^{-4}$

$$= 54 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

Example 2. Decomposition of $\text{N}_2\text{O}_5(\text{g})$ into $\text{NO}_2(\text{g})$ and $\text{O}_2(\text{g})$ is a first order reaction. If initial concentration of $\text{N}_2\text{O}_5(\text{g})$, i.e., $[\text{N}_2\text{O}_5]_0$ is $0.03 \text{ mol litre}^{-1}$, what will be its concentration after 30 minutes? Rate constant of the reaction is $1.35 \times 10^{-4} \text{ s}^{-1}$.

Solution: $k = \frac{2.303}{t} \log_{10} \frac{[A_0]}{[A]}$

$$1.35 \times 10^{-4} = \frac{2.303}{30 \times 60} \log_{10} \frac{0.03}{[A]}$$

$$[A] = 0.0235 \text{ mol litre}^{-1}$$

Example 3. Rate constant for the decomposition of ethylene oxide into CH_4 and CO may be described by the equation, $\log k (\text{s}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$

(a) What is the energy of activation of this reaction?

(b) What is the value of k at 670 K?

Solution: (a) We know that,

$$\log_{10} k = \log_{10} A - \frac{E}{2.303RT} \quad \dots (i)$$

$$\log_{10} k (\text{s}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T} \quad \dots (ii)$$

Comparing eq. (i) and eq. (ii), we get

$$\frac{E}{2.303R} = 1.25 \times 10^4$$

$$E = 1.25 \times 10^4 \times 2.303 \times 8.314 \times 10^{-3}$$

$$E = 239.339 \text{ kJ/mol}$$

(b) Substituting the value of T , i.e., at 670 K, in equation (ii), we get,

$$\log k (\text{s}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{670} = -4.3167$$

$$k = 4.82 \times 10^{-5} \text{ s}^{-1}$$

Example 4. A drug becomes ineffective after 30% decomposition. The original concentration of a sample was 5 mg/mL, which becomes 4.2 mg/mL during 20 months. Assuming the decomposition of first order, calculate the expiry time of the drug in months. What is the half life of the product?

Solution: $k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right) = \frac{2.303}{20} \log_{10} \left(\frac{5}{4.2} \right)$

$$= 0.00872 \text{ month}^{-1}$$

Expiry time ' t ' may be calculated as:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$0.00872 = \frac{2.303}{t} \log_{10} \frac{100}{70}$$

$$t = 40.9 \approx 41 \text{ month}$$

$$t_{1/2} = \frac{0.693}{0.00872} = 79.4 \text{ month}$$

Example 5. Two reactions of the same order have equal exponential factors but their activation energies differ by 24.9 kJ/mol. Calculate the ratio between the rate constants of these reactions at 27°C. ($R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$) (Dhanbad 1990)

Solution: We know that,

$$\log_{10} k = \log_{10} A - \frac{E}{2.303RT}$$

So, $\log_{10} k_2 = \log_{10} A - \frac{E_2}{2.303RT}$

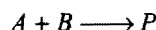
and $\log_{10} k_1 = \log_{10} A - \frac{E_1}{2.303RT}$

$$\log_{10} \left(\frac{k_2}{k_1} \right) = \frac{(E_1 - E_2)}{2.303RT}$$

$$\log_{10} \left(\frac{k_2}{k_1} \right) = \frac{24.9 \times 1000}{2.303 \times 8.314 \times 300}$$

$$\frac{k_2}{k_1} = 2.199 \times 10^4$$

Example 6. Pseudo first order rate for the reaction,

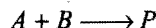


when studied in 0.1 M of B is given by

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

where, $k = 1.85 \times 10^4 \text{ sec}^{-1}$. Calculate the value of second order rate constant.

Solution:



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

$$-\frac{d[A]}{dt} = 1.85 \times 10^4 \times [A] \quad \dots (i)$$

Assuming the reaction to be of second order,

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

$$-\frac{d[A]}{dt} = k'[A][0.1] \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii), we get

$$1 = \frac{1.85 \times 10^4}{k'[0.1]}$$

$$k' = 1.85 \times 10^5 \text{ litre mol}^{-1} \text{ sec}^{-1}$$

Example 7. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9 \text{ sec}^{-1}$, calculate its rate constant at 318 K and also the energy of activation. (IIT 1997)

Solution: We know that,

$$k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$$

At 298 K, $x = 10, a = 100,$

$$k_{298} = \frac{2.303}{t_1} \log_{10} \frac{100}{90} \quad \dots (i)$$

At 308 K, $a = 100, x = 25, (a-x) = 75$

$$k_{308} = \frac{2.303}{t_2} \log_{10} \left(\frac{100}{75} \right) \quad \dots (ii)$$

$t_1 = t_2$, dividing eq. (ii) by eq. (i)

$$\frac{k_{308}}{k_{298}} = 2.73$$

$$\log \frac{k_{308}}{k_{298}} = \frac{E}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log 2.73 = \frac{E}{2.303 \times 8.314} \left(\frac{1}{308} - \frac{1}{298} \right)$$

$$E = 76.622 \text{ kJ/mol}$$

Similarly, we can solve for k_{318} which is equal to $9.22 \times 10^{-4} \text{ s}^{-1}$.

Example 8. The rate constant of a reaction is $1.5 \times 10^7 \text{ s}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ s}^{-1}$ at 100°C. Calculate the Arrhenius parameter A and E_a . (IIT 1998)

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

$$\log_{10} \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{323} - \frac{1}{373} \right)$$

$$E_a = 2.2 \times 10^4 \text{ J/mol}$$

We know that,

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

$$\log_{10} (1.5 \times 10^7) = \log_{10} A - \frac{2.2 \times 10^4}{2.303 \times 8.314 \times 323}$$

$$A = 5.42 \times 10^{10} \text{ s}^{-1}$$

Example 9. In hydrogenation reaction at 25°C, it is observed that hydrogen gas pressure falls from 2 atm to 1.2 atm in 50 min. Calculate the rate of reaction in molarity per sec. ($R = 0.0821 \text{ litre-atm degree}^{-1} \text{ mol}^{-1}$)

Solution:

$$\text{Rate} = \frac{dP}{dt} = \frac{2-1.2}{50 \times 60}$$

$$= 2.666 \times 10^{-4} \text{ atm s}^{-1}$$

$$PV = nRT$$

$$\frac{P}{\text{sec}} = \left(\frac{n}{V} \right) \frac{RT}{\text{sec}}$$

$$\left[\frac{n}{V}\right] \frac{1}{\text{sec}} = \left[\frac{P}{\text{sec}}\right] \frac{1}{RT}$$

$$\text{Rate (molarity/sec)} = \frac{2.666 \times 10^{-4}}{0.0821 \times 298}$$

$$= 1.09 \times 10^{-5} \text{ mol litre}^{-1} \text{ s}^{-1}$$

Example 10. A drop of solution (volume 0.05 mL) contains 3×10^{-6} mole H^+ ions. If the rate of disappearance of the H^+ ions is $1 \times 10^7 \text{ mol litre}^{-1} \text{ sec}^{-1}$, how long would it take for H^+ ions in the drop to disappear?

Solution:

$$\text{Concentration of drop} = \frac{\text{mole}}{\text{volume in mL}} \times 1000$$

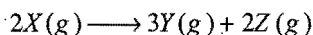
$$= \frac{3 \times 10^{-6}}{0.05} \times 1000 = 0.06 \text{ mol litre}^{-1}$$

$$\text{Rate of disappearance} = \frac{\text{conc. change}}{\text{time}}$$

$$/ \quad 1 \times 10^7 = \frac{0.06}{\text{time}}$$

$$\text{Time} = 6 \times 10^{-9} \text{ sec}$$

Example 11. A constant temperature and volume X decomposes as,



P_X is the partial pressure of X .

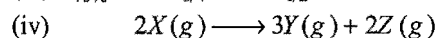
Observation No.	Time (min)	P_X (in mm Hg)
1	0	800
2	100	400
3	200	200

- What is the order of the reaction with respect to X ?
- Find the rate constant.
- Find the time for 75% completion of the reaction.
- Find the total pressure when pressure of X is 700 mm Hg. (IIT 2005)

Solution: (i) Data shows that half life of the reaction is constant, i.e., 100 min; hence, it is a first order reaction.

$$(ii) k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ min}^{-1}$$

$$(iii) t_{75\%}, \text{ i.e., } t_{3/4} = 2 \times t_{1/2} = 2 \times 100 = 200 \text{ min}$$



$$t = 0 \quad 800 \quad 0 \quad 0$$

$$dt \quad 800 - 2X \quad 3X \quad 2X$$

$$\text{Total pressure} = 800 - 2X + 3X + 2X = 800 + 3X \dots (i)$$

$$800 - 2X = 700$$

$$X = 50$$

$$\therefore \text{Total pressure} = 800 + 3 \times 50 = 950 \text{ mm Hg}$$

Example 12. Suppose 50 bacteria are placed in a flask containing nutrients for the bacteria so that they can multiply.

A study at 35°C gave the following results:

Time (minute)	0	15	30	45	60
Number of bacteria	50	100	200	400	800

Show that the rate of production of bacteria is of first order. How many bacteria will be there after 3 hours?

Solution: For bacterial growth,

$$k = -\frac{2.303}{t} \log_{10} \left(\frac{a}{a+x} \right)$$

$$\text{At 15 minutes: } k = -\frac{2.303}{15} \log_{10} \left(\frac{50}{100} \right)$$

$$= 0.0462 \text{ min}^{-1}$$

$$\text{At 30 minutes: } k = -\frac{2.303}{30} \log_{10} \left(\frac{50}{200} \right)$$

$$= 0.0462 \text{ min}^{-1}$$

$$\text{At 45 minutes: } k = -\frac{2.303}{45} \log_{10} \left(\frac{50}{400} \right) = 0.0462 \text{ min}^{-1}$$

Same values of rate constants show that the process corresponds to first order.

Let there be ' n ' bacteria after 3 hrs.

$$k = -\frac{2.303}{t} \log_{10} \left(\frac{a}{a+x} \right)$$

$$0.0462 = -\frac{2.303}{180} \log_{10} \frac{50}{n}$$

$$n = 2.04 \times 10^5$$

Example 13. A viral preparation was inactivated in a chemical bath. The inactivation process was found to be of first order in virus concentration, and at the beginning of the experiment 2.0% of the virus was found to be inactivated per minute. Evaluate ' k ' for the inactivation process.

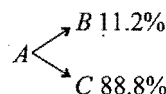
Solution: $a = 100$, $a - x = 98$, $t = 60 \text{ sec}$

$$k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$$

$$= \frac{2.303}{60} \log_{10} \left(\frac{100}{98} \right) = 3.3 \times 10^{-4} \text{ sec}^{-1}$$

Example 14. Trans-1,2-dideuterocyclopropane (A) undergoes a first order decomposition. The observed rate constant at a certain temperature, measured in terms of disappearance of ' A ' was $1.52 \times 10^{-4} \text{ sec}^{-1}$. Analysis of products showed that the reaction followed two parallel paths, one leading to dideuteropropane (B) and the other to cis-1,2-dideuterocyclopropane (C). (B) was found to constitute 11.2% of the reaction product, independently of extent of reaction. What is the order of reaction for each path and what is the value of the rate constant for the formation of each of the products?

Solution:



In case of parallel path reaction,

$$k_B = k_A \times \text{fractional yield of } B \\ = 1.52 \times 10^{-4} \times 0.112 = 1.7 \times 10^{-5} \text{ sec}^{-1}$$

$$k_C = k_A \times \text{fractional yield of } C \\ = 1.52 \times 10^{-4} \times 0.888 = 1.35 \times 10^{-4} \text{ sec}^{-1}$$

The reaction will be first order for each individual path.

Example 15. In milk, at 37°C , *Lactobacillus acidophilus* has a generation time of about 75 minutes. Calculate the population relative to the initial value at 30, 60, 75, 90 and 150 minutes.

Solution: For growth kinetics,

$$k = -\frac{2.303}{t} \log_{10} \left(\frac{a}{a+x} \right)$$

$$k = -\frac{2.303}{t} \log_{10} \left(\frac{N_0}{N} \right)$$

Generation time = 75 minutes; $a = 1$, $a + x = 2$

$$k = -\frac{2.303}{75} \log_{10} \left(\frac{1}{1+1} \right) = 0.00924 \text{ min}^{-1}$$

After 30 minutes,

$$k = \frac{-2.303}{t} \log_{10} \left(\frac{N_0}{N} \right)$$

$$0.00924 = -\frac{2.303}{30} \log_{10} \left(\frac{N_0}{N} \right)$$

$$\frac{N}{N_0} = 1.319 \approx 1.32$$

Similarly, we may calculate after 60, 75, 90 and 150 minutes.

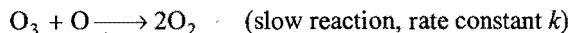
Example 16. Rate law for ozone layer depletion is,

$$\frac{d[\text{O}_3]}{dt} = \frac{K[\text{O}_3]^2}{[\text{O}_2]}$$

Give the probable mechanism of reaction?

Solution: $\text{O}_3 \rightleftharpoons \text{O}_2 + \text{O}$ (fast reaction)

(equilibrium constant K_c)



$$\text{Rate} = k[\text{O}_3][\text{O}] \quad \dots (i)$$

$$K_c = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \text{ or } [\text{O}] = K_c \frac{[\text{O}_3]}{[\text{O}_2]},$$

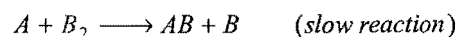
putting the value in eq. (i)

From eq. (i),

$$\text{Rate} = k \cdot [\text{O}_3] \cdot K_c \frac{[\text{O}_3]}{[\text{O}_2]} = k \cdot K_c \cdot \frac{[\text{O}_3]^2}{[\text{O}_2]} = K \cdot \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

Here, $K = k \times K_c$

Example 17. In hypothetical reaction $A_2 + B_2 \longrightarrow 2AB$, follows the mechanism as given below:



Give the rate law and order of reaction.

Solution: Slowest step is rate determining.

$$\text{Rate} = k[A][B_2] \quad \dots (i)$$

Here, $[A]$ should be eliminated.

$$K_c = \frac{[A][A]}{[A_2]} = \frac{[A]^2}{[A_2]}$$

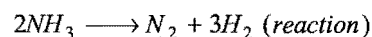
$$[A] = K_c^{1/2} [A_2]^{1/2}$$

From eq. (i), $\text{Rate} = k K_c^{1/2} [A_2]^{1/2} [B_2]$

$$= K [A_2]^{1/2} [B_2]; \quad [K = k \cdot K_c]$$

$$\text{Order} = 1 + 1/2 = 3/2$$

Example 18. Calculate order of reaction from the following data:



Pressure (mm Hg)	50	100	200
Half lives (min)	3.52	1.82	0.93

Solution: We know that,

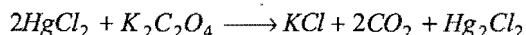
$$n = 1 + \frac{\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2}{\log_{10} p_2 - \log_{10} p_1}$$

$$= 1 + \frac{\log_{10} 3.52 - \log_{10} 1.82}{\log_{10} 100 - \log_{10} 50}$$

$$= 1.95 \approx 2$$

Similarly, we may calculate for other set of conditions.

Example 19. The chemical reaction between mercuric chloride and potassium oxalate proceeds as under:



the mass of Hg_2Cl_2 precipitated from different solutions in a given time, at 100°C was as follows:

Expt. No.	HgCl_2 (mol L ⁻¹)	$\text{K}_2\text{C}_2\text{O}_4$ (mol L ⁻¹)	Time (minutes)	Hg_2Cl_2 precipitated (mole)
(1)	0.0836	0.404	65	0.0068
(2)	0.0836	0.202	120	0.0031
(3)	0.0418	0.404	60	0.0032

From these data calculate order of the reaction.

Solution: $\text{Rate} = k[\text{HgCl}_2]^\alpha [\text{K}_2\text{C}_2\text{O}_4]^\beta$

$$\frac{0.0068}{65} = k[0.0836]^\alpha [0.404]^\beta; \quad \dots (i)$$

$$\frac{0.0031}{120} = k[0.0836]^\alpha [0.202]^\beta; \quad \dots (ii)$$

$$\frac{0.0032}{60} = k[0.0418]^\alpha [0.404]^\beta \quad \dots (iii)$$

Dividing eq. (i) by eq. (ii), we get $4 = 2^\beta; \beta = 2$

Dividing eq. (i) by eq. (iii), we get $2 = 2^\alpha; \alpha = 1$

Thus, overall order $= \alpha + \beta = 3$

Example 20. The rate constant of the reaction $A \rightarrow B$ is $k = 0.5$; the initial concentration of A being 1 mol/litre. Calculate the degree of conversion of substance 'A' within 1 hour if the reaction is of zeroth, first and second order. How does the degree of conversion depend on the order of reaction?

Solution: Zero order:

$$x = kt$$

$$x = 0.5 \times 1 = 0.5$$

First order:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$k = 0.5; t = 1 \text{ hr}; a = 1 \text{ M}$$

$$0.5 = \frac{2.303}{1} \log_{10} \frac{1}{(1-x)}$$

$$x = 0.39$$

Second order:

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

$$0.5 = \frac{1}{1} \frac{x}{1(1-x)}$$

$$x = 0.33$$

Example 21. Two first order reactions proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75°C .

Solution: For first order reaction, $r_1 = k[A]^1$

$$\therefore r_1 / r_2 = k_1 / k_2 = \text{temperature coefficient}$$

Let the rate of reaction for Ist at 25°C be R_1 and the rate of reaction for IInd at 25°C be R_2 .

Also,

$$R_1 = R_2$$

Rates of reaction

At 25°C	R_1	R_2
35°C	$2R_1$	$3R_2$
45°C	$(2)^2 R_1$	$(3)^2 R_2$
55°C	$(2)^3 R_1$	$(3)^3 R_2$
65°C	$(2)^4 R_1$	$(3)^4 R_2$
75°C	$(2)^5 R_1$	$(3)^5 R_2$

$$\therefore \text{Temperature coefficient for 1st reaction} = \frac{k_{35}}{k_{25}} = \frac{R_{35}}{R_{25}} = 2$$

i.e., for each 10°C rise in temperature, rate becomes 2 times.

Similarly, for 2nd reaction it becomes 3 times,

$\therefore$ At 75°C

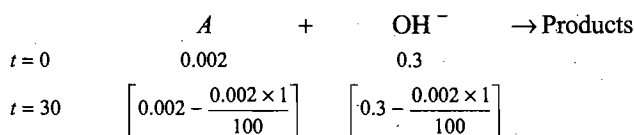
$$\frac{\text{rate of reaction for 2nd}}{\text{rate of reaction for 1st}} = \frac{(3)^5 R_2}{(2)^5 R_1} = 7.5937 (\because R_1 = R_2)$$

Example 22. The reaction, $A + \text{OH}^- \rightarrow \text{Products}$, obeys rate law expression as:

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

If initial concentrations of $[A]$ and $[\text{OH}^-]$ are 0.002 M and 0.3 M respectively and if it takes 30 sec for 1% A to react at 25°C , calculate the rate constant for the reaction.

Solution:



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

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

$$k = 1.12 \times 10^{-3} \text{ litre mol}^{-1} \text{ s}^{-1}$$

Example 23. A hydrogenation reaction is carried out at 500 K . If the same reaction is carried out in 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} . (IIT 2000)

Solution: Arrhenius equation may be given as,

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

Let k_{500} and k_{400} be the rate constants at temperatures 500 K and 400 K (in presence of catalyst) respectively. E_{500} and E_{400} be the activation energies at temperatures 500 K and 400 K respectively.

$$k_{500} = Ae^{-E_{500}/R \times 500} \quad \dots (i)$$

$$k_{400} = Ae^{-E_{400}/R \times 400} \quad \dots (ii)$$

Given, $k_{500} = k_{400}$ (same rates in presence and absence of a catalyst).

On comparing eq. (i) with eq. (ii),

$$\frac{E_{500}}{R \times 500} = \frac{E_{400}}{R \times 400}$$

$$\text{or } \frac{E_{500}}{5} = \frac{E_{400}}{4}$$

$$\text{or } E_{500} = \frac{E_{400}}{4} \times 5 \quad \dots (iii)$$

$$\text{Given, } E_{500} = E_{400} + 20$$

Substituting in eq. (iii),

$$E_{400} + 20 = E_{400} \times 1.25$$

or
$$E_{400} = \frac{20}{0.25} = 80 \text{ kJ mol}^{-1}$$

So,
$$E_{500} = 80 + 20 = 100 \text{ kJ mol}^{-1}$$

Example 24. Some $\text{PH}_3(\text{g})$ is introduced into a flask at 600°C containing an inert gas. PH_3 proceeds to decompose into $\text{P}_4(\text{g})$ and $\text{H}_2(\text{g})$ and the reaction goes to completion. Total pressure is given below as a function of time. Find the order of the reaction and calculate the rate constant,

Time (sec)	0	60	120	∞
Pressure (mm Hg)	262.40	272.90	275.51	276.40

(IIT 2001)

Solution: $4\text{PH}_3(\text{g}) + \text{Inert gas} \rightarrow \text{P}_4(\text{g}) + 6\text{H}_2(\text{g}) + \text{Inert gas}$

$t = 0$	P	P_i	0	0	0
$t = t$	$(P - x)$	P_i	$x/4$	$6x/4$	P_i
$t = \infty$	0	P_i	$P/4$	$6P/4$	P_i

At $t = 0$, $262.40 = P + P_i$... (i)

$t = 60 \text{ sec}$ $272.90 = P_{\text{PH}_3(\text{left})} + P_{\text{P}_4(\text{g})} + P_{\text{H}_2(\text{g})} + P_i$

$t = 120 \text{ sec}$ $275.51 = P_{\text{PH}_3(\text{left})} + P_{\text{P}_4(\text{g})} + P_{\text{H}_2(\text{g})} + P_i$

$t = \infty$ $276.40 = P_{\text{P}_4(\text{g})} + P_{\text{H}_2(\text{g})} + P_i$

$$276.40 = \frac{P}{4} + \frac{6P}{4} + P_i$$

$$276.40 \times 4 = 7P + 4P_i \quad \dots \text{(ii)}$$

At $t = 0$, $262.40 = P + P_i$... (iii)

On solving eqs. (ii) and (iii), we get

$$P = 18.66 \text{ mm}, P_i = 243.74 \text{ mm}$$

At 60°C : $272.90 = (P - x) + P_i + \frac{x}{4} + \frac{6x}{4}$

$$272.90 = 18.66 - x + 243.74 + \frac{7x}{4}$$

$$x = 14 \text{ mm}$$

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right) = \frac{2.303}{60} \log \frac{18.66}{18.66 - 14}$$

$$k = 2.32 \times 10^{-2} \text{ sec}^{-1}$$

Similarly, at 120 sec $k = 2.30 \times 10^{-2} \text{ sec}^{-1}$ (do yourself)

Since, $\therefore$ values of ' k ' are same, hence the reaction belongs to first order.

Example 25. For the given reaction, $A + B \rightarrow \text{Products}$ following data were obtained:

	$[A_0]$	$[B_0]$	$R_0 \text{ mol litre}^{-1} \text{ sec}^{-1}$
1.	0.1 M	0.2 M	0.05
2.	0.2 M	0.2 M	0.10
3.	0.1 M	0.1 M	0.05

(i) Write the rate law expression.

(ii) Find the rate constant. [IIT 2004 (Memory based)]

Solution: Let order with respect to A and B are α and β respectively. Rate law expression may be given as,

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

$$0.05 = k[0.1]^\alpha [0.2]^\beta \quad \dots \text{(i)}$$

$$0.10 = k[0.2]^\alpha [0.2]^\beta \quad \dots \text{(ii)}$$

$$0.05 = k[0.1]^\alpha [0.1]^\beta \quad \dots \text{(iii)}$$

Dividing eq. (i) by eq. (ii), we get

$$\frac{1}{2} = \left[\frac{1}{2} \right]^\alpha, \text{ i.e., } \alpha = 1$$

Dividing eq. (i) by eq. (iii), we get

$$1 = [2]^\beta, \text{ i.e., } \beta = 0$$

$$\therefore \text{Rate} = k[A]^1 [B]^0$$

Substituting the value of α and β in eq. (i), we get

$$0.05 = k[0.1]^1 [0.2]^0$$

$$k = 0.5 \text{ sec}^{-1}$$

Example 26. $A + 2B \rightarrow 3C + 2D$

The rate of disappearance of B is $1 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1}$. What will be the (i) rate of the reaction and (ii) rate of change in concentration of A and C ? [CBSE (Mains) 2005]

Solution: (i) $\text{Rate} = -\frac{1}{2} \frac{d[B]}{dt}$

$$= -\frac{1}{2} [-1 \times 10^{-2}]$$

$$= 0.5 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

(ii) $-\frac{d[A]}{dt} = -\frac{1}{2} \left[\frac{d[B]}{dt} \right] = 0.5 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1}$

$$\frac{1}{3} \frac{d[C]}{dt} = -\frac{1}{2} \frac{d[B]}{dt}$$

$$\frac{d[C]}{dt} = -\frac{3}{2} \times (-1 \times 10^{-2})$$

$$= 1.5 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

Example 27. For the reaction, $A + B \rightarrow \text{Products}$, rate is given as, $\text{rate} = k[A][B]^2$.

How will the rate change if volume of the reaction mixture is reduced to 1/3rd of its original volume? (BCECE 2006)

Solution: When volume is reduced to 1/3rd, then concentration will increase three times.

$$\therefore r_1 = k[A][B]^2 \quad \dots \text{(i)}$$

$$r_2 = k[3A][3B]^2 \quad \dots \text{(ii)}$$

From eqs. (i) and (ii),

$$\frac{r_1}{r_2} = \frac{1}{27}$$

$$r_2 = 27r_1$$

$\therefore$ Rate will increase 27 times.

Example 28. For first order reaction, if rate constant at 17°C is $2.8 \times 10^{-5} \text{ s}^{-1}$ and at 27°C is $2.8 \times 10^{-4} \text{ s}^{-1}$.

(i) Write the equation for calculation of activation energy.

(ii) Calculate the activation energy.

($R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$)

[AIPMT (Mains) 2008]

Solution. We know,

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

$$\begin{aligned} \log \frac{2.8 \times 10^{-4}}{2.8 \times 10^{-5}} &= \frac{E_a}{2.303 \times 8.3} \left[\frac{1}{290} - \frac{1}{300} \right] \\ E_a &= \frac{2.303 \times 8.3 \times 290 \times 300}{10} \\ &= 166299.6 \text{ J mol}^{-1} \\ &= 166.3 \text{ kJ mol}^{-1} \end{aligned}$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Chemical kinetics: It is the branch of chemistry which deals with the rates of reactions, the factors which influence it and the mechanism by which the reactions occur.

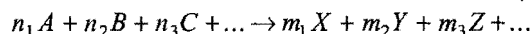
2. Rate of reaction: It is the speed with which the reactants are converted into products. It may be expressed in terms of rate of disappearance of any of the reactants or rate of appearance of any of the products.

The rate measured over a long time interval is called the average rate.

$$\begin{aligned} \text{Average rate of reaction} &= - \frac{\text{Decrease in conc. of reactant}}{\text{Time taken}} \\ &= + \frac{\text{Increase in conc. of product}}{\text{Time taken}} \end{aligned}$$

A -ve sign signifies a decrease in concentration of the reactant and +ve sign indicates an increase in concentration of the product.

In general, for a reaction,



$$-\frac{1}{n_1} \frac{\Delta A}{\Delta t} = -\frac{1}{n_2} \frac{\Delta B}{\Delta t} = -\frac{1}{n_3} \frac{\Delta C}{\Delta t} = \dots$$

$$\frac{1}{m_1} \frac{\Delta X}{\Delta t} = \frac{1}{m_2} \frac{\Delta Y}{\Delta t} = \frac{1}{m_3} \frac{\Delta Z}{\Delta t} = \dots$$

Average rate is not very useful as it does not remain constant throughout its life span. It is more appropriate to express instantaneous rate.

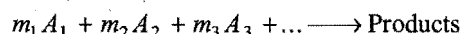
Rate of reaction with reference to a particular instant of time is called instantaneous rate of reaction. It is defined as the rate of change of concentration of any one of the reactant or product species over a small interval of time.

$$\text{Rate of reaction} = -\frac{dx}{dt} \text{ or } +\frac{dx}{dt}$$

Units of rate of reaction are conc. time^{-1} , e.g., $\text{mol L}^{-1} \text{ s}^{-1}$ or $\text{mol L}^{-1} \text{ hr}^{-1}$, etc.

3. Law of mass action: It was presented by Guldberg and Waage in 1864. At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the active

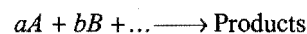
masses of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction. Consider the following general reaction,



$$\text{Rate of reaction} \propto [A_1]^{m_1} [A_2]^{m_2} [A_3]^{m_3} \dots$$

4. Rate constant: It is equal to rate of reaction when concentration of each reactant is unity, i.e., one mole litre⁻¹. It is a constant for a particular reaction at a given temperature and also known as specific rate constant or specific reaction rate.

Consider a general reaction,



$$\frac{dx}{dt} = k[A]^a [B]^b \dots$$

$$\text{If } C_A = C_B = 1 \text{ or } [A] = [B] = 1$$

$$\text{Then, } \frac{dx}{dt} = k$$

5. Collision theory of reaction rate: A chemical reaction occurs when the existing bonds of the reactants are broken down and new bonds come into existence in the molecules of products. The basic requirement for a reaction to occur is that there should be physical contact between reacting species, i.e., they must collide with one another. Effective collisions which bring chemical change are few in spite of large number of actual collisions. For a collision to be effective, the following two conditions must be satisfied:

(i) Reacting species must possess adequate energy to overcome the energy barrier.

(ii) Reacting molecules must be properly oriented at the time of collision.

The minimum amount of energy which the colliding particles must possess as to make the chemical reaction to occur is called threshold energy. The excess energy (over and above the average energy of the reacting species) required by the reacting species to undergo chemical reaction is called activation energy (E_a).

$$\text{Activation energy} = \text{Threshold energy} - \text{Average kinetic energy of the reacting molecules}$$

Every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before the reactants can be transformed into products. The reacting molecules must have sufficient energy as to cross this energy barrier. The effective collisions increase with increase of temperature, i.e., rate of reaction increases with increase of temperature.

6. Factors influencing the reaction rate: The chief factors which influence the rates of reactions are:

(i) Nature of reactants: The reactants with weak bonds react quickly whereas the reactions involving reactants with strong bonds are slow. The molecular reactions are generally slow while ionic reactions are fast.

(ii) Concentration of reactants: The rate of reaction increases with increase in concentration of reactants as the number of collisions increases.

(iii) Catalyst: Positive catalysts increase the reaction rate by providing an alternative path involving lesser amount of activation energy.

(iv) Temperature: The rate of reaction increases with an increase in temperature. The number of effective collisions increases with increase of temperature. The rates of many reactions are approximately doubled or tripled for every 10° C rise in temperature. The temperature coefficient is defined as the ratio of specific reaction rates of a reaction at two temperatures differing by 10° C.

$$\text{Temp. coefficient} = \frac{k_{t+10}}{k_t} \quad (\text{value lies generally between 2 and 3})$$

Arrhenius suggested an equation which describes k as a function of temperature, i.e.,

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

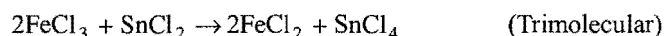
where, k = rate constant, A = a frequency factor (constant), E_a = energy of activation, R = gas constant and T = temperature.

At two temperatures T_1 and T_2 ,

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

7. Molecularity and order of reaction:

(i) Molecularity of reaction: The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of the reaction. The reactions are termed as unimolecular, bimolecular or trimolecular, etc., depending upon the number of reacting particles as 1, 2, 3, etc., in the rate determining step. Simultaneous collisions involving more than three molecules are very rare and hence reactions with molecularity more than three are also rare.

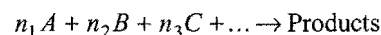


In simple reactions involving one step only, the molecularity is equal to the sum of number of molecules of the reactants

involved in the balanced equation. There are number of reactions which are complex in nature and occur in several steps; the molecularity of such reactions is determined by the slowest step. Thus, molecularity depends upon the mechanism of the reaction.

(ii) Order of reaction: Rate equation or rate law is an experimentally determined mathematical expression relating the molar concentrations of the reactants to the actual reaction rate.

Consider a general reaction,



The rate law or rate equation is

$$\text{Rate} = -\frac{dx}{dt} = k[A]^x[B]^y[C]^z \dots$$

Order of reaction is the sum of the exponents (powers) to which molar concentration terms are raised in the rate law.

$$\text{Order of reaction} = (x + y + z + \dots)$$

The value of $(x + y + z + \dots)$ usually ranges between 0 and 2 and even 3. It may have positive, negative, zero and fractional values. It is termed overall order. The reactions are classified as zero, first, second, third order according as $(x + y + z + \dots)$ is zero, one, two or three respectively. The order can be expressed either in terms of the order of the specific reactant or in terms of overall order of the reaction.

The reactions which obey a first order rate equation, although they are not unimolecular, are said to be pseudo first order.

8. Reactions of various orders: In such reactions, the concentrations of various reactants except one remain practically constant during the course of reaction.

(i) Zero order reactions: A reaction in which the rate is independent of the concentration of the reactant molecules, i.e., the rate is proportional to the zeroth power of the concentration of the reactants.

$$-\frac{dx}{dt} = k[A]_0 = k$$

i.e., the reaction velocity remains constant throughout the progress of the reaction. The concentration decreases linearly with time.

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

$$t_{\text{completion}} = \frac{[A]_0}{k} = \frac{\text{Initial concentration}}{\text{Rate constant}}$$

The units of k are $\text{mol L}^{-1} \text{time}^{-1}$.

(ii) First order reactions: The rate depends upon the concentration of one reactant only.

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

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

t = time, a = initial concentration and $(a-x)$ = concentration at time t .

A change in concentration unit does not affect the numerical value of k . Thus, for first order reactions, any quantity which is

proportional to concentration can be used in place of concentration in the integrated equation.

The time taken for the completion of same fraction of change is independent of initial concentration. When $x = 0.5a$ and $t = t_{1/2}$,

$$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{0.5a} = \frac{2.303}{t_{1/2}} \log_{10} 2 = \frac{0.693}{t_{1/2}}$$

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

Thus, $t_{1/2}$ is independent of initial concentration.

The equation of the first order can also be written in the following form when initial concentration is not known.

$$k = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{(a - x_1)}{(a - x_2)} = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{[A]_{t_1}}{[A]_{t_2}}$$

The unit of k is time^{-1} .

(iii) **Second order reactions:** Reaction rate depends upon the concentration of two reactants.

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

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

[($a - x$) and ($b - x$) are the concentrations of A and B after time interval t .]

When concentrations of both the reactants are same,

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

(x is the concentration changed in time interval t)

Half life period, $t_{1/2} = \frac{1}{ka}$, i.e., inversely proportional to initial concentration. The units of k are $\text{litre mol}^{-1} \text{time}^{-1}$.

(iv) **Third order reactions:** Expression for third order reactions of the type

$$3A \rightarrow \text{Products}$$

$$\frac{dx}{dt} = k[A]^3$$

$$k = \frac{1}{t} \cdot \frac{x(2a-x)^2}{2a^2(a-x)^2}$$

The units of k are $\text{L}^2 \text{mol}^{-2} \text{time}^{-1}$.

9. Methods for the determination of order of a reaction:

(i) **Initial rate method:** A number of experiments are carried out by varying concentration of a reactant w.r.t. which the order is to be determined keeping the concentrations of all other reactants constant. The initial rate of the reaction at each concentration is determined by concentration-time curves. The order of the reactant is then calculated from the rates at various

concentrations. The experiments are repeated with other reactants in a similar way. Likewise, the orders w.r.t. all reactants are determined. The overall order is the sum of the orders of all the reactants.

(ii) **Integration method:** The quantities a , x and t are determined and substituted in the kinetic equations of various orders. The equation which gives the most consistent values for the specific rate constant (k) for a series of time intervals is the one corresponding to order of reaction.

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \quad \text{for first order reactions}$$

$$k = \frac{1}{t} \cdot \left[\frac{a}{a(a-x)} \right] \quad \text{for second order reactions}$$

$$\text{Rate} = k \quad \text{for zero order reactions}$$

(iii) **Graphical method:** If the plot of $\log(a-x)$ versus ' t ' is a straight line, the reaction follows first order.

If a plot of $\frac{1}{(a-x)}$ versus ' t ' is a straight line, the reaction follows second order.

If a plot of $\frac{1}{(a-x)^2}$ versus ' t ' is a straight line, the reaction follows third order.

(iv) **Half life method:** Starting with two different concentrations a_1 and a_2 for the same reaction, the half lives $(t_{1/2})_1$ and $(t_{1/2})_2$ are determined.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1} \right)^{n-1} \quad \text{or} \quad n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1}$$

n is the order of reaction.

(v) **van't Hoff differential method:** For two different initial concentrations C_1 and C_2 equations can be written in the form

$$-\frac{dC_1}{dt} = kC_1^n \quad \text{and} \quad -\frac{dC_2}{dt} = kC_2^n$$

Taking logarithms of two equations and then subtracting

$$n = \frac{\log \left(-\frac{dC_1}{dt} \right) - \log \left(-\frac{dC_2}{dt} \right)}{\log C_1 - \log C_2}$$

10. Mechanism: An intelligent guess depending upon the observed rates of reactions about the series of steps (known as elementary processes) leading to the formation of products is called the reaction mechanism. The overall reaction is the summation of all elementary steps. The slowest step is taken as the rate determining step.

Questions

1. Matrix Matching Problems:

(According to the new pattern of IIT Screening)

[A] Match the reactions of List-I with their orders in List-II:

List-I	List-II
(a) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$	(p) Pseudo first order
(b) $CH_3COOC_2H_5 \xrightarrow[H^+ \text{ or } OH^-]{HOH} CH_3COOH + C_2H_5OH$	(q) Zero order
(c) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$	(r) Second order
(d) $CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$	(s) First order

[B] Match the reactions in Column-I with the units of their rate constant in Column-II:

Column-I (Reactions)	Column-II (Unit of k)
(a) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$	(p) sec^{-1}
(b) $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$	(q) min^{-1}
(c) $2H_2O_2 \longrightarrow 2H_2O + O_2$	(r) $L \text{ mol}^{-1} \text{ min}^{-1}$
(d) $H_2O_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2$	(s) $L \text{ mol}^{-1} \text{ s}^{-1}$

[C] Match the kinetic equations of Column-I with the units of their rate constant in Column-II:

Column-I (Kinetic equations)	Column-II (Units of rate constant)
(a) $x = kt$	(p) sec^{-1}
(b) $k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$	(q) $L \text{ mol}^{-1} \text{ sec}^{-1}$
(c) $k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right]$	(r) $\text{mol L}^{-1} \text{ sec}^{-1}$
(d) $k = \frac{2.303}{t(a-b)} \log \left[\frac{b(a-x)}{a(b-x)} \right]$	(s) $\text{atm}^{-1} \text{ sec}^{-1}$

[D] Match the half lives in Column-I with the orders in Column-II:

Column-I (Half life)	Column-II (Order)
(a) $t_{1/2} = \text{constant}$	(p) First order
(b) $t_{1/2} \propto a$	(q) Pseudo first order
(c) $t_{1/2} \propto \frac{1}{a}$	(r) Second order
(d) $t_{1/2} \propto p^{-1}$	(s) Zero order

where, a = Initial concentration of the reactant
 p = Initial pressure of the reactant

[E] Match the reactions of List-I with the increase in rate when concentration is raised two times in List-II:

List-I (Reactions)	List-II (Increase in rate when conc. of reactant is doubled)
(a) $CH_3CHO \longrightarrow CH_4 + CO$	(p) 2 times
(b) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$	(q) $2^{1.5}$ times
(c) $2H_2O_2 \longrightarrow 2H_2O + O_2$	(r) 2 times in acid medium
(d) $CH_3COOC_2H_5 \xrightarrow{HOH} CH_3COOH + C_2H_5OH$	(s) 2^2 times in basic medium

[F] Match the List-I with List-II and List-III:

List-I	List-II	List-III
(a) x is plotted against 't' in zero order reaction	(p) Slope = $-k/2.303$	(u) Intercept = $\frac{1}{a}$
(b) $\log(a-x)$ is plotted against 't' in first order reaction	(q) Slope = $2k$	(v) Intercept = $1/a$
(c) $(a-x)^{-1}$ is plotted against 't' in second order reaction	(r) Slope = $-k$ (when log is natural)	(w) Intercept = $1/a^2$
(d) $(a-x)^2$ is plotted against 't' in second order reaction	(s) Slope = k	(x) Intercept = $\log_{10} a$

where, a = Initial concentration of reactant
 x = Extent of reaction in time 't' sec

[G] Match the List-I with List-II:

List-I	List-II
(a) Molecularity	(p) 0
(b) Order	(q) 1/2
(c) Temperature coefficient	(r) Between 2 to 3
(d) Activation energy for participation of all reactant molecules	(s) 2

[H] Match the Column-I with Column-II:

Column-I (Rate law)	Column-II (Order)
(a) Rate = $k \times \text{Intensity of light}$	(p) Second order
(b) Rate = $k[A]^1[B]^1$	(q) Zero order
(c) Rate = $k[A]^{3/2}[B]^{1/2}$	(r) First order when A is excess
(d) Rate = $k[A]^2[B]^1$	(s) Second order when B is excess

[I] Match the Column-I with Column-II:

Column-I	Column-II
(a) $t_{1/2} = \frac{0.693}{k}$	(p) Zero order
(b) $t_{1/2} = \frac{a}{2k}$	(q) First order
(c) $\tau = \frac{1}{k}$	(r) Average life
(d) $t_{3/4} = 2t_{1/2}$	(s) 75% completion
	(t) 25% completion

[J] Match the Column-I with Column-II:

Column-I	Column-II
(a) $t_{3/4} = \frac{3}{2} \times t_{1/2}$	(p) 99% completion
(b) $t_{3/4} = 2 \times t_{1/2}$	(q) Zero order
(c) $6.909/k$	(r) First order
(d) $2.303/k$	(s) 90% completion

Here, $t_{1/2}$ = half life $t_{3/4}$ = 3/4th life k = rate constant

[K] Match the Column-I with Column-II:

Column-I	Column-II
(a) First order reaction	(p) $C_0 = 0.1 M$; $t_{1/2} = 25$ min $C_0 = 0.05 M$; $t_{1/2} = 12.5$ min
(b) Second order reaction	(q) $C_0 = 0.1 M$; $t_{1/2} = 12$ min $C_0 = 0.05 M$; $t_{1/2} = 24$ min
(c) Zero order reaction	(r) Radioactive decay
(d) $t_{1/2}$ varies inversely to the concentration of the reactants	(s) $C_0 = 0.1 M$; $t_{1/2} = 8$ min $C_0 = 0.05 M$; $t_{1/2} = 8$ min

Answers

1. [A] (a-p), (b-r, s), (c-q), (d-r)
 [B] (a-p, q), (b-r, s), (c-p, q), (d-r, s)
 [C] (a-r), (b-p), (c-q, s), (d-q, s)
 [D] (a-p, q), (b-s), (c-r, s), (d-r, s)
 [E] (a-q), (b-p), (c-p), (d-r, s)
 [F] (a-s-u), (b-p, r-x), (c-s-v), (d-q-w)

- [G] (a-s), (b-p, q, s), (c-r), (d-p)
 [H] (a-q), (b-p), (c-p), (d-r, s)
 [I] (a-q), (b-p), (c-q, r), (d-q, s)
 [J] (a-q), (b-r), (c-p, r), (d-r, s)
 [K] (a-r, s), (b-q), (c-p), (d-q)

● PRACTICE PROBLEMS ●

1. For the reaction $A \rightarrow B$, it was found that the concentration of B increased by 0.3 mol L^{-1} in 2 hours. What is the average rate of reaction?

[Ans. $0.15 \text{ mol L}^{-1} \text{ hr}^{-1}$]

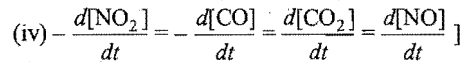
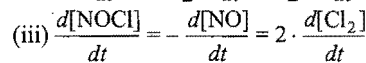
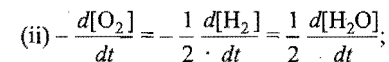
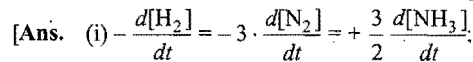
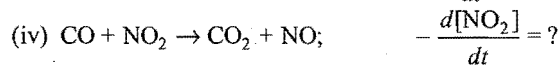
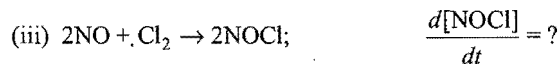
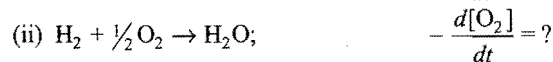
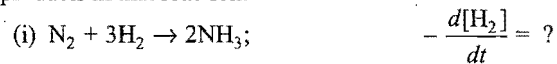
2. In the reaction $X \rightarrow Y$, the initial concentration of X is 2.5 mol L^{-1} and its concentration after 3 hours is 0.7 mol L^{-1} . What is the average rate of the reaction?

[Ans. $6.0 \times 10^{-1} \text{ mol L}^{-1} \text{ hr}^{-1}$]

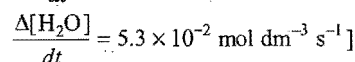
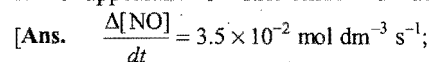
3. For the reaction $2A + B \rightarrow C$, the rate of formation of C is $0.25 \text{ mol L}^{-1} \text{ hr}^{-1}$. What is the rate of disappearance of A and B ?

[Ans. $0.5 \text{ mol L}^{-1} \text{ hr}^{-1}$; $0.25 \text{ mol L}^{-1} \text{ hr}^{-1}$]

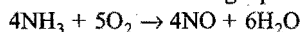
4. For each of the following reactions express the given rate of change of the concentration of the reactant or product in terms of the rate of change of concentration of the other reactants or products in that reaction.



5. When ammonia is treated with O_2 at elevated temperatures, the rate of disappearance of ammonia is found to be $3.5 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$ during a measured time interval. Calculate the rate of appearance of nitric oxide and water.



[Hint: Consider the following equation:



The equality in this case is

$$-\frac{1}{4} \frac{\Delta[\text{NH}_3]}{dt} = \frac{1}{4} \frac{\Delta[\text{NO}]}{dt} = \frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{dt}]$$

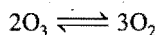
6. In a reaction, $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$,

the rate of disappearance of N_2O_5 is $6.5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$.

Compute the rates of formation of NO_2 and O_2 .

[Ans. $\frac{d[\text{NO}_2]}{dt} = 1.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$;
 $\frac{d[\text{O}_2]}{dt} = 3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$]

7. For the reaction,

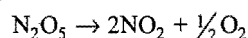


$-\frac{\Delta[\text{O}_3]}{dt}$ was found to be $4.0 \times 10^{-4} \text{ atm s}^{-1}$.

Determine the value of $\frac{\Delta[\text{O}_2]}{\Delta t}$ in atm s^{-1} during this period of time.

[Ans. $6.0 \times 10^{-4} \text{ atm s}^{-1}$]

8. The following reaction was carried out at 44°C :



The concentration of NO_2 is $6.0 \times 10^{-3} \text{ M}$ after 10 minutes of the start of the reaction. Calculate the rate of production of NO_2 over the first ten minutes of the reaction.

[Ans. $6.0 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$]

9. The rate of a particular reaction doubles when temperature changes from 27°C to 37°C . Calculate the energy of activation for such reaction. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

[Ans. $53.59 \text{ kJ mol}^{-1}$]

10. The rate constant of a reaction is $2 \times 10^{-2} \text{ s}^{-1}$ at 300 K and $8 \times 10^{-2} \text{ s}^{-1}$ at 340 K . Calculate the energy of activation of the reaction.

[Ans. $29.39 \text{ kJ mol}^{-1}$]

11. For a chemical reaction the energy of activation is 85 kJ mol^{-1} . If the frequency factor is $4.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, what is the rate constant at 400 K ?

[Ans. $k = 3.19 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$]

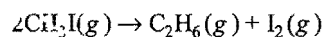
12. The energy of activation of a reaction is 140 kJ mol^{-1} . If its rate constant at 400 K is $2.0 \times 10^{-6} \text{ s}^{-1}$, what is the value at 500 K ?

[Ans. $9.06 \times 10^{-3} \text{ s}^{-1}$]

13. Calculate the ratio of the catalysed and uncatalysed rate constant at 20°C if the energy of activation of a catalysed reaction is 20 kJ mol^{-1} and for the uncatalysed reaction is 75 kJ mol^{-1} .

[Ans. 6.4×10^9]

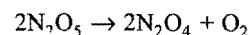
14. The decomposition of methyl iodide,



at 273°C has a rate constant of $2.418 \times 10^{-5} \text{ s}^{-1}$. If activation energy for the reaction is $+179.9 \text{ kJ mol}^{-1}$, what is the value of collision factor 'A' at 273°C ?

[Ans. $3.9 \times 10^{12} \text{ s}^{-1}$]

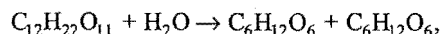
15. The reaction,



occurs in carbon tetrachloride. The rate constant is $2.35 \times 10^{-4} \text{ sec}^{-1}$ at 20°C and $9.15 \times 10^{-4} \text{ sec}^{-1}$ at 30°C . Calculate the activation energy of the reaction.

[Ans. $100.343 \text{ kJ mol}^{-1}$]

16. For the inversion of cane sugar,



the rate constant is $2.12 \times 10^{-4} \text{ L mol}^{-1} \text{ sec}^{-1}$ at 27°C . The activation energy of the reaction is $1.07 \times 10^5 \text{ J mol}^{-1}$. What is the rate constant of the reaction at 37°C ?

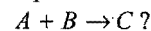
[Ans. $8.46 \text{ L mol}^{-1} \text{ sec}^{-1}$]

17. From the data given below for the reaction $2\text{A} + \text{B} \rightarrow 3\text{C}$ at 298 K , find out the rate law expression for the reaction.

Expt. No.	[A] (mol L ⁻¹)	[B] (mol L ⁻¹)	Rate of formation of C
1.	0.10	0.10	4.0×10^{-4}
2.	0.30	0.30	1.2×10^{-3}
3.	0.10	0.30	4.0×10^{-4}
4.	0.20	0.40	8.0×10^{-4}

[Ans. Rate = $k[\text{A}]$]

18. What is the rate law expression for the reaction,

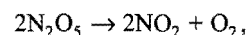


The following data were collected from the experiments:

Expt. No.	Initial [A] (mol L ⁻¹)	Initial [B] (mol L ⁻¹)	Rate of formation of C
1.	0.10	0.10	4.0×10^{-4}
2.	0.20	0.20	3.2×10^{-3}
3.	0.10	0.20	1.6×10^{-3}

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

19. The reaction,



was studied and the following data were collected:

Expt. No.	[N ₂ O ₅] (mol L ⁻¹)	Rate of disappearance of N ₂ O ₅ (mol L ⁻¹ min ⁻¹)
1.	1.13×10^{-2}	34×10^{-5}
2.	0.84×10^{-2}	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

Determine (i) order of the reaction (ii) the rate law and (iii) rate constant for the reaction.

[Hint: Let the rate law for the reaction be

$$\text{Rate} = k[\text{N}_2\text{O}_5]^x$$

$$34 \times 10^{-5} = k[1.13 \times 10^{-2}]^x$$

$$25 \times 10^{-5} = k[0.84 \times 10^{-2}]^x$$

$$\text{or } \frac{34 \times 10^{-5}}{25 \times 10^{-5}} = \frac{[1.13 \times 10^{-2}]^x}{[0.84 \times 10^{-2}]^x}$$

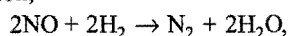
$$1.36 = [1.345]^x$$

$$x = 1$$

Order of the reaction is 1. Rate law = $k[\text{N}_2\text{O}_5]$

$$k = \frac{\text{Rate}}{[\text{N}_2\text{O}_5]} = \frac{34 \times 10^{-5}}{1.13 \times 10^{-2}} = 30.08 \times 10^{-3} \text{ min}^{-1}$$

20. For the reaction,



the following kinetic data were obtained:

Expt. No.	$[\text{H}_2]$ (mol L ⁻¹)	$[\text{NO}]$ (mol L ⁻¹)	Rate of reaction (mol L ⁻¹ s ⁻¹)
1.	0.12	0.12	0.25×10^{-4}
2.	0.12	0.24	1.0×10^{-4}
3.	0.24	0.24	2.0×10^{-4}

Determine the rate law and the rate constant.

$$[\text{Ans. Rate} = k[\text{H}_2][\text{NO}]^2; k = 1.45 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}]$$

21. Fill in the blanks in the following table which treats reaction of a compound A with a compound B, that is of the first order with respect to A and zero order with respect to B:

Expt. No.	$[A]$ (mol L ⁻¹)	$[B]$ (mol L ⁻¹)	Initial rate (mol L ⁻¹ s ⁻¹)
1.	0.1	0.1	2.0×10^{-2}
2.	...	0.2	4.0×10^{-2}
3.	0.4	0.4	...
4.	...	0.2	2.0×10^{-2}

$$[\text{Ans. (2)} [A] = 0.2 \text{ mol L}^{-1}]$$

$$(3) \text{ Rate} = 8.0 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$(4) [A] = 0.1 \text{ mol L}^{-1}]$$

22. The reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, follows the rate law = $k[\text{NO}]^2[\text{O}_2]$. What is the order of the reaction? If $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$, what is the rate of the reaction when $[\text{NO}] = 0.04 \text{ mol L}^{-1}$ and $[\text{O}_2] = 0.2 \text{ mol L}^{-1}$?

$$[\text{Ans. Order of the reaction} = 3;$$

$$\text{Rate} = 6.4 \times 10^{-10} \text{ mol L}^{-1} \text{ s}^{-1}]$$

23. From the following data of initial concentrations and rates, calculate the order of reaction $aA \rightarrow \text{Products}$; and its rate constant.

$[A] \text{ mol L}^{-1}$	0.1	0.2	0.4
Rate $\text{mol L}^{-1} \text{ s}^{-1}$	9×10^{-5}	36×10^{-5}	144×10^{-5}

$$[\text{Ans. Order of reaction} = 2;$$

$$\text{Rate constant} = 9.0 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}]$$

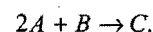
24. For a reaction $aA + bB \rightarrow mM + nN$, the rate of reaction is given as $k[A]^x[B]^y$.

Calculate the order of the reaction and the rate constant from the given initial concentrations and the corresponding rates.

$[A] \text{ mol L}^{-1}$	0.1	0.1	0.2
$[B] \text{ mol L}^{-1}$	0.2	0.4	0.2
Rate $\text{mol L}^{-1} \text{ s}^{-1}$	4×10^4	16×10^4	8×10^4

$$[\text{Ans. Order of the reaction} = 3, k = 1.0 \times 10^7 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}]$$

25. The data given in the following table pertain to the reaction,

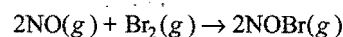


Determine the form of the rate equation and the value of the rate constant.

Expt. No.	Initial concentration (mol L ⁻¹)		Initial rate (mol L ⁻¹ s ⁻¹)
	$[A]$	$[B]$	
1.	1×10^{-3}	1×10^{-3}	7×10^{-6}
2.	1×10^{-3}	2×10^{-3}	14×10^{-6}
3.	1×10^{-3}	3×10^{-3}	21×10^{-6}
4.	2×10^{-3}	3×10^{-3}	84×10^{-6}

$$[\text{Ans. Rate} = k[A]^2[B]; k = 7 \times 10^3]$$

26. The following initial rate data were obtained for the reaction:



Run	$[\text{NO}]/M$	$[\text{Br}_2]/M$	Rate/ $M \text{ min}^{-1}$
1.	1.0	1.0	1.30×10^{-3}
2.	2.0	1.0	5.20×10^{-3}
3.	4.0	2.0	4.16×10^{-2}

Determine the reaction rate law and the value of the rate constant. (Dhanbad 1992)

$$[\text{Ans. } -\frac{dx}{dt} = k[\text{NO}]^2[\text{Br}_2]; K = 1.30 \times 10^{-3} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}]$$

27. The data below are for the reaction of NO and Cl₂ to form NOCl at 295 K.

Expt. No.	$[\text{Cl}_2]$ (mol L ⁻¹)	$[\text{NO}]$ (mol L ⁻¹)	Initial rate (mol L ⁻¹ s ⁻¹)
1.	0.05	0.05	1.0×10^{-3}
2.	0.15	0.05	3.0×10^{-3}
3.	0.05	0.15	9.0×10^{-3}

(a) What is the order w.r.t. NO and Cl₂ in the reaction?

(b) Write the rate expression.

(c) Calculate the rate constant.

(d) Determine the reaction rate when concentrations of Cl₂ and NO are 0.2 M and 0.4 M respectively. (IIT 1993)

$$[\text{Ans. (a) Order w.r.t. NO} = 2; \text{ order w.r.t. Cl}_2 = 1]$$

$$(b) \text{ Rate expression, } r = k[\text{NO}]^2[\text{Cl}_2]$$

$$(c) k = 8.0 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

$$(d) \text{ Rate} = 0.256 \text{ mol L}^{-1} \text{ s}^{-1}]$$

28. In the hydrolysis of propyl acetate in presence of dilute HCl in aqueous solution, the following data were recorded:
- | | | |
|-----------------------------|-------|-------|
| Time from start (in minute) | 60 | 350 |
| % of ester decomposed | 18.17 | 69.12 |
- Calculate the rate constant of decomposition and time in which half of the ester was decomposed.
[Ans. $3.34 \times 10^{-3} \text{ min}^{-1}$; 207.6 min]
29. In a first order reaction the concentration of the reactant is reduced to one-fourth of its initial value in 50 seconds. Calculate the rate constant of the reaction.
[Ans. $2.77 \times 10^{-2} \text{ s}^{-1}$]
30. For a first order reaction, the rate constant is 0.1 s^{-1} . How much time will it take to reduce the concentration from initial value of 0.6 mol L^{-1} to 0.06 mol L^{-1} ?
[Ans. 23.0 second]
31. A substance decomposes following first order reaction. If the half life period of the reaction is 35 minutes, what is the rate constant of this reaction?
[Ans. $1.98 \times 10^{-2} \text{ min}^{-1}$]
32. For a certain first order reaction, it takes 5 minutes for the initial concentration of 0.6 mol L^{-1} to become 0.2 mol L^{-1} . What is the rate constant for this reaction? [$\log 3 = 0.4771$].
[Ans. 0.2197 min^{-1}]
33. Find the two-thirds life ($t_{2/3}$) of a first order reaction in which $k = 5.48 \times 10^{-1} \text{ sec}^{-1}$ ($\log 3 = 0.4771$; $\log 2 = 0.3010$).
[Ans. 2.005 s]
[Hint: $t_{2/3} = \frac{2.303}{k} \log_{10} \frac{a}{a - \frac{2}{3}a}$]
34. A first order reaction has a specific rate of 10^{-3} sec^{-1} . How much time will it take from 10 g of the reactant to reduce to 7.5 g ($\log 2 = 0.3010$; $\log 4 = 0.6020$ and $\log 6 = 0.7782$)?
[Ans. 287.7 s]
35. In a reaction 5 g ethyl acetate is hydrolysed per litre in presence of dilute HCl in 300 min. If the reaction is of first order and initial concentration is 22 g per litre, calculate the rate constant for the reaction.
[Ans. $k = 8.59 \times 10^{-4} \text{ min}^{-1}$]
36. Calculate the half life of the reaction $A \rightarrow B$, when the initial concentration of A is 0.01 mol L^{-1} and initial rate is $0.00352 \text{ mol L}^{-1} \text{ min}^{-1}$. The reaction is of the first order.
[Ans. 1.969 min]
[Hint: Evaluate k from $\frac{dx}{dt} = k[A]$]
37. In a reaction, $A \rightarrow B + C$, the following data were obtained:
- | | | | |
|----------------------|------|------|------|
| t in seconds | 0 | 900 | 1800 |
| Concentration of A | 50.8 | 19.7 | 7.62 |
- Prove that it is a first order reaction.
[Hint: Calculate the value of k in both cases by using first order equation.]
38. The first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C . If the reaction is allowed to run for 10 hours at the same temperature, what percentage of the initial concentration would have changed into the product? What is the half life period of this reaction?
[Ans. $t_{1/2} = 128.3 \text{ hours}$; 5.27%]
39. A first order reaction is 20% completed in 10 minutes. Calculate (i) the specific rate constant of the reaction and (ii) the time taken for the reaction to go to 75% completion.
[Ans. $k = 2.232 \times 10^{-2} \text{ min}^{-1}$; $t = 62.12 \text{ min}$]
40. The rate constant of a reaction with respect to reactant A is 6 min^{-1} . If we start with $[A] = 0.8 \text{ mol L}^{-1}$, when would $[A]$ reach the value of 0.08 mol L^{-1} ?
[Ans. 0.3838 min]
41. What will be the initial rate of a reaction if the rate constant is 10^{-3} min^{-1} and the concentration is 0.2 mol dm^{-3} ? How much of the reactant will be converted into the product in 200 minutes?
[Ans. Initial rate = $2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$; 0.036 mol]
42. A substance A decomposes by the first order reaction. Starting initially with $[A] = 2.00 M$, after 200 minutes $[A] = 0.25 M$. For this reaction what is $t_{1/2}$ and k ?
[Ans. $t_{1/2} = 66.66 \text{ min}$, $k = 0.01039 \text{ min}^{-1}$]
43. The specific rate constant for the concentration of H_2 and I_2 to form HI is $0.0234 \text{ mol}^{-1} \text{ L s}^{-1}$ at 400°C and $750 \text{ mol}^{-1} \text{ L s}^{-1}$ at 500°C . Calculate the activation energy of the reaction.
[Ans. 107.9 kcal]
[CEE (Bihar) 1993]
44. For a certain reaction it takes 10 minutes for the initial concentration of 2.0 mol L^{-1} to become 1.0 mol L^{-1} and another 10 minutes to become 0.5 mol L^{-1} . Calculate the rate constant of the reaction.
[Ans. 0.0693 min^{-1}]
45. The catalytic decomposition of H_2O_2 was studied by titrating it at different intervals with KMnO_4 and the following data were obtained:
- | | | | |
|-----------------------------|------|------|------|
| t (seconds) | 0 | 600 | 1200 |
| V of KMnO_4 (mL) | 22.8 | 13.8 | 8.3 |
- Calculate the velocity constant for the reaction assuming it to be a first order reaction.
[Ans. $8.4 \times 10^{-3} \text{ s}^{-1}$]
[Hint: Volume of KMnO_4 used $\propto$ concentration of H_2O_2
Hence, $k = \frac{2.303}{t} \log_{10} \frac{V_0}{V_t}$]
46. The half life of a first order reaction is 10 seconds. Calculate the time for completion of 99.9% of the reaction.
[Ans. 99.7 sec $\approx$ 100 sec]
47. A first order reaction is 40% complete after 8 min. How long will it take before it is 90% complete? What is the value of the rate constant?
[Ans. $k = 0.06386 \text{ min}^{-1}$; $t = 36.06 \text{ min}$]
48. The reaction $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$ is a first order gas reaction with $k = 2.2 \times 10^{-5} \text{ s}^{-1}$ at 573 K . What per cent of SO_2Cl_2 is decomposed on heating at 573 K for 90 min?
[Ans. 11.2]

49. The decomposition of $AB(g) \rightarrow A(g) + B(g)$, is first order reaction with a rate constant $k = 4 \times 10^{-4} \text{ s}^{-1}$ at 318 K. If AB has 26664.5 Pa pressure at the initial stage, what will be the partial pressure of AB after half an hour?

[Ans. 12981.7 Pa]

50. In the first order reaction $A(g) \rightarrow B(g) + C(g)$, the initial pressure of A is 11200 Pa and the total pressure at the end of 16 minutes is 14667 Pa. Calculate the half life period of reaction.

[Ans. 30 min]

51. It was found that a solution of cane sugar was hydrolysed to the extent of 25% in 1 hr. Calculate the time taken for the sugar to be 50% hydrolysed assuming that the reaction is of first order.

[Ans. 2.408 hours]

52. A reaction is 20% complete in 20 minutes. How long will it take for 80% completion if the order of reaction is (a) zero and (b) one?

[Ans. (a) 80 minutes (b) 144.27 minutes]

53. A second order reaction where $a = b$ is 20% completed in 500 seconds. How long will the reaction take to be 60% complete?

[Hint: Apply

$$k = \frac{x}{ta(x-x)} = \frac{20}{500[100 \times (100 - 20)]} = \frac{1}{200000} \text{ mol}^{-1} \text{ L s}^{-1}$$

$$t = \frac{60}{k \times 100 \times 40} = \frac{60 \times 200000}{100 \times 40} = 3000 \text{ seconds}]$$

54. At a certain temperature, the half life periods of a reaction at different initial pressures were as follows:

p (kPa)	100	66.67	33.33
t (min)	105	235	950

Find out the order of the reaction.

[Ans. 3]

55. The time for half change for a gaseous reaction was measured for various initial pressures and the following data were obtained:

p (kPa)	26.6	40	53.3
t (min)	150	99.8	75.3

Find out the order of the reaction.

[Ans. 2]

56. Show that for a first order reaction the time required for 99% completion is twice the time required for the completion of 90% of the reaction.

57. Show that for a first order reaction the time required to complete 99.9% of the reaction is 10 times that required for half the reaction.

58. Show that for a first order reaction, the time required for a 50% reaction is half that for 75% reaction.

59. The decomposition of an aqueous solution of ammonium nitrite was studied. The volume of nitrogen gas collected at different intervals of time was as follows:

Time (minutes)	10	15	20	∞
Vol. of N_2 (mL)	6.25	9.00	11.40	35.05

From the above data prove that the reaction is of the first order.

[Hint: $[A]_0$ = volume of nitrogen at ∞ = 35.05

$$[A]_t = V_{\infty} - V_t$$

$$\text{when } t = 10, \quad k = \frac{2.303}{10} \log \frac{35.05}{(35.05 - 6.25)} = 0.0196$$

when $t = 15, \quad k = 0.0198$

when $t = 20, \quad k = 0.0196$

60. Optical rotation of sucrose in 1 N HCl at various times was found as shown below:

Time (sec)	0	7.18	18.0	27.05	∞
Rotation (deg)	+24.09	+21.7	+17.7	+15.0	-10.74

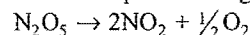
Show that the inversion of sucrose is a first order reaction.

[Hint: Initial concentration, $[A]_0 = r_0 - r_{\infty}$

$$\text{At time } t, \quad [A]_t = r_t - r_{\infty}$$

$$k = 11.8 \times 10^{-3} \text{ s}^{-1}$$

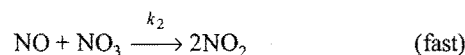
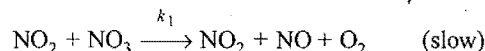
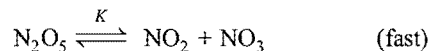
61. The rate law for the decomposition of gaseous N_2O_5



is observed to be:

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

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



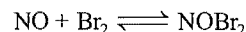
Show that the mechanism is consistent with the observed law.

[Hint: $r = k_1[NO_2][NO_3]$,

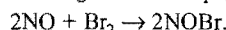
$$K = \frac{[NO_2][NO_3]}{[N_2O_5]} \quad \text{or} \quad [NO_3] = \frac{K[N_2O_5]}{[NO_2]}$$

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

62. Write the overall reaction and the rate law equation from the following elementary steps:



[Hint: Adding both the steps, we get overall reaction,



The second step is slow and, therefore, a rate determining step.

$$r = k'[NOBr_2][NO]$$

$$K = \frac{[NOBr_2]}{[NO][Br_2]} \quad \text{or} \quad [NOBr_2] = K[NO][Br_2]$$

$$r = k'K[NO]^2[Br_2]$$

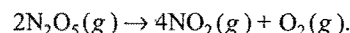
63. The reaction, $2NO + O_2 \rightarrow 2NO_2$ proceeds in two steps. If one elementary reaction is $NO + O_2 \rightarrow NO_3$, write the second elementary reaction. Write the rate law of the reaction.

[Ans. $NO + NO_3 \rightarrow 2NO_2$, rate = $k[NO]^2[O_2]$]

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

[Ans. 20.39 min]

65. Calculate the average rate of decomposition of N_2O_5 by the reaction,



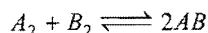
During the time interval from $t = 600 \text{ s}$ to $t = 1200 \text{ s}$ using the following data:

Time	$[\text{N}_2\text{O}_5]$
600 s	$1.24 \times 10^{-2} \text{ M}$
1200 s	$0.93 \times 10^{-2} \text{ M}$

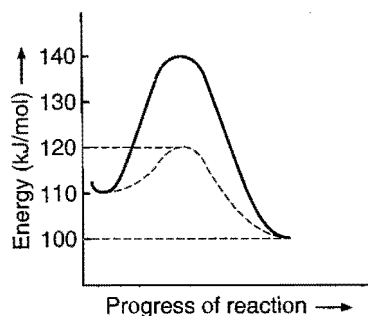
[CET (Bihar) 1995]

[Ans. $5.166 \times 10^{-6} \text{ M s}^{-1}$]

66. Consider the diagram for reaction:



- Calculate the ΔH of the reaction.
- Calculate the energy of activation for forward and backward reaction.
- The dotted line curve is the path in the presence of a catalyst. What is the energy of activation for the forward and backward reactions in the presence of the catalyst?



What is the lowering in activation energy in the presence of the catalyst?

- (d) Will the catalyst change the extent of the reaction?

[Ans. (a) $\Delta H = -10 \text{ kJ/mol}$;

(b) $E_f = 30 \text{ kJ/mol}$; $E_b = 40 \text{ kJ/mol}$;

(c) $E_f = 10 \text{ kJ/mol}$; $E_b = 20 \text{ kJ/mol}$; 20 kJ/mol ;

(d) no]

67. Temperature coefficient, $\mu = \frac{k_{35^\circ\text{C}}}{k_{25^\circ\text{C}}}$ of a reaction is

1.82. Calculate the energy of activation in calories. ($R = 1.987 \text{ cal degree}^{-1} \text{ mol}^{-1}$).

[Ans. 10.924 kcal/mol]

68. For first order gaseous reaction, $\log k$ when plotted against $\frac{1}{T}$

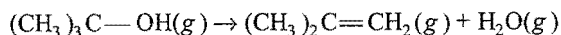
gives a straight line with a slope of -8000 . Calculate the activation energy of the reaction.

[Ans. 36.6 kcal]

69. The rate at 27°C of a chemical reaction increases 1000 times when a suitable catalyst is introduced. Calculate the change in the energy of activation that the catalyst has brought in.

[Ans. 4118 cal]

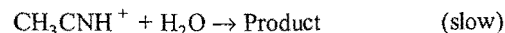
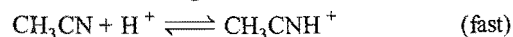
70. Dehydration of tertiary butyl alcohol follows a first order reaction,



the rate constant at 300°C is $2.27 \times 10^{-8} \text{ s}^{-1}$. Calculate the rate constant at 400°C if the energy of activation for the reaction is 58 kcal .

[Ans. $4.392 \times 10^{-5} \text{ s}^{-1}$]

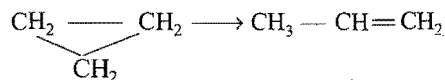
71. Let us consider the following mechanism:



What would be the rate law?

[Ans. $\text{Rate} = k[\text{CH}_3\text{CN}][\text{H}_2\text{O}][\text{H}^+]$]

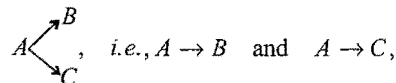
72. The thermal isomerization of cyclopropane occurs according to the equation:



The specific reaction rate constant for this reaction at 499°C was $5.95 \times 10^{-4} \text{ sec}^{-1}$. What is the half life of the reaction? What fraction of the cyclopropane will remain after 1 hour at 499.5°C ?

[Ans. 1165 s ; 11.7%]

73. A substance 'A' was found to undergo two parallel first order reactions,



with rate constants $1.26 \times 10^{-4} \text{ s}^{-1}$ and $3.8 \times 10^{-5} \text{ s}^{-1}$ respectively. What were the percentage distributions of B and C?

[Ans. 76.83% of B and 23.17% of C]

74. Two reactions proceed at 25°C at the same rate; the temperature coefficient of the rate of the first reaction is 2 and that of the second reaction is 2.5. Find the ratio of rates of these reactions at 95°C .

[Ans. 5 times]

75. The population of India in the year 1988 was 800 million. Growth rate is 25 per thousand per year. What will be the population in the year 2000 if the growth follows first order kinetics?

[Ans. 1075 million]

76. Half lives against initial pressure are given below. Calculate the order of the reaction.

p (mm)	750	500	250
t (min)	105	235	950

Find out the order of the reaction.

[Ans. 3]

77. For a given reaction at temperature T , the velocity constant k , is expressed as:

$$k = Ae^{-27000 k'/T} \quad (k' = \text{Boltzmann constant})$$

Given, $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$. Calculate the value of energy of activation. Comment on the results.

[Ans. $E = 18 \times 10^{-20} \text{ cal}$]

[Hint: Compare the equation with Arrhenius equation

$$k = Ae^{-E_a/RT} \quad \dots (i)$$

$$k = Ae^{-27000k'/T} \quad \dots (ii)$$

$$\frac{E_a}{RT} = \frac{27000k'}{T}$$

$$E_a = 27000Rk'$$

$$= 27000 R \times \frac{R}{N} = \frac{27000 \times (2)^2}{6.023 \times 10^{23}}$$

$$= 18 \times 10^{-20} \text{ cal}$$

Activation energy is low, therefore reaction will be fast.]

78. If the activation energy of a reaction is 80.9 kJ mol^{-1} , calculate the fraction of molecules at 400°C which have enough energy to react to form the products.

[Ans. 5.257×10^{-7}]

[Hint: Fraction of total molecules which are active at a temperature is given as,

$$\begin{aligned} \frac{k}{A} &= e^{-E_a/RT} \\ \log \frac{k}{A} &= \frac{-E_a}{2.303 RT} \\ \frac{k}{A} &= \text{antilog} \left(\frac{-E_a}{2.303 RT} \right) \end{aligned}$$

Substituting the values of E and T we can solve the problem.]

79. The following data were obtained for a given reaction at 300 K :

Reaction **Energy of activation (kJ/mol)**

- | | |
|----------------|----|
| 1. Uncatalysed | 76 |
| 2. Catalysed | 57 |

Calculate by what factor the rate of catalysed reaction is increased?

[Ans. 2000]

[Hint: Use: $\frac{k_p}{k_a} = \text{antilog} \left(\frac{\Delta E}{2.303 RT} \right)$

k_p = rate constant in presence of catalyst

k_a = rate constant in absence of catalyst

$\Delta E = 76 - 57 = 19 \text{ kJ/mol}$]

80. The Arrhenius equations for *cis-trans* isomerization of but-2-ene ($\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$) and but-2-ene, 1-nitrile ($\text{CH}_3 - \text{CH} = \text{CH} - \text{CN}$) are,

$$k(\text{s}^{-1}) = 10^{13.8} \exp(-263.5 \text{ kJ mol}^{-1} / RT)$$

$$k^{-1}(\text{s}^{-1}) = 10^{11} \exp(-214.5 \text{ kJ mol}^{-1} / RT)$$

Calculate the temperature at which $k = k^{-1}$.

[Ans. 914 K]

81. The half life for a reaction between fixed concentration of reactants varies with temperature as follows:

$t^\circ\text{C}$	520	533	555	574
$t_{1/2} \text{ sec}$	1288	813	562	477

Calculate the activation energy of this reaction.

[Ans. $86.47 \text{ kJ mol}^{-1}$]

[Hint: Use: $\log \left(\frac{k_2}{k_1} \right) = \frac{E}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

$$k_2 = 0.693 / t_2$$

$$k_1 = 0.693 / t_1$$

$$\therefore \log \left(\frac{t_1}{t_2} \right) = \frac{E}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

82. What percentage of reactant molecules will crossover the energy barrier at 325 K ? Heat of reaction is 0.12 kcal and activation energy of backward reaction is 0.02 kcal .

[Hint: Activation energy of forward reaction = $0.12 - 0.02$
= 0.10 kcal

Fraction of molecules which are active

or which crossover the energy barrier $\left(\frac{k}{A} \right) = e^{-E/RT}$

$$\begin{aligned} \log_e \left(\frac{k}{A} \right) &= -\frac{E}{RT} \\ \frac{k}{A} &= \text{antilog} \left[\frac{-E}{2.303 RT} \right] \\ &= \text{antilog} \left[\frac{-0.10 \times 1000}{2.303 \times 2 \times 325} \right] \\ &= \text{antilog} [-0.06680] = 0.8574 \end{aligned}$$

$\therefore$ Percentage of reactant molecules crossing over the barrier
= $0.8574 \times 100 = 85.74$]

83. In a milk at 37°C *Lactobacillus acidophilus* has a generation time of about 75 minutes. Calculate the population relative to the initial value at 30, 60, 75, 90 and 150 minutes.

[Ans.

t_{min}	30	60	75	90
N/N_0	1.32	1.74	2	2.30

]

[Hint: In the case of population growth we have to use growth kinetics.

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

a = initial population

x = growth in population in time ' t '

Here, $N_0 = a$; $N = a + x$]

84. Two reactions of same order have equal pre-exponential factors but their activation energies differ by 41.9 J/mol . Calculate the ratios between rate constants of these reactions at 600 K .

[Ans. 0.002]

[Hint: Use the relation,

$$\log_{10} k = \log_{10} A - \frac{E}{2.303 RT} \quad \dots (i)$$

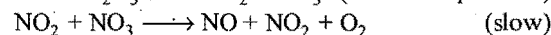
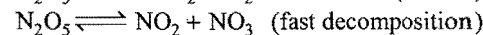
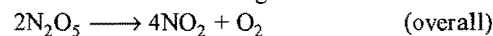
$$\log_{10} k_1 = \log_{10} A - \frac{E_1}{2.303 \times 8.314 \times 600} \quad \dots (ii)$$

$$\log_{10} k_2 = \log_{10} A - \frac{E_2}{2.303 \times 8.314 \times 600} \quad \dots (iii)$$

$$E_1 - E_2 = 41.95 / \text{mol} \quad \dots (iv)$$

Subtract eq. (iii) from eq. (ii) to determine the ratio.]

85. A decomposition reaction has following mechanism



Determine rate law, is the mechanism corresponds to first order reaction.

$$[\text{Ans. } \frac{-d[\text{N}_2\text{O}_5]}{dt} = \frac{2k_1 k_3}{k_1 + k_3} [\text{N}_2\text{O}_5]]$$

86. Rate constant of a reaction changes by 2% by 0.1°C rise in temperature at 25°C . The standard heat of reaction is $121.6 \text{ kJ mol}^{-1}$. Calculate E_a of reverse reaction.

[Ans. 24.7 kJ/mol]

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

$$\log \frac{102}{100} = \frac{E}{2.303 \times 8.314} \left(\frac{1}{298} - \frac{1}{298.1} \right)$$

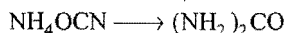
$$E = 1.463 \times 10^5 \text{ J/mol} = 146.3 \text{ kJ/mol}$$

$$\Delta H = E_f - E_b$$

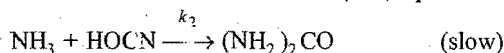
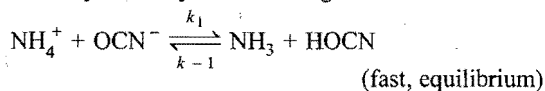
$$121.6 = 146.3 - E_b$$

$$E_b = 24.7 \text{ kJ/mol}$$

87. Urea $(\text{NH}_2)_2\text{CO}$ can be prepared by heating ammonium cyanate NH_4OCN .



The reaction may occur by the following mechanism:



What is rate law predicted by this mechanism?

[Ans. Rate = $\frac{k_2 k_1}{k-1} [\text{NH}_4^+][\text{OCN}^-] = k[\text{NH}_4^+][\text{OCN}^-]$]

88. For the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$, under certain conditions of pressure and temperature of the reactants, the rate of formation of NH_3 is 0.001 kg hr^{-1} . Calculate the rate of reaction for N_2 and H_2 .

[Ans. $1.76 \times 10^{-4} \text{ kg hr}^{-1}$]

[Hint: $-\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$]

$$\frac{d[\text{NH}_3]}{dt} = 0.001 \text{ kg hr}^{-1} = \frac{0.001 \times 1000}{17} \text{ mol hr}^{-1}$$

$$= 0.058 \text{ mol hr}^{-1}$$

$$-\frac{d[\text{N}_2]}{dt} = \frac{1}{2} \times 0.058 \text{ mol hr}^{-1}$$

$$= 0.029 \text{ mol hr}^{-1}$$

$$= 0.029 \times 28 \times 10^{-3} \text{ kg hr}^{-1}$$

$$= 8.12 \times 10^{-4} \text{ kg hr}^{-1}$$

Similarly, $-\frac{d[\text{H}_2]}{dt} = 1.76 \times 10^{-4} \text{ kg hr}^{-1}$

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. Chemical kinetics, a branch of physical chemistry, deals with:

- (a) heat changes in a reaction
- (b) physical changes in a reaction
- (c) rates of reactions
- (d) structure of molecules

2. The rate at which a substance reacts depends upon its:

- (a) atomic mass
- (b) equivalent mass
- (c) molecular mass
- (d) active mass

3. The rate of a chemical reaction:

- (a) increases as the reaction proceeds
- (b) decreases as the reaction proceeds
- (c) may increase or decrease during the reaction
- (d) remains constant as the reaction proceeds

4. For the reaction, $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$, rate is expressed as:

- (a) $-3 \frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{3}{2} \frac{d[\text{NH}_3]}{dt}$
- (b) $-\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$
- (c) $-\frac{d[\text{N}_2]}{dt} = -\frac{3d[\text{H}_2]}{dt} = \frac{2d[\text{NH}_3]}{dt}$
- (d) $-\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$

5. For the reaction, $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$, rate is expressed as:

- (a) $-\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$
- (b) $-\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$

(c) $-\frac{2d[\text{NO}_2]}{dt} = \frac{2d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$

(d) $-\frac{d[\text{NO}_2]}{dt} = \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$

6. The rate of reaction that does not involve gases, is not dependent on:

- (a) pressure
- (b) temperature
- (c) concentration
- (d) catalyst

7. For the reaction, $A + B \longrightarrow 2C + D$, which one is the incorrect statement?

- (a) Rate of disappearance of A = Rate of disappearance of B
- (b) Rate of disappearance of A = Rate of appearance of D
- (c) Rate of disappearance of B = $2 \times$ rate of appearance of C
- (d) Rate of disappearance of B = $\frac{1}{2} \times$ rate of appearance of C

8. In a reaction, $2A_2 + B_2 \longrightarrow 2A_2B$, the reactant A will disappear at:

- (a) half the rate that B will decrease
- (b) the same rate that B will decrease
- (c) double the rate that A_2B will form
- (d) twice the rate that B will decrease

9. In the reaction $3A \rightarrow 2B$, rate of reaction + $\frac{d[B]}{dt}$ is equal to:

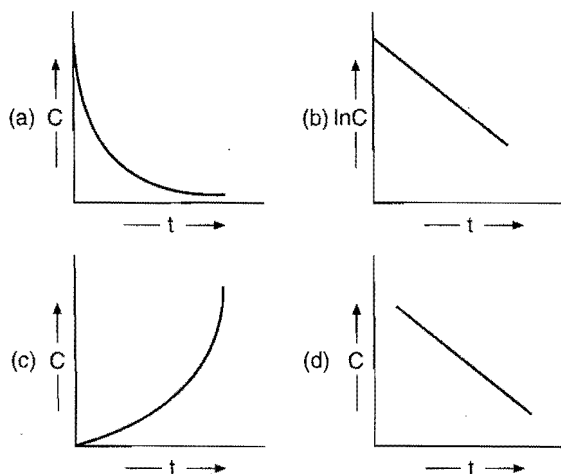
[JEE (WB) 2008]

(a) $-\frac{1}{3} \frac{d[A]}{dt}$ (b) $-\frac{2}{3} \frac{d[A]}{dt}$ (c) $+2 \frac{d[A]}{dt}$ (d) $-\frac{3}{2} \frac{d[A]}{dt}$

10. For the reaction, $2\text{NO} \longrightarrow \text{N}_2 + \text{O}_2$, the expression

$-\frac{1}{2} \frac{d[\text{NO}]}{dt}$ represents:

- (a) the rate of formation of NO
 (b) the average rate of the reaction
 (c) the instantaneous rate of the reaction
 (d) all of the above
11. The term $-\frac{dx}{dt}$ in the rate expression refers to the:
 (a) instantaneous rate of reaction
 (b) average rate of reaction
 (c) increase in the concentration of reactants
 (d) concentration of reactants
12. According to collision theory of reaction rates:
 (a) every collision between reactant molecules leads to a chemical reaction
 (b) rate of reaction is proportional to the velocity of the molecules
 (c) rate of reaction is proportional to the average energy of the molecules
 (d) rate of reaction is proportional to the number of collisions per second
13. According to collision theory:
 (a) all collisions are sufficiently violent
 (b) all collisions are responsible for product formation
 (c) all collisions are effective
 (d) only a fraction of collisions are effective which have enough energy to form products
14. Which of the following has been used to explain the subject of chemical kinetics?
 (a) Collision theory of bimolecular reactions
 (b) The activated complex theory
 (c) Arrhenius equation
 (d) All of the above
15. The activation energy for a chemical reaction depends upon:
 (a) temperature
 (b) nature of reacting species
 (c) concentration of the reacting species
 (d) collision frequency
16. In a reaction, the threshold energy is equal to:
 (a) activation energy + normal energy of reactants
 (b) activation energy - normal energy of reactants
 (c) normal energy of reactants - activation energy
 (d) average kinetic energy of molecules of reactants
17. The influence of temperature on the rate of reaction is determined by:
 (a) Nernst's equation (b) Gibbs-Helmholtz equation
 (c) Arrhenius equation (d) van't Hoff equation
18. According to the collision theory of reaction rates, the rate of reaction increases with temperature due to:
 (a) greater number of collisions
 (b) higher velocity of reacting molecules
 (c) greater number of molecules having the activation energy
 (d) decrease in the activation energy
19. The temperature coefficient of a reaction is:
 (a) ratio of rate constants at two temperatures differing by 1°C
 (b) ratio of rate constants at temperature 35°C and 25°C
 (c) ratio of rate constants at temperature 30°C and 25°C
 (d) specific reaction rate at 25°
20. In general, with every 10°C rise in temperature, the rate of reaction becomes approximately
 (a) ten times (b) double
 (c) half (d) one tenth
21. Activation energy of the reaction is:
 (a) the energy released during the reaction
 (b) the energy evolved when activated complex is formed
 (c) minimum amount of energy needed to overcome the potential barrier
 (d) the energy needed to form one mole of the product
22. The temperature coefficient of most of the reactions lies between:
 (a) 2 and 3 (b) 1 and 2
 (c) 2 and 4 (d) 3 and 4
23. According to Arrhenius equation, rate constant of a chemical reaction is equal to:
 (a) $Ae^{-E_a/RT}$ (b) $Ae^{E_a/RT}$
 (c) Ae^{RT/E_a} (d) Ae^{-RT/E_a}
24. The correct expression for Arrhenius equation showing the effect of temperature on the rate constant is ($T_2 > T_1$):
 (DCE 2009)
 (a) $\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_1 T_2}{T_2 - T_1} \right]$
 (b) $\log_{10} \frac{k_2}{k_1} = \frac{R}{2.303E_a} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$
 (c) $\log_{10} \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$
 (d) $\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$
25. In order to react, a molecule, at the time of collision, must possess a certain amount of energy known as:
 (a) free energy (b) kinetic energy
 (c) threshold energy (d) internal energy
26. The activation energy of a reaction is zero. The rate constant of the reaction:
 (IIT (Ph) 1991)
 (a) increases with increase of temperature
 (b) decreases with decrease of temperature
 (c) decreases with increase of temperature
 (d) is nearly independent of temperature
27. The activation energy of a reaction can be lowered by:
 (a) using a positive catalyst
 (b) increasing temperature
 (c) decreasing temperature
 (d) increasing concentration of the reactants
28. The activation energy for a hypothetical reaction $A \longrightarrow \text{Product}$ is 12.49 kcal/mol. If temperature is raised from 295 to 305, the rate of reaction increases by:
 (a) 60% (b) 100%
 (c) 50% (d) 20%
29. The plot between concentration versus time for a zero order reaction is represented by: (AMU (Engg.) 2009)



30. The rate of reaction increases with rise in temperature because of: [Comed (Karnataka) 2008]

(a) increase in the number of activated molecules
(b) increase in the activation energy
(c) decrease in the activation energy
(d) increase in the number of molecular collisions

31. Which of the following is a first order reaction?

(a) $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$ (b) $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$
(c) $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ (d) $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$

32. Which one of the following is not a first order reaction?

(a) $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$
(b) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
(c) $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
(d) $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$

33. Rate expression of a chemical change is $-\frac{dx}{dt} = k[A]^2[B][C]^0$.

The order of reaction is:

(a) 3 (b) 2 (c) 1 (d) zero

34. For a reaction, $2A + B \longrightarrow C + D$, the concentration of B is kept constant and that of A is tripled the new rate of reaction will be:

(a) nine times (b) three times
(c) same (d) zero

35. The rate of the reaction, $A + B + C \longrightarrow \text{Products}$, is given by

$$-\frac{d[A]}{dt} = k[A]^{1/2}[B]^{1/3}[C]^{1/4}$$

The order of the reaction is:

(a) 1/2 (b) 13/12
(c) 1 (d) 2

36. Which of the following rate laws has an overall order of 0.5 for the reaction involving substances x, y and z?

(a) $\text{Rate} = k[C_x][C_y][C_z]$
(b) $\text{Rate} = k[C_x]^{0.5}[C_y]^{0.5}[C_z]^{0.5}$
(c) $\text{Rate} = k[C_x]^{1.5}[C_y]^{-1}[C_z]^0$
(d) $\text{Rate} = k[C_x][C_y]^{-2}[C_z]^0$

37. If the rate of reaction between A and B is given by rate $= k[A][B]^2$, then the reaction is:

(a) first order in A (b) second order in B
(c) third order overall (d) all are correct

38. For the reaction $A \longrightarrow B$, the rate of reaction is quadrupled when the concentration of A is doubled; the rate of the reaction is $r = k[A]^n$; the value of n is:

(a) 1 (b) zero (c) 3 (d) 2

39. Select the rate law that corresponds to the data shown for the following reaction: $A + B \longrightarrow C$ (CBSE 1994)

Expt. No.	$[A]_0$	$[B]_0$	Initial rate
1.	0.012	0.035	0.10
2.	0.024	0.070	0.80
3.	0.024	0.035	0.10
4.	0.012	0.070	0.80

(a) $\text{rate} = k[B]^3$ (b) $\text{rate} = k[B]^4$
(c) $\text{rate} = k[A][B]^3$ (d) $\text{rate} = k[A]^2[B]^2$

40. For a chemical reaction, $A \longrightarrow E$, it is found that rate of reaction is doubled when the concentration of A is increased four times. The order of the reaction is:

(a) 1 (b) 2
(c) 1/2 (d) zero

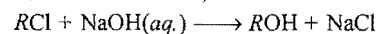
41. The rate of reaction, $A + B \longrightarrow \text{Products}$, is given by the equation, $r = k[A][B]$. If B is taken in large excess, the order of reaction would be: (BIT 1992)

(a) 2 (b) 1
(c) zero (d) unpredictable

42. The rate of reaction between A and B increases by a factor of 100, when the concentration of A is increased 10 folds. The order of reaction with respect to A is:

(a) 10 (b) 2 (c) 1 (d) 20

43. The rate law for the reaction,



is given by, $\text{Rate} = k[\text{RCl}]$. The rate of reaction will be:

(a) unaffected by increasing temperature of the reaction
(b) doubled on doubling the concentration of NaOH
(c) halved on reducing the concentration of NaOH to one half
(d) halved on reducing the concentration of RCl to one half

44. A zero order reaction is one:

(a) in which reactants do not react
(b) in which one of the reactants is in large excess
(c) whose rate is uniform and not affected by time
(d) whose rate increases with time

45. The rates of a certain reaction at different time intervals are as follows:

Time (second)	0	10	20
Rate	1.8×10^{-2}	1.82×10^{-2}	$1.79 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$

The reaction is of:

(a) zero order (b) first order
(c) second order (d) third order

46. For which of the following, the units of rate and rate constant of the reaction are identical?

(a) First order reaction (b) Zero order reaction
(c) Second order reaction (d) Fractional order reaction

47. The unit of rate constant for a zero order reaction is:
 (a) mol time^{-1} (b) L time^{-1}
 (c) $\text{mol L}^{-1} \text{time}^{-1}$ (d) $\text{L mol}^{-1} \text{time}^{-1}$
48. For a zero order reaction: (IIT JEE 1990)
 (a) $t_{1/2} \propto a$ (b) $t_{1/2} \propto \frac{1}{a}$ (c) $t_{1/2} \propto a^2$ (d) $t_{1/2} \propto \frac{1}{a^2}$
49. The rate of the first order reaction, $A \longrightarrow \text{Products}$, is $7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, when the concentration of A is 0.2 mol L^{-1} . The rate constant of the reaction is:
 (a) $2.5 \times 10^{-5} \text{ s}^{-1}$ (b) $8.0 \times 10^{-4} \text{ s}^{-1}$
 (c) $6.0 \times 10^{-4} \text{ s}^{-1}$ (d) $3.75 \times 10^{-3} \text{ s}^{-1}$
50. If the concentration is expressed in mole per litre and time in second, the units of rate constant for a first order reaction is:
 (a) $\text{mol L}^{-1} \text{ sec}^{-1}$ (b) sec^{-1}
 (c) mol L^{-1} (d) mol^{-1}
51. Which one of the following formula represents a first order reaction?
 (a) $k = \frac{2.303}{t} \log \frac{[A]_t}{[A]_0}$ (b) $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$
 (c) $k = \frac{2.303}{t} \log \frac{a}{a-x}$ (d) $k = \frac{2.303}{t} \log \frac{a}{x}$
52. 75% of a first order reaction was completed in 32 minute; when was 50% of the reaction completed?
 (a) 4 min (b) 8 min (c) 24 min (d) 16 min
53. The first order rate constant for the decomposition of N_2O_5 is $6.2 \times 10^{-4} \text{ s}^{-1}$. The half life period for this decomposition is: (IIT JEE 1991)
 (a) 1117.7 s (b) 1117 s (c) 223.4 s (d) 160.9 s
54. The half life period of a first order reaction is:
 (a) $\frac{0.693}{a}$ (b) $\frac{0.693}{k}$ (c) $\frac{0.693}{t}$ (d) $\frac{0.693}{ak}$
55. The specific rate constant of a first order reaction depends on:
 (a) concentration of the reactants
 (b) concentration of the products
 (c) time
 (d) temperature
56. For a given reaction of first order, it takes 20 minutes for the concentration to drop from 1.0 M to 0.6 M . The time required for the concentration to drop, from 0.6 M to 0.36 M will be:
 (a) more than 20 minutes (b) less than 20 minutes
 (c) equal to 20 minutes (d) infinity
57. For the first order reaction $A \longrightarrow \text{Product}$, the half life is 200 seconds. The rate constant of the reaction is:
 (a) $3.46 \times 10^{-2} \text{ s}^{-1}$ (b) $3.46 \times 10^{-3} \text{ s}^{-1}$
 (c) $3.46 \times 10^{-4} \text{ s}^{-1}$ (d) $3.46 \times 10^{-5} \text{ s}^{-1}$
58. The following data were obtained for the thermal decomposition of nitrous oxide on finely divided gold:

t (minutes)	0	20	40	60	80
Concentration of N_2O (mol L^{-1})	0.10	0.08	0.06	0.04	0.02

 The order of reaction is:
 (a) zero (b) 1 (c) 2 (d) 3
59. The following data are for the decomposition of ammonium nitrite in aqueous solution:

Vol. of N_2 in cm^3	6.25	9.0	11.42	13.65	35.02
Time (min)	10	15	20	25	∞

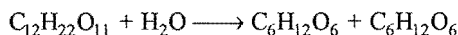
 The order of reaction is:
 (a) 3 (b) 2 (c) 1 (d) zero
 [Hint: $a = 35.02$, $(a-x) = 35.02 - V_t$
 Apply, $k = \frac{2.303}{t} \log \frac{35.02}{(35.02 - V_t)}$]
60. In the first order reaction, the concentration of reactant decreases from 1.0 M to 0.25 M in 20 minutes. The value of specific rate is:
 (a) 69.32 (b) 6.932 (c) 0.6932 (d) 0.06932
61. The half life period of a first order reaction is 10 minutes. The time required for the concentration of the reactant to change from 0.08 M to 0.02 M is: (IIT 1990)
 (a) 10 min (b) 20 min (c) 30 min (d) 40 min
62. The rate constant for the hydrolysis reaction of an ester by dilute acid is $0.6931 \times 10^{-3} \text{ s}^{-1}$. The time required to change the concentration of ester from 0.04 M to 0.01 M is:
 (a) 6931 sec (b) 4000 sec
 (c) 2000 sec (d) 1000 sec
63. The rate of a gaseous reaction is given by the expression $k[A][B]$. If the volume of reaction vessel is suddenly reduced to one-fourth of the initial volume, the reaction rate relative to the original rate will be: (IIT 1992)
 (a) 1/16 (b) 1/8 (c) 8 (d) 16
64. The velocity of a reaction is doubled for every 10°C rise in temperature. If the temperature is raised to 50°C , the reaction velocity increases by about:
 (a) 12 times (b) 16 times (c) 32 times (d) 50 times
65. If the rate expression for a reaction is $\frac{dx}{dt} = k[A]^{1/2}[B]^{3/2}$, the overall order of the reaction is: [CEE (Bihar) 1992]
 (a) 2 (b) 1/2 (c) 3/2 (d) 1
66. The rates of a certain reaction at different times are as follows:

Time (second)	0	10	20	30
Rate ($\text{mol L}^{-1} \text{ s}^{-1}$)	2.8×10^{-2}	2.78×10^{-2}	2.81×10^{-2}	2.79×10^{-2}

 The reaction is of:
 (a) third order (b) second order
 (c) first order (d) zero order
67. The second order rate constant is usually expressed as:
 (a) $\text{mol L}^{-1} \text{ s}^{-1}$ (b) $\text{mol}^{-1} \text{ L}^{-1} \text{ s}^{-1}$
 (c) $\text{mol}^{-1} \text{ L s}^{-1}$ (d) mol L s^{-1}
68. The hydrolysis of ethyl acetate is a reaction of:

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$
 (a) zero order (b) first order
 (c) second order (d) third order

69. The inversion of cane sugar is represented by,



It is a reaction of:

[PMT (MP) 1993]

- (a) second order (b) unimolecular
(c) pseudo-unimolecular (d) zero order
70. In a second order reaction, the time needed for the initial concentration of the reactant to reduce to half that value is:
(a) independent of the initial concentration
(b) proportional to the initial concentration
(c) inversely proportional to initial concentration
(d) proportional to the square of the initial concentration
71. Which of the following statements regarding molecularity of the reaction is wrong?
(a) It may be either whole number or fractional
(b) It is calculated from the reaction mechanism
(c) It depends on the rate determining step
(d) It is number of molecules of reactants taking part in a single step chemical reaction
72. For the reaction, $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, the reaction rate is:

$$rate = k[H_2][Br_2]^{1/2}$$

Which one of the following statements is true for this reaction?

- (a) The reaction is of second order
(b) The molecularity of the reaction is 3/2
(c) The unit of k is sec^{-1}
(d) The molecularity of the reaction is two
73. Molecularity of the reaction:
(a) is always a whole number
(b) is never a whole number
(c) can have a fractional value
(d) can be zero
74. For a single step reaction, $A + 2B \longrightarrow$ Products, the molecularity is:
(a) zero (b) three (c) two (d) one
75. The hypothetical reaction, $A_2 + B_2 \longrightarrow 2AB$, follows the following mechanism:

$$\begin{array}{ll} A_2 \longrightarrow A + A & \text{(fast)} \\ A + B_2 \longrightarrow AB + B & \text{(slow)} \\ A + B \longrightarrow AB & \text{(fast)} \end{array}$$

 The order of the overall reaction is: [PMT (Ph.) 1991]
 (a) zero (b) 1 (c) 2 (d) 3/2
76. The molecularity of a reaction is:
(a) same as its order
(b) different from order
(c) may be same or different as compared to order
(d) always zero
77. The chemical reaction, $2O_3 \longrightarrow 3O_2$ proceeds as follows:

$$\begin{array}{ll} O_3 \longrightarrow O_2 + O & \text{(fast)} \\ O + O_3 \longrightarrow 2O_2 & \text{(slow)} \end{array}$$

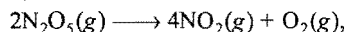
The rate law expression should be:

- (a) $r = k[O_3]^2$ (b) $r = k[O_3]^2[O_2]^{-1}$
(c) $r = k[O_3][O_2]$ (d) $r = [O_3][O_2]^2$

[Hint: $r = k'[O_3][O] = \frac{k'k''[O_3][O_3]}{[O_2]} = k[O_3]^2[O_2]^{-1}$]

78. Time required to decompose half of the substance for n th order reaction is inversely proportional to:
(a) a^{n+1} (b) a^{n-1}
(c) a^{n-2} (d) a^n
79. What is the order of the reaction which obeys the expression $t_{1/2} = \frac{1}{ka}$?
(a) Zero (b) Third
(c) First (d) Second
80. The order of reaction can be deduced from:
(a) experiment (b) chemical equation
(c) rate constant (d) thermochemical equations
81. The order of a reaction may be determined by:
(a) differential method (b) initial rate method
(c) graphical method (d) all of these
82. A graph between time (t) and the substance consumed at any time is found to be a straight line passing through the origin. This indicates that the reaction is of:
(a) second order (b) first order
(c) zero order (d) fractional order
83. A plot of $\log(a-x)$ against time ' t ' is a straight line. This indicates that the reaction is of:
(a) zero order (b) first order
(c) second order (d) third order
84. For the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, the value of rate of disappearance of N_2O_5 is given as $6.25 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as: [CBSE (PMT) 2010]
 (a) $6.25 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$ and $6.25 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$
 (b) $1.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$ and $3.125 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$
 (c) $6.25 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$ and $3.125 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$
 (d) $1.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$ and $6.25 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$
- [Hint: $\frac{-d[N_2O_5]}{dt} = +\frac{1}{2} \frac{d[N_2O_5]}{dt} = +2 \frac{d[O_2]}{dt}$]
 $\therefore \frac{d[N_2O_5]}{dt} = 2 \left[\frac{-d[N_2O_5]}{dt} \right] = 2 \times 6.25 \times 10^{-3}$
 $= 1.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$
 $\frac{d[O_2]}{dt} = \frac{1}{2} \left[\frac{-d[N_2O_5]}{dt} \right] = \frac{1}{2} \times 6.25 \times 10^{-3}$
 $= 3.125 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$]
85. The ratio of the time required for $\frac{3}{4}$ th of the reaction of first order to complete to that required for half of the reaction:
(a) 4 : 3 (b) 3 : 2
(c) 2 : 1 (d) 1 : 2
86. In pseudo-unimolecular reactions:
(a) one of the reactants is present in large excess
(b) both the reactants have same concentration
(c) both the reactants are present in low concentration
(d) one of the reactants is less reactive

87. The reaction,



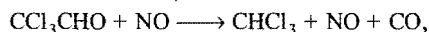
is first order with respect to N_2O_5 . Which of the following graph, would yield a straight line?

- (a) $\log(p_{\text{N}_2\text{O}_5})$ versus time with -ve slope
 (b) $(p_{\text{N}_2\text{O}_5})^{-1}$ versus time
 (c) $(p_{\text{N}_2\text{O}_5})$ versus time
 (d) $\log(p_{\text{N}_2\text{O}_5})$ versus time with +ve slope
88. Consider the following statements :
- (i) increase in concentration of reactant increases the rate of a zero order reaction
 (ii) rate constant k is equal to collision frequency ' A ' if $E_a = 0$
 (iii) rate constant k is equal to collision frequency A if $E_a = \infty$
 (iv) $\log_e k$ vs T is a straight line
 (v) $\log_e k$ vs $1/T$ is a straight line
- Correct statement are : [PMT (Kerala) 2010]
- (a) (i) and (iv) (b) (ii) and (v)
 (c) (iii) and (iv) (d) (ii) and (iii)
 (e) (i) and (v)

89. If we plot a graph between $\log k$ and $\frac{1}{T}$ by Arrhenius equation, the slope is: [EAMCET (Engg.) 2010]

(a) $-E_a/R$ (b) $+E_a/R$ (c) $-\frac{E_a}{2.303R}$ (d) $+\frac{E_a}{2.303R}$

90. The rate of the reaction,



is given by the equation, $\text{rate} = k[\text{CCl}_3\text{CHO}][\text{NO}]$. If concentration is expressed in mol / litre, the units of k are:

[PMT (MP) 1993]

- (a) $\text{mol}^{-2} \text{L}^2 \text{s}^{-1}$ (b) $\text{mol L}^{-1} \text{s}^{-1}$
 (c) $\text{L mol}^{-1} \text{s}^{-1}$ (d) s^{-1}
91. In a reaction, $2A + B \longrightarrow A_2B$, the reactant A will disappear at: [PMT (MP) 1993]
- (a) half the rate that B will decrease
 (b) twice the rate that B will decrease
 (c) the same rate that B will decrease
 (d) the same rate that A_2B will form
92. The rate of the reaction, $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$, at 25°C is $0.028 \text{ mol L}^{-1} \text{s}^{-1}$. The experimental rate is given by

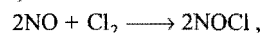
$$r = k[\text{NO}]^2[\text{O}_2]$$

If the initial concentrations of the reactants are $\text{O}_2 = 0.040 \text{ mol L}^{-1}$ and $\text{NO} = 0.01 \text{ mol L}^{-1}$, the rate constant of the reaction is:

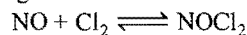
- (a) $7.0 \times 10^{-2} \text{ L mol}^{-1} \text{s}^{-1}$ (b) $7.0 \times 10^{-4} \text{ L}^2 \text{mol}^{-2} \text{s}^{-1}$
 (c) $7.0 \times 10^2 \text{ L}^2 \text{mol}^{-2} \text{s}^{-1}$ (d) $7.0 \times 10^3 \text{ L}^2 \text{mol}^{-2} \text{s}^{-1}$

[Hint: $0.028 = k[0.01]^2[0.040]$]

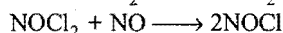
93. For the reaction,



the following mechanism has been proposed.



(fast)



(slow)

The rate law for the reaction is:

- (a) $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$ (b) $\text{rate} = k[\text{NO}][\text{Cl}_2]^2$
 (c) $\text{rate} = k[\text{NOCl}_2]$ (d) $\text{rate} = k[\text{NOCl}]^2$

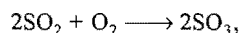
[Hint:

$$\text{rate} = k'[\text{NO}][\text{NOCl}_2] = k'K[\text{NO}][\text{NO}][\text{Cl}_2] = k[\text{NO}]^2[\text{Cl}_2]$$

94. The rate of a reaction can be increased in general by all the following factors except:

- (a) by increasing the temperature
 (b) using a suitable catalyst
 (c) by increasing the concentration of reactants
 (d) by an increase in activation energy

95. How will the rate
- $r = k[\text{SO}_2][\text{O}_2]$
- of reaction,



change if the volume of the reaction vessel is tripled?

- (a) It will be $\frac{1}{3}$ rd of its initial value
 (b) It will be 3 times of its initial value
 (c) It will be 9 times of its initial value
 (d) It will be $\frac{1}{9}$ th of its initial value

96. Radioactive disintegration is an example of:

- (a) zero order reaction (b) first order reaction
 (c) second order reaction (d) third order reaction

97. In the formation of sulphur trioxide by the contact process,
- $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$
- , the rate of reaction was measured as

$$-\frac{d[\text{O}_2]}{dt} = 3.0 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}.$$

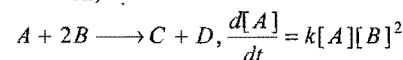
The rate of reaction expressed in terms of SO_3 will be:

- (a) $3.0 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$ (b) $6.0 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$
 (c) $1.5 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$ (d) $4.5 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$

98. The rate constant for a first order reaction is
- 6.909 min^{-1}
- . Therefore, the time required in minutes for the participation of 75% of the initial reactant is: [PET (J&K) 2009]

- (a) $\frac{2}{3} \log 2$ (b) $\frac{2}{3} \log 4$ (c) $\frac{3}{2} \log 2$ (d) $\frac{3}{2} \log 4$

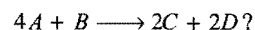
99. For the reaction,



the expression for $\frac{d[B]}{dt}$ will be:

- (a) $2k[A][B]^2$ (b) $\frac{1}{2} k[A][B]^2$
 (c) $k[A][B]^2$ (d) $k[A][B/2]^2$

100. Which of the following statements is not correct for the reaction,



- (a) The rate of appearance of C is one-half the rate of disappearance of B
 (b) The rate of disappearance of B is one-fourth of the rate of disappearance of A
 (c) The rate of formation of D is one-half of the rate of consumption of A
 (d) The rates of formation of C and D are equal

101. The overall rate of a reaction is governed by:
 (a) the rate of the fastest intermediate step
 (b) the sum total of the rates of all the intermediate steps
 (c) the average of the rates of all the intermediate steps
 (d) the rate of the slowest intermediate step
102. The rate constant of a reaction does not depend upon:
 (a) temperature
 (b) activation energy
 (c) catalyst
 (d) concentration of reactants and products
103. 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 : ($\log 2 = 0.301$) (AIEEE 2009)
 (a) 230.3 minutes (b) 23.03 minutes
 (c) 46.06 minutes (d) 460.6 minutes
104. For the chemical reaction $x \longrightarrow y$, it is found that the rate of reaction increases 2.25 times when the concentration of x is increased 1.5 times. What is the order of reaction?
 (a) One (b) Two (c) Three (d) Zero
 [Hint: $r = k[x]^a$ and $2.25r = k[1.5x]^a$
 So, $2.25 = (1.5)^a$ or $a = 2$]
105. The half life period of a reaction is constant for:
 (a) zero order (b) first order
 (c) second order (d) none of these
106. From different sets of data of $t_{1/2}$ at different initial concentrations say 'a' for a given reaction, the $[t_{1/2} \times a]$ is found to be constant. The order of reaction is:
 (a) zero (b) 1 (c) 2 (d) 3
107. Diazonium salt decomposes as

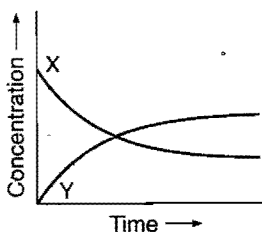
$$\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \longrightarrow \text{C}_6\text{H}_5\text{Cl} + \text{N}_2$$

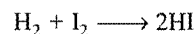
 At 0°C , the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is: (MLNR 1994)
 (a) a first order reaction
 (b) a second order reaction
 (c) independent of the initial concentration of the salt
 (d) a zero order reaction
108. For the reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$, under certain conditions of temperature and pressure of the reactants, the rate of formation of ammonia is 0.001 kg hr^{-1} . The rate of consumption of hydrogen under the same conditions is kg hr^{-1} .
 (a) 0.001 (b) 0.003 (c) 0.002 (d) 0.0015
109. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively. The value of rate constant at $T \longrightarrow \infty$ is: (IIT 1996)
 (a) $2.0 \times 10^{18} \text{ s}^{-1}$ (b) $6.0 \times 10^{14} \text{ s}^{-1}$
 (c) infinity (d) $3.6 \times 10^{30} \text{ s}^{-1}$
110. In the reaction

$$\text{BrO}_3^-(\text{aq.}) + 5\text{Br}^-(\text{aq.}) + 6\text{H}^+ \longrightarrow 3\text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$$

 The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following:
 [CBSE (PMT) 2009]

- (a) $\frac{d[\text{Br}_2]}{dt} = \frac{3}{5} \frac{d[\text{Br}^-]}{dt}$ (b) $\frac{d[\text{Br}_2]}{dt} = -\frac{3}{5} \frac{d[\text{Br}^-]}{dt}$
 (c) $\frac{d[\text{Br}_2]}{dt} = -\frac{5}{3} \frac{d[\text{Br}^-]}{dt}$ (d) $\frac{d[\text{Br}_2]}{dt} = +\frac{5}{3} \frac{d[\text{Br}^-]}{dt}$

111. Given that k is the rate constant for some order of any reaction at temp. T , then the value of $\lim_{T \rightarrow \infty} \log k$, (where, A is the Arrhenius constant) is:
 (a) $A / 2.303$ (b) A (c) $2.303A$ (d) $\log A$
112. The curve depicts the change in concentration of species X and Y as a function of time. The point of intersection of the two curves represents:

 (a) $t_{1/2}$
 (b) $t_{3/4}$
 (c) $t_{2/3}$
 (d) data insufficient to predict
113. In gaseous reactions, important for the understanding of the upper atmosphere H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and E_a is 77 kJ mol^{-1} ; then E_a for the bimolecular recombination of two OH radicals to form H_2O and O is:
 (a) 3 kJ mol^{-1} (b) 4 kJ mol^{-1}
 (c) 5 kJ mol^{-1} (d) 7 kJ mol^{-1}
114. From the following data, the activation energy for the reaction (cal/mol) is:



$T (\text{K})$	$1/T (\text{K}^{-1})$	$\log K$
769	1.3×10^{-3}	2.9
667	1.5×10^{-3}	1.1

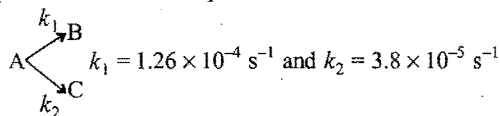
- (a) 4×10^4 (b) 2×10^4
 (c) 8×10^4 (d) 3×10^4
115. The hydrolysis of an ester was carried out separately with 0.05 N HCl and $0.05 \text{ N H}_2\text{SO}_4$. Which of the following will be true?
 (a) $k_{\text{HCl}} > k_{\text{H}_2\text{SO}_4}$ (b) $k_{\text{H}_2\text{SO}_4} > k_{\text{HCl}}$
 (c) $k_{\text{H}_2\text{SO}_4} = 2k_{\text{HCl}}$ (d) $k_{\text{H}_2\text{SO}_4} = k_{\text{HCl}}$
116. For an endothermic reaction, where, ΔH represents the enthalpy of the 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
117. In the following first order competing reactions;

$$\text{A} + \text{Reagent} \longrightarrow \text{Product}$$

$$\text{B} + \text{Reagent} \longrightarrow \text{Product}$$

 The ratio of k_1/k_2 if only 50% of B will have been reacted when 94% of A has been reacted is:
 (a) 4.06 (b) 3.06
 (c) 2.06 (d) 0.06
118. Two reactions $A \rightarrow \text{Products}$ and $B \rightarrow \text{Products}$, have rate constants k_A and k_B at temperature T and activation energies E_A and E_B respectively. If $k_A > k_B$ and $E_A < E_B$ and assuming that A for both the reactions is same, then:

- (a) at higher temperatures k_A will be greater than k_B
 (b) at lower temperatures k_A and k_B will be close to each other in magnitude
 (c) as temperature rises, k_A and k_B will be close to each other in magnitude
 (d) at lower temperature $k_B > k_A$
119. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as:



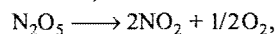
The percentage distributions of B and C are:

- (a) 80% B and 20% C (b) 76.83% B and 23.17% C
 (c) 90% B and 10% C (d) 60% B and 40% C
120. Inversion of a sugar follows first order rate equation which can be followed by noting the change in rotation of the plane of polarisation of light in a polarimeter. If r_∞ , r_t and r_0 are the rotations at $t = \infty$, $t = t$ and $t = 0$, then first order reaction can be written as:
- (a) $k = \frac{1}{t} \log_e \frac{r_t - r_\infty}{r_0 - r_\infty}$ (b) $k = \frac{1}{t} \log_e \frac{r_0 - r_\infty}{r_t - r_\infty}$
 (c) $k = \frac{1}{t} \log_e \frac{r_\infty - r_0}{r_\infty - r_t}$ (d) $k = \frac{1}{t} \log_e \frac{r_\infty - r_t}{r_\infty - r_0}$

121. Rate of a chemical reaction can be kept constant by:
 (BHU 1993)

- (a) stirring the compounds
 (b) keeping the temperature constant
 (c) both (a) and (b)
 (d) none of the above
122. The number of molecules of the reactants taking part in a single step of the reaction tells about: (AMU 1992)
 (a) molecularity of the reaction
 (b) mechanism of the reaction
 (c) order of reaction
 (d) all of the above
123. Number of moles of a substance present in 1 litre volume is known as: [PMT (MP) 1993]
 (a) activity (b) molar concentration
 (c) active mass (d) none of these
124. The inversion of cane sugar into glucose and fructose is:
 (a) I order (b) II order (c) III order (d) zero order
125. The unit of rate constant obeying the rate expression $r = k[A]^x[B]^{2/3}$ is:
 (a) $\text{mol}^{-2/3} \text{ litre}^{2/3} \text{ time}^{-1}$ (b) $\text{mol}^{2/3} \text{ litre}^{-2/3} \text{ time}^{-1}$
 (c) $\text{mol}^{-5/3} \text{ litre}^{5/3} \text{ time}^{-1}$ (d) none of these

126. For the reaction,



$$-\frac{d[\text{N}_2\text{O}_5]}{dt} = k_1[\text{N}_2\text{O}_5]$$

$$\frac{d[\text{NO}_2]}{dt} = k_2[\text{N}_2\text{O}_5]$$

$$\frac{d[\text{O}_2]}{dt} = k_3[\text{N}_2\text{O}_5]$$

The relation in between k_1 , k_2 and k_3 is:

- (a) $2k_1 = k_2 = 4k_3$ (b) $k_1 = k_2 = k_3$
 (c) $2k_1 = 4k_2 = k_3$ (d) none of these
127. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which one is true for the rates of the three reactions if the concentration of the reactant is greater than 1 M?
 (a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$
 (c) $r_1 < r_2 < r_3$ (d) All of these
128. In the Q.No. 127, if the concentration of the reactant is less than 1 M, then:
 (a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$
 (c) $r_1 < r_2 < r_3$ (d) all of these
129. In the Q.No. 127, if the concentration of the reactant is 1 M, then:
 (a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$
 (c) $r_1 < r_2 < r_3$ (d) all of these
130. For a first order reaction, $A \longrightarrow \text{Product}$, the rate of reaction at $[A] = 0.2 \text{ mol L}^{-1}$ is $1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$. The half life period for the reaction is: (IIT 1999)
 (a) 832 s (b) 440 s (c) 416 s (d) 14 s
131. The rate constant of a first order reaction, $A \longrightarrow \text{Products}$, is $60 \times 10^{-4} \text{ min}^{-1}$. Its rate at $[A] = 0.01 \text{ mol L}^{-1}$ would be: (IIT 1997)
 (a) $60 \times 10^{-6} \text{ mol L}^{-1} \text{ min}^{-1}$ (b) $36 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$
 (c) $60 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$ (d) $36 \times 10^{-1} \text{ mol L}^{-1} \text{ min}^{-1}$
132. For a first order reaction, the half life is independent of: (CBSE 1999)
 (a) initial concentration
 (b) cube root of initial concentration
 (c) first power of final concentration
 (d) square root of final concentration
133. Activation energy of a chemical reaction can be determined by: (CBSE 1998)
 (a) changing concentration of reactants
 (b) evaluating rate constant at standard temperature
 (c) evaluating rate constants at two different temperatures
 (d) evaluating velocities of reaction at two different temperatures

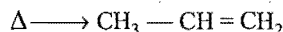
134. The experimental data for the reaction $2A + B_2 \rightarrow 2AB$, is:

Expt. No.	[A]	[B ₂]	Rate (mol s ⁻¹)
1.	0.50	0.50	1.6×10^{-4}
2.	0.50	1.00	3.2×10^{-4}
3.	1.0	1.00	3.2×10^{-4}

The rate equation for the above data is: (CBSE 1997)

- (a) rate = $k[B_2]^2$ (b) rate = $k[B_2]$
 (c) rate = $k[A]^2[B]^2$ (d) rate = $k[A]^2[B]$
135. For the reaction $A \rightarrow B$, the rate law is: rate = $k[A]$. Which of the following statements is incorrect? [PMT (Pb.) 1998]
 (a) The reaction follows first order kinetics
 (b) The $t_{1/2}$ of the reaction depends on initial concentration
 (c) k is constant for the reaction at a constant temperature
 (d) The rate law provides a simple way of predicting the concentration of reactants at any time after the start of the reaction

136. Cyclopropane rearranges to form propene:

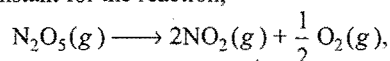


This follows first order kinetics. The rate constant is $2.714 \times 10^{-3} \text{ sec}^{-1}$. The initial concentration of cyclopropane is 0.29 M. What will be the concentration of cyclopropane after 100 sec?

[JEE (Orissa) 2009]

- (a) 0.035 M (b) 0.22 M
(c) 0.145 M (d) 0.0018 M

137. The rate constant for the reaction,



is $2.3 \times 10^{-2} \text{ sec}^{-1}$. Which equation given below describes the change of $[\text{N}_2\text{O}_5]$ with time $[\text{N}_2\text{O}_5]_0$ and $[\text{N}_2\text{O}_5]_t$ correspond to concentration of N_2O_5 initially and time 't'? (AIIMS 2004)

- (a) $[\text{N}_2\text{O}_5]_0 = [\text{N}_2\text{O}_5]_t e^{kt}$
(b) $\log_e \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = kt$
(c) $\log_{10} [\text{N}_2\text{O}_5]_t = \log_{10} [\text{N}_2\text{O}_5]_0 - kt$
(d) $[\text{N}_2\text{O}_5]_t = [\text{N}_2\text{O}_5]_0 + kt$

138. The reaction, $X \longrightarrow Y$ (Product) follows first order kinetics.

In 40 minutes, the concentration of X changes from 0.1 M to 0.025 M, then the rate of reaction when concentration of X is 0.01 M is:

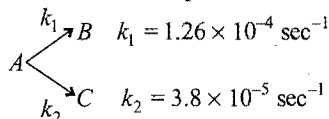
[IIT (S) 2004]

- (a) $1.73 \times 10^{-4} \text{ M/min}$ (b) $3.47 \times 10^{-5} \text{ M/min}$
(c) $3.47 \times 10^{-4} \text{ M/min}$ (d) $1.73 \times 10^{-5} \text{ M/min}$

139. In a first order reaction, the concentration of the 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:

- (a) 30 min (b) 15 min (c) 7.5 min (d) 60 min

140. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as;



The percentage distribution of B and C are:

[PMT (Kerala) 2004]

- (a) 75% B and 25% C (b) 80% B and 20% C
(c) 60% B and 40% C (d) 90% B and 10% C
(e) 76.83% B and 23.17% C

141. For a reaction $2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$, it is observed that $-\frac{d(\text{NH}_3)}{dt} = k_1(\text{NH}_3)$, $\frac{d(\text{N}_2)}{dt} = k_2(\text{NH}_3)$, $\frac{d(\text{H}_2)}{dt} = k_3(\text{NH}_3)$.

What is the relation between k_1 , k_2 and k_3 ?

- (a) $k_1 = k_2 = k_3$ (b) $3k_1 = 6k_2 = 2k_3$
(c) $2k_1 = 3k_2 = 6k_3$ (d) $6k_1 = 3k_2 = 2k_3$

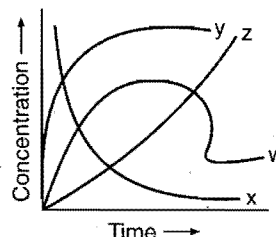
142. In Arrhenius equation $k = Ae^{-E_a/RT}$, factor $e^{-E_a/RT}$ is known as:

- (a) frequency factor (b) activation factor
(c) pre-exponential factor (d) Boltzmann factor

143. Unit of frequency factor (A) is:

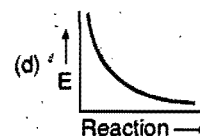
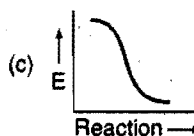
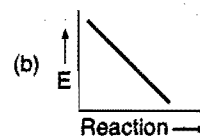
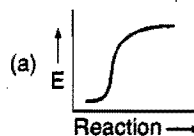
- (a) moles/lit (b) moles/lit/sec
(c) depends upon order (d) no unit

144. For the reaction $A + B \longrightarrow C + D$, the variation of the concentration of the products is given by the curve:



- (a) x (b) y (c) z (d) w

145. Which graph shows zero activation energy?



146. $E_{\text{Threshold}}$ can never be:

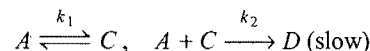
- (a) $> E_R$ (b) $> E_P$
(c) $< E_P$ (d) $> E_R$ as well as $> E_P$

147. A reaction takes place in three steps; the rate constants are k_1 , k_2 and k_3 . The overall rate constant $k = \frac{k_1 k_3}{k_2}$. If energies

of activation are 40, 30 and 20 kJ, the overall energy of activation is:

- (a) 10 (b) 15 (c) 30 (d) 60

148. For hypothetical reaction $A \longrightarrow B$ takes place according to



Rate law will be:

- (a) $k_2[A][C]$ (b) $k_1 k_2[A]$ (c) $k_1 k_2[A]^2$ (d) $k_1 k_2[A][C]$

149. If concentration of reactant is increased by 'm'; then k becomes:

- (a) $e^{k/m}$ (b) k (c) k/m (d) mk

150. $aA + bB \longrightarrow P$; $dx/dt = k[A]^a \cdot [B]^b$. If conc. of A is doubled, rate is doubled. If B is doubled, rate becomes four times. Which is correct?

- (a) $\frac{-d[A]}{dt} = \frac{-d[B]}{dt}$ (b) $\frac{-d[A]}{dt} = \frac{-2d[B]}{dt}$
(c) $\frac{-2d[A]}{dt} = \frac{-d[B]}{dt}$ (d) None of these

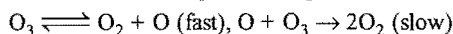
151. A drop of solution (volume 0.05 mL) contains 3×10^{-6} mole of H^+ . If the rate constant of disappearance of H^+ is $10^7 \text{ mol litre}^{-1} \text{ sec}^{-1}$, how long would it take for H^+ in the drop to disappear?

(a) $6 \times 10^{-8} \text{ sec}$ (b) $6 \times 10^{-9} \text{ sec}$
(c) $6 \times 10^{-10} \text{ sec}$ (d) $6 \times 10^{-12} \text{ sec}$

152. For the reaction, $H_2 + I_2 \xrightleftharpoons[k_2]{k_1} 2HI$. The rate law expression is:

(a) $-\frac{1}{2} \frac{d[HI]}{dt} = k_1[H_2][I_2]$
(b) $-\frac{1}{2} \frac{d[HI]}{dt} = \frac{k_1[HI]^2}{k_2[H_2][I_2]}$
(c) $-\frac{1}{2} \frac{d[HI]}{dt} = k_1[H_2][I_2] - k_2[HI]^2$
(d) $-\frac{1}{2} \frac{d[HI]}{dt} = k_1 k_2 [H_2][I_2]$

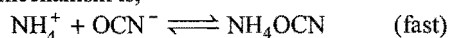
153. The chemical reaction, $2O_3 \rightarrow 3O_2$ proceeds as;



The rate law expression will be:

(a) rate = $k[O][O_3]$ (b) rate = $k[O_3]^2$
(c) rate = $k[O_3]^2[O_2]^{-1}$ (d) can't be determined

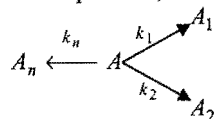
154. For the reaction $NH_4^+ + OCN^- \rightarrow NH_2CONH_2$, the probable mechanism is,



The rate law will be:

(a) rate = $k[NH_2CONH_2]$ (b) rate = $k[NH_4^+][OCN^-]$
(c) rate = $k[NH_4OCN]$ (d) none of these

155. For a 1st order decomposition,



overall k will be given by:

(a) $k = k_1 + k_2 + \dots + k_n$ (b) $k = (k_1 + k_2 + \dots + k_n)/n$
(c) $k = k_1 \times k_2 \times \dots \times k_n$ (d) none of these

156. For a reaction $A + 3B \rightarrow P$, Rate = $\frac{-d[A]}{dt}$, the expression for the rate of reaction in terms of change in the concentration of B , $\frac{-d[B]}{dt}$ will be:

(a) $k[A]^2[B]$ (b) $k[A]^2[3B]$
(c) $3k[A]^2[B]$ (d) $(1/3)k[A]^2[B]$

157. Which of the following statements is correct?

(a) Rate of reaction $\propto \frac{1}{E_a}$
(b) At lower temp., increase in temp. causes more change in the value of k
(c) Both (a) and (b) are correct
(d) None is correct

158. For $X \rightarrow Y$; $k = 10^{10} e^{-500/T}$, and for $W \rightarrow Z$; $k = 10^{12} e^{-1000/T}$ at what temperature ' T ' both reactions will have same value of k ?

(a) 500 K (b) 1500 K
(c) $\frac{4.606}{500} \text{ K}$ (d) $\frac{2.303}{5000} \text{ K}$

159. For a reversible reaction where the forward reaction is exothermic, which of the following statements is correct?

[JEE (WB) 2010]

(a) The backward reaction has higher activation energy than the forward reaction
(b) The backward and the forward processes have same activation energy
(c) The backward reaction has lower activation energy
(d) No activation energy is required at all since energy is liberated in the process

160. For the reaction, $A + 3B \rightarrow 2C + D$

which one of the following is not correct?

[EAMCET (Med.) 2010]

(a) Rate of disappearance of A = Rate of formation of D
(b) Rate of formation of $C = \frac{2}{3} \times$ Rate of disappearance of B
(c) Rate of formation of $D = \frac{1}{3} \times$ Rate of disappearance of B
(d) Rate of disappearance of $A = 2 \times$ Rate of formation of C

161. $2A \rightarrow B + C$, would be a zero order reaction when:

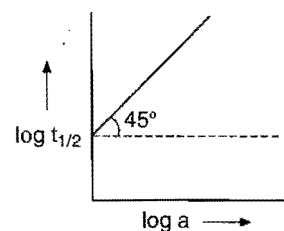
[CBSE (PMT) 2002]

(a) the rate of reaction is proportional to square of concentration of ' A '
(b) the rate of reaction is same at any concentration of ' A '
(c) the rate remains unchanged at any concentration of ' B ' and ' C '
(d) the rate of reaction doubles if concentration of ' B ' is increased to double

162. Units of rate constants for first and zero order reactions in terms of molarity M unit are respectively: (AIEEE 2002)

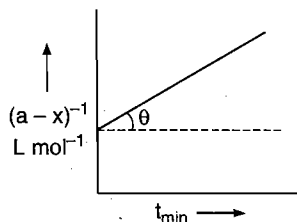
(a) $\text{sec}^{-1}, M \text{ sec}^{-1}$ (b) sec^{-1}, M
(c) $M \text{ sec}^{-1}, \text{sec}^{-1}$ (d) M, sec^{-1}

163. Following is the graph between $\log t_{1/2}$ and $\log a$ (a = initial concentration) for a given reaction at 27°C . Hence, order is:



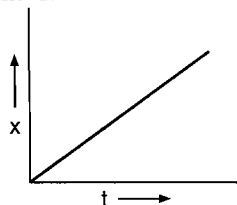
(a) 0 (b) 1 (c) 2 (d) 3

164. Following is the graph between $(a-x)^{-1}$ and time t for second order reaction. $\theta = \tan^{-1}(1/2)$; $OA = 2 \text{ L mol}^{-1}$, hence rate at the start of reaction will be:

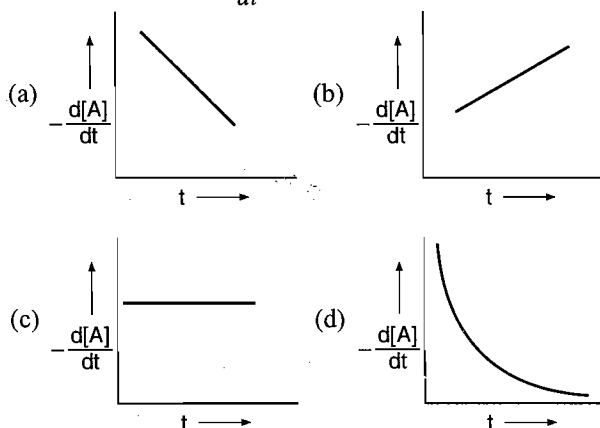


- (a) $1.25 \text{ L mol}^{-1} \text{ min}^{-1}$ (b) $0.5 \text{ mol L}^{-1} \text{ min}^{-1}$
(c) $0.125 \text{ mol L}^{-1} \text{ min}^{-1}$ (d) $1.25 \text{ mol L}^{-1} \text{ min}^{-1}$

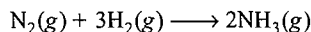
165. Graph between concentration of the product 'x' and time 't' for $A \rightarrow B$ is given ahead:



The graph between $-\frac{d[A]}{dt}$ and time will be of the type:



166. Consider the chemical reaction,

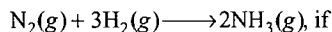


The rate of reaction can be expressed in terms of time derivative of concentration of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$ or $\text{NH}_3(\text{g})$. Identify the correct relationship amongst the rate expressions:

(IIT 2002)

- (a) $\text{rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$
(b) $\text{rate} = -\frac{d[\text{N}_2]}{dt} = -3 \frac{d[\text{H}_2]}{dt} = +2 \frac{d[\text{NH}_3]}{dt}$
(c) $\text{rate} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$
(d) $\text{rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$

167. For the reaction,



$\frac{d[\text{NH}_3]}{dt} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, the value of $-\frac{d[\text{H}_2]}{dt}$ would be:

[CBSE (PMT) 2009]

- (a) $1 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ (b) $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
(c) $4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ (d) $6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

168. Temperature dependent equation can be written as:

[JEE (Orissa) 2005]

- (a) $\ln k = \ln A - \frac{E_a}{RT}$ (b) $\ln k = \ln A + \frac{E_a}{RT}$
(c) $\ln k = \ln A - \frac{RT}{E_a}$ (d) all of these

169. If the rate of reaction $A \rightarrow B$ doubles on increasing the concentration of A by 4 times, the order of reaction is:

[CET (J&K) 2005]

- (a) 2 (b) 1 (c) 1/2 (d) 4

170. For the reaction: $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ if the concentration of NO_2 increases by $5.2 \times 10^{-3} \text{ M}$ in 100 sec, then the rate of reaction is:

[PET (Kerala) 2005]

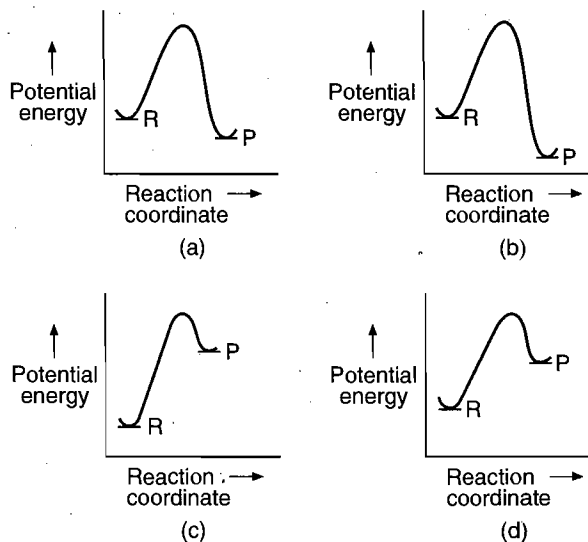
- (a) $1.3 \times 10^{-5} \text{ M s}^{-1}$ (b) $5 \times 10^{-4} \text{ M s}^{-1}$
(c) $7.6 \times 10^{-4} \text{ M s}^{-1}$ (d) $2 \times 10^{-3} \text{ M s}^{-1}$
(e) $2.5 \times 10^{-5} \text{ M s}^{-1}$

171. A first order reaction is 10% complete in 20 min. The time taken for 19% completion is:

[PET (Kerala) 2005]

- (a) 30 min (b) 40 min (c) 50 min (d) 38 min
(e) 45 min

172. An endothermic reaction with high activation energy for the forward reaction is given by the diagram: (AIIMS 2005)



173. For reaction $aA \rightarrow xP$, when $[A] = 2.2 \text{ m-M}$, the rate was found to be 2.4 m M s^{-1} . On reducing concentration of A to half, the rate changes to 0.6 m M s^{-1} . The order of reaction with respect to A is:

(AIIMS 2005)

- (a) 1.5 (b) 2.0 (c) 2.5 (d) 3.0

[Hint: $\text{Rate} = k[A]^a$

$$2.4 = k[2.2]^a \quad \dots (i)$$

$$0.6 = k[1.1]^a \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii), $a = 2 \therefore \text{order} = 2$

174. According to the law of mass action, rate of a chemical reaction is proportional to:

(AFMC 2005)

- (a) concentration of reactants
- (b) molar concentration of reactants
- (c) concentration of products
- (d) molar concentration of products

175. Consider the endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for backward and forward reactions, respectively. In general: (AIEEE 2005)

- (a) $E_b < E_f$
- (b) $E_b > E_f$
- (c) $E_b = E_f$
- (d) there is no definite relation between E_f and E_b

176. Which one of the following statements for order of reaction is not correct? [IIT (S) 2005]

- (a) Order can be determined experimentally
- (b) Order of reaction is equal to sum of powers of concentration terms in differential rate law
- (c) It is not affected by the stoichiometric coefficient of the reactants
- (d) Order cannot be fractional

177. The rate constant of a reaction is found to be $3 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$. The order of the reaction is: [CET (J&K) 2006]

- (a) zero (b) 1 (c) 2 (d) 1.5

[Hint: Unit of rate and rate constants are same for zero order reaction.]

178. In the first order reaction, the concentration of the reactants is reduced to 25% in one hour. The half life period of the reaction is: [UGET (Manipal) 2005]

- (a) 2 hrs (b) 4 hrs (c) 1/2 hr (d) 1/4 hr

$$[\text{Hint: } k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)]$$

$$k = \frac{2.303}{1} \log \left(\frac{100}{25} \right) = 2 \times 0.693$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2 \times 0.693} = \frac{1}{2} \text{ hr}]$$

179. A substance reacts with initial concentration of a mol dm^{-3} according to zero order kinetics. The time it takes for the completion of the reaction is: (k = rate constant)

[Hint: $k = \frac{dx}{dt}$; CET (Karnataka) 2009]

- (a) $\frac{k}{a}$ (b) $\frac{a}{2k}$ (c) $\frac{a}{k}$ (d) $\frac{2k}{a}$

(e) ka

[Hint: $x = k \times t$

$$t = \frac{x}{k}$$

Time for completion of reaction (when $x = a$), i.e., $t = \frac{a}{k}$]

180. Rate of a reaction can be expressed by Arrhenius equation as, $k = Ae^{-E/RT}$. In this equation, E represents: (AIEEE 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 reaction

181. The rate constant of a first order reaction at 27°C is 10^{-3} min^{-1} . The temperature coefficient of this reaction is 2. What is the rate constant (in min^{-1}) at 17°C for this reaction?

[ET 2006]

- (a) 10^{-3} (b) 5×10^{-4} (c) 2×10^{-3} (d) 10^{-2}

$$[\text{Hint: } \frac{k_{T_2}}{k_{T_1}} = (\mu)^{\Delta T/10}]$$

$$\frac{10^{-3}}{k_{T_1}} = (\mu)^{10/10} = 2$$

$$k_{T_1} = \frac{10^{-3}}{2} = 0.5 \times 10^{-3} \\ = 5 \times 10^{-4} \text{ min}^{-1}]$$

182. In a chemical reaction, two reactants take part. The rate of reaction is directly proportional to the concentration of one of them and inversely proportional to the concentration of the other. The order of the reaction is: [PMT (Raj.) 2006]

- (a) zero (b) 1 (c) 2 (d) 4

183. According to Arrhenius equation, the rate constant (k) is related to temperature (T) as: (VITEEE 2007)

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

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

$$(c) \ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} + \frac{1}{T_2} \right)$$

$$(d) \ln \left(\frac{k_2}{k_1} \right) = -\frac{E_a}{R} \left(\frac{1}{T_1} + \frac{1}{T_2} \right)$$

184. Consider a reaction $aG + bH \rightarrow \text{Products}$. When concentration of both the reactants G and H are doubled, the rate increases by eight times. However, when the concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of reaction is:

[IIT 2007]

- (a) 0 (b) 1 (c) 2 (d) 3

[Hint: Order with respect to ' G ' will be two and with respect to ' H ' the order will be one.

$$\text{Rate} = k[G]^2[H]^1$$

When concentration of both G and H are doubled, the rate will increase eight times.]

185. 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 plotting: [MS 2007]

- (a) $\log k$ vs T (b) $\log k$ vs $\frac{1}{T}$ (c) k vs T (d) k vs $\frac{1}{\log T}$

186. Consider the reaction, $2A + B \rightarrow \text{Products}$. 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: (AIEEE 2007)

- (a) s^{-1} (b) $\text{L mol}^{-1}\text{s}^{-1}$ (c) unitless (d) $\text{mol L}^{-1}\text{s}^{-1}$

[Hint: Concentration change in 'B' does not change half life, it means the reaction is first order with respect to B. When concentration of only 'A' is doubled, the rate of reaction becomes double, thus order with respect to A will also be one.]

Overall order of reaction = 2

unit of rate constant = $\text{L mol}^{-1}\text{s}^{-1}$

187. In a first order reaction $A \longrightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M then half life is:

[CBSE (Med) 2007]

- (a) $\frac{\log 2}{k}$ (b) $\frac{\log 2}{k\sqrt{0.5}}$ (c) $\frac{\ln 2}{k}$ (d) $\frac{0.693}{0.5k}$

188. For the first order reaction, half life is 14 sec, the time required for the initial concentration to reduce to 1/8 of its value is:

[CET (J&K) 2007]

- (a) $(14)^3$ sec (b) 28 sec (c) 42 sec (d) $(14)^2$ sec

189. 75% of a first order reaction was completed in 32 min, when was 50% of the reaction completed? [BHU (Mains) 2007]

- (a) 24 min (b) 16 min (c) 8 min (d) 48 min

190. For a zero order reaction,
 $A \longrightarrow P$

$t_{1/2}$ is: (k is rate constant) [BHU (Mains) 2007]

- (a) $\frac{[A]_0}{2k}$ (b) $\frac{\ln 2}{k}$ (c) $\frac{1}{k[A]_0}$ (d) $\frac{\ln 2}{[A]_0 k}$

191. The rate constants k_1 and k_2 for two different reactions are $10^{16} e^{-2000/T}$ and $10^{15} e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is:

[CBSE (PMT) 2008]

- (a) 2000 K (b) $\frac{1000}{2.303}$ K (c) 1000 K (d) $\frac{2000}{2.303}$ K

[Hint: $10^{15} e^{-1000/T} = 10^{16} e^{-2000/T}$

$$\frac{e^{-2000/T}}{e^{-1000/T}} = \frac{10^{15}}{10^{16}}$$

$$e^{-1000/T} = 10^{-1}$$

$$\log_e e^{-1000/T} = \log_e 10^{-1}$$

$$\frac{-1000}{T} = 2.303 \log_{10} 10^{-1}$$

$$= -2.303$$

$$T = \frac{1000}{2.303} \text{ K}$$

192. Under the same reaction conditions, initial concentration of $1.386 \text{ mol dm}^{-3}$ of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constant for first order (k_1)

and zero order (k_0) of the reaction is: (IIT 2008)

- (a) $0.5 \text{ mol}^{-1} \text{ dm}^3$ (b) $1 \text{ mol} \text{ dm}^{-3}$
(c) $1.5 \text{ mol} \text{ dm}^{-3}$ (d) $2 \text{ mol}^{-1} \text{ dm}^3$

[Hint: $t_{1/2} = \frac{0.693}{k_1}$

$$t_{1/2} = \frac{a_0}{2k_0}$$

$$40 = \frac{0.693}{k_1}$$

$$20 = \frac{1.386}{2k_0} = \frac{0.693}{k_0}$$

$$\frac{20}{40} = \frac{0.693/k_0}{0.693/k_1} = \frac{k_1}{k_0}$$

$$\frac{k_1}{k_0} = 0.5 \frac{\text{sec}^{-1}}{\text{mol dm}^{-3} \text{ sec}^{-1}} = 0.5 \text{ mol}^{-1} \text{ dm}^3$$

193. The decomposition of HI on the surface of gold is:

[Comed (Karnataka) 2008]

- (a) Pseudofirst order (b) zero order
(c) first order (d) second order

194. Consider following two reactions



k_1 and k_2 are expressed in terms of molarity (mol L^{-1}) and time (s^{-1}) as:

[BHU (Mains) 2008]

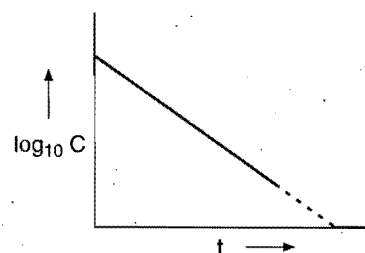
- (a) $\text{s}^{-1}, M \text{ s}^{-1} \text{ L}^{-1}$ (b) $M \text{ s}^{-1}, M \text{ s}^{-1}$
(c) $\text{s}^{-1}, M^{-1} \text{ s}^{-1}$ (d) $M \text{ s}^{-1}, \text{s}^{-1}$

195. If a plot of $\log_{10} C$ versus t gives a straight line for a given reaction, then the reaction is:

(VITEEE 2008)

- (a) zero order (b) first order (c) second order (d) third order

[Hint:



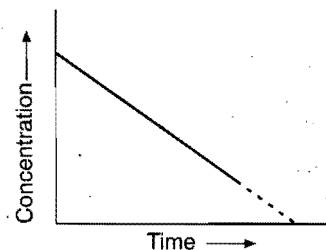
In first order reaction, $\log_{10} C$ when plotted against time 't' then we get straight line. Slope of the line $\left(\frac{2.303}{k}\right)$ gives the value of rate constant.]

196. For a zero order reaction the plot of concentration of reactant versus time is: (intercept refers to concentration axis)

[PET (Kerala) 2008]

- (a) linear with +ve slope and zero intercept
(b) linear with -ve slope and zero intercept
(c) linear with -ve slope and non zero intercept
(d) linear with +ve slope and non zero intercept
(e) a curve asymptotic to concentration axis

[Hint:



Linear with negative slope and non zero intercept.]

197. T_{50} of first order reaction is 10 min. Starting with 10 mol L^{-1} , rate after 20 min is:

(AIIMS 2008)

- (a) $0.0693 \text{ mol L}^{-1} \text{ min}^{-1}$
(b) $0.0693 \times 2.5 \text{ mol L}^{-1} \text{ min}^{-1}$

(c) $0.0693 \times 5 \text{ mol L}^{-1} \text{ min}^{-1}$

(d) $0.0693 \times 10 \text{ mol L}^{-1} \text{ min}^{-1}$

[Hint : Remaining concentration of reactant after 20 min

$$= \frac{1}{4} \times 10 = 2.5 \text{ mol L}^{-1}$$

Rate = $k \times [\text{Reactant}]$

$$= \frac{0.693}{t_{1/2}} \times [\text{Reactant}]$$

$$= \frac{0.693}{10} \times 2.5 = 0.0693 \times 2.5 \text{ mol L}^{-1} \text{ min}^{-1}]$$

198. For the decomposition of AB at 600 K, the following data were obtained

[AB] mol dm ⁻³	Rate of decomposition of AB in mol dm ⁻³ s ⁻¹
0.20	2.75×10^{-8}
0.40	11×10^{-8}
0.60	24.75×10^{-8}

The order of the decomposition of AB is :

[CET (Karnataka) 2009]

- (a) 0 (b) 1 (c) 2 (d) 1.5

199. For a reaction between A and B, the initial rate of reaction is measured for various initial concentrations of A and B. The data provided are: (DCE 2009)

Exp. No.	[A]	[B]	Initial reaction rate (mol L ⁻¹ s ⁻¹)
1.	0.2 M	0.3 M	5×10^{-5}
2.	0.2 M	0.1 M	5×10^{-5}
3.	0.4 M	0.05 M	7.5×10^{-5}

The overall order of the reaction is:

(DCE 2009)

- (a) one (1) (b) two (2)
(c) two and a half (2.5) (d) between 1 and 2

200. For a first order reaction $A \longrightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation:

$$\log k = -(2000) \frac{1}{T} + 6.0$$

The pre exponential factor A and the activation energy E_a respectively, are : (IIT 2009)

(a) $1 \times 10^6 \text{ s}^{-1}$ and 9.2 kJ mol^{-1}

(b) 6 s^{-1} and 16.6 kJ mol^{-1}

(c) $1 \times 10^6 \text{ s}^{-1}$ and 16.6 kJ mol^{-1}

(d) $1 \times 10^6 \text{ s}^{-1}$ and 38.3 kJ mol^{-1}

[Hint : $\log k = \log_{10} A - \frac{E_a}{2.303} \times \frac{1}{T}$

Comparing this equation with the given equation we get,

$$A = 10^6 \text{ s}^{-1}, E_a = 38.3 \text{ kJ mol}^{-1}]$$

201. The time for half-life period of a certain reaction, $A \rightarrow \text{Product}$ is 1 hour. When the initial concentration of the reactant 'A' is 2 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? (AIEEE 2010)

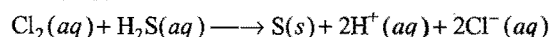
- (a) 0.25 h (b) 1 h (c) 4 h (d) 0.5 h

[Hint : $\frac{t_1}{t_2} = \left(\frac{a_2}{a_1} \right)^{n-1}$

$$\frac{1}{t_2} = \left(\frac{0.5}{2} \right)^{0-1}$$

$$t_2 = 0.25 \text{ h}]$$

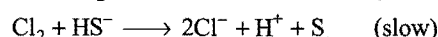
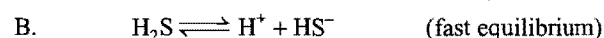
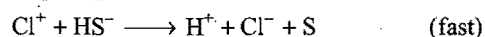
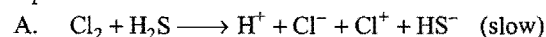
202. Consider the reaction :



The rate equation for this reaction is :

Rate = $k [\text{Cl}_2][\text{H}_2\text{S}]$

Which of these mechanisms is/are consistent with this rate equation?



(AIEEE 2010)

- (a) neither A nor B (b) A only
(c) B only (d) both A and B

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as 'Assertion' (A) and 'Reason' (R). While answering these questions you are required to choose any one of the following four options:

- (a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
 - (b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
 - (c) If (A) is correct but (R) is incorrect.
 - (d) If (A) is incorrect but (R) is correct.
1. (A) The rate of reaction sometimes does not depend on concentration.
(R) The order of reaction can be negative.
 2. (A) The rate of reaction increases generally by 2 to 3 times for every 10°C rise in temperature.
(R) Increase in temperature increases the collision frequency.
 3. (A) Hydrolysis of ethyl acetate in presence of acid is a reaction of first order whereas in presence of alkali, it is a reaction of second order.
(R) Acid acts as catalyst only whereas alkali acts as one of the reactant.
 4. (A) The molecularity of the reaction,

$$\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$$
 is 2.
(R) The order of this reaction is 3/2.
 5. (A) Positive catalysts lower the activation energy of the reaction whereas heat of reaction remains same.
(R) Heat of reaction is equal to the difference between activation energies for forward and the backward reactions.
 6. (A) Positive catalysts increase the rate of reaction.
(R) Catalysts decrease the value of ΔG° .
 7. (A) $k = Ae^{-E_a/RT}$, the Arrhenius equation represents the dependence of rate constant with temperature.
(R) Plot of $\log k$ against $1/T$ is linear and the activation energy can be calculated with this plot.
 8. (A) If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
(R) Lower the activation energy, faster is the reaction.
 9. (A) Order with respect to any reactant or product can be zero, positive, negative and fractional.
(R) Rate cannot decrease with increase in concentration of a reactant or product.
 10. (A) Formation of HI is a bimolecular reaction.
(R) Two molecules of reactants are involved in this reaction.
 11. (A) The order of the reaction,

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$
 is 2.
(R) The molecularity of this reaction is 2.
 12. (A) For: $aA + bB \longrightarrow \text{Product}$. The order of the reaction is equal to $(a + b)$.
(R) Rate of reaction $= k[A]^a[B]^b$.
 13. (A) The hydrolysis of methyl acetate by dil HCl is a pseudo first order reaction.
(R) HCl acts as a catalyst for the hydrolysis. (AIIMS 2007)
 14. (A) The order of a reaction can have fractional value.
(R) The order of a reaction cannot be written from balanced equation of a reaction. (AIIMS 2008)

Answers : OBJECTIVE QUESTIONS

- | | | | | | | | |
|----------|----------|----------|----------|----------|-------------|----------|----------|
| 1. (c) | 2. (d) | 3. (b) | 4. (b) | 5. (a) | 6. (a) | 7. (c) | 8. (d) |
| 9. (b) | 10. (c) | 11. (a) | 12. (d) | 13. (d) | 14. (d) | 15. (b) | 16. (a) |
| 17. (c) | 18. (c) | 19. (b) | 20. (b) | 21. (c) | 22. (a) | 23. (a) | 24. (d) |
| 25. (c) | 26. (d) | 27. (a) | 28. (b) | 29. (d) | 30. (d) | 31. (d) | 32. (b) |
| 33. (a) | 34. (a) | 35. (b) | 36. (c) | 37. (d) | 38. (d) | 39. (a) | 40. (c) |
| 41. (b) | 42. (b) | 43. (d) | 44. (c) | 45. (a) | 46. (b) | 47. (c) | 48. (a) |
| 49. (d) | 50. (b) | 51. (c) | 52. (d) | 53. (a) | 54. (b) | 55. (d) | 56. (c) |
| 57. (b) | 58. (a) | 59. (c) | 60. (d) | 61. (b) | 62. (c) | 63. (d) | 64. (c) |
| 65. (a) | 66. (d) | 67. (c) | 68. (b) | 69. (c) | 70. (c) | 71. (a) | 72. (d) |
| 73. (a) | 74. (b) | 75. (d) | 76. (c) | 77. (b) | 78. (b) | 79. (d) | 80. (a) |
| 81. (d) | 82. (c) | 83. (b) | 84. (b) | 85. (c) | 86. (a) | 87. (a) | 88. (b) |
| 89. (c) | 90. (c) | 91. (b) | 92. (d) | 93. (a) | 94. (d) | 95. (d) | 96. (b) |
| 97. (b) | 98. (a) | 99. (a) | 100. (a) | 101. (d) | 102. (d) | 103. (c) | 104. (b) |
| 105. (b) | 106. (c) | 107. (a) | 108. (d) | 109. (b) | 110. (b) | 111. (d) | 112. (a) |
| 113. (c) | 114. (a) | 115. (a) | 116. (c) | 117. (a) | 118. (a, c) | 119. (b) | 120. (b) |
| 121. (b) | 122. (a) | 123. (c) | 124. (a) | 125. (a) | 126. (a) | 127. (c) | 128. (b) |
| 129. (a) | 130. (a) | 131. (a) | 132. (a) | 133. (c) | 134. (b) | 135. (b) | 136. (b) |
| 137. (b) | 138. (c) | 139. (a) | 140. (e) | 141. (c) | 142. (d) | 143. (b) | 144. (b) |
| 145. (c) | 146. (c) | 147. (c) | 148. (c) | 149. (b) | 150. (c) | 151. (b) | 152. (c) |
| 153. (c) | 154. (b) | 155. (a) | 156. (c) | 157. (c) | 158. (c) | 159. (a) | 160. (d) |
| 161. (b) | 162. (a) | 163. (a) | 164. (c) | 165. (c) | 166. (a) | 167. (b) | 168. (a) |
| 169. (c) | 170. (a) | 171. (b) | 172. (c) | 173. (b) | 174. (b) | 175. (a) | 176. (d) |
| 177. (a) | 178. (c) | 179. (c) | 180. (b) | 181. (b) | 182. (a) | 183. (a) | 184. (d) |
| 185. (b) | 186. (b) | 187. (c) | 188. (c) | 189. (b) | 190. (a) | 191. (b) | 192. (a) |
| 193. (b) | 194. (d) | 195. (b) | 196. (c) | 197. (b) | 198. (c) | 199. (d) | 200. (d) |
| 201. (a) | 202. (b) | | | | | | |

Answers : ASSERTION-REASON TYPE QUESTIONS

- | | | | | | | | |
|--------|---------|---------|---------|---------|---------|--------|--------|
| 1. (b) | 2. (b) | 3. (a) | 4. (b) | 5. (b) | 6. (c) | 7. (a) | 8. (b) |
| 9. (c) | 10. (a) | 11. (d) | 12. (b) | 13. (b) | 14. (b) | | |

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS

for

IIT ASPIRANTS

- Which of the following is correct?
 - Molecularity of a reaction can be fractional
 - Zero order reaction never stops
 - A first order reaction must be homogeneous
 - The frequency factor 'A' in Arrhenius equation ($k = Ae^{-E_a/RT}$) increases with increase in temperature

- The rate constant of the reaction,

$$2\text{H}_2\text{O}_2(\text{aq.}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}),$$
 is $3 \times 10^{-3} \text{ min}^{-1}$.

At what concentration of H_2O_2 , the rate of the reaction will be $2 \times 10^{-4} \text{ M s}^{-1}$?

- $6.67 \times 10^{-3} \text{ M}$
- 2 M
- 4 M
- 0.08 M

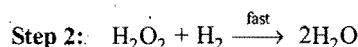
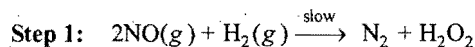
[Hint: Rate = $k [\text{H}_2\text{O}_2]^1$]

$$2 \times 10^{-4} = \frac{3 \times 10^{-3}}{60} \times [\text{H}_2\text{O}_2]$$

$$[\text{H}_2\text{O}_2] = 4 \text{ M}$$

- The mechanism of the reaction,

$$2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}),$$
 is:



- rate = $k [\text{NO}]^2 [\text{H}_2]^2$
- rate = $k [\text{H}_2\text{O}_2] [\text{H}_2]$
- on doubling the concentration of H_2 , keeping the concentration of NO constant, the rate will become double
- if the initial concentration of H_2 and NO is C_0 and after time 't' the concentration of N_2 is x, then

$$\text{Rate} = k(C_0 - 2x)^x$$

[Hint: Slowest step is rate determining]

$$\therefore \text{Rate} = k [\text{NO}]^2 [\text{H}_2]$$

$\therefore$ On doubling the concentration of H_2 without changing the concentration of NO, the rate will become double.]

- The rate law for a reaction between A and B is given by:

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

On doubling the concentration of A and halving the concentration of B, the ratio of new rate to the earlier rate of the reaction will be as:

- $n - m$
- 2^{n-m}
- $2^{1/(n+m)}$
- 2^{m-n}

- The reaction $A \xrightarrow{k} \text{Product}$, is zero order while the reaction $B \xrightarrow{k} \text{Product}$, is first order reaction. For what initial concentration of A are the half lives of the two reactions equal?

- $(\log_e 4) \text{ M}$
- 2 M
- $2 \log 2 \text{ M}$
- $\ln 2 \text{ M}$

[Hint: For zero order reaction,

$$x = kt$$

$$\therefore \frac{a}{2} = k \times t_{1/2}, \text{ i.e., } t_{1/2} = \frac{a}{2k} \quad \dots (i)$$

For first order reaction,

$$t_{1/2} = \frac{\log_e 2}{k} \quad \dots (ii)$$

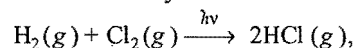
From eqs. (i) and (ii), $\frac{a}{2k} = \frac{\log_e 2}{k}$

$$a = \log_e 4 \text{ M}]$$

- Which of the following is pseudo-unimolecular reaction?

- $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{HOH} \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl}$
- $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
- $2\text{O}_3 \longrightarrow 3\text{O}_2$

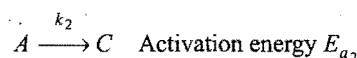
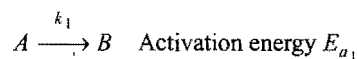
- The order and molecularity of the chain reaction,



are:

- 2, 0
- 0, 2
- 1, 1
- 3, 0

- A reactant (A) forms two products:



If $E_{a2} = 2E_{a1}$, then k_1 and k_2 will be related as:

- $k_2 = k_1 e^{E_{a1}/RT}$
- $k_2 = k_1 e^{E_{a2}/RT}$
- $k_1 = A k_2 e^{E_{a1}/RT}$
- $k_1 = 2k_2 e^{E_{a2}/RT}$

[Hint: $k_2 = A e^{-E_{a2}/RT}$

$$k_1 = A e^{-E_{a1}/RT}$$

$$\therefore \frac{k_2}{k_1} = e^{(-E_{a2} + E_{a1})/RT}$$

$$\frac{k_2}{k_1} = e^{E_{a1}/RT}$$

$$\text{Since, } E_{a2} = 2E_{a1}$$

$$k_2 = k_1 e^{E_{a1}/RT}]$$

- Collision theory is satisfactory for:

- first order reactions
- second order reactions
- bimolecular reactions
- zeroth order reactions

- Initial concentration of reactant for n th order reaction is 'a'. Which of the following relations is correct about $t_{1/2}$ of the reaction?

- $\ln t_{1/2} = \ln (\text{constant}) - (n-1) \log_e a$
- $\ln t_{1/2} = \ln n + \ln (\text{constant}) - \ln a$
- $t_{1/2} \ln n = \ln (\text{constant}) + \ln a_0$
- $\ln t_{1/2} = n \ln a_0$

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

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

$$\ln t_{1/2} = \ln k - (n-1) \log_e a$$

11. Half life of a reaction becomes half when initial concentrations of reactants are made double. The order of the reaction will be:

(a) 1 (b) 2 (c) 0 (d) 3

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

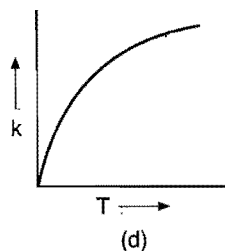
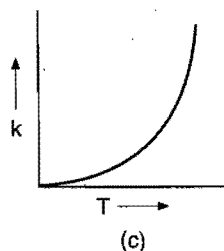
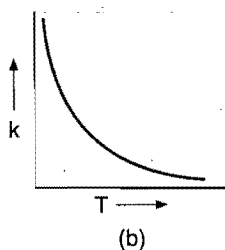
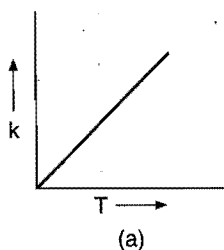
$$t_{1/2} \propto \frac{1}{a}$$

where, n = order of reaction for second order reaction.]

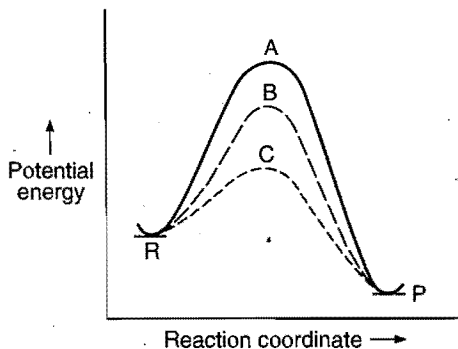
12. Arrhenius equation is:

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

Which of the following graphs represents the variation of rate constant k against temperature T ? (IIT 2010)

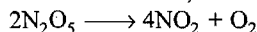


13. If a homogeneous catalytic reaction follows three alternative paths A, B and C, then which of the following indicates the relative ease with which the reaction moves?



(a) $A > B > C$ (b) $C > B > A$ (c) $A > C > B$ (d) $A = B = C$

14. The rate constant for the reaction,



is $3 \times 10^{-5} \text{ sec}^{-1}$. If the rate is $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$, then the concentration of N_2O_5 in mol litre^{-1} will be:

(a) 1.4 (b) 2.1 (c) 1.27 (d) 0.8

[Hint: Rate = $k[\text{N}_2\text{O}_5]$

$$2.4 \times 10^{-5} = 3 \times 10^{-5} [\text{N}_2\text{O}_5]$$

$$[\text{N}_2\text{O}_5] = 0.8 \text{ M}$$

15. Consider the following statements:

1. The rate of reaction is always proportional to the concentrations of reactants.
2. The order of an elementary chemical reaction step can be determined by examining its stoichiometry.
3. The first order reactions follow an exponential time course.

Of these statements:

- (a) 1, 2 and 3 are correct (b) 1 and 2 are correct
(c) 2 and 3 are correct (d) 1 and 3 are correct

[Hint: Statement (1) cannot be correct because the rate of zero order reactions does not depend on concentration of reactant.]

16. Two different first order reactions have rate constants k_1 and k_2 at T_1 ($k_1 > k_2$). If temperature is increased from T_1 to T_2 , then new constants become k_3 and k_4 respectively. Which among the following relations is correct?

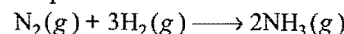
- (a) $k_1 > k_2 = k_3 = k_4$ (b) $k_1 < k_3$ and $k_2 < k_4$
(c) $k_1 = k_3 = k_4$ (d) $k_1 > k_2 > k_3 > k_4$

17. In the reaction, $A + B \longrightarrow C + D$, the rate $\left(\frac{dx}{dt}\right)$ when

plotted against time ' t ' gives a straight line parallel to time axis. The order and rate of reaction will be:

- (a) 1, $k+1$ (b) 0, k (c) 1, $k+1$ (d) $k, k+1$

18. In the Haber's process of ammonia manufacture,



the rate of appearance of NH_3 is:

$$\frac{d[\text{NH}_3]}{dt} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

The rates of the reaction expressed in terms of N_2 and H_2 will be:

	Rates in terms of H_2 ($\text{mol L}^{-1} \text{ sec}^{-1}$)	Rates in terms of N_2 ($\text{mol L}^{-1} \text{ sec}^{-1}$)
(a)	3×10^{-4}	2×10^{-4}
(b)	3×10^{-4}	1×10^{-4}
(c)	1×10^{-4}	3×10^{-4}
(d)	2×10^{-4}	2×10^{-4}

- (a) 3×10^{-4} 2×10^{-4}
(b) 3×10^{-4} 1×10^{-4}
(c) 1×10^{-4} 3×10^{-4}
(d) 2×10^{-4} 2×10^{-4}

[Hint: Rate = $+\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$

$$\frac{-d[\text{H}_2]}{dt} = \frac{3}{2} \times \frac{d[\text{NH}_3]}{dt} = \frac{3}{2} \times 2 \times 10^{-4} = 3 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\frac{-d[\text{N}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{1}{2} \times 2 \times 10^{-4} = 1 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}]$$

19. A reaction $A \longrightarrow B$, involves following mechanism:



The rate law of the reaction may be given as:

- (a) rate = $k_1[A]$ (b) rate = $k_2[B]$
 (c) rate = $k_3[C]$ (d) rate = $k_1k_2k_3[B][C]$

20. For a gaseous reaction, the following data were recorded:

Concentration in mol L ⁻¹	0.1	0.05	0.025	0.0125
Half life in sec	30	29.9	30.1	30

The order of reaction is:

- (a) second (b) first (c) zero (d) fractional

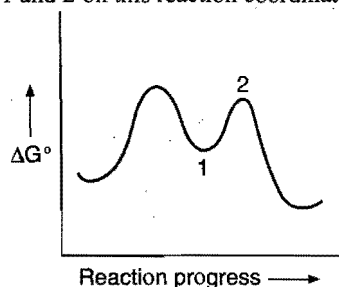
21. The half life of second order reaction is:

- (a) inversely proportional to the square of the initial concentration of the reactants
 (b) inversely proportional to the initial concentration of reactants
 (c) proportional to the initial concentration of reactants
 (d) independent of the initial concentration of reactants

[Hint: $t_{1/2} \propto \frac{1}{a^{n-1}}$; where, a = initial conc., n = order

$$t_{1/2} \text{ (second order)} \propto \frac{1}{a}]$$

22. What names apply to chemical species corresponding to locations 1 and 2 on this reaction coordinate diagram?



Location 1

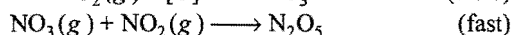
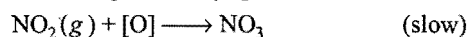
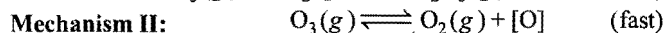
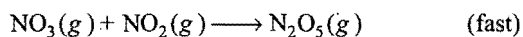
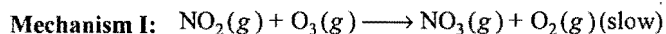
Location 2

- | | |
|---------------------------|-------------------|
| (a) Activated complex | Activated complex |
| (b) Reaction intermediate | Activated complex |
| (c) Activated complex | Intermediate |
| (d) Reaction intermediate | Intermediate |

23. Consider this reaction:

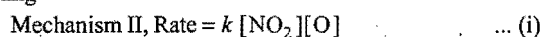


The reaction of nitrogen dioxide and ozone represented is first order in $\text{NO}_2(\text{g})$ and in $\text{O}_3(\text{g})$. Which of these possible reaction mechanisms is consistent with the rate law?



- (a) I only (b) II only
 (c) Both I and II (d) Neither I nor II

[Hint: Mechanism I, Rate = $k[\text{NO}_2][\text{O}_2]$. Slow step is rate determining

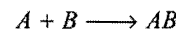


$$K = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]}, [\text{O}] = K \frac{[\text{O}_2]}{[\text{O}_3]}$$

From eq. (i), Rate = $kK[\text{NO}_2][\text{O}_2][\text{O}_2]^{-1}$

∴ Both mechanisms show that reaction is first order with respect to NO_2 and O_3 .

24. Use the experimental data in the table to determine the rate law for this reaction:



These data were obtained when the reaction was studied:

[A]	[B]	$\frac{\Delta[AB]}{\Delta t} \text{ mol L}^{-1} \text{ sec}^{-1}$
0.1 M	0.1 M	2×10^{-4}
0.2 M	0.1 M	2×10^{-4}
0.3 M	0.3 M	1.8×10^{-3}

What is the rate equation for the reaction?

- (a) Rate = $k[A][B]$ (b) Rate = $k[A]^2$
 (c) Rate = $k[B]$ (d) Rate = $k[B]^2$

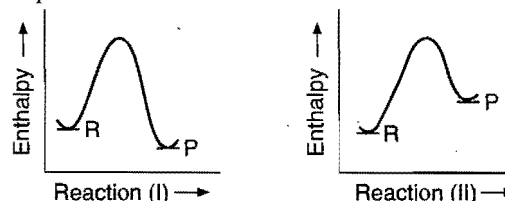
25. In which of the following reactions, the increase in the rate of reaction will be maximum?

E_a

Temperature rise

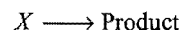
- | | |
|-----------------------------|-----------|
| (a) 40 kJ/mol | 200–210 K |
| (b) 90 kJ/mol | 300–320 K |
| (c) 80 kJ/mol | 300–310 K |
| (d) All will have same rate | |

26. Which of the reactions represented in these diagrams will show the greatest increase in rate for a given increase in temperature?



- (a) Reaction I forward (b) Reaction I reversed
 (c) Reaction II forward (d) Reaction II reversed

27. Which function of $[X]$, plotted against time, will give a straight line for a second order reaction?

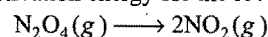


- (a) $[X]$ (b) $[X]^2$ (c) $\ln [X]$ (d) $\frac{1}{[X]}$

28. Decomposition of H_2O_2 is a first order reaction. A 16 volume solution of H_2O_2 of half life 30 min is present at start. When will the solution become one volume?

- (a) After 120 min (b) After 90 min
 (c) After 60 min (d) After 150 min

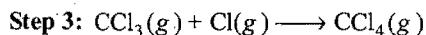
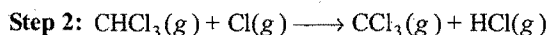
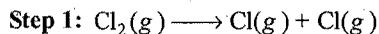
29. What is the activation energy for the reverse of this reaction?



Data for the given reaction is: $\Delta H = +54 \text{ kJ}$ and $E_a = +57.2 \text{ kJ}$:

- (a) -54 kJ (b) $+3.2 \text{ kJ}$ (c) $+60.2 \text{ kJ}$ (d) $+111.2 \text{ kJ}$

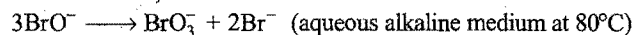
30. The reaction between chloroform, $\text{CHCl}_3(\text{g})$ and chlorine $\text{Cl}_2(\text{g})$ to form $\text{CCl}_4(\text{g})$ and $\text{HCl}(\text{g})$ is believed to occur by this series of steps:



If this reaction is first order in CHCl_3 and half order in Cl_2 , which statement about the relative rates of steps 1, 2 and 3 is correct?

- (a) Step 1 is the slowest
 (b) Steps 1 and 2 must both be slow
 (c) Step 2 must be slower than step 1
 (d) Step 3 must be the slowest

31. In the reaction,



the value of the rate constant in the rate law in terms of $-\frac{d}{dt}[\text{BrO}^-]$ is $0.056 \text{ L mol}^{-1} \text{ s}^{-1}$. What will be the rate

constant when the rate law is stated in terms of $\frac{d}{dt}[\text{BrO}_3^-]$?

- (a) $18.7 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ (b) $37.4 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$
 (c) $0.0187 \text{ L mol}^{-1} \text{ s}^{-1}$ (d) $18.7 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$

[Hint: $-\frac{1}{3} \frac{d[\text{BrO}^-]}{dt} = \frac{d[\text{BrO}_3^-]}{dt} = +\frac{1}{2} \frac{d[\text{Br}^-]}{dt}$]

Required rate constant $= \frac{1}{3} \times 0.056 \text{ L mol}^{-1} \text{ s}^{-1}$
 $= 0.0187 \text{ L mol}^{-1} \text{ s}^{-1}$

32. The dependence of the rate constant for a reaction on temperature is given by the equation $k = Ae^{-E_a/RT}$.

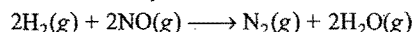
Under what conditions is the rate constant k the smallest?

- (a) High T and large E_a (b) High T and small E_a
 (c) Low T and large E_a (d) Low T and small E_a

33. The activation energy of a certain reaction is 87 kJ mol^{-1} . What is the ratio of the rate constants for this reaction when the temperature is decreased from 37°C to 15°C ?

- (a) 5/1 (b) 8.3/1 (c) 13/1 (d) 24/1

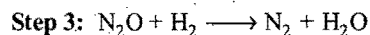
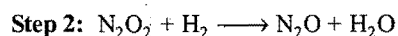
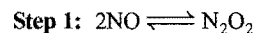
34. Consider this reaction,



The rate law for this reaction is:

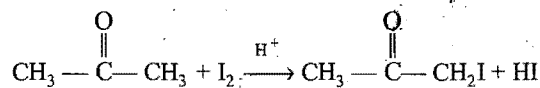
$\text{Rate} = k[\text{H}_2][\text{NO}]^2$

Under what conditions could these steps represent the mechanism?



- (a) These steps cannot be the mechanism under any circumstances
 (b) These steps could be the mechanism if step 1 is the slow step
 (c) These steps could be the mechanism if step 2 is the slow step
 (d) These steps could be the mechanism if step 3 is the slow step

35. Propanone reacts with iodine in acid medium according to the following equation:



These data were obtained when the reaction was studied:

$[\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3], M$	$[\text{I}_2], M$	$[\text{H}^+], M$	Relative rate
0.010	0.010	0.010	1
0.020	0.010	0.010	2
0.020	0.020	0.010	2
0.020	0.010	0.020	4

What is the rate equation for the reaction?

- (a) $\text{Rate} = k[\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3][\text{I}_2]$
 (b) $\text{Rate} = k[\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3]^2$
 (c) $\text{Rate} = k[\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3][\text{I}_2][\text{H}^+]$
 (d) $\text{Rate} = k[\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3][\text{H}^+]$

36. Arrhenius equation $k = Ae^{-E_a/RT}$

If the activation energy of the reaction is found to be equal to RT , then:

- (a) the rate of reaction does not depend upon initial concentration
 (b) the rate constant becomes about 37% of the Arrhenius constant A
 (c) the rate constant becomes equal to 73% of the Arrhenius constant A
 (d) the rate of the reaction becomes infinite or zero

37. At 25°C , the values of rate constant, activation energy and Arrhenius constant of a reaction are $3 \times 10^{-4} \text{ sec}^{-1}$, 129 kJ/mol and $2 \times 10^{15} \text{ sec}^{-1}$ respectively.

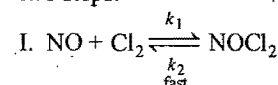
The value of rate constant as $T \rightarrow \infty$ is:

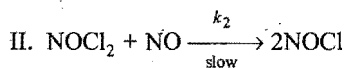
- (a) zero (b) 2×10^{15} (c) 3×10^{-4} (d) 6×10^{11}

38. The observed rate of a chemical reaction is substantially lower than the collision frequency. One or more of the following statements is/are true to account for this fact.

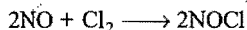
- A. the reactants do not have the required energy.
 B. the partners do not collide in the proper orientation
 C. collision complex exists for a very short time.
 D. collision frequency over estimates the number of effective collisions
 (ISAT 2010)
 (a) A, B and C (b) A, B and D
 (c) B, C and D (d) A, C and D

39. The reaction between NO and Cl_2 takes place in the following two steps:





The rate law of overall reaction,

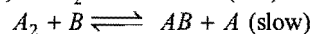
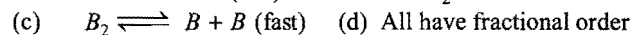
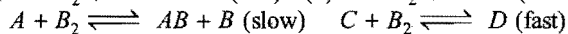
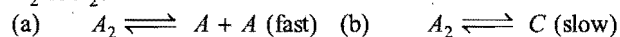


can be given by:

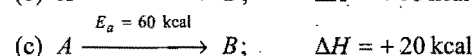
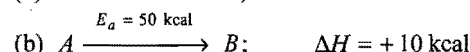
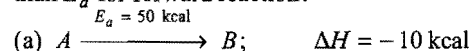
(a) rate = $k[\text{NO}]^2[\text{Cl}_2]$ (b) rate = $k[\text{NO}][\text{Cl}_2]$

(c) rate = $k[\text{NOCl}][\text{NO}]$ (d) rate = $k[\text{NO}][\text{Cl}_2]^2$

40. Which of the following reactions will have fractional order for A_2 or B_2 ?



41. In which of the following, E_a for backward reaction is greater than E_a for forward reaction?



(d) All of the above

[Hint: $\Delta H = (E_a)_f - (E_a)_b$

$(E_a)_b = (E_a)_f - \Delta H = 50 + 10 = 60 \text{ kcal}$]

42. For n th order reaction $t_{1/2}$ depends on ($n \neq 1$):

(a) initial concentration only

(b) 'n' only

(c) initial concentration and 'n' both

(d) sometimes 'n' and sometimes initial concentration

[Hint: Time for fractional change $\propto \frac{1}{a^{n-1}}$]

43. For a second order reaction, $2A \longrightarrow \text{Products}$, a plot of $\log t_{1/2}$ vs $\log a$ (where, a is initial concentration) will give an intercept equal to which one of the following? (SCRA 2007)

(a) $\frac{1}{k}$ (b) $\log \left(\frac{1}{2k} \right)$

(c) $\log \left(\frac{1}{k} \right)$ (d) $\log k$

[Hint: Kinetic equation for second order reaction is:

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

when $x = \frac{a}{2}, t = t_{1/2}$

$$\therefore t_{1/2} = \frac{1}{k} \times \frac{1}{a}$$

$$\log t_{1/2} = -\log k - \log a$$

44. For a reaction taking place in three steps, the rate constants are k_1, k_2 and k_3 . The overall rate constant $k = \frac{k_1 k_2}{k_3}$. If the energy of activation values for the first, second and third stages are

respectively 40, 50 and 60 kJ mol^{-1} , then the overall energy of activation in kJ mol^{-1} is: [PMT (Kerala) 2008]

- (a) 30 (b) 40 (c) 60 (d) 50
(e) 150

[Hint: $k = \frac{k_1 k_2}{k_3}$

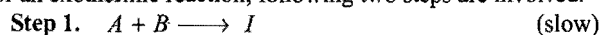
$$Ae^{-E/RT} = \frac{Ae^{-E_1/RT} \times Ae^{-E_2/RT}}{Ae^{-E_3/RT}}$$

$$e^{-E/RT} = e^{(-E_1 - E_2 + E_3)/RT}$$

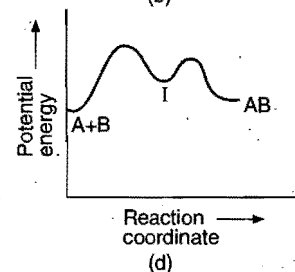
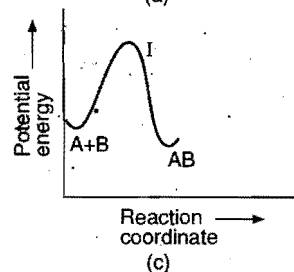
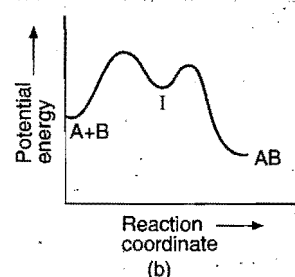
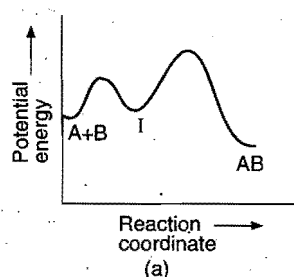
$$E = E_1 + E_2 - E_3$$

$$= 40 + 50 - 60 = 30 \text{ kJ mol}^{-1}$$

45. For an exothermic reaction, following two steps are involved.



Which of the following graphs correctly represent this reaction?



46. A reaction takes place in three steps with individual rate constant and activation energy,

	Rate constant	Activation energy
Step 1	k_1	$E_{a1} = 180 \text{ kJ/mol}$
Step 2	k_2	$E_{a2} = 80 \text{ kJ/mol}$
Step 3	k_3	$E_{a3} = 50 \text{ kJ/mol}$

overall rate constant, $k = \left(\frac{k_1 k_2}{k_3} \right)^{2/3}$

overall activation energy of the reaction will be:

- (a) 140 kJ/mol (b) 150 kJ/mol
(c) 130 kJ/mol (d) 120 kJ/mol

[Hint: $Ae^{-E_a/RT} = \left[\frac{Ae^{-E_{a1}/RT} Ae^{-E_{a2}/RT}}{Ae^{-E_{a3}/RT}} \right]^{2/3}$

$$E_a = \frac{2}{3} [E_{a1} + E_{a2} - E_{a3}]$$

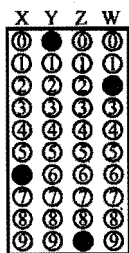
$$= \frac{2}{3} [180 + 80 - 50] = 140 \text{ kJ/mol}$$

Answers

- | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|------------|
| 1. (d) | 2. (c) | 3. (c) | 4. (b) | 5. (a) | 6. (b) | 7. (b) | 8. (a) |
| 9. (c) | 10. (a) | 11. (b) | 12. (c) | 13. (b) | 14. (d) | 15. (c) | 16. (b) |
| 17. (b) | 18. (b) | 19. (b) | 20. (b) | 21. (b) | 22. (b) | 23. (c) | 24. (d) |
| 25. (b) | 26. (b) | 27. (d) | 28. (a) | 29. (b) | 30. (c) | 31. (c) | 32. (c) |
| 33. (c) | 34. (c) | 35. (d) | 36. (b) | 37. (b) | 38. (a) | 39. (a) | 40. (a, c) |
| 41. (a) | 42. (c) | 43. (d) | 44. (a) | 45. (a) | 46. (a) | | |

Integer Answer TYPE QUESTIONS

This section contains 10 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



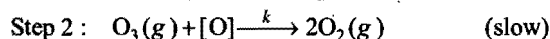
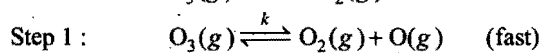
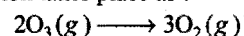
- In the reaction, $A \longrightarrow B$ when the initial concentration of reactant is halved, the half-life increases by a factor of eight, what will be the order of the reaction?
- Rate of a chemical reaction increases by 1024 times by 100°C rise in temperature; the temperature coefficient of the reaction will be:
- The rate of a reaction at 10 sec intervals are as follows :

Time (sec)	Rate ($\text{mol L}^{-1} \text{sec}^{-1}$)
0	4.8×10^{-2}
10	4.79×10^{-2}
20	4.78×10^{-2}
30	4.81×10^{-2}

What will be the order of the reaction?

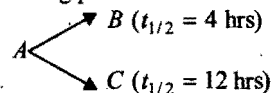
- How many times of the half-life will require to complete 75% of a reaction of first order?

- Ozone depletion takes place as :



order of the reaction will be :

- If the $t_{1/2}$ for a first order reaction is 0.4 min, the time of or 99.9% completion of the reaction is min.
- Consider following parallel first order reactions



The half-life for the decay of A ishrs.

- The half-life period of a first order reaction is 1 hr. What is the time in hour taken for 87.5% completion of the reaction?
- The half-life of a reaction is doubled when the initial concentration is doubled. The order of reaction is :
- For the reaction $A_2 + 2B \longrightarrow 2AB$, the following data were observed :

Exp. No.	$[A_2]$	$[B]$	Rate ($\text{mol L}^{-1} \text{s}^{-1}$)
1.	0.1	0.01	1.5×10^{-3}
2.	0.1	0.04	6.0×10^{-3}
3.	0.2	0.01	3.0×10^{-3}

The overall order of the reaction will be :

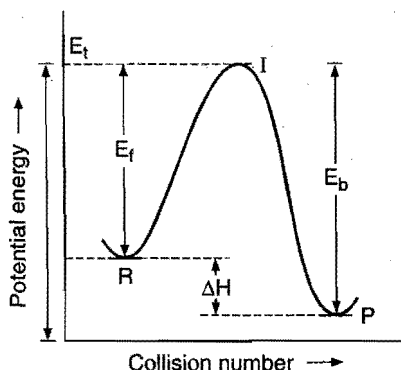
Answers

- | | | | | | | | |
|--------|---------|--------|--------|--------|--------|--------|--------|
| 1. (4) | 2. (2) | 3. (0) | 4. (2) | 5. (1) | 6. (4) | 7. (3) | 8. (3) |
| 9. (0) | 10. (2) | | | | | | |

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

A collision between reactant molecules must occur with a certain minimum energy before it is effective in yielding product molecules. This minimum energy is called activation energy E_a . Larger is the value of activation energy, smaller is the value of rate constant. Larger is the value of activation energy, greater is the effect of temperature rise on rate constant k .



E_f = Activation energy of forward reaction

E_b = Activation energy of backward reaction

$\Delta H = E_f - E_b$

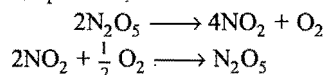
E_t = Threshold energy

Answer the following questions:

- If a reaction, $A + B \longrightarrow C$, is exothermic to the extent of 30 kJ/mol and the forward reaction has an activation energy of 249 kJ/mol, the activation energy for reverse reaction in kJ/mol is:

(a) 324 (b) 279 (c) 40 (d) 100

- For the following reaction at a particular temperature, according to the equations,



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) $\sqrt{E_1 E_2} = 1$

- In a hypothetical reaction, $A \rightarrow Y$, the activation energies for the forward and backward reactions are 15 and 9 kJ mol⁻¹ respectively. The potential energy of A is 10 kJ mol⁻¹. Which of the following is wrong?

(a) Threshold energy of the reaction is 25 kJ
 (b) The potential energy of B is 16 kJ
 (c) Heat of reaction is 6 kJ
 (d) The reaction is exothermic

- For two reactions, activation energies are E_{a1} and E_{a2} ; rate constants are k_1 and k_2 at the same temperature. If $k_1 > k_2$, then:

(a) $E_{a1} > E_{a2}$ (b) $E_{a1} = E_{a2}$ (c) $E_{a1} < E_{a2}$ (d) $E_{a1} \geq E_{a2}$

- The rate constant of a certain reaction is given by $k = Ae^{-E_a/RT}$ (where A = Arrhenius constant). Which factor should be lowered so that the rate of reaction may increase?

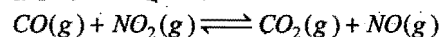
(a) T (b) Z (c) A (d) E_a

- The activation energies for forward and backward reactions in a chemical reaction are 30.5 and 45.4 kJ mol⁻¹ respectively. The reaction is:

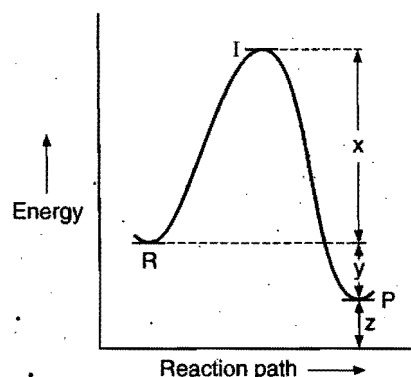
(a) exothermic
 (b) endothermic
 (c) neither exothermic nor endothermic
 (d) independent of temperature

Passage 2

The energy profile diagram for the reaction:



is given below:



Answer the following questions:

- The activation energy of the forward reaction is:
 (a) x (b) y (c) $x + y$ (d) $x - y$
- The activation energy of the backward reaction is:
 (a) x (b) y (c) $x + y$ (d) $x - y$
- The heat of the reaction is:
 (a) x (b) y (c) $x + y$ (d) $x - y$
- The threshold energy of the reaction is:
 (a) $x + y - z$ (b) $x - y + z$ (c) $x + y + z$ (d) $x - y - z$

Passage 3

Population growth of humans and bacteria follows first order growth kinetics. Suppose 50 bacteria are placed in a flask containing nutrients for the bacteria so that they can multiply. A study at 35°C gave the following results:

Time (minutes)	0	15	30	45	60
Number of bacteria	100	200	400	800	1600

Answer the following questions:

- The rate constant for the first order growth of bacteria can be calculated using:

(a) $k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$ (b) $k = -\frac{2.303}{t} \log \left(\frac{a}{a+x} \right)$

- (c) $k = \frac{0.693}{t}$ (d) $k = \frac{x}{t}$
2. Unit of rate constant for first order growth is:
 (a) min^{-1} (b) min^{-2} (c) min^{-3} (d) unitless
3. The rate constant for the reaction is:
 (a) 0.0462 min^{-1} (b) 0.462 min^{-1}
 (c) 4.62 min^{-1} (d) 46.2 min^{-1}
4. The rate of growth initially is:
 (a) 4.62 bacteria per min (b) 23.1 bacteria per min
 (c) 23.1 bacteria per sec (d) 0.231 bacteria per sec
5. At what time, there will be 6400 bacteria in the flask?
 (a) 150 min (b) 90 min (c) 160 min (d) 120 min

● Passage 4

Order of reaction is an experimentally determined quantity. It may be zero, positive, negative and fractional. The kinetic equation of n th order reaction is:

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

Half life of n th order reaction depends on initial concentration according to the following relation:

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

Unit of the rate constant varies with the order but general relation for unit of n th order reaction is:

$$\text{Unit of } k = \left[\frac{1}{\text{conc.}} \right]^{n-1} \times \text{time}^{-1}$$

The differential rate law for n th order reaction may be given as:

$$\frac{dx}{dt} = k[A]^n$$

where, A denotes the reactant.

Answer the following questions:

1. The unit of rate and rate constant are same for a:
 (a) zero order reaction (b) first order reaction
 (c) second order reaction (d) half order reaction
2. The rate constant for zero order reaction is:
 (a) $k = \frac{C_0}{2t}$ (b) $k = \frac{C_0 - C_t}{t}$
 (c) $k = \ln \frac{C_0 - C_t}{2t}$ (d) $k = \frac{C_0}{C_t}$

where C_0 and C_t are concentrations of reactants at respective times.

3. The half life for a zero order reaction equals to:

(a) $\frac{1}{2} \frac{k}{a^2}$ (b) $\frac{a^2}{2k}$ (c) $\frac{2k}{a}$ (d) $\frac{a}{2k}$

4. For a reaction:



in an aqueous medium, the rate of the reaction is given by

$$\frac{d[\text{IO}^-]}{dt} = k \frac{[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}$$

The overall order of the reaction is:

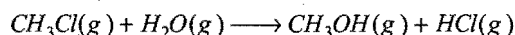
(a) -1 (b) 1 (c) zero (d) 2

5. In a chemical reaction $A \longrightarrow B$, it is found that the rate of the reaction doubles when the concentration of A is increased four times. The order of the reaction with respect to A is:

(a) 0 (b) 1/2 (c) 1 (d) 2

● Passage 5

Consider the reaction represented by the equation:



These kinetic data were obtained for the given reaction concentrations:

Initial conc. (M)		Initial rate of disappearance of CH_3Cl M s^{-1}
$[\text{CH}_3\text{Cl}]$	$[\text{H}_2\text{O}]$	
0.2	0.2	1
0.4	0.2	2
0.4	0.4	8

Answer the following questions based on these data:

1. The rate law for the reaction will be:
 (a) $r = k[\text{CH}_3\text{Cl}][\text{H}_2\text{O}]$ (b) $r = k[\text{CH}_3\text{Cl}]^2[\text{H}_2\text{O}]$
 (c) $r = k[\text{CH}_3\text{Cl}][\text{H}_2\text{O}]^2$ (d) $r = k[\text{CH}_3\text{Cl}]^2[\text{H}_2\text{O}]^4$
2. Order with respect to $[\text{CH}_3\text{Cl}]$ will be:
 (a) 0 (b) 1 (c) 2 (d) 3
3. Overall order of the reaction will be:
 (a) 0 (b) 1 (c) 2 (d) 3
4. Unit of rate constant will be:
 (a) sec^{-1} (b) $\text{litre}^2 \text{ mol}^{-2} \text{ sec}^{-1}$
 (c) $\text{litre mol}^{-1} \text{ sec}^{-1}$ (d) $\text{mol litre}^{-1} \text{ sec}^{-1}$
5. If H_2O is taken in large excess, the order of the reaction will be:
 (a) 1 (b) 0 (c) 3 (d) 2

Answers

Passage 1.	1. (d)	2. (a)	3. (d)	4. (c)	5. (d)	6. (a)
Passage 2.	1. (a)	2. (c)	3. (b)	4. (c)		
Passage 3.	1. (b)	2. (a)	3. (a)	4. (a)	5. (b)	
Passage 4.	1. (a)	2. (b)	3. (d)	4. (b)	5. (b)	
Passage 5.	1. (c)	2. (b)	3. (d)	4. (b)	5. (a)	

SELF ASSESSMENT

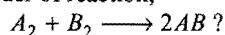
ASSIGNMENT NO. 8

SECTION-I

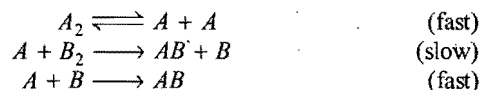
Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. What is the order of reaction,



Mechanism:



- (a) 2 (b) 1 (c) $\frac{3}{2}$ (d) $\frac{1}{2}$
2. For a gaseous reaction, $A(g) \longrightarrow \text{Product}$, which one of the

following is correct relation among $\frac{dP}{dt}$, $\frac{dn}{dt}$ and $\frac{dc}{dt}$?

($\frac{dP}{dt}$ = Rate of reaction in atm sec⁻¹; $\frac{dc}{dt}$ = Rate of reaction in

molarity sec⁻¹; $\frac{dn}{dt}$ = Rate of reaction in mol sec⁻¹)

- (a) $\frac{dc}{dt} = \frac{dn}{dt} = -\frac{dP}{dt}$ (b) $-\frac{dc}{dt} = -\frac{1}{V} \frac{dn}{dt} = -\frac{dP}{dt}$
 (c) $\frac{dc}{dt} = \frac{V}{RT} \frac{dn}{dt} = \frac{dP}{dt}$ (d) None of these

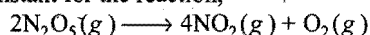
3. The rate law for a reaction between the substances A and B is given by the, rate = $k[A]^n[B]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as:

- (a) $\frac{1}{2^{m+n}}$ (b) $m+n$ (c) $n-m$ (d) $2^{(n-m)}$

4. A substance having initial concentration 'a' reacts according to zero order kinetics. What will be the time for the reaction to go to completion?

- (a) $\frac{a}{k}$ (b) $\frac{k}{a}$ (c) $\frac{a}{2k}$ (d) $\frac{2k}{a}$

5. The rate constant for the reaction,



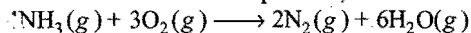
is $3 \times 10^{-5} \text{ sec}^{-1}$. If the rate of reaction is $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$, then the concentration of N_2O_5 in mol litre^{-1} is:

- (a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8

6. Half life of a reaction is inversely proportional to cube of initial concentration. The order of reaction is:

- (a) 4 (b) 3 (c) 5 (d) 2

7. The oxidation of ammonia takes place as,



if the rate of formation of N_2 is 0.7 M/s , determine the rate at which NH_3 is consumed:

- (a) $1.4 \text{ mol L}^{-1} \text{ s}^{-1}$ (b) $0.7 \text{ mol L}^{-1} \text{ s}^{-1}$
 (c) $1.5 \text{ mol L}^{-1} \text{ s}^{-1}$ (d) none of these

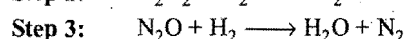
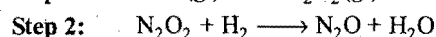
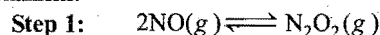
8. Consider the reaction:



The rate law for this reaction is:

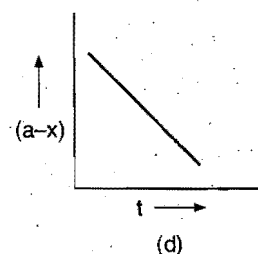
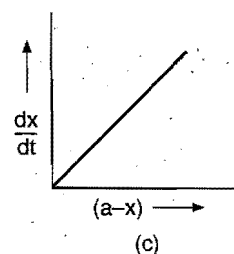
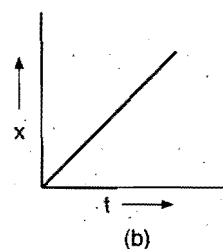
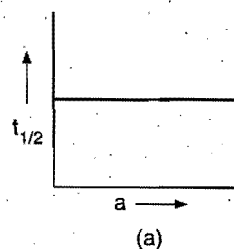
$$\text{Rate} = k[H_2][NO]^2$$

Under what conditions could these steps represent the mechanism?



- (a) These steps can never satisfy the rate law
 (b) Step 1 should be the slowest step
 (c) Step 2 should be the slowest step
 (d) Step 3 should be the slowest step

9. Which of the following is not for zero order reaction?



10. I. $E_a = 15 \text{ kJ mol}^{-1}$; $\Delta H = -70 \text{ kJ mol}^{-1}$
 II. $E_a = 30 \text{ kJ mol}^{-1}$; $\Delta H = -15 \text{ kJ mol}^{-1}$
 III. $E_a = 60 \text{ kJ mol}^{-1}$; $\Delta H = +20 \text{ kJ mol}^{-1}$

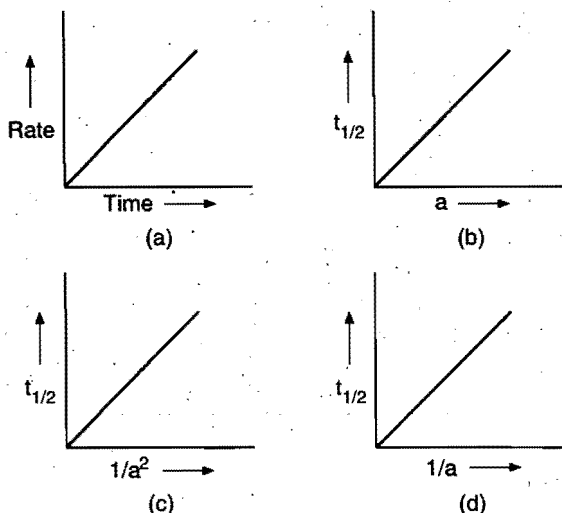
If above reactions are at same frequency factor then fastest and slowest reactions are:

- (a) III is fastest, II is slowest
 (b) I is fastest, III is slowest
 (c) II is fastest, III is slowest
 (d) III is fastest, I is slowest

SECTION-II

Multiple Answers Type Objective Questions

11. Which of the following graphs are correct?



Here 'a' denotes initial concentration of reactants.

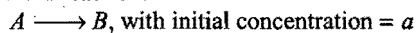
12. Arrhenius equation may be given as:

- (a) $\ln \frac{A}{k} = \frac{E_a}{RT}$ (b) $\log A = \log k + \frac{E_a}{2.303 RT}$
 (c) $\log \left[\frac{-E_a}{RT} \right] = \frac{k}{a}$ (d) $\frac{d \ln k}{dt} = \frac{E_a}{RT}$

13. Which of the following is/are correct for second order reaction?

- (a) $t_{1/2}$ is inversely proportional to initial concentration
 (b) $k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right]$
 (c) $k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$
 (d) $k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$

14. For a 1st order reaction:



- (a) $t_{1/2} = \frac{k}{a}$ (b) $t_{3/4} = 2t_{1/2}$
 (c) $t_{1/2} = \frac{0.693}{k}$ (d) $t_{1/2} = k \times 0.693$

15. Select the correct statement for Arrhenius equation

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

- (a) 'A' may be termed as the rate constant at very high temperature
 (b) 'A' may be termed as the rate constant at zero activation energy
 (c) E_a is the activation energy of reaction
 (d) k is rate of reaction at zero concentration

SECTION-III

Assertion-Reason Type Questions

This section contains 3 questions. Each question of this section contains **Statement-1** (Assertion) and **Statement-2**

(Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

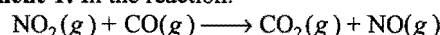
- (a) Statement-1 is true; Statement-2 is true; Statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; Statement-2 is true; Statement-2 is not a correct explanation for Statement-1.
 (c) Statement-1 is true; Statement-2 is false.
 (d) Statement-1 is false; Statement-2 is true.

16. **Statement-1:** If temperature does not affect the rate of reaction, $E_a = 0$.

Because

Statement-2: Lesser is the activation energy, slower is the rate.

17. **Statement-1:** In the reaction:



$$\text{Rate} = k [\text{NO}_2]^2$$

The rate of reaction does not depend on the concentration of CO.

Because

Statement-2: Carbon monoxide is involved in fast step.

18. **Statement-1:** The reciprocal of time in which 66% of the reactant is converted to product is equal to the rate constant of first order reaction.

Because

Statement-2: The rate constant for first order reaction depends on initial concentration of reactants.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q); and (d-s), then correct bubbled 4×4 matrix should be as follows:

	p	q	r	s
a	☒ p	☐ q	☐ r	☒ s
b	☐ p	☒ q	☒ r	☐ s
c	☒ p	☒ q	☐ r	☐ s
d	☐ p	☐ q	☐ r	☒ s

19. Match the Column-I with Column-II:

Column-I

- (a) Rate of reaction
 (b) Rate constant
 (c) Order of reaction
 (d) Molecularity of reaction

Column-II

- (p) May be fractional
 (q) Whole number
 (r) Independent of temperature
 (s) Increase with temperature

20. Match the Column-I with Column-II:

Column-I
(Order of reaction)

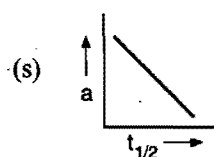
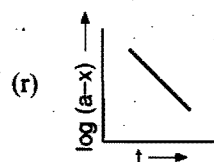
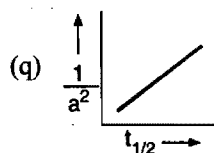
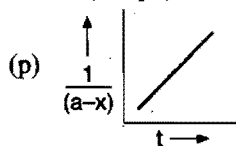
(a) First order

(b) Second order

(c) Third order

(d) Zero order

Column-II
(Graph)



21. Match the Column-I with Column-II:

Column-I

- (a) First order
(b) Pseudo first order
(c) Third order
(d) Second order

Column-II

- (p) Unit of $k = \text{sec}^{-1}$
(q) Unit of $k = \text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$
(r) $t_{1/2} \propto 1/a^2$
(s) $t_{1/2} \propto \frac{1}{a}$

Answers

- | | | | | | | | |
|---------|---------|---------------------------------|-----------------------------|-------------------------------|-----------|-------------|---------|
| 1. (c) | 2. (b) | 3. (d) | 4. (a) | 5. (d) | 6. (a) | 7. (a) | 8. (c) |
| 9. (c) | 10. (b) | 11. (b,c) | 12. (a,b) | 13. (a,b) | 14. (b,c) | 15. (a,b,c) | 16. (c) |
| 17. (a) | 18. (c) | 19. (a-s) (b-s) (c-p,r) (d-q,r) | 20. (a-r) (b-p) (c-q) (d-s) | 21. (a-p) (b-p) (c-q,r) (d-s) | | | |