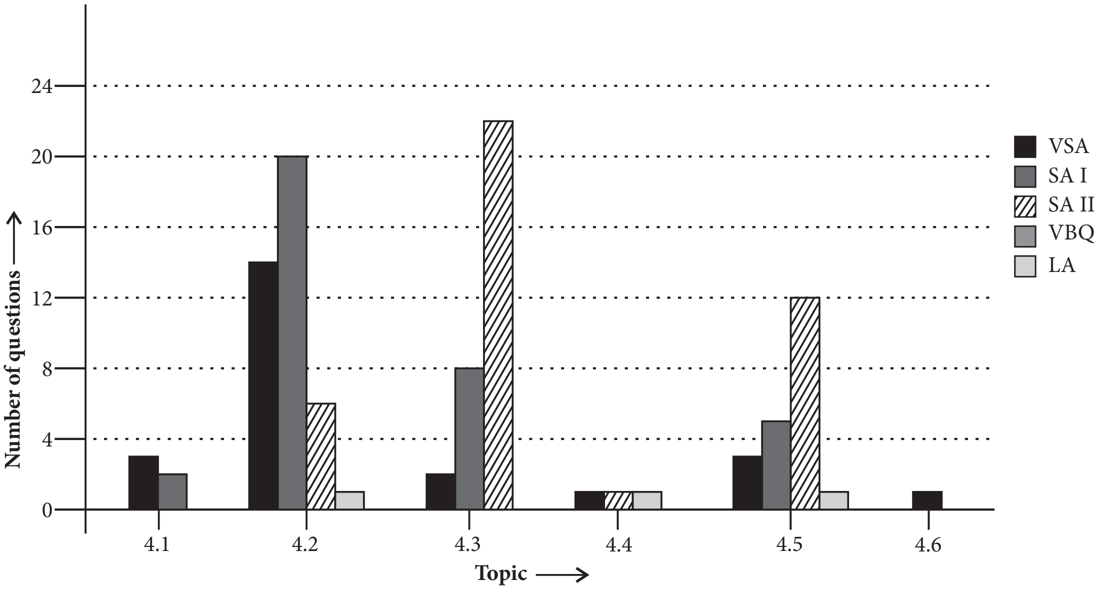
# 04

# Chemical Kinetics

4.1 Rate of a Chemical Reaction
4.2 Factors Influencing Rate of a Reaction
4.3 Integrated Rate Equations
4.4 Pseudo First Order Reaction
4.5 Temperature Dependence of the Rate of a Reaction
4.6 Collision Theory of Chemical Reactions

## Topicwise Analysis of Last 10 Years' CBSE Board Questions



- Maximum total weightage is of *Integrated Rate Equations.*
- Maximum SA I type questions were asked from *Factors Influencing Rate of a Reaction.*
- Maximum SA II type questions were asked from *Integrated Rate Equations.*

## QUICK RECAP

- **Chemical kinetics :** It is the branch of chemistry which deals with the study of reaction rates and their mechanisms.
- **Rate of a reaction :** The rate of a reaction can be defined as the change in concentration of a reactant or a product in unit time. For the reaction,

$$R \longrightarrow P,\ \text{Rate} = -\frac{\Delta[R]}{\Delta t} \text{ or } +\frac{\Delta[P]}{\Delta t}$$

- **Units of rate :** Concentration time$^{-1}$ *i.e.*, mol L$^{-1}$ s$^{-1}$ or atm s$^{-1}$ for gaseous reactions.

**Average rate of reaction :** It is the average value during a large time interval.

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

**Instantaneous rate of reaction :** It is the rate of a reaction at a particular instant of time *i.e.*, when $\Delta t$ approaches zero.

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

**Factors influencing rate of a reaction :**

- **Concentration :** Greater the concentrations of the reactants, faster is the rate of reaction.
- **Physical state of reactants :** Reactions involving gaseous reactants are faster than reactions containing solid and liquid reactants.
- **Temperature :** The rate of reaction increases with increase of temperature. For most of the reactions, rate of reaction becomes almost double with 10° C rise of temperature.
- **Presence of catalyst :** A catalyst generally increases the speed of a reaction.
- **Surface area of reactants :** For a reaction involving a solid reactant or catalyst, the greater is the surface area, the faster is the reaction.
- **Presence of light :** Photochemical reactions take place in the presence of light only.
- **Activation energy :** Lower the activation energy faster is the reaction.

**Rate law and rate constant :** The equation that correlates the rate of reaction with concentration of reactants is known as *rate law*.

- For a simple reaction, $A + B \rightarrow C + D$
  Rate = $k[A][B]$ where $k$ is the *rate constant* which is equal to the rate of reaction when concentration of each of the reactant is unity.

**Order and molecularity :**

| Molecularity of reaction | Order of reaction |
|---|---|
| It is the total number of species taking part in a chemical reaction. | It is the sum of the powers of the concentration terms of reacting species in the rate law equation. |
| It is a theoretical concept. | It is an experimental quantity. |
| It is derived from the mechanism of reaction. | It is derived from the rate expression. |
| It can neither be zero nor fractional. It is always a whole number. | It may be zero, fractional or an integer (may range from 0 to 3). |
| It is applicable only to elementary reactions. The overall molecularity of a complex reaction has no significance. | It is applicable to elementary as well as complex reactions. |

**Half life of reaction :** The time in which the concentration of a reactant is reduced to one half of its initial concentration is called *half life of the reaction.*

$t_{1/2} \propto \frac{1}{a^{n-1}}$ where $n$ is the order of the reaction.

**Rate law, integrated rate law, half-life, units of rate constant and graph for the reactions of different orders :**

| Order | Rate law | Integrated rate law | Half-life | Units of rate constant | Graph |
|---|---|---|---|---|---|
| 0 | Rate = $k[A]^0$ | $[A]_t = -kt + [A]_0$ | $t_{1/2} = [A]_0/2k$ | mol $L^{-1}$ $s^{-1}$ | $[A]$ *vs* $t$; slope = $-k$ |
| 1 | Rate = $k[A]^1$ | $\ln[A]_t = -kt + \ln[A]_0$ | $t_{1/2} = 0.693/k$ | $s^{-1}$ | $\ln[A]$ *vs* $t$; slope = $-k$ |
| 2 | Rate = $k[A]^2$ | $1/[A]_t = kt + 1/[A]_0$ | $t_{1/2} = 1/k[A]_0$ | L $mol^{-1}$ $s^{-1}$ | $1/[A]$ *vs* $t$; slope = $k$ |
| 2 | Rate = $k[A][B]$ | $kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$ | – | L $mol^{-1}$ $s^{-1}$ | $1/[A]$ *vs* $t$; slope = $k$ |
| $n$ | Rate = $k[A]^n$ | $(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}$ | $t_{1/2} = \frac{2^{n-1}-1}{k(n-1)[A]_0^{n-1}}$ | $(\text{mol L}^{-1})^{1-n}$ $s^{-1}$ | $\frac{1}{[A]^{n-1}}$ *vs* $t$; slope = $k$ |

**Pseudo first order reactions :** Those reactions which are not truly of the first order but under certain conditions become reactions of the first order are called *pseudo first order reactions.*

*e.g.*

- **Acid hydrolysis of ethyl acetate :**

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

Rate = $k'[CH_3COOC_2H_5][H_2O]$

$= k[CH_3COOC_2H_5]$

where $k = k'[H_2O]$

- **Acid catalysed inversion of cane sugar :**

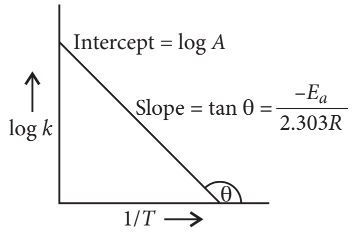
$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Rate = $k[C_{12}H_{22}O_{11}]$

**Effect of temperature on rate of reaction :**

- For a chemical reaction with rise in temperature by 10° C, the rate constant is nearly doubled.
- **Arrhenius equation :** $k = Ae^{-E_a/RT}$

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



where, $k$ = Rate constant,

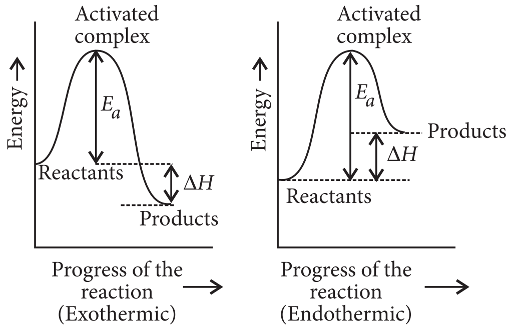
$A$ = Pre-exponential factor (frequency factor),

$E_a$ = Activation energy,

$T$ = Temperature

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

**Activation energy :** The minimum amount of energy required by reactant molecules to participate in a reaction is called *activation energy* ($E_a$).



- Activation energy = Threshold energy – Average kinetic energy of reacting molecules
- Activation energy ($E_a$) $= E_{(\text{activated complex})} - E_{(\text{ground state})}$
- $\Delta H$ = Activation energy of forward reaction – Activation energy of backward reaction

**Collision theory of chemical reactions :**

- Reaction occurs due to collision of molecules.
- All collisions are not effective.
- *Effective collisions* are those collisions in which molecules collide with sufficient kinetic energy (called *threshold energy* which is equal to activation energy + energy possessed by reacting species) and proper orientation.
- Rate = $PZ_{AB}e^{-E_a/RT}$ where, $P$ = probability or steric factor which takes into account the fact that in a collision, molecules must be properly oriented and $Z_{AB}$ = collision frequency (*i.e.*, the no. of collisions per second per unit volume of the reaction mixture) of reactants, $A$ and $B$.

# Previous Years' CBSE Board Questions

## 4.1 Rate of a Chemical Reaction

**VSA (1 mark)**

**1.** Express the rate of the following reaction in terms of the formation of ammonia.
$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ *(Delhi 2013C)*

**2.** Define elementary step in a reaction. *(1/5, Foreign 2011)*

**3.** Why does the rate of a reaction not remain constant throughout the reaction process? *(AI 2009C)*

**SA I (2 marks)**

**4.** What is meant by rate of reaction? Differentiate between average rate and instantaneous rate of reaction. *(AI 2012C)*

**5.** Explain the difference between the average rate and instantaneous rate of chemical reaction. *(2/5, AI 2010C)*

## 4.2 Factors Influencing Rate of a Reaction

**VSA (1 mark)**

**6.** Define the rate constant. *(1/5, Foreign 2015, Delhi 2015C)*

**7.** Define the specific rate of reaction. *(AI 2014C)*

**8.** For a reaction $A + B \rightarrow P$, the rate law is given by,
$r = k[A]^{1/2}[B]^2$
What is the order of this reaction? *(AI 2013)*

**9.** If the rate constant of reaction is $k = 3 \times 10^{-4} s^{-1}$, then identify the order of the reaction. *(Delhi 2013C, 2011C)*

**10.** Define 'order of a reaction'. *(AI 2011)*

**11.** Identify the reaction order from the following rate constant :
$k = 2.3 \times 10^{-5}$ L mol$^{-1}$s$^{-1}$ *(Delhi, AI 2011C)*

**12.** Distinguish between molecularity and order of a reaction. *(1/5, AI 2010C)*

**13.** Define the term 'order of reaction' for chemical reactions. *(Delhi, AI 2008)*

**14.** For the reaction, $Cl_{2(g)} + 2NO_{(g)} \rightarrow 2NOCl_{(g)}$ the rate law is expressed as
Rate = $k[Cl_2]\,[NO]^2$
What is the overall order of this reaction? *(Delhi 2007)*

**15.** Express the rate of the following reaction in terms of disappearance of hydrogen in the reaction :
$3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}$ *(AI 2007)*

**SA I (2 marks)**

**16.** For a reaction : $2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$
Rate = $k$
(i) Write the order and molecularity of this reaction.
(ii) Write the unit of $k$. *(Delhi 2016)*

**17.** For a reaction : $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$
Rate = $k$
(i) Write the order and molecularity of this reaction
(ii) Write the unit of $k$. *(AI 2016)*

**18.** For a reaction $A + B \longrightarrow P$, the rate is given by
Rate = $k[A][B]^2$
(i) How is the rate of reaction affected if the concentration of $B$ is doubled?
(ii) What is the overall order of reaction if $A$ is present in large excess? *(2/5, Delhi 2015)*

**19.** Define rate of reaction. Write two factors that affect the rate of reaction. *(AI 2015)*

**20.** Write units of rate constants for zero order and for the second order reactions if the concentration is expressed in mol L$^{-1}$ and time in second. *(AI 2015C)*

**21.** Write two differences between 'order of reaction' and 'molecularity of reaction'. *(Delhi 2014, 2011C)*

**22.** (i) For a reaction, $A + B \rightarrow$ Product, the rate law is given by, Rate = $k[A]^1[B]^2$. What is the order of the reaction ?

(ii) Write the unit of rate constant '$k$' for the first order reaction. *(Delhi 2014C)*

**23.** A reaction is of second order with respect to its reactant. How will its reaction rate be affected if the concentration of the reactant is (i) doubled (ii) reduced to half ? *(AI 2014C, 2012, Delhi 2009)*

**24.** What do you understand by the 'order of a reaction'? Identify the reaction order from each of the following units of reaction rate constant.
(i) $L^{-1}$ mol $s^{-1}$ (ii) L $mol^{-1}$ $s^{-1}$ *(Delhi 2012)*

**25.** Distinguish between 'rate expression' and 'rate constant' of a reaction. *(Delhi 2011)*

**26.** What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are :
(i) $L^{-1}$ mol $s^{-1}$ (ii) L $mol^{-1}$ $s^{-1}$ *(AI 2011)*

**27.** Express clearly what do you understand by 'rate expression' and 'rate constant' of a reaction *(2/5, Foreign 2011)*

**28.** Explain the term 'order of reaction'. Derive the unit for first order rate constant. *(Delhi 2009C)*

**29.** What is meant by the 'rate constant, $k$' of a reaction? If the concentration be expressed in mol $L^{-1}$ units and time in seconds. What would be the units for $k$ (i) for a zero order reaction and (ii) for a first order reaction? *(Delhi 2008)*

**30.** List the factors on which the rate of a chemical reaction depends. *(2/5, Delhi, AI 2008)*

**31.** Distinguish between order and molecularity of a reaction. When could order and molecularity of a reaction be the same? *(Delhi 2008C)*

## SA II (3 marks)

**32.** A reaction is second order in $A$ and first order in $B$.
(i) Write the differential rate equation.
(ii) How is the rate affected on increasing the concentration of $A$ three times?
(iii) How is the rate affected when the concentration of both $A$ and $B$ are doubled? *(3/5, Delhi 2013)*

**33.** The reaction, $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ contributes to air pollution whenever a fuel is burnt in air at a high temperature. At 1500 K, equilibrium constant $K$ for it is $1.0 \times 10^{-5}$. Suppose in a case $[N_2] = 0.80$ mol $L^{-1}$ and $[O_2] = 0.20$ mol $L^{-1}$ before any reaction occurs. Calculate the equilibrium concentrations of the reactants and the product after the mixture has been heated to 1500 K. *(AI 2012)*

**34.** (i) A reaction is first order in $A$ and second order in $B$.
(a) Write differential rate equation.
(b) How is rate affected when concentration of $B$ is tripled?
(c) How is rate affected when concentration of both $A$ and $B$ is doubled?
(ii) What is molecularity of a reaction? *(AI 2012C)*

**35.** $A + 2B \rightarrow 3C + 2D$. The rate of disappearance of $B$ is $1 \times 10^{-2}$ mol/L/s.
What will be (i) rate of the reaction (ii) rate of change in concentration of $A$ and $C$ ? *(3/5, AI 2008)*

**36.** The data given below is for the reaction,
$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$ at 298 K :

| **S. No.** | **$[N_2O_5]$ (mol $L^{-1}$)** | **Rate of disappearance of $N_2O_5$(mol $L^{-1}$ $min^{-1}$)** |
|---|---|---|
| 1. | $1.13 \times 10^{-2}$ | $34 \times 10^{-5}$ |
| 2. | $0.84 \times 10^{-2}$ | $25 \times 10^{-5}$ |
| 3. | $0.62 \times 10^{-2}$ | $18 \times 10^{-5}$ |

Determine for this reaction :
(i) order of reaction
(ii) rate constant
(iii) rate law. *(AI 2008C)*

**37.** The decomposition of $NH_3$ on platinum surface :
$2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$
is a zero order reaction with $k = 2.5 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$
What are the rates of production of $N_2$ and $H_2$? *(Delhi 2007)*

## LA (5 marks)

**38.** The following results have been obtained during the kinetic studies of the reaction :

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

| **Experi-ment No.** | [$A$] | [$B$] | **Inital rate of formation of $D$** |
|---|---|---|---|
| 1. | 0.1 M | 0.1 M | $6.0 \times 10^{-3}$ M min$^{-1}$ |
| 2. | 0.3 M | 0.2 M | $7.2 \times 10^{-2}$ M min$^{-1}$ |
| 3. | 0.3 M | 0.4 M | $2.88 \times 10^{-1}$ M min$^{-1}$ |
| 4. | 0.4 M | 0.1 M | $2.40 \times 10^{-2}$ M min$^{-1}$ |

Calculate the rate of formation of $D$ when $[A] = 0.5$ mol L$^{-1}$ and $[B] = 0.2$ mol L$^{-1}$. *(Delhi 2010C)*

## 4.3 Integrated Rate Equations

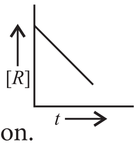
### VSA (1 mark)

**39.** Define the half-life period of reaction ($t_{1/2}$). *(Delhi 2014)*

**40.** If half-life period of a first order reaction is $x$ and 3/4th life period of the same reaction is $y$, how are $x$ and $y$ related to each other? *(1/5, Delhi 2013C)*

### SA I (2 marks)

**41.** For a chemical reaction $R \rightarrow P$, the variation in the concentration [$R$] *vs*. time ($t$) plot is given as



(i) Predict the order of the reaction.
(ii) What is the slope of the curve? *(AI 2014)*

**42.** Define half-life of a reaction. Write the expression of half-life for
(i) zero order reaction and
(ii) first order reaction. *(Foreign 2014)*

**43.** For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction. *(2/5, Delhi 2013)*

**44.** Rate constant $k$ for a first order reaction has been found to be $2.54 \times 10^{-3}$ sec$^{-1}$. Calculate its 3/4th life. (log 4 = 0.6020) *(Delhi 2013C)*

**45.** The thermal decomposition of $HCO_2H$ is a first order reaction with a rate constant of $2.4 \times 10^{-3}$ s$^{-1}$ at a certain temperature. Calculate how long will it take for three-fourth of initial quantity of $HCO_2H$ to decompose. (log 0.25 = – 0.6021) *(AI 2011)*

**46.** In a first order reaction, the concentration of the reactant is reduced from 0.6 mol L$^{-1}$ to 0.2 mol L$^{-1}$ in 5 minutes. Calculate the rate constant of the reaction. *(AI 2011C)*

**47.** Show that for a first order reaction, the time required for half the change (half-life period) is independent of initial concentration. *(Delhi 2009C)*

**48.** A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value. *(Delhi, AI 2008)*

### SA II (3 marks)

**49.** For the first order thermal decomposition reaction, the following data were obtained :
$C_2H_5Cl_{(g)} \longrightarrow C_2H_{4(g)} + HCl_{(g)}$

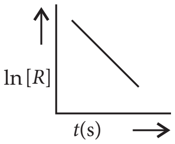
| Time/sec | Total pressure/atm |
|---|---|
| 0 | 0.30 |
| 300 | 0.50 |

Calculate the rate constant.
(Given : $\log 2 = 0.301, \log 3 = 0.4771, \log 4 = 0.6021$) *(AI 2016)*

**50.** A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. (log 2 = 0.3010) *(3/5, Delhi 2015)*

**51.** A first order reaction takes 10 minutes for 25% decomposition. Calculate $t_{1/2}$ for the reaction. (Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021) *(3/5, Foreign 2015)*

**52.** For a chemical reaction $R \longrightarrow P$, the variation in the concentration, ln [$R$] vs. time (s) plot is given as



(i) Predict the order of the reaction.
(ii) What is the slope of the curve?
(iii) Write the unit of the rate constant for this reaction. *(3/5, Foreign 2015)*

**53.** The rate constant for a first order reaction is 60 s$^{-1}$. How much time will it take to reduce the initial concentration of the reactant to its 1/10th value? *(AI 2015C, 2007)*

**54.** The following data were obtained during the first order thermal decomposition of $SO_2Cl_2$ at a constant volume :
$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$

| Experiment | Time/s | Total pressure/atm |
|---|---|---|
| 1 | 0 | 0.4 |
| 2 | 100 | 0.7 |

Calculate the rate constant.

(Given : log 4 = 0.6021, log 2 = 0.3010)

*(Delhi, AI, Foreign 2014)*

**55.** Hydrogen peroxide, $H_2O_{2(aq)}$ decomposes to $H_2O_{(l)}$ and $O_{2(g)}$ in a reaction that is first order in $H_2O_2$ and has a rate constant $k = 1.06 \times 10^{-3}\ \text{min}^{-1}$.

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

(ii) How long will it take for 85% of the sample to decompose? *(Delhi 2014C)*

**56.** The first order reaction take 100 minutes for completion of 60% of the reaction. Find the time when 90% of the reaction will be completed.

*(3/5, Delhi 2013C)*

**57.** For the reaction :

$2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}$

The following data were collected. All the measurements were taken at 263 K.

| Exp. No. | Initial [NO](M) | Initial $[Cl_2]$ (M) | Initial rate of disapp. of $Cl_2$ (M/min) |
|---|---|---|---|
| 1. | 0.15 | 0.15 | 0.60 |
| 2. | 0.15 | 0.30 | 1.20 |
| 3. | 0.30 | 0.15 | 2.40 |
| 4. | 0.25 | 0.25 | ? |

(i) Write the expression for rate law.

(ii) Calculate the value of rate constant and specify its units.

(iii) What is the initial rate of disappearance of $Cl_2$ in exp. 4? *(Delhi 2012)*

**58.** A first order reaction is 15% completed in 20 minutes. How long will it take to complete 60% of the reaction? *(3/5, Delhi 2012C)*

**59.** Nitrogen pentoxide decomposes according to equation :

$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$

This first order reaction was allowed to proceed at 40° C and the data below were collected :

| $[N_2O_5]$ (M) | Time (min) |
|---|---|
| 0.400 | 0.00 |
| 0.289 | 20.0 |
| 0.209 | 40.0 |
| 0.151 | 60.0 |
| 0.109 | 80.0 |

(i) Calculate the rate constant. Include units with answer.

(ii) What will be the concentration of $N_2O_5$ after 100 minutes?

(iii) Calculate the initial rate of reaction.

*(Delhi 2011)*

**60.** Nitrogen pentoxide decomposes according to the equation :

$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$

This first order reaction was allowed to proceed at 40°C and the data given below were collected :

| $[N_2O_5]$ (M) | Time (min) |
|---|---|
| 0.400 | 0.00 |
| 0.289 | 20.00 |
| 0.209 | 40.00 |
| 0.151 | 60.00 |
| 0.109 | 80.00 |

(i) Calculate the rate constant for the reaction. Include units with your answer.

(ii) Calculate the initial rate of reaction.

(iii) After how many minutes will $[N_2O_5]$ be equal to 0.350 M? *(3/5, Delhi 2011)*

**61.** A first order reaction has a rate constant value of 0.00510 $\text{min}^{-1}$. If we begin with 0.10 M concentration of the reactant, how much of the reactant will remain after 3.0 hours?

*(3/5, Foreign 2011)*

**62.** A reactant has a half-life of 10 minutes.

(i) Calculate the rate constant for the first order reaction.

(ii) What fraction of the reactant will be left after an hour of the reaction has occurred?

*(Delhi 2011C)*

**63.** The decomposition of a compound is found to follow a first order rate law. If it takes 15 minutes for 20 per cent of original material to react, calculate

(i) the rate constant.
(ii) the time at which 10% of the original material remains unreacted.

*(3/5, Delhi 2010C)*

**64.** The half-life for a first order reaction is $5 \times 10^4$ s. What percentage of the initial reactant will react in 20 hours? *(3/5, AI 2009C)*

**65.** A first order reaction is 20% complete in 5 minutes. Calculate the time taken for the reaction to be 60% complete. *(AI 2009C)*

**66.** The half-life for decay of radioactive $^{14}C$ is 5730 years. An archaeological artifact containing wood has only 80% of the $^{14}C$ activity as found in living trees. Calculate the age of the artifact. *(Delhi, AI 2008)*

## 4.4 Pseudo First Order Reaction

### VSA (1 mark)

**67.** Define the following term :
Pseudo first order reaction *(1/2, Delhi 2014)*

### SA II (3 marks)

**68.** In a pseudo first order hyrolysis of ester in water, the following results are obtained :

| ***t* in seconds** | 0 | 30 | 60 | 90 |
|---|---|---|---|---|
| **[Ester]M** | 0.55 | 0.31 | 0.17 | 0.085 |

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

*(3/5, AI 2010C)*

### LA (5 marks)

**69.** For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained :

| ***t*/s** | 0 | 30 | 60 |
|---|---|---|---|
| **[$CH_3COOCH_3$]/mol $L^{-1}$** | 0.60 | 0.30 | 0.15 |

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.
(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(Given : log 2 = 0.3010, log 4 = 0.6021)

*(Delhi 2015)*

## 4.5 Temperature Dependence of the Rate of a Reaction

### VSA (1 mark)

**70.** Define the following :
Energy of activation of reaction.

*(1/5, Foreign 2015, AI 2014C, 2008)*

### SA I (2 marks)

**71.** How does a change in temperature affect the rate of a reaction? How can this effect on the rate constant of reaction be represented quantitatively? *(AI 2014C)*

**72.** With the help of diagram, explain the physical significance of energy of activation ($E_a$) in chemical reactions. *(AI 2013C)*

**73.** With the help of a labelled diagram explain the role of activated complex in a reaction.

*(2/5, Delhi 2012C)*

**74.** The rate of most of the reactions becomes double when their temperature is raised from 298 K to 308 K. Calculate their activation energy.
[Given $R = 8.314$ J mol$^{-1}$ K$^{-1}$] *(Delhi 2011C)*

**75.** Define "order of a reaction" and "activation energy of a reaction". *(AI 2009)*

### SA II (3 marks)

**76.** The rate constant for the first order decomposition of $H_2O_2$ is given by the following equation :

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} \text{K}$$

Calculate $E_a$ for this reaction and rate constant $k$ if its half-life period be 200 minutes.
(Given : $R = 8.314$ J K$^{-1}$ mol$^{-1}$) *(Delhi 2016)*

**77.** The rate constant of a first order reaction increases from $2 \times 10^{-2}$ to $4 \times 10^{-2}$ when the temperature changes from 300 K to 310 K. Calculate the energy of activation ($E_a$).
(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

*(Delhi 2015)*

**78.** The rate constants of reaction at 500 K and 700 K are 0.02 s$^{-1}$ and 0.07 s$^{-1}$ respectively. Calculate the value of activation energy, $E_a$ ($R = 8.314$ J K$^{-1}$ mol$^{-1}$). *(Delhi 2015C, 2008)*

**79.** For a decomposition reaction, the values of $k$ at two different temperatures are given below :

$k_1 = 2.15 \times 10^{-8}$ L/(mol.s) at 650 K

$k_2 = 2.39 \times 10^{-8}$ L/(mol.s) at 700 K

Calculate the value of $E_a$ for the reaction.

($R = 8.314$ J K$^{-1}$ mol$^{-1}$) *(AI 2014C, 2009)*

**80.** Rate constant '$k$' of a reaction varies with temperature '$T$' according to the equation :

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

where $E_a$ is the activation energy. When a graph is plotted for log $k$ *vs* $\frac{1}{T}$, a straight line with a slope of – 4250 K is obtained. Calculate '$E_a$' for the reaction.

($R = 8.314$ J K$^{-1}$ mol$^{-1}$). *(3/5, Delhi 2013)*

**81.** The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation ($E_a$) of the reaction assuming that it does not change with temperature.

[$R = 8.314$ J K$^{-1}$ mol$^{-1}$, log 4 = 0.6021] *(AI 2013)*

**82.** The decomposition of $A$ into products has a value of $k$ as $4.5 \times 10^3$ s$^{-1}$ at 10°C and energy of activation is 60 kJ mol$^{-1}$. At what temperature would $k$ be $1.5 \times 10^4$ s$^{-1}$? *(3/5, Delhi 2013C)*

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

[$R = 8.314$ J/K$^{-1}$ mol$^{-1}$] *(AI 2012C)*

**84.** The decomposition of phosphine,

$4PH_{3(g)} \longrightarrow P_{4(g)} + 6H_{2(g)}$

has the rate law, Rate = $k[PH_3]$.

The rate constant is $6.0 \times 10^{-4}$s$^{-1}$ at 300 K and activation energy is $3.05 \times 10^5$ J mol$^{-1}$. Calculate the value of rate constant at 310 K.

[Given : $R = 8.314$ J K$^{-1}$ mol$^{-1}$] *(Delhi 2008C)*

**85.** The first order rate constant for the decomposition of ethyl iodide by the reaction :

$$C_2H_5I_{(g)} \rightarrow C_2H_{4(g)} + HI_{(g)}$$

at 600 K is $1.6 \times 10^{-5}$ s$^{-1}$. Its energy of activation is 209 kJ mol$^{-1}$.

Calculate the rate constant of reaction at 700 K. *(AI 2007)*

**LA (5 marks)**

**86.** (i) What is the physical significance of energy of activation? Explain with diagram.

(ii) In general, it is observed that the rate of a chemical reaction doubles with every 10 degree rise in temperature. If the generalisation holds good for the reaction in the temperature range of 295 K to 305 K, what would be the value of activation energy for this reaction?

[$R = 8.314$ J/K$^{-1}$ mol$^{-1}$] *(Delhi 2012C)*

## 4.6 Collision Theory of Chemical Reactions

**VSA (1 mark)**

**87.** In some cases it is found that a large number of colliding molecules have energy more than threshold energy, yet the reaction is slow, Why? *(Delhi 2013C)*

## Detailed Solutions

**1.** $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

$$\frac{-d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

**2.** **Elementary step :** Each step of a complex reaction is called an elementary step.

**3.** The rate of a reaction does not remain constant throughout the reaction process because the rate of the reaction depends upon concentration of reactants which keeps on decreasing.

**4.** Change in concentration *i.e.*, either (decrease in concentration of reactant or increase in concentration of product) per unit time is called rate of reaction.

$$\text{Rate of reaction} = \frac{C_2 - C_1}{t_2 - t_1} = \frac{\Delta C}{\Delta t}$$

The ratio of change of concentration of reactants to the time consumed in that change is called average rate of reaction.

$$r_{av} = \frac{\Delta x}{\Delta t} = -\frac{C_2 - C_1}{t_2 - t_1}$$

The rate of reaction at a particular instant (time) is called instantaneous rate of reaction.

$$r_{ins} = \frac{dx}{dt}$$

$dx$ = small change in concentration
$dt$ = small time interval

**5.** *Refer to answer 4.*

**6.** Rate constant is the proportionality factor in the rate law expression for a chemical reaction. It is defined as the rate of a chemical reaction for which the concentration of each of the reacting species is unity.

**7.** At a given temperature, rate is equal to the rate constant of reaction when concentration of the reactant in unity. Thus rate constant is also known as specific reaction rate.
In the case of two reactants, the reaction may be written as :

$$A + B \rightarrow \text{Products}$$

$$r = \frac{dx}{dt} = k\,C_A C_B$$

where all the terms have their usual meaning as :
if $C_A = C_B = 1$ then $r = k$.

**8.** $A + B \rightarrow$ Product
Rate law, $r = k[A]^{1/2}[B]^2$

Order of reaction is sum of the powers of concentration terms,

$$\therefore \text{ Order of reaction} = \frac{1}{2} + 2 = \frac{5}{2} = 2.5$$

**9.** First order reaction.

**10.** It is defined as "the sum of the powers or exponents to which the concentration terms are raised in the rate law expression."
If rate = $k[A]^m[B]^n$, then order = $m + n$.

**11.** Second order reaction :

$$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{L mol}^{-1}\text{s}^{-1}$$

**12.** Distinction between order and molecularity of a reaction : (*any one*)

| Order of a reaction | Molecularity of a reaction |
|---|---|
| 1. It is the sum of powers of the concentration of the reactants in the rate law expression. | 1. It is the number of reacting species(atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction. |
| 2. It need not be a whole number. | 2. It is always a whole number. |

Generally, in a complex reaction the order of reaction is equal to the molecularity of the slowest step.

**13.** *Refer to answer 10.*

**14.** Rate = $k[Cl_2][NO]^2$
Hence order of the reaction = 1 + 2 = 3

**15.** Rate $= \dfrac{-1}{3}\dfrac{d[H_2]}{dt}$

**16.** (i) The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.
In this reaction, platinum metal acts as a catalyst.

At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.

However, two molecules of ammonia react to give products thus, the molecularity is two.
(ii) For a zero order reaction, unit of rate constant is mol $L^{-1}$ $sec^{-1}$.

**17.** (i) Rate = $k$
Experimentally, it is found that the rate of reaction is independent of the concentration of $H_2$ and $Cl_2$. Hence, it is a zero order reaction.
Molecularity = 2
(ii) Unit of $k$ = mole $litre^{-1}$ $sec^{-1}$

**18.** (i) From the rate law equation, order of reaction w.r.t. $B$ is 2. Hence, if concentration of $B$ is doubled, rate will become four times.
(ii) If $A$ is present in large excess, rate of reaction will be independent of concentration of $A$ and hence, order of reaction will be 2.

**19.** *Refer to answer 4.*

Following factors affect the rate of a chemical reaction :

**(i) Concentration of reactants :** Higher the concentration of reactants, faster would be the rate of reaction.

Rate = $k\,C^n$, where $C$ = concentration of reactant.

**(ii) Temperature :** The rate of reaction increases with the temperature. For every 10°C rise in temperature rate of reaction increases 2 to 3 times.

**20.** Unit of rate constant ($k$), for zero order reaction.
$\text{Rate} = k[A]^0 \Rightarrow k = \text{mol L}^{-1}\text{ s}^{-1}$
Unit of rate constant ($k$), for second order reaction
$\text{Rate} = k[A]^2 \Rightarrow k = \text{mol}^{-1}\text{ L s}^{-1}$

**21.** *Refer to answer 12.*

**22.** (i) Order of reaction is sum of powers of concentration terms,
$\therefore$ Order of reaction = 1 + 2 = 3
(ii) *Refer to answer 28.*

**23.** Let the concentration of the reactant $[A] = a$
Order of reaction = 2 so that
$$\text{Rate of reaction} = k\,[A]^2 \qquad ...(1)$$
$$= ka^2$$
(i) Given that concentration of the reactant is doubled
So, that $[A] = 2a$,
Putting the value in equation (1) we get
New rate of reaction, $R_1 = k(2a)^2 = 4ka^2$
Hence, rate of reaction will increased to 4 times.
(ii) Given that concentration of the reactant is reduced to half
So that $[A] = (1/2)a$
Putting the value in equation (1), we get
New rate of reaction $R_2 = k((1/2)a)^2$
$= (1/4)ka^2$
Hence, rate of reaction will reduced to 1/4.

**24. Order of a reaction :** *Refer to answer 10.*
(i) $L^{-1}$mol $s^{-1}$ – Zero order reaction
(ii) L $mol^{-1}$ $s^{-1}$ – Second order reaction

**25.** Rate expression is a way of expressing rate of reaction in terms of concentration of reactants, *e.g.*, for a general reaction, $aA + bB \longrightarrow cC + dD$
$$\text{Rate} = k[A]^x\,[B]^y$$
Rate constant ($k$) is equal to the rate of reaction when molar concentration of reactant is unity. Its units depends upon the order of reaction.

**26.** *Refer to answers 25 and 24.*

**27.** *Refer to answer 25.*

**28. Order of a reaction :** *Refer to answer 10.*
Unit for first order rate constant :
For first order reaction,
$$\text{Rate} = \frac{dx}{dt} = k[A]$$
$$\frac{\text{mol L}^{-1}}{\text{sec}} = k.\,\text{mol L}^{-1} \Rightarrow k = \frac{1}{\text{sec}} = \text{sec}^{-1}.$$

**29.** *Refer to answer 6.*
Unit for $k$ :
(i) For a zero order reaction : mol $L^{-1}$ $s^{-1}$
(ii) For a first order reaction : $s^{-1}$.

**30.** Factors affecting the rate of a chemical reaction :
**(i) Concentration of reactants :** In general the rate of a reaction increases when concentration of reactants is increased.
$$\text{Rate} = kC^n$$

**(ii) Temperature :** Most of the chemical reactions are accelerated by increase in temperature.

**(iii) Catalyst :** Rate of a reaction increases in presence of a catalyst.

**(iv) Nature of reactants :** Reactions involving ionic reactants are fast as compared to those involving covalent reactants.

**(v) Surface area of the reactants :** In case of solid reactants, the rate of reaction increases with the surface area of the particles of the reactants.

**(vi) Light :** In case of photochemical reactions, the rate of reaction increases with increasing the intensity of light.

**31.** *Refer to answer 12.*

**32.** Since the reaction is second order in $A$ and first order in $B$

(i) Differential rate equation is

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

(ii) The new concentration of $A = [3A]$

$\therefore$ New rate = $k[3A]^2[B] = 9k[A]^2[B]$

$\therefore$ New rate = 9 times of the original rate

(iii) New concentration of $A = [2A]$

New concentration of $B = [2B]$

$\therefore$ New rate = $k[2A]^2[2B] = 8k[A]^2[B]$

$\therefore$ New rate = 8 times of the original rate.

**33.** Given reaction is

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \,;\, K = 1.0 \times 10^{-5}$$

Initially : $0.80 \text{ mol L}^{-1}$ $0.20 \text{ mol L}^{-1}$ $0$

At equil.: $0.80 - x$ $0.20 - x$ $2x$

According to law of mass action,

$$K = \frac{[NO]^2}{[N_2][O_2]}$$

$$\text{or} \quad 1.0 \times 10^{-5} = \frac{(2x)^2}{(0.80 - x)(0.20 - x)}$$

$x$ is very small hence can be neglected in the denominator. Thus,

$$1.0 \times 10^{-5} = \frac{4x^2}{0.8 \times 0.2} \text{ or } 1.0 \times 10^{-5} = \frac{4x^2}{0.16}$$

or, $4x^2 = 1.0 \times 10^{-5} \times 0.16$ or $4x^2 = 16 \times 10^{-7}$

or, $x^2 = 4 \times 10^{-7}$ or $x = 6.32 \times 10^{-4}$

$\therefore$ $[N_2] = 0.80 - 0.000632 = 0.7994 \text{ mol L}^{-1}$

$[O_2] = 0.20 - 0.000632 = 0.199 \text{ mol L}^{-1}$

$[NO] = 2x = 2 \times 0.000632 = 0.001264 \text{ mol L}^{-1}$

**34.** (i) (a) Differential rate equation of reaction is

$$\frac{dx}{dt} = k[A]^1[B]^2 = k[A][B]^2$$

When conc. of $B$ is tripled, it means conc. of $B$ becomes $[3 \times B]$

$\therefore$ New rate of reaction, $\frac{dx'}{dt} = k[A][3B]^2$

$$= 9k[A][B]^2 = 9\left(\frac{dx}{dt}\right)$$

*i.e.,* the rate of reaction will become 9 times.

(i) When conc. of $A$ is doubled and that of $B$ is also doubled, then conc. of $A$ becomes $[2A]$ and that of $B$ becomes $[2B]$.

$\therefore$ Now rate of reaction, $\frac{dx'}{dt} = k[2A][2B]^2$

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

*i.e.*, the rate of reaction will become 8 times.

(ii) Molecularity of a reaction is the number of reacting particles which collide simultaneously to bring about the chemical change. It is a theoretical concept.

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

$= 0.5 \times 10^{-2}$ mol/L/s.

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

Rate of change in concentration of $A$,

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

$= 0.5 \times 10^{-2}$ mol/L/s.

Rate of change in concentration of $C$,

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

$= 1.5 \times 10^{-2}$ mol/L/s.

**36.** (i) Let rate law for the disappearance of $N_2O_5$ is

Rate = $k[N_2O_5]^a$

$$\text{Then } \frac{r_1}{r_2} = \frac{34 \times 10^{-5}}{25 \times 10^{-5}} = \frac{k\,(1.13 \times 10^{-2})^a}{k(0.84 \times 10^{-2})^a}$$

$$\text{or, } \frac{34}{25} = \left(\frac{113}{84}\right)^a \text{ or } a = 1$$

Thus, order of reaction = 1

(ii) $r = k[N_2O_5]$ or, $34 \times 10^{-5} = k \times 1.13 \times 10^{-2}$

$$\text{or,} \quad k = \frac{34 \times 10^{-5}}{1.13 \times 10^{-2}} = 3.0 \times 10^{-2} \text{ min}^{-1}$$

(iii) Rate law = $k[N_2O_5]$

**37.** The reaction is

$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

Here : $k = 2.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$

The order of reaction is 0 *i.e.*,

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

Rate = $2.5 \times 10^{-4} \times 1 = 2.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$

$$\text{Rate of reaction} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$$

The rate of formation of $N_2 = 2.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$

$$\text{Again, } 2.5 \times 10^{-4} = \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\therefore \quad \frac{d[H_2]}{dt} = 7.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Therefore, rate of formation of $H_2$

$= 7.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$

**38.** Suppose order with respect to $A$ is $m$ and with respect to $B$ is $n$. Then the rate law will be

Rate = $k[A]^m[B]^n$

Substituting the value of experiments 1 to 4, we get

Expt. 1 : Rate = $6.0 \times 10^{-3} = k\,(0.1)^m\,(0.1)^n$ ...(i)

Expt. 2 : Rate = $7.2 \times 10^{-2} = k\,(0.3)^m\,(0.2)^n$ ...(ii)

Expt. 3 : Rate = $2.88 \times 10^{-1} = k\,(0.3)^m\,(0.4)^n$ ...(iii)

Expt. 4 : Rate = $2.4 \times 10^{-2} = k\,(0.4)^m\,(0.1)^n$ ...(iv)

Comparing equation (i) and equation (iv),

$$\therefore \quad \frac{(\text{Rate})_1}{(\text{Rate})_4} = \frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{k(0.1)^m\,(0.1)^n}{k(0.4)^m\,(0.1)^n}$$

$$\text{or, } \quad \frac{1}{4} = \frac{(0.1)^m}{(0.4)^m} = \left(\frac{1}{4}\right)^m \quad \therefore\ m = 1$$

Comparing equation (ii) and equation (iii)

$$\frac{(\text{Rate})_2}{(\text{Rate})_3} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k(0.3)^m\,(0.2)^n}{k(0.3)^m\,(0.4)^n}$$

$$\text{or, } \quad \left(\frac{1}{2}\right)^2 = \frac{(0.2)^n}{(0.4)^n} = \left(\frac{1}{2}\right)^n \quad \therefore\ n = 2$$

$\therefore$ Rate law expression is : Rate = $k[A][B]^2$

The rate constant can be calculated from the given data of any experiment using expression :

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

$$\text{From Expt. 1, } k = \frac{6.0 \times 10^{-3}}{0.1 \times (0.1)^2} = 6.0$$

$\therefore$ Rate constant $k = 6.0\ \text{mol}^{-2}\ \text{L}^2\ \text{min}^{-1}$

$$\text{Unit of } k,\ \frac{dx}{dt} = k[A]^1[B]^2 = 6.0[0.5][0.2]^2$$

$$= 6 \times 5 \times 4 \times 10^{-3}$$

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

**39.** The time taken for half of the reaction to complete, *i.e.*, the time in which the concentration of a reactant is reduced to half of its original value Is called half-life period of the reaction.

$$t = t_{1/2} \text{ when } [R] = \frac{[R_0]}{2}$$

**40.** For a first order reaction, $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{x}$

For $\frac{3}{4}$ th life period, $a = a$

$$a - x = a - \frac{3}{4}a = \frac{1}{4}a$$

$$\therefore \quad k = \frac{2.303}{y}\log\frac{a}{(a-x)}$$

$$\frac{0.693}{x} = \frac{2.303}{y}\log\frac{a}{a/4}$$

$$\frac{0.693}{x} = \frac{2.303}{y}2\log 2$$

$$\frac{0.693}{x} = \frac{0.693 \times 2}{y}$$

$y = 2x$

**41.** (i) The reaction is of zero order.

(ii) Slope of the straight line graph gives '$k$'

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

**42.** *Refer to answer 39.*

(i) For zero order reaction rate constant is given by :

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

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

In zero order reaction, $t_{1/2}$ is directly proportional to $[R]_0$.

(ii) For first order reaction,

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}, \quad \text{At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$\therefore\ k = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]_0/2} \quad \text{or, } t_{1/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} \Rightarrow t_{1/2} = \frac{0.693}{k}$$

In first order reaction, $t_{1/2}$ is independent of initial concentration.

**43.** For first order reaction, $t = \dfrac{2.303}{k} \log \dfrac{[R_0]}{[R_t]}$

For 99% completion of reaction

$t = t_{0.99}$, $[R]_0 = 1$, $[R]_t = (1 - 0.99) = 0.01 = 10^{-2}$

$$t_{0.99} = \frac{2.303}{k} \log \frac{1}{10^{-2}} = \frac{2.303}{k} \log 10^2 = \frac{2.303}{k} \times 2 \quad \text{...(i)}$$

For 90% completion of reaction

$t = t_{0.90}$, $[R]_0 = 1$, $[R]_t = (1-0.9) = 0.1 = 10^{-1}$

$$t_{0.90} = \frac{2.303}{k} \log \frac{1}{10^{-1}} = \frac{2.303}{k} \log 10 = \frac{2.303}{k} \quad \text{...(ii)}$$

Comparing equations (i) and (ii),

$$t_{0.99} = 2 \times t_{0.90}$$

**44.** The integrated rate equation for first order reaction is

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

$$k = \frac{2.303}{t} \log \frac{a}{a - \frac{3}{4}a}$$

$$k = \frac{2.303}{t} \log \frac{a}{0.25a}$$

$$t_{3/4} = \frac{2.303}{2.54 \times 10^{-3}\,\text{sec}^{-1}} \times \log \frac{1}{0.25}$$

$$t_{3/4} = 546 \text{ s}$$

Therefore, the 3/4th life of the reaction is 546 seconds.

**45.** For a first order reaction,

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

Given $k = 2.4 \times 10^{-3}\ \text{s}^{-1}$

$[R] = \dfrac{[R]_0}{4}$, $t = ?$

Substituting these values in the equation, we get

$$t = \frac{2.303}{2.4 \times 10^{-3}\ \text{s}^{-1}} \log \frac{[R]_0}{[R]}$$

$$t = \frac{2.303}{2.4 \times 10^{-3}\ \text{s}^{-1}} \log 4 = \frac{2.303}{2.4 \times 10^{-3}} \times 0.6021 \text{ s}$$

$t = 577.7$ s = 578 s.

**46.** $a = 0.6$ mol/L, $(a - x) = 0.4$ mol/L

$t = 5$ min

$$k = \frac{2.303}{5\text{ min}} \log \frac{0.6}{0.4} = 0.0811 \text{ min}^{-1}$$

**47.** *Refer to answer 42(ii).*

**48.** Here $t = 40$ min, $t_{1/2} = ?$

Let $a = 100$ ∴ $x = 30\%$ of $100 = 30$

Using the formula,

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

$$\Rightarrow 40 = \frac{2.303}{k} \log \frac{100}{100-30}$$

$$40 = \frac{2.303}{k} \log \frac{100}{70}$$

$$\Rightarrow 40 = \frac{2.303}{k} (\log 10 - \log 7)$$

$$40 = \frac{2.303}{k} (1 - 0.8451)$$

$$\Rightarrow 40 = \frac{2.303}{k} \times 0.1549 \Rightarrow k = \frac{0.357}{40} = 0.0089 \text{ min}^{-1}$$

$$\therefore\ t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0089} = 77.86 \text{ min.}$$

**49.** The given reaction is

| | $C_2H_5Cl_{(g)}$ | $\longrightarrow$ | $C_2H_4{}_{(g)}$ | + | $HCl_{(g)}$ |
|---|---|---|---|---|---|
| At time $t = 0$ | 0.30 atm | | 0 | | 0 |
| At time $t = 300$ sec | $0.30 - x$ | | $x$ | | $x$ |

Total pressure $= 0.30 - x + x + x = 0.50$

or $0.30 + x = 0.50$

∴ $x = 0.50 - 0.30 = 0.20$

∴ Initial pressure, $P_0 = 0.30$ atm

Pressure of $C_2H_5Cl$ after 300 sec, $P_t = 0.30 - 0.20 = 0.10$ atm

Using formula for first order reaction,

$$k = \frac{2.303}{t} \log \frac{P_0}{P_t}$$

$$k = \frac{2.303}{300} \log \frac{0.30}{0.10}$$

$$k = \frac{2.303}{300} \log 3 = \frac{2.303 \times 0.4771}{300} = 3.66 \times 10^{-3} \text{ sec}^{-1}$$

**50.** $t_{50\%}$ or $t_{1/2} = 30$ minutes

$$\Rightarrow\ k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{100-90} = \frac{2.303}{0.0231} \log 10$$

$$= 99.69 \text{ minutes}$$

**51.** For a first order reaction,

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

$$k=\frac{2.303}{10}\log\frac{100}{100-25}$$

$$k=\frac{2.303}{10}\times 0.124=0.02$$

$$\therefore\quad t_{1/2}=\frac{0.693}{k}=\frac{0.693}{0.02}=34.65\text{ min}$$

**52.** (i) The reaction is of 1st order.
(ii) For first order reaction
$\ln[R]=-kt+\ln[R]_0$
comparing *eqn.* $y=m\times x+c$
we get a straight line with slope = $-k$ and intercept equal to $\ln[R]_0$.
(iii) Unit of rate constant for first order reaction

$$\frac{\text{mol L}^{-1}}{\text{s}}\times\frac{1}{(\text{mol L}^{-1})^1}=\text{s}^{-1}$$

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

$\Rightarrow\ k=60\,\text{s}^{-1},\ [R]=\dfrac{1}{10}[R]_0$

or, $[R]_0=10\,[R]$

$$t=\frac{2.303}{60}\log\frac{10[R]}{[R]}\Rightarrow\ t=\frac{2.303}{60}\log 10$$

$$\Rightarrow\ t=\frac{2.303\times 1}{60}$$

$t=0.0384$ second

**54.** The given reaction is

$$\begin{array}{llll} & SO_2Cl_{2(g)} \longrightarrow & SO_{2(g)}\ + & Cl_{2(g)}\\ \text{At } t=0 & 0.4\text{ atm} & 0 & 0\\ \text{At time } t & (0.4-x)\text{ atm} & x\text{ atm} & x\text{ atm}\end{array}$$

Total pressure at time $t$ will be
$P_T=(0.4-x)+x+x=0.4+x$
$x=(P_T-0.4)$
Pressure of $SO_2Cl_2$ at time $t$ will be
$p_{SO_2Cl_2}=0.4-x=0.4-(P_T-0.4)=0.8-P_T$
At time $t=100$ s, $P_T=0.7$ atm
$\therefore\ p_{SO_2Cl_2}=0.8-0.7=0.1$ atm
According to first order kinetic equation

$$k=\frac{2.303}{t}\log\frac{p_{SO_2Cl_2\text{(initial)}}}{p_{SO_2Cl_2\text{(after reaction)}}}$$

$$=\frac{2.303}{100}\log\left(\frac{0.4}{0.1}\right)=1.3\times 10^{-2}\ \text{s}^{-1}$$

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

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

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

$$t=\frac{2303}{1.06}[2\log 10-\log 85]\text{min}$$

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

$t=153.39$ min $=153.4$ min.

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

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

$$=\frac{2303}{1.06}[2\log 10-\log 15]\text{min}$$

$$=\frac{2303}{1.06}[2\times 1-1.1761]=\frac{2303\times 0.8231}{1.06}\text{min}=1788\text{ min}$$

**56.** For the first order reaction,

Rate constant, $k=\dfrac{2.303}{100}\log\dfrac{a}{a-x}$

For 60% completion of the reaction, if $a=100\%$
$a-x=100-60=40\%$

Then, $k=\dfrac{2.303}{100}\log\dfrac{100}{40}$ ...(i)

For 90% completion of the reaction,
$a=100\%$
and $a-x=100-90=10\%$

Then, $k=\dfrac{2.303}{t}\log\dfrac{100}{10}$ ...(ii)

Substituting the value of $k$ in eq. (ii),

we have, $\dfrac{2.303}{100}\log\dfrac{100}{40}=\dfrac{2.303}{t}$ $[\because\ \log 10=1]$

or $\dfrac{1}{t}=\dfrac{1}{100}\log\dfrac{100}{40}$

$$\frac{1}{t}=\frac{0.3979}{100}$$

$$t=\frac{100}{0.3979}$$

$t=251$ min

**57.** Given reaction :
$2NO_{(g)}+Cl_{2(g)}\longrightarrow 2NOCl_{(g)}$

| Exp. No. | Initial [NO] (M) | Initial [$Cl_2$] (M) | Initial rate of disapp. of $Cl_2$ (M/min) |
|---|---|---|---|
| 1. | 0.15 | 0.15 | 0.60 |
| 2. | 0.15 | 0.30 | 1.20 |
| 3. | 0.30 | 0.15 | 2.40 |
| 4. | 0.25 | 0.25 | ? |

(i) Let rate of this reaction $r = k[NO]^m[Cl_2]^n$

then $\frac{r_1}{r_2} = \frac{0.60}{1.20} = \frac{k(0.15)^m(0.15)^n}{k(0.15)^m(0.30)^n}$

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

Again from $\frac{r_2}{r_3} = \frac{1.20}{2.40} = \frac{k(0.15)^m(0.30)^1}{k(0.30)^m(0.15)^1}$

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

Hence, expression for rate law is

$r = k[NO]^2\,[Cl_2]^1$

(ii) Substituting the values in experiment (1),

$0.60 \text{ M min}^{-1} = k(0.15 \text{ M})^2\,(0.15 \text{ M})^1$

or $k = \frac{0.60 \text{ M min}^{-1}}{0.0225 \times 0.15 \text{ M}^3} = 177.77 \text{ M}^{-2} \text{ min}^{-1}$

(iii) $r = 177.7 \text{ M}^{-2} \text{ min}^{-1} \times (0.25 \text{ M})^2\,(0.25 \text{ M})$

$= 2.77 \text{ M min}^{-1}$

**58.** $k = \frac{2.303}{20 \text{ min}} \log \frac{100}{100-15}$

$\frac{2.303}{20 \text{ min}} \log \frac{100}{100-15} = \frac{2.303 \times 0.0706}{20} \text{min}$

$t = \frac{2.303}{k} \log \frac{100}{100-60} = \frac{2.303 \times 20}{2.303 \times 0.0706} \log \frac{100}{40}$

$= \frac{20}{0.0706} \times 0.3979 = 112.7 \text{ min}$

**59.** (i) When $t = 20$ min, $[R] = 0.289 \text{ mol L}^{-1}$

$[R]_0 = 0.400 \text{ mol L}^{-1}$

For a first order reaction,

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

$\therefore\ k = \frac{2.303}{20} \log \frac{0.400}{0.289}$

$\Rightarrow\ k = \frac{2.303}{20} \log \frac{4.00}{2.89}$

$\Rightarrow\ k = \frac{2.303}{20} [\log 4.00 - \log 2.89]$

$\Rightarrow\ k = \frac{2.303}{20} [0.6021 - 0.4609]$

$\Rightarrow\ k = \frac{2.303}{20} \times 0.1412$

$\Rightarrow\ k = 2.303 \times 0.00706$

$\Rightarrow\ k = 1.626 \times 10^{-2} \text{ min}^{-1}$

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

Here, $[R]_0 = 0.400 \text{ mol L}^{-1}$, $t = 100$ min,

$k = 1.626 \times 10^{-2} \text{ min}^{-1}$, $[R] = ?$

$\therefore\ 100 = \frac{2.303}{1.626 \times 10^{-2}} \log \frac{0.400}{[R]}$

$\frac{100 \times 1.626 \times 10^{-2}}{2.303} = \log \frac{0.4}{[R]}$

$0.7060 = \log \frac{0.4}{[R]}$

or Antilog $(0.7060) = \frac{0.4}{[R]}$

$5.082 = \frac{0.4}{[R]} \Rightarrow [R] = \frac{0.4}{5.082} = 0.079 \text{ M}$

(iii) Initial rate, *i.e.*, rate of reaction when $t = 0$

When $t = 0.00$ min, $[R] = 0.400 \text{ mol L}^{-1}$

Also, $k = 1.626 \times 10^{-2} \text{ min}^{-1}$

$\therefore$ Initial rate $= k[R]$

$= 1.626 \times 10^{-2} \text{ min}^{-1} \times 0.400 \text{ mol L}^{-1}$

$= 6.504 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$

**60.** (i) *Refer answer 59(i).*

(ii) *Refer answer 59(iii).*

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

Here, $k = 1.6259 \times 10^{-2} \text{ min}^{-1}$, $[R]_0 = 0.400$ M,

$[R] = 0.350$ M

Substituting these values in the equation, we get

$t = \frac{2.303}{1.6259 \times 10^{-2}} \log \frac{0.400}{0.350}$

$= \frac{2.303}{1.6259 \times 10^{-2}} [\log 40 - \log 35]$

$= 141.583\,[1.6021 - 1.5441] = 141.583 \times 0.0580$

$= 8.21$ min

**61.** Given : $k = 5.10 \times 10^{-3}\ \text{min}^{-1}$,
$t = 3 \times 60\ \text{min} = 180\ \text{min}$
$[R]_0 = 0.1\ \text{M}$
Substituting these values in the equation

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

We get, $180\,\text{min} = \dfrac{2.303}{5.1 \times 10^{-3}\ \text{min}^{-1}} \log \dfrac{0.1}{[R]}$

$$\log \frac{0.1}{[R]} = \frac{180\,\text{min} \times 5.1 \times 10^{-3}\ \text{min}^{-1}}{2.303} = 0.398$$

$$\frac{0.1}{[R]} = \text{Antilog } 0.398 = 2.50$$

$[R] = 0.1/2.5 = 0.04\ \text{M}$

**62.** (i) $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{10} = 0.0693$

(ii) $N = N_0 \left(\dfrac{1}{2}\right)^n$

where, $n = \dfrac{\text{Total time}}{t_{1/2}} = \dfrac{60}{10} = 6$

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^6 = \frac{1}{64} \qquad \text{...(1)}$$

[where $N_0$ = initial amount of reactant and $N$ = amount of reactant left after time, $t$].

**63.** 20% decomposition means that $x$ = 20% of $a = 0.20\,a$

For first order reaction, $k = \dfrac{2.303}{t} \log \dfrac{a}{a - x}$

$$= \frac{2.303}{15} \log \frac{a}{a - 0.20a} = \frac{2.303}{15} \log \frac{a}{0.80a}$$

$$= \frac{2.303}{15} \log 1.25$$

$$= \frac{2.303}{15} \times 0.0969 = 0.0148\,\text{min}^{-1}$$

**64.** Here $t_{1/2} = 5 \times 10^4$ s and $t$ = 2 hours
= 2 × 60 × 60 = 7200 s

$$k = \frac{0.693}{t_{1/2}} \text{ and } k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\therefore \quad \frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\frac{0.693}{5 \times 10^4} = \frac{2.303}{7200} \log \frac{[A]_0}{[A]}$$

$$\therefore \quad \log \frac{[A]_0}{[A]} = \frac{0.693}{5 \times 10^4} \times \frac{7200}{2.303} = \frac{4989.6}{11.515 \times 10^4}$$

$$= \frac{4989.6}{115150} = 0.0433$$

$$\frac{[A]_0}{[A]} = \text{antilog } 0.0433 = 1.105$$

$$\Rightarrow \frac{[A]}{[A_0]} = \frac{1}{1.105} \times 100 = 90.49\%$$

**65.** For the first order reaction :

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

Let $[A]_0 = x$
then $[A] = x - 20\%$ of $x = x - 0.20\,x = 0.80\,x$

$$\therefore \quad k = \frac{2.303}{5} \log \frac{x}{0.80x}$$

$$k = \frac{2.303}{5} \log 1.25 \qquad \text{...(i)}$$

In second case, let $[A]_0 = x$ then
$[A] = x - 60\%$ of $x = x - 0.60\,x = 0.40\,x$

$$\therefore \quad k = \frac{2.303}{t} \log \frac{x}{0.40x}$$

$$k = \frac{2.303}{t} \log 2.5 \qquad \text{...(ii)}$$

From (i) and (ii), we have

$$\frac{2.303}{t} \log 2.5 = \frac{2.303}{5} \log 1.25$$

$$\frac{\log 2.5}{t} = \frac{\log 1.25}{5} \Rightarrow t = \frac{5 \times \log 2.5}{\log 1.25}$$

$$\therefore \quad t = \frac{5 \times 0.3979}{0.0969} = 20.53 \text{ minutes}$$

**66.** Radioactive decay follows first order kinetics.
Let $[A]_0 = 100$
$\therefore$ $[A] = 100 \times 80\% = 80$

Decay constant $(k) = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{5730}$

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} = \frac{2.303}{0.693/5730} \log \frac{100}{80}$$

$$= \frac{2.303 \times 5730}{0.693} \times \log 1.25 = \frac{2.303 \times 5730}{0.693} \times 0.0969$$

$$= \frac{1278.7108}{0.693} = 1845.18 \approx 1845 \text{ years}$$

**67.** A reaction of second order which obeys the first order rate law is known as pseudo first order reaction.

*e.g.*, Inversion of cane sugar :

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Rate = $k[C_{12}H_{22}O_{11}]^1[H_2O]^0$

**68.** (i) Average rate of reaction between the time interval 30 to 60 seconds is

$$r_{av} = \frac{-[0.17-0.31]}{60-30} = \frac{0.14}{30}$$

$= 4.67 \times 10^{-3}\ s^{-1}$ [Taking only difference]

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

At $t = 30$ s,

$$k = \frac{2.303}{30}\log\frac{0.55}{0.31} = \frac{2.303}{30}\times 0.249 = 1.91\times 10^{-2}\ s^{-1}$$

At $t = 60$ s,

$$k = \frac{2.303}{60}\log\frac{0.55}{0.17} = \frac{2.303}{90}\times 0.5099 = 1.96\times 10^{-2}\ s^{-1}$$

At $t = 90$ s

$$k = \frac{2.303}{90}\log\frac{0.55}{0.085}$$

$$k = \frac{2.303}{90}\times 0.8109 = 2.07\times 10^{-2}\ s^{-1}$$

∴ Average value of $k$

$$= \frac{1.91\times 10^{-2} + 1.96\times 10^{-2} + 2.07\times 10^{-2}}{3} = 1.98\times 10^{-2} s^{-1}$$

**69.** (i) For a first order reaction,

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

When $t = 30$ s

$$k = \frac{2.303}{30}\log\frac{0.60}{0.30} = \frac{2.303}{30}\times 0.3010 = 0.0231\ s^{-1}$$

When $t = 60$ s

$$k = \frac{2.303}{60}\log\frac{0.60}{0.15} = \frac{2.303}{60}\times 0.602 = 0.0231\ s^{-1}$$

As the value of $k$ is constant at different time intervals, the reaction is first order w.r.t. ester when $[H_2O]$ is constant. Hence, it is pseudo first order reaction.

(ii) Average rate $= -\frac{C_2 - C_1}{t_2 - t_1} = \frac{-(0.15-0.30)}{60-30}$

$$= \frac{0.15}{30} = 5\times 10^{-3}\ \text{mol L}^{-1}s^{-1}$$

**70.** The minimum extra energy which must be supplied to the reactants to enable them to cross over the potential energy barrier between reactants and products is called activation energy. It is denoted by $E_a$.

$$E_a = E_T - E_R$$

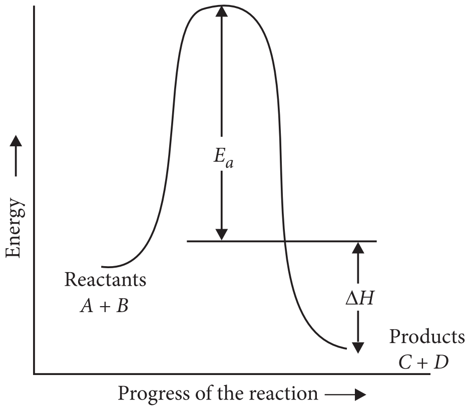
**71.** The rate constant is nearly doubled with a rise in temperature by 10° for a chemical reaction.

The temperature effect on the rate constant can be represented quantitatively by Arrherius equation :

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

where $k \rightarrow$ Rate constant
$A \rightarrow$ Arrhenius factor
$R \rightarrow$ Gas constant
$T \rightarrow$ Temperature
$E_a \rightarrow$ Energy of activation for the reaction.

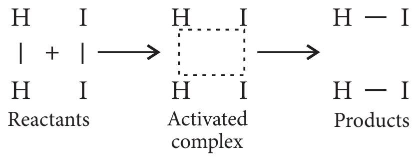
**72.** The energy required to form activated complex is called activation energy. It is the difference between the threshold energy and the average energy possessed by the reacting molecules.



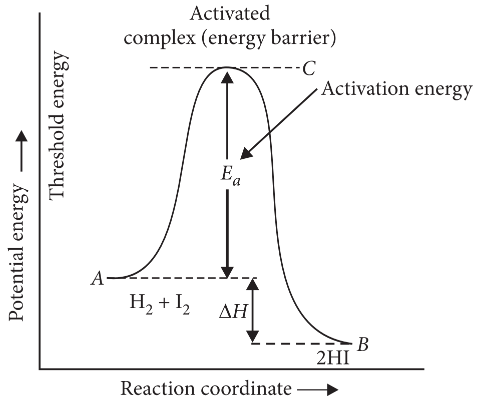
Activation energy ($E_a$) = Threshold energy – Average energy possessed by reacting molecules.

**73.** When the colliding molecules possess the kinetic energy equal to $E_a$, the atomic configuration of species formed at this stage is different from the reactant as well as the products. This stage is called the activated state and the specific configuration bearing state is called activated complex.

For example, in the reaction between $H_{2(g)}$ and $I_{2(g)}$, activated complex has configuration in which H—H and I—I bonds are breaking and H—I bonds, are forming as shown below.



Potential energy diagram of this reaction is shown below :



**74.** Here $k_2 = 2k_1$, $T_1 = 298$ K, $T_2 = 308$ K
$E_a = ?$

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

$$\log\frac{2k_1}{k_1} = \frac{E_a}{2.303R}\left[\frac{308-298}{308\times298}\right]$$

$$\log 2 = \frac{E_a}{2.303R}\left[\frac{10}{91784}\right]$$

$$0.3010 = \frac{1.089\times10^{-4}E_a}{2.303\times8.314}$$

$$E_a = \frac{0.3010\times2.303\times8.314}{1.089\times10^{-4}} = 52922.77\,\text{J mol}^{-1}$$

**75.** (i) Order of a reaction : *Refer to answer 10.*
(ii) Activation energy of a reaction : *Refer to answer 70.*

**76.** For first order reaction, $t_{1/2} = \dfrac{0.693}{k}$

$$t_{1/2} = 200\,\text{min} = 200\times60 = 12000\text{ s}$$

$$\Rightarrow \; k = \frac{0.693}{12000\text{ s}} = 5.8\times10^{-5}\text{ s}^{-1}$$

Also, for first order decomposition of $H_2O_2$, rate constant is

$$\log k = 14.2 - \frac{1.0\times10^4}{T}\text{K}$$

Comparing the above equation with the Arrhenius equation,

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

$$\Rightarrow \; E_a = 2.303\times8.314\times1.0\times10^4 = 1.91\times10^5\text{ J mol}^{-1}$$

**77.** Given, $T_1 = 300$ K, $T_2 = 310$ K
$k_1 = 2\times10^{-2}$, $k_2 = 4\times10^{-2}$, $E_a = ?$
Using Arrhenius equation,

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

$$\text{or} \quad \log\frac{4\times10^{-2}}{2\times10^{-2}} = \frac{E_a}{2.303\times8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$$

$$\text{or} \quad \log 2 = \frac{E_a}{2.303\times8.314}\times\left[\frac{310-300}{310\times300}\right]$$

$$\text{or} \quad E_a = \frac{0.301\times2.303\times8.314\times310\times300}{10}$$

$$= 53598\text{ J mol}^{-1} = 53.598\text{ kJ mol}^{-1}$$

**78.** $k_1 = 0.02\text{ s}^{-1}$, $k_2 = 0.07\text{ s}^{-1}$
$T_1 = 500$ K, $T_2 = 700$ K

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_2T_1}\right]$$

$$\log\frac{0.07}{0.02} = \frac{E_a}{2.303R}\left[\frac{700-500}{700\times500}\right]$$

$$E_a = \frac{0.544\times2.303\times8.314\times700\times500}{200}$$

$$= 18228.07\text{ J mol}^{-1}$$

**79.** $\log\dfrac{k_2}{k_1} = \dfrac{E_a}{2.303R}\left(\dfrac{T_2 - T_1}{T_1T_2}\right)$

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

$$E_a = \frac{2.303\times8.314\,\text{J mol}^{-1}\text{K}^{-1}\times650\,\text{K}\times700\,\text{K}}{700\,\text{K} - 650\,\text{K}} \times\log\frac{2.39\times10^{-8}}{2.15\times10^{-8}}$$

$$E_a = \frac{19.147\times650\times700}{50}(\log 23.9 - \log 2.15)\text{ J mol}^{-1}$$

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

$$= 174237.7\times1.0459\text{ J mol}^{-1}$$

$$= 1822235.2\text{ J mol}^{-1} = 182.24\text{ kJ mol}^{-1}$$

**80.** Given : Slope, $m = -4250$ K,
$R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$
$E_a = ?$

Using formula,

$$\log k = \log A - \frac{E_a}{2.303\,R}\left(\frac{1}{T}\right)$$

Comparing with $y = mx + c$ [straight line equation]

$$-\frac{E_a}{2.303\,R} = \frac{-\,4250}{1}$$

$E_a = 2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 4250\ \text{K}$

$= 81{,}375.35\ \text{J mol}^{-1} = 81.37\ \text{kJ mol}^{-1}$

**81.** Since the rate of a reaction quadruples when temperature changes from 293 K to 313 K.

$\therefore\ \ k_2 = 4k_1$

$T_1 = 293$ K and $T_2 = 313$ K

According to Arrhenius equation

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

Putting the values

$$\log\frac{4k_1}{k_1} = \frac{E_a}{2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}}\left[\frac{(313 - 293)\text{K}}{293\text{K} \times 313\ \text{K}}\right]$$

$$0.6021 = \frac{E_a \times 20}{2.303 \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 293\ \text{K} \times 313\ \text{K}}$$

$$\therefore\ \ E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}\ \text{J mol}^{-1}$$

$= 52863.3\ \text{J mol}^{-1} = 52.86\ \text{kJ mol}^{-1}$

**82.** $k_1 = 4.5 \times 10^3\ \text{s}^{-1}, T_1 = 10 + 273\ \text{K}, k_2 = 1.5 \times 10^4\ \text{s}^{-1}$

$T_2 = ?\ E_a = 60\ \text{kJ mol}^{-1}$

From Arrhenius equation,

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

$$\text{or}\log\frac{1.5\times10^4}{4.5\times10^3} = \frac{60000\ \text{J mol}^{-1}}{2.303\times8.314\ \text{JK}^{-1}\ \text{mol}^{-1}}\left[\frac{T_2 - 283}{283T_2}\right]$$

$$\text{or}\ \log 3.333 = 3133.63\left[\frac{T_2 - 283}{283T_2}\right]$$

$$\text{or}\ \ \frac{0.5228}{3133.63} = \frac{T_2 - 283}{283T_2}$$

or $\quad 0.0472T_2 = T_2 - 283$ or $0.9528T_2 = 283$

$$\text{or}\quad T_2 = \frac{283}{0.9528} = 297\text{K}\ \ \text{or}\ (297 - 273)°\text{C} = 24°\text{C}$$

**83.** $T_1 = 295$ K, $k_1 = k$ (say)

$T_2 = 305$ K, $k_2 = 2k$, $E_a = ?$

Using Arrhenius equation,

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

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

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

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

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

**84.** $k_1 = 6.0 \times 10^{-4}\ \text{s}^{-1}, T_1 = 300\ \text{K}, E_a = 3.05 \times 10^5\ \text{J mol}^{-1}$

$k_2 = ?$, $T_2 = 310$ K

Using Arrhenius equation,

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

$$\text{or, }\log\frac{k_2}{k_1} = \frac{3.05 \times 10^5\ \text{J mol}^{-1}}{2.303 \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}} \times \left[\frac{310 - 300}{300 \times 310}\right]$$

$$\log\frac{k_2}{k_1} = \frac{3.05\times10^5\text{J mol}^{-1}\times10\ \text{K}}{1780684.2\ \text{JK}^{-1}\text{mol}^{-1}}$$

$$\log\frac{k_2}{k_1} = 1.71 \Rightarrow \frac{k_2}{k_1} = \text{antilog}(1.71)$$

$$\frac{k_2}{6\times10^{-4}} = 51.28$$

$k_2 = 3.07 \times 10^{-2}\ \text{s}^{-1}$

**85.** Here $T_1 = 600$ K, $T_2 = 700$ K

$E_a = 209\ \text{kJ/mol} = 209000\ \text{J mol}^{-1}$

$k_1 = 1.6 \times 10^{-5}\ \text{s}^{-1}$

Using formula,

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

$$\log k_2 - \log k_1 = \frac{209000}{2.303 \times 8.314}\left[\frac{700 - 600}{700 \times 600}\right]$$

$\log k_2 - \log\,(1.60 \times 10^{-5}) = 2.598$

$\log k_2 = 2.598 + \log\,(1.6 \times 10^{-5})$

$\log k_2 = -\,4.796 + 2.598 = -\,2.198$

$\quad k_2 = \text{Antilog}\ (-\,2.198)$

or, $\ k_2 = 6.34 \times 10^{-3}\ \text{s}^{-1}$

**86.** (i) *Refer to answer 72.*

(ii) *Refer to answer 83.*

**87.** It is due to improper orientation. Energy more than threshold energy and proper orientation are the two main factors which are responsible for a reaction to occur.