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# CHEMISTRY

**For NEET (UG)**
**Aligned with Latest NCERT & NEET Pattern**

## CHEMICAL KINETICS

# 3. Chemical Kinetics

## 1. INTRODUCTION

In the thermodynamics, we have studied whether a reaction will take place or not and if it does then upto what extent (chemical equilibrium), In this chapter we will study about how fast a chemical reaction takes place and what are the different factors affecting this rate of chemical reaction. How to optimize the conditions as to maxims the output in optimum time. The last part of chapter will be dealing with the mechanism of a chemical reaction and catalysis.

Rate/Velocity of chemical reaction:

The rate of change of concentration with time of different chemical species taking part in a chemical reaction is known as **<u>rate of reaction of that species.</u>**

Rate = $\frac{\Delta c}{\Delta t} = \frac{\text{mol / lit.}}{\text{sec}}$ = mol lit$^{-1}$ time$^{-1}$ = mol dm$^{-3}$ time$^{-1}$

Rate is always defined in such a manner so that it is always a positive quantity.

Types of Rates of chemical reaction :

For a reaction R $\longrightarrow$ P

Average rate

$$= \frac{\text{Total change in concentration}}{\text{Total time taken}}$$

$$= \frac{\Delta c}{\Delta t} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

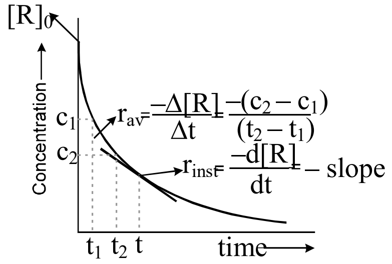
Instantaneous rate :

rate of reaction at a particular instant.

$$R_{\text{instantaneous}} = \lim_{t\to 0}\left[\frac{\Delta c}{\Delta t}\right] = \frac{dc}{dt} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Instantaneous rate can be determined by drawing a tangent at time t on curve drawn for concentration versus time.

**Initial Rate :** Instantaneous rate at 't = 0' is called initial rate [slope of tangent at t = 0].



Relation between reaction rates of different species involved in a reaction :

For the reaction : $N_2 + 3H_2 \longrightarrow 2NH_3$

Rate of reaction of $N_2 = -\frac{d[N_2]}{dt}$

Rate of reaction of $H_2 = -\frac{d[H_2]}{dt}$

Rate of reaction of $NH_3 = \frac{d[NH_3]}{dt}$

These rates are not all equal. Therefore by convention the rate of a reaction is defined as

Rate of reaction

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

✍ **Note:** Rate of reaction value is dependent on the stoichiometic coefficients used in the reaction while rate of any species will be fixed value under given conditions.

**Example : 01**

From the concentrations of R at different times given below, calculate the average rate of the reaction: R→P during different intervals of time.

| t/s | $10^3 \times$ [R]/mol L$^{-1}$ |
|---|---|
| 0 | 160 |
| 5 | 80 |
| 10 | 40 |
| 20 | 10 |
| 30 | 2.5 |

**Solution:**

We can determine the difference in concentration over different intervals of time and thus determine the rate by dividing Δ[R] by Δt

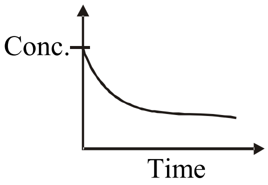
| $\frac{[R]_1 \times 10^3}{\text{mol L}^{-1}}$ | $\frac{[R]_2 \times 10^3}{\text{mol L}^{-1}}$ | $\frac{t_2}{s}$ | $\frac{t_1}{s}$ | $\frac{r_{av} \times 10^3}{\text{mol L}^{-1}\text{ s}^{-1}}$ $= \frac{-[R_2 - R_1]\times 10^3}{[t_2 - t_1]}$ |
|---|---|---|---|---|
| 160 | 80 | 5 | 0 | 16 |
| 80 | 40 | 10 | 5 | 8 |
| 40 | 10 | 20 | 10 | 3 |
| 10 | 2.5 | 30 | 20 | 0.75 |

## 2. FACTORS AFFECTING RATE OF CHEMICAL REACTION

1. Concentration
2. Temperature
3. Nature of reactants & products
4. Catalyst
5. pH of the solution
6. Dielectric constant of the medium.
7. Radiations/light
8. Pressure
9. Electrical & Magnetic field.

The first four factors generally affect rate of almost all reactions while other factors are specific to some reactions only. The common examples of these reactions are:

❖ **Concentration :** We known from law of mass action that Rate is proportional to concentration of reactants. “So, generally rate of reaction decreases with passage of time, since concentration of reactants decreases.



❖ Temperature :

❖ Nature of reactants & Products :

Physical state of reactants :

Gaseous state > Liquid state > Solid state

Decreasing order of rate of reaction.

**Physical size of reactants :** As we decreases the particle size rate of reaction increases since surface area increases.

**Chemical nature of reactants :**

- If more bonds are to be broken, the rate of reaction will be slow.
- Similarly bond strength is more, rate of reaction will be slow.

❖ Catalyst :

- Presence of positive catalyst lower down the activation energy hence increases the rate of reaction.
- Presence of negative catalyst increases activation energy hence decreases the rate of reaction.

❖ pH of solution :

Eg. $Fe(CN)_6^{4-} \xrightarrow{(Tl^{3+})} [Fe(CN)_6]^{3-}$

This reaction takes place with appreciable rate in acidic medium, but does not take place in basic medium.

❖ **Dielectric constant of the medium :**

More is the dielectric constant of the medium greater will be the rate of ionic reactions.

❖ **Radiations/light :**

Radiation are useful for photochemical reaction.

❖ **Pressure :**

Pressure is important factor for gaseous reaction.

❖ **Electrical & Magnetic field :**

Electric & magnetic fields are rate determining factors if a reaction involves polar species.

Rate Law (Dependence of rate on concentration of reactants) :

The representation of rate of reaction in terms of the concentration of the reactants is called the rate law.

It can only be established by experiments.

Generally rate law expressions are not simple and these may differ for the same reaction on conditions under which the reaction is being carried out.

But for large number of reactions starting with pure reactants we can obtain simple rate laws.

For these reactions: **Rate $\propto$ (conc.)$^{\text{order}}$**

Rate = K (conc.)$^{\text{order}}$ – differential rate equation or rate expression

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity

unit of K = (conc)$^{1-\text{order}}$ time$^{-1}$

✍ **Note:**

Value of K is a constant for a given reaction, depends only on temperature

- **Order of reaction:**

Let there be a reaction $m_1A + m_2B \longrightarrow$ products.

Now, if on the basis of experiment, we find that

$R \propto [A]^P [B]^q$

Where p may or may not be equal to $m_1$ & similarly q may or may not be equal to $m_2$.

p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and (p + q) is overall order of the reaction.

✍ **Note:**

Order of a reaction can be ‘zero’ or any whole number, can be a fractional number and it can even be negative with respect to a particular reactant. But overall order is not found to be negative for any reaction till observed.

**Examples showing different values of order of reactions :**

| Reaction | Rate law | Order |
|---|---|---|
| $2N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g)$ | $R = K\,[N_2O_5]^1$ | 1 |
| $5Br^-\,(aq) + BrO_3^-\,(aq) + 6H^+\,(aq) \longrightarrow 3Br_2\,(\ell) + 3H_2O\,(\ell)$ | $R = K\,[Br^-]\,[BrO_3^-]\,[H^+]^2$ | 1 + 1 + 2 = 4 |
| $H_2\,(Para) \longrightarrow H_2\,(ortho)$ | $R = K\,[H_{2\,(Para)}]^{3/2}$ | 3/2 |
| $NO_2\,(g) + CO\,(g) \longrightarrow NO\,(g) + CO_2\,(g)$ | $R = K\,[NO_2]^2\,[CO]^o$ | 2 + 0 = 2 |
| $2O_3\,(g) \longrightarrow 3O_2\,(g)$ | $R = K\,[O_3]^2\,[O_2]^{-1}$ | 2 – 1 = 1 |
| $H_2 + Cl_2 \xrightarrow{hv} 2\,HCl$ | $R = K\,[H_2]^0[Cl_2]^0$ | 0 + 0 = 0 |

The reaction (2) does not take place in one single step. It is almost impossible for all the 12 molecules of the reactants to be in a state of encounter simultaneously. Such a reaction is called complex reaction and takes places in a sequence of a number of elementary reactions. For an elementary reaction the sum of stoichiometric coefficients = order of the reactions. But for complex reactions order is to be experimentally calculated.

**Example : 02**

The reaction $2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$ is second order in NO and first order in $Cl_2$. In a volume of 2 $dm^3$, 5 mole of nitric oxide and 2 mol of $Cl_2$ were brought together, and the initial rate was $2.4 \times 10^{-3}$ mole $dm^{-3}\,s^{-1}$. What will be the rate when half of the chlorine has reacted?

**Solution:**

$4.32 \times 10^{-4}$ M $sec^{-1}$

$2NO + Cl_2 \longrightarrow 2NaCl$

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$$R = k\left(\frac{5}{2}\right)^2 2.4 \times 10^{-3} = k\left(\frac{15}{4}\right)$$

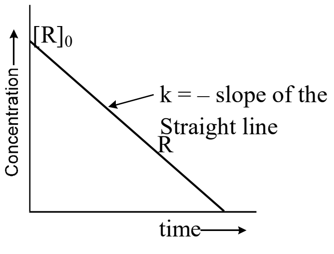
$$R = \frac{4 \times 2.4 \times 10^{-3}}{25}$$

$$R = \frac{4 \times 2.4 \times 10^{-3}}{25}\left[\frac{3}{2}\right]^2 \left[\frac{1}{2}\right]$$

$$R = \frac{4 \times 2.4 \times 10^{-3}}{25} \times \frac{9 \times 1}{8} = 4.32 \times 10^{-4} \text{ M sec}^{-1}$$

## 3. INTEGRATED RATE LAWS

### (1) Zero order reactions :



For a zero order reaction

General rate law is, Rate = k $[conc.]^o$ = constant

If $C_0$ is the initial concentration of a reactant and $C_t$ is the concentration at time 't' then

$$Rate = k = \frac{C_0 - C_t}{'t'} \text{ or } kt = C_0 - C_t \text{ or } C_t = C_0 - kt$$

Unit of K = same as that of Rate = mol $lit^{-1}$ $sec^{-1}$.

$$\text{Time for completion} = \frac{C_0}{k}$$

$t_{1/2}$ (half life period)

$$\text{at } t_{1/2},\ C_t = \frac{C_0}{2}, \text{ so } kt_{1/2} = \frac{C_0}{2}$$

$$\Rightarrow \quad \mathbf{t_{1/2}} = \frac{C_0}{2k}$$

$\therefore\ t_{1/2} \propto C_0$

- Examples of zero order reactions :
  Generally decomposition of gases on metal surfaces at high concentrations follow zero order kinetics.

  $2PH_3\,(g) \xrightarrow{Ni} 2\,P + 3\,H_2$ Rate = K $[PH_3]^o$

  $2HI\,(g) \xrightarrow{Au} H_2 + I_2$

  $2NH_3(g) \xrightarrow{N} N_2 + 3H_2$ $H_2 + Cl_2 \xrightarrow{hv} 2\,HCl$

  Rate = R $[H_2]^o\,[Cl_2]^o$

### (2) First Order Reactions:

(i) Let a 1st order reaction is

$A \longrightarrow$ Products

conc. 'a' 0 t = 0 'a–x' ......

t = 't'

Let $\frac{dx}{dt}$ be the rate of reaction at time 't'

$$\therefore \frac{dx}{dt} = k\,(a–x)^1 \text{ or } \frac{dx}{a-x} = kdt.$$

On solving

$$t = \frac{2.303}{k} \log \frac{a}{a-x}\ k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

$$\boxed{K = \frac{2.303}{t}\log\frac{C_0}{C_t}}$$

$$\boxed{\begin{array}{c}\text{Wilhemy formula:}\\ C_t = C_0\,e^{-kt}\end{array}}$$

$$\boxed{\begin{array}{l}\text{Interval formula:}\\ K = \dfrac{2.303}{(t_2 - t_1)}\log\dfrac{C_1}{C_2}\end{array}}$$

- If any substance is growing/increasing following first order kinetics then:

  $$k = \frac{2.303}{t} \log\left(\frac{a+x}{a}\right)$$

  Where a is initial concentration of the substance and x is the increment in its concentration after time t.

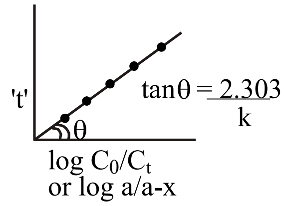
Half life time ($t_{1/2}$) $k = \frac{2.303}{t_{1/2}} \log \frac{2C_0}{C_0}$

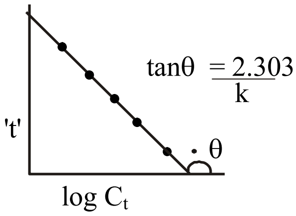
$$\Rightarrow t_{1/2} = \frac{2.303\log 2}{k} = \frac{\ell n2}{k} = \frac{0.693}{k}$$

∴ Half life period for a 1st order reaction is a constant quantity.

- Graphical Representation:

$$t = -\frac{2.303}{k}\log C_t + \frac{2.303}{R}\log C_0$$





❖ First order growth reaction :

For bacteria multiplication or virus growth use following concept

Consider a growth reaction

| Time | Population (or colony) |
|---|---|
| 0 | a |
| dt | (a + x) |

$$\frac{dx}{dt} = k(a+x) \text{ or } \frac{dx}{(a+x)} = kdt$$

on integration

$\log_e(a+x) = kt + C$

at $t = 0$ ; $x = 0 \Rightarrow C = \log_e a$

$$kt = -\log_e \frac{a}{(a+x)} \quad \text{or}$$

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

or $\boxed{K = \frac{2.303}{t}\log_{10}\left(\frac{a+x}{a}\right)}$

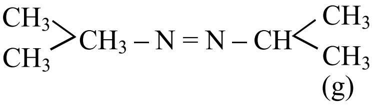
❖ Generation time:

At t = generation time, x = a

$$\therefore \; t = \frac{0.693}{K}$$

❖ Examples of 1st order reactions:

1. Decomposition of azoisopropane

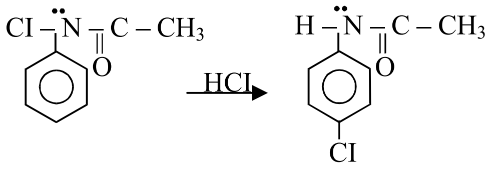


$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH_3-N=N-CH\!\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

(g)

$$(g)\xrightarrow{\Delta}N_2(g)+C_6H_{14}(g)$$

2. Conversion of N–chloro acetanilide into p–chloroacetanilide



3. $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$
4. $NH_4NO_2 \longrightarrow 2H_2O + N_2$
5. Radioactive decay

- All radioactive decays are always first order kinetics.

$${}^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn + 2H_4$$

**Example : 03**

Calculate $\frac{t_{0.75}}{t_{0.50}}$ for a 1st order reaction

**Solution:**

$$k = \frac{2.303}{t_{1/4}}\log\frac{C_0}{\frac{1}{4}C_0} = \frac{2.303}{t_{1/2}}\log\frac{C_0}{\frac{C_0}{2}}$$

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

**Example : 04**

At least how many half-lives should elapse for a 1st order reaction A products so that the reaction is at least 95% completed? (log 2 = 0.3)

(1) 4 (2) 5 (3) 6 (4) 7

**Solution: (2)**

$$\underset{0\%}{100}\xrightarrow{t_{1/2}}\underset{50\%}{50}\xrightarrow{t_{1/2}}\underset{75\%}{25}\xrightarrow{t_{1/2}}\underset{87.5\%}{12.5}\xrightarrow{t_{1/2}}$$

$$\underset{93.75\%}{6.25}\xrightarrow{t_{1/2}}\underset{96.875\%}{3.125}$$

**(3) Second order reaction :**

2nd order Reactions

Two types

$A + A \longrightarrow$ products

a a

(a – x) (a – x)

$$\therefore \frac{dx}{dt} = k(a-x)^2 \Rightarrow \int_0^x \frac{dx}{(a-x)^2} = \int kdt$$

$$\Rightarrow \left(\frac{-1}{(a-x)}\right)_0^1 = kt$$

$$\Rightarrow \frac{1}{(a-x)} - \frac{1}{a} = kt$$

$A + B \longrightarrow$ products.

a b 0

a – x b – x

Rate law;

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

$$\int_0^x \frac{dx}{(a-x)\quad(b-x)} = \int_0^t k\,dt$$

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

**(4) Psuedo first order reaction :**

A second order (or of higher order) reactions can be converted into a first order reaction if the other reactant is taken in large excess. Such first order reactions are known as psuedo first order reactions.

∴ For $A + B \longrightarrow$ Products [Rate = $K\,[A]^1\,[B]^1$]

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

Now if 'B' is taken in large excess b > > a.

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

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

∵ 'b' is very large can be taken as constant

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

$$\Rightarrow k' = \frac{2.303}{t} \log \frac{a}{a-x}$$

- k' is psuedo first order rate constant
- K' will have units of first order.
- K will have units of second order.
- Examples of Pseudo 1st order reactions:

Hydrolysis of canesugar

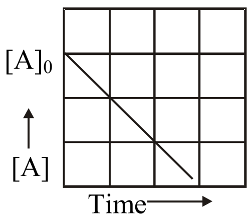
$$\underset{\text{sucrose}}{C_{12}H_{12}O_{11}} + \underset{\text{excess}}{H_2O} \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

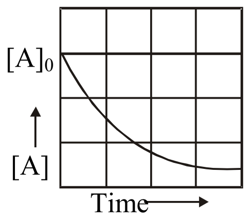
**(2) Hydrolysis of esters**

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

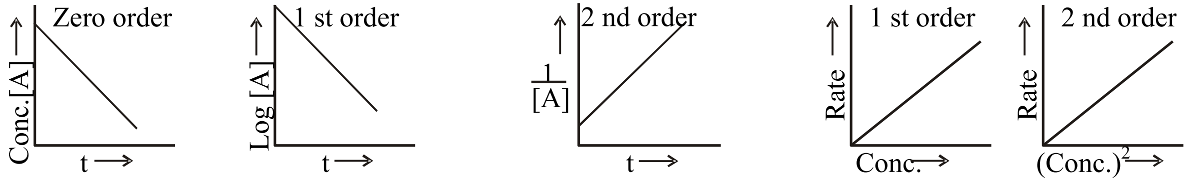
**Table: Characterstics of First-and Second-Order Reactions of the Type A Products**

| | **Zero Order** | **First-Order** | **Second-Order** | **n$^{th}$ order** |
|---|---|---|---|---|
| Differential Rate law | $\frac{-\Delta A}{\Delta t} = k[A]^\circ$ | $-\frac{\Delta[A]}{\Delta t} = k[A]$ | $-\frac{\Delta[A]}{\Delta t} = k[A]^2$ | $-\frac{\Delta A}{\Delta t} = k\ [A]^n$ |
| (Integrated Rate law) | $[A]_t = [A]_0 - kt$ | $\ln\,[A]_t = -kt + \ln\,[A]_0$ | $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ | $\frac{1}{(A_t)^{n-1}} - \frac{1}{(A_0)^{n-1}} = (n-1)\ kt$ |
| Linear graph | $[A]_t$ versus t | $\ln\,[A]$ versus t | $\frac{1}{[A]}$ versus t | $\frac{1}{(A_t)^{n-1}}$ v/s t |
| Half-life | $t_{1/2} = \frac{[A]_0}{2k}$<br>(Depends on $[A]_0$) | $t_{1/2} = \frac{0.693}{k}$<br>(Independent of $[A]_0$) | $t_{1/2} = \frac{1}{k[A]_0}$<br>(Depends on $[A]_0$) | $t_{1/2} \propto \frac{1}{(A_0)^{n-1}}$ |





Graphical comparison of different orders



## 4. METHODS TO DETERMINE ORDER OF A REACTION

**(1) Initial rate method:**

- By comparison of different initial rates of a reaction by varying the concentration of one of the reactants while others are kept constant
  $r = k\,[A]^a\,[B]^b\,[C]^c$ if
  $[B]$ = constant
  $[C]$ = constant
  then for two different initial concentrations of A we have
  $r_{0_1} = k\,[A_0]_1^{\,a}$ $r_{0_2} = k\,[A_0]_2^{\,a}$

$$\Rightarrow \quad \frac{r_{0_1}}{r_{0_2}} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^x$$

or in log form we have $\boxed{a = \dfrac{\log (r_{0_1}/r_{0_2})}{\log ([A_0]_1/[A_0]_2)}}$

**Example : 05**

The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below:

| t/s | p/Pa |
|---|---|
| 0 | $4.00 \times 10^3$ |
| 100 | $3.50 \times 10^3$ |
| 200 | $3.00 \times 10^3$ |
| 300 | $2.5 \times 10^3$ |

Determine the order of reaction, its rate constant and half-life period.

**Solution:** It Can be seen that rate of reaction between different time intervals is :

0–100 s,

$$\text{rate} = \frac{[3.50-4.00]\times 10^3 \;\; \text{Pa}}{100} = 5 \text{ Pa/s } 100\text{–}200\text{s},$$

$$\text{rate} = -\frac{[3.00-3.50]\times 10^3 \;\; \text{Pa}}{100\text{s}} = 5 \text{ Pa/s } 200\text{–}300\text{s},$$

$$\text{rate} = -\frac{[2.50-3.00]\times 10^3 \;\; \text{Pa}}{100} = 5 \text{ Pa/s}$$

We notice that the rate remains constant and therefore, reaction is of zero order. Alternatively, if we plot a p against t, it is a straight line again indicating it is a zero order reaction.

k = rate = 5 Pa/s

$$t_{1/2} = \frac{\text{initial concentration or pressure}}{2k}$$

$$= \frac{4.00\times 10^3\,\text{Pa}}{2\times 5 \;\; \text{Pa}\,\text{s}^{-1}} = 400\text{s}$$

**(2) Integrated rate law method :**

- It is method of hit and trial. By checking where the kinetic data (experimental data) best fits into which integrated rate law, we determine the order. It can also be done graphically.

**Example : 06**

The rate of decomposition of $N_2O_5$ in $CCl_4$ solution has been studied at 318 K and the following results have been obtained :

| t/min | 0 | 135 | 342 | 683 | 1693 |
|---|---|---|---|---|---|
| c/M | 2.08 | 1.91 | 1.67 | 1.35 | 0.57 |

Find the order of the reaction and calculate its rate constant. What is the half-life period?

**Solution:**

It can be shown that the rate of the reaction. We now try integrated first order equation i.e.,

$$k = \frac{\ln \; (c_0/c)}{t}$$

| t/min | c/M | $k = \dfrac{\ln \; (c_0/c)}{t}\,\text{min}^{-1}$ |
|---|---|---|
| 0 | 2.08 | $6.32 \times 10^{-4}$ |
| 135 | 1.91 | $6.30 \times 10^{-4}$ |
| 339 | 1.68 | $6.32 \times 10^{-4}$ |
| 683 | 1.35 | $6.32 \times 10^{-4}$ |
| 1680 | 0.72 | $6.31 \times 10^{-4}$ |

It can be seen that the value of k is almost constant for all the experimental results and hence it is first order reaction with

$k = 6.31 \times 10^{-4}\ \text{min}^{-1}$ .

$$t_{1/2} = \frac{0.69}{6.31\times 10^{-4}\ \text{min}^{-1}} = 1.094 \times 10^3\ \text{min}^{-1}$$

Graphical method : Alternatively, if we draw a graph between $\ell$n c against t, we obtain a straight line with slope = – k.

**(3) Method of half lives :**

- The half lives of each order is unique so by comparing half lives we can determine order
  for n^th order reaction $t_{1/2} \propto \dfrac{1}{[R_0]^{n-1}}$

$$\boxed{\frac{t_{1/2}}{t'_{1/2}} = \frac{(R'_0)^{n-1}}{(R_0)^{n-1}}}$$

**Example : 07**

In the reduction of nitric gas with hydrogen, the reaction was found to be 50% complete in 210 seconds when the initial pressure of the mixture was 200mm. In a second experiment the time of half reaction was 140 seconds when the initial pressure was 300mm. Calculate the total order of the reaction.

**Solution:** For a nth order reaction ($n \neq 1$), $t_{1/2} \propto \dfrac{1}{c_0^{\,n-1}}$

$$\frac{210}{140} = \left(\frac{300}{200}\right)^{n-1} \quad n = 2$$

**(4) Ostwald's isolation method :**

- This method is employed in determining the order of complicated reaction by isolating one of the reactants so far in its influence on the rate of reaction is concerned. Suppose the reaction under consideration is A + B + C Products

The order of the reaction is determined with respect to A, B and C. For the determination of the order w.r.t A, B & C are taken in large excess so there conc. does not affected during the reaction. The order of reaction is then determined by using any method described above.

Like wise the order of reaction w.r.t B & C is determined.

If $n_A$ , $n_B$ & $n_C$ are the order w.r.t A, B & C

The order of reaction n = $n_A + n_B + n_C$

**Example : 08**

The reaction :

$CH_3COF + H_2O = CH_3COOH + HF$

has been studied under the following initial conditions:

| **Case I** | **Case II** |
|---|---|
| $c^0_{H_2O} = 1.00$ M | $c^0_{H_2O} = 0.02$ M |
| $c^0_{CH_3COF} = 0.01$ M | $c^0_{CH_3COF} = 0.80$ M |

Concentrations were monitored as a function of time and are given below:

| **Case I** | | **Case II** | |
|---|---|---|---|
| **t/min** | $c_{CH_3COF}$ **/ M** | **t/min** | $c_{CH_2}$ **/M** |
| 0 | 0.01000 | 0 | 0.0200 |
| 10 | 0.00857 | 10 | 0.0176 |
| 20 | 0.00735 | 20 | 0.0156 |
| 40 | 0.00540 | 40 | 0.0122 |

Determine the order of the reaction and the rate constant for the reaction.

**Solution:**

Let rate = k $(c_{CH_3COF})^a (c_{H_2O})^b$

We shall use here Ostwald isolation method, as in one set of experimental conditions, $c^0_{H_2O} >> c^0_{CH_3COF}$ and in the second case, $c^0_{H_2O} << c^0_{CH_3COF}$ . In the first case we determine the order of the reaction with respect to $CH_3COF$. We note that the reaction is not of zero order as rate of reaction changes with time. We now, apply first order equation and find,

| t/min | $c_{CH_3COF}$ / M | $\dfrac{k(c_{H_2O})^b}{\min^{-1}} = \dfrac{\ln\left(\dfrac{c^0_{CH_3COF}}{c_{CH_3COF}}\right)}{t}$ |
|---|---|---|
| 0 | 0.01000 | – |
| 10 | 0.00857 | 0.0154 |
| 20 | 0.00735 | 0.0154 |
| 40 | 0.00540 | 0.0154 |

Therefore, k $(c_{H_2O})$ = 0.0154 $\min^{-1}$

as we note the order of reaction with respect to $CH_3COF$ is 1. Now we determine the order of reaction with respect to water. Again we try for first order equation.

| t/min | $c_{H_2O}$ / M | $\dfrac{k(c_{CH_3COF})^b}{\min^{-1}} = \dfrac{\ln\left(\dfrac{c^0_{H_2O}}{c_{H_2O}}\right)}{t}$ |
|---|---|---|
| 0 | 0.0200 | – |
| 10 | 0.0176 | 0.0128 |
| 20 | 0.0156 | 0.0124 |
| 40 | 0.0122 | 0.0124 |

Average = 0.0125 $\min^{-1}$

The reaction is first order in $H_2O$ and we have

$k(c_{CH_3COF}) = 0.01125 \min^{-1}$

Now in case I,

$$k = \frac{0.0154 \min^{-1}}{1.00} = 0.0154\ M^{-1}\ \min^{-1}$$

and in case II

$$= 0.0125\ \frac{0.0154 \min^{-1}}{1.00}\ 0.800$$

$$= 0.0156\ M^{-1}\ \min^{-1}.$$

## 5. Methods to monitor the progress of the reaction

**(1) Pressure measurement :**

Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature.

This method can applied for those reaction also in which a gas is produced because of decomposition of a solid or liquid. We can get an idea about the concentration of reacting species at a particular time by measuring pressure.

- The pressure data can be given in terms of
  (i) Partial pressure of the reactant
  (ii) Total pressure of the reaction system
  (iii) Pressure at only some points of time

**Example : 09**

Find the expression for K in terms of $P_0$ , $P_t$ and n

**Solution:**

Let there is a 1st order reaction,

Let initial pressure at time t

| A(g) $\longrightarrow$ | nB(g) | |
|---|---|---|
| $P_0$ | 0 | t = 0 |
| $P_A = (P_0 - x)$ | nx | t = t |
| – | $nP_0$ | t = ∞ |

$\therefore$ $P_t$ (Total pressure at time 't')

$= P_0 - x + nx$

$= P_0 + (n - 1)\ x$

$$\therefore\ x = \frac{P_t - P_0}{n-1}$$

$$\therefore\ P_A = P_0 - \frac{P_t - P_0}{n-1} = \frac{P_0 n - P_t}{n-1}$$

$\therefore$ $a \propto p_0$ &

$$a - x \propto P_A = \frac{nP_0 - P_t}{n-1}$$

$$\therefore \quad k = \frac{2.303}{t} \log \frac{P_0(n-1)}{nP_0 - P_t}$$

$$\text{or} \quad K = \frac{2.303}{t} \log \frac{P_\infty - P_0}{P_\infty - P_t}$$

Final total pressure after infinite time = $P_f = nP_0$

- Formula is not applicable when n = 1, the value of n can be fractional also.
- Do not remember the formula but derive it for each question.

**Example : 10**

For the decomposition of azoisopropane at 270ºC it was found that at t = 0, the total pressure was 33.15 mm of Hg and after 3 minutes the total pressure was found to be 46.3 mm of Hg. Calculate the value of 'k' for this reaction.

**Solution:**

$$k = \frac{2.303}{3} \log \frac{33.15\ (2-1)}{2 \times 33.15 - 46.3}$$

$= 0.1684\ \text{min}^{-}$

**(2) Volume measurement :**

(i) By measuring the volume of product formed we can monitor the progress of reactions.

**Example : 11**

Study of a reaction whose progress is monitored by measuring the volume of a escaping gas.

$$NH_4NO_2\ (s) \xrightarrow{\Delta} 2H_2O\ (\ell) + N_2\ (g)$$

**Solution:**

Let, $V_t$ be the volume of $N_2$ collected at time 't'

$V_\infty$ = be the volume of $N_2$, collected at the end of the reaction.

$a \propto V_\infty$

$(a - x) \propto V_\infty - V_t$

$$\therefore \quad k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

**(ii) By titration method :**

By measuring the volume of titrating agent we can monitor amount of reactant remaining or amount of product formed at any time. It is the titre value. Here the milliequilivents or millimoles are calculated using valence factors.

**Example : 12**

Study of acid hydrolysis of an ester.

$$CH_3COOCH_3 + \underset{\text{(excess)}}{H2O} \xrightarrow[\text{(HCl)}]{H^+} CH_3COOH + CH_3OH$$

The progress of this reaction is monitered or dertermined by titrating the reaction mixture at different time intervals against a standard solution of NaOH using phenolphthalein as indicator. Find out rate constant of the reaction in terms of volume of NaOH consumed at t = 0, $V_0$ , at t = ∞, $V_\infty$ & at time t, $V_t$ .

**Solution:**

Let,

$V_0$ = vol. of NaOH used at t = 0

[this is exciusively for HCl.]

$V_t$ = vol. of NaOH used at 't'

$V_\infty$ = vol. of NaOH used at t = ∞

$a \propto V_\infty - V_0$

$a - x \propto V_\infty - V_t$ ; $x \propto V_t - V_0$

$$a \propto V_\infty - V_0 ;\ k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

(3) Optical rotation measurment :

It is used for optically active sample. It is applicable if there is at least one optically active species involved in chemical reaction.

- The optically active species may be present in reactant or product.

It is found that $\begin{matrix} (r_\infty - r_0) \propto a \\ (r_\infty - r_t) \propto (a - x) \end{matrix}$

(a = concentration , x = amount consumed)

where are $r_0$, $r_t$, $r_\infty$ are angle of optical rotation at time t = 0, t = t and t = ∞

**Example : 13**

Study of hydrolysis of sucrose : Progress of this reaction is monitored with the help of polarimeter because a solution of sucrose is dextrorotatory and on hydrolysis, the mixture of glucose as fructose obtained becomes leavorotary. That's why this reaction is also known as inversion of cane sugar.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

excess glucose fructose

Sp. rotation +66.5º +52.7º –92.4º

Let the readings in the polarimeters are

t = 0, $\theta_0$ ; t = 't', $\theta_t$ and at t = ∞, $\theta_\infty$

Then calculate rate constant 'k' in terms of these readings.

**Solution:**

The principle of the experiment is that change in the rotation is directly proportional to the amount of sugar hydrolysed.

$\therefore\ a \propto \theta_1 - \theta_\infty$ ; $a - x \propto \theta_t - \theta_\infty$ ;

$$k = \frac{2.303}{t} \log \left( \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty} \right)$$

## 6. Effect of temperature on rate of reaction

In early days the effect of temperature on reaction rate was expressed in terms of temperature coefficient which was defined as the ratio of rate of reaction at two different temperature differing by $10^0$C(usually these temperatures were taken as $25^0$C and $35^0$C)

$$\text{T.C.} = \frac{K_t + 10}{K_t} \approx 2 \text{ to } 3 \text{ (for most of the reactions)}$$

For some reactions temperature coefficient is also found to be less than unity. for example $2NO + O_2 \rightarrow 2NO_2$ rate of reaction decreases on increasing temperature.

**Example : 14**

For a reaction T.C. = 2, Calculate $\frac{k_{40^\circ C}}{k_{25^\circ C}}$ for this reaction.

**Solution:**

$$\frac{k_2}{k_1} = (T.C.)^{\frac{\Delta t}{10}} = (2)^{\frac{15}{10}} = (2)^{\frac{3}{2}} = \sqrt{8}$$

- But the method of temperature coefficient was not exact and to explain the effect of temperature on reaction rate new theory was evolved

## 7. Arhenius theroy of reaction rate

It was developed by max Trautz and William Lewis.

It gives insight in to the energetics and mechanistic aspects of reactions.

It is based upon kinetic theory of gases.

Arrhenius proposed a theory of reaction rate which states as follows :

- A chemical reaction takes place due to the 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).
- Every collision does not bring a chemical change. The collision that actually produce the products are effective collision. For a collision to be effective the following two barriers are to be effective the following two barriers are to be cleared.

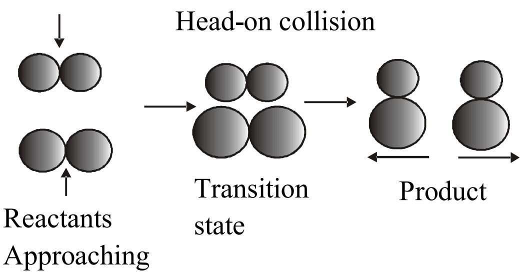
❖ Energy barrier :

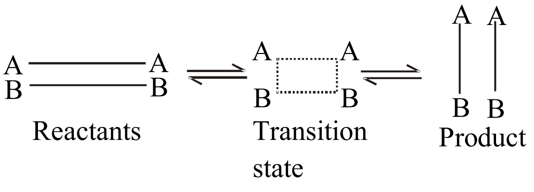
The minimum amount of energy which the colliding molecules must posses as to make the chemical reaction to occur is known as threshold energy.

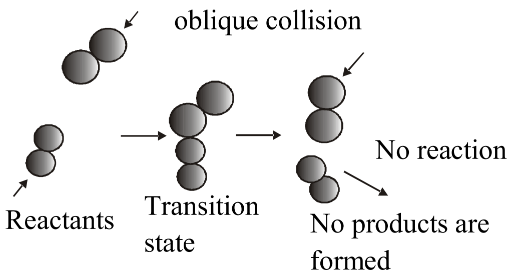
“The minimum amount of extra energy required by reactant molecules to participate in a reaction is called activation energy ($E_a$)”

❖ Orientation barrier :

Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper direction to make collision effective. Following diagrams can explain importance of suitable direction for collision.





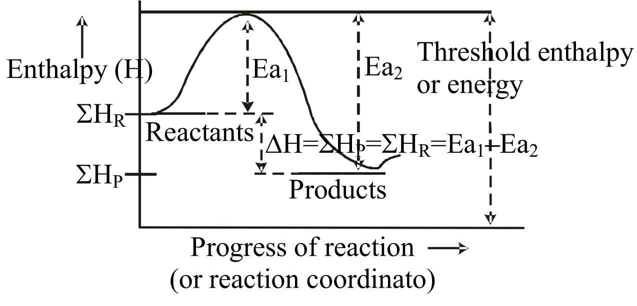


- Collision to be effective the colliding molecules must posses some certain minimum energy called threshold energy of the reaction.
- Reactant molecules having energy equal or greater than the threshold are called active molecules and those having energy less than the threshold are called passive molecules.
- At a given temperature there exists a dynamic equilibrium between active and passive molecules. The process of transformation from passive to active molecules being endothermic, increase of temperature increases the number of active molecules and hence the reaction.

  Passive molecules → Active molecules, $\Delta H = +ve$
- Concept of energy of activation ($E_a$)
- The extra amount of energy which the reactant molecules (having energy less than the threshold) must acquire so that their mutual collision may lead to the breaking of bond(s) and hence the energy is known as energy of activation of the reaction. It is denoted by the symbol $E_a$. Thus,

  $E_a$ = Threshold energy – Actual average energy

  $E_a$ is expressed in kcals $mole^{-1}$ or kJ $mole^{-1}$.
- The essence of Arrhenius Theory of reaction rate is that there exists an energy barrier in the reaction path between reactant(s) and product(s) and for reaction to occur the reactant molecules must climb over the top of the barrier which they do by collision. The existence of energy barrier and concept of $E_a$ can be understood from the following diagram.



$\Sigma H_R$ = Summation of enthalpies of reactants

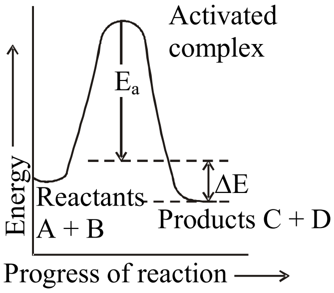
$\Sigma H_P$ = Summation of enthalpies of reactants

$\Delta H$ = Enthalpy change during the reaction

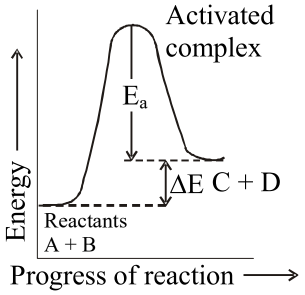
$Ea_1$ = Energy of activation of the forward reaction

$Ea_2$ = Energy of activation of the backward reaction

From the figure above it can be concluded that the minimum activation energy of any exothermic reaction will be zero while minimum activation energy for any endothermic reaction will be equal to ΔH. Greater the height of energy barrier, greater will be the energy of activation and more slower will be the reaction at a given temperature.



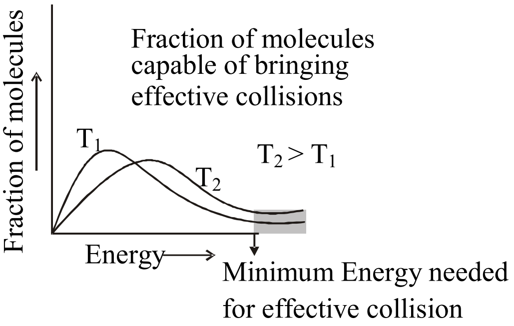
(Exothermic)



(Endothermic)

Rate of any chemical reaction = Collision frequency × fraction of the total number of effective collision= Collision frequency × fraction of the total number of collision in which K.E. of the colliding molecules equals to $E_a$ or exceeds over it.

Collision frequency is the number of collisions per unit volume per unit time. It is denoted by the symbol Z. Z is directly proportional to $\sqrt{T}$. By 10ºC rise in temperature, so it is the fraction of the total number of effective collision that increases markedly resulting into marked increase in the reaction rate.



Arrhenius equation $\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$

Integrating equation 4 assuming $E_a$ to be constant we get,

$$\ln k = \frac{Ea}{RT} + \ln A \text{ or } \ln\frac{k}{A} = \frac{Ea}{RT}$$

$$\text{or } k = A\ e^{\frac{-Ea}{RT}}$$

This is integrated form of Arrhenius equation.

Where :

Constant A = pre–exponential factor it is a constant for a given reaction.

From this equation it is evident that as T → ∞, k → A. Thus, the constant A is the rate constant of reaction at infinity temperature. The rate constant goes on increasing with temperature.

So, when T approaches inifinty, k will be maximum. That is to say, A is the maximum rate constant of a reaction.

- The expontential term i.e. $e^{-Ea/RT}$ measures the fraction of total number of molecules in the activated state or fraction of the total number of effective collisions.

  $\frac{n_{E_a}}{n} = e^{-E_a/RT}$ Where

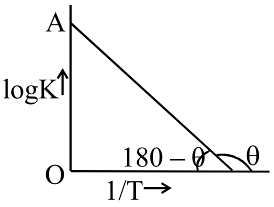
  $n_{Ea}$ = no. of molecules of reactant in the activated state

  n = total no. of molecules of the reactant in the reaction

- From Arrhenius Equation we have,

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

  So from this it is evident that a plot of log k versus $\frac{1}{T}$ will be a straight line of the slope equal to $-\frac{E_a}{2.303\ R}$ and intercept equal to log A as shown below :



Thus, from this plot $E_a$ and A both can be determined accurately.

If $k_1$ and $k_2$ be the rate constant of a reaction at two different temperature $T_1$ and $T_2$ respectively, then we have

$$\log k_1 = -\frac{E_a}{2.303\ R}.\frac{1}{T_1} + \log A \text{ and}$$

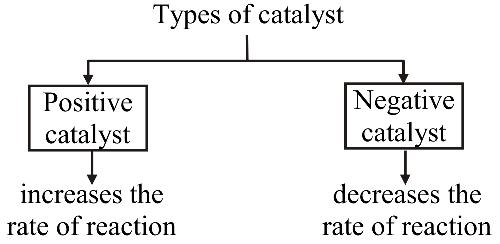
$$\log k_2 = -\frac{E_a}{2.303\ R}.\frac{1}{T_1} + \log A$$

Subtracting we get

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

## 8. CATALYST AND CATALYSIS :

A catalyst is a substance, which increases the rate of a reaction without itself being consumed at the end of the reaction, and the phenomenon is called catalysis.



Catalyst are generally foreign substances but sometimes one of the product may act as a catalyst and such catalyst is called **"auto catalyst"** and the phenomena is called **auto catalysis**.

**Examples of catalysis:**

(1) Thermal decomposition of $KClO_3$ is found to be accelerated by the presence of $MnO_2$. Here $MnO_2$ (foregin substance) acts as a catalyst.

$$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2\uparrow + [MnO_2]$$

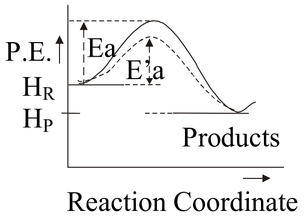
- $MnO_2$ can be received in the same composition and mass at the end of the reaction.

(2) In the permanganate titration of oxalic acid intially there is slow discharge of the colour of permanganate solution but afterwards the discharge of the colour become faster. This is due to the formation of $MnSO_4$ during the reaction which acts as a catalyst for the same reaction. Thus, $MnSO_4$ is an **"auto catalyst"** for this reaction. This is an example of auto catalyst.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_2 \longrightarrow K_2SO_4 + 8H_2O + 10CO_2$$

General characteristics of catalyst :

- A catalyst does not initiate the reaction. It simply fastens it.
- Only a small amount of catalyst can catalyse the reaction.



- A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence $\Delta G^o$. It simply lowers the time needed to attain equilibrium. This means if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst also the reaction will go to 75% of completion before the attainment of equilibrium but the time needed for this will be less than 20 minutes.

- A catalyst drives the reaction through a low energy path and hence $E_a$ is less. That is, the function of the catalyst is to lower down the activation energy.
  $E_a$ = Energy of activation in absence of catalyst.
  $E'_a$ = Energy of activation in presence of catalyst.
  $E_a - E'_a$ = lowering of activation energy by catalyst.

**Comparison of rates of reaction in presence and absence of catalyst :**

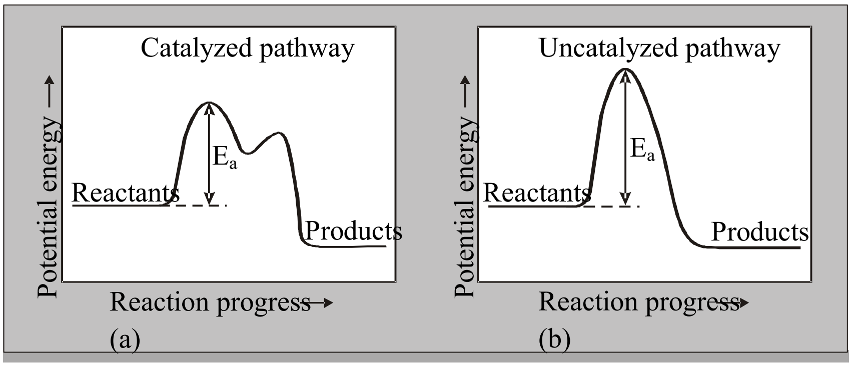
If k and $k_{cat}$ be the rate constant of a reaction at a given temperature T, and $E_a$ and $E'_a$ are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{cat}}{k} = \frac{Ae^{-E'a/RT}}{Ae^{-Ea/RT}} = Ae^{(E_a - E'_a)/RT}$$

Since $E_a - E'_a$ is positive so $k_{cat} > k$. the ratio $\frac{k_{cat}}{k}$ gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature.

The rate of reaction in the presence of catalyst at any temperature $T_1$ may be made equal to the rate of reaction in absence of catalyst but for this sake we will have to raise the temperature. Let this temperature be $T_2$ this

$$e^{-E'_a/RT_1} = e^{-E_a/RT_2} \text{ or } \frac{E'_a}{T_1} = \frac{E_a}{T_2}$$



(a) (b)

**Example : 15**

**For the reaction $CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$ under the same concentration conditions of the reactants, the rate of the reaction at 250°C is 1500 times as fast as the same reaction at 150°C. Calculate the activation energy of the reaction. If the frequency factor is $2.0 \times 10^{10}$ $M^{-1}$ $sec^{-1}$, calculate the rate constant of the reaction at 150°C.**

**Solution:**

$$\log\frac{K_2}{K_1} = \frac{E}{2.303R}\left[\frac{T_2 - T_1}{T_1\ T_2}\right]$$

$$\log 1500 = \frac{E}{2.303\times 2}\times\frac{100}{523\times 423}$$

$$E = \frac{3.1761\times 2.303\times 2\times 523\times 423}{100}$$

$= 32.36$ kcal $mol^{-1}$

$$\log K = \log A - \frac{E}{2.303RT}$$

$$= \log(2.0\times 10^{10}) - \frac{32360}{2.303\times 2\times 423}$$

$= 10.301 - 16.609 = -6.308$

$K = 4.92\times 10^{-7}$ liters $mol^{-1}$ $sec^{-1}$

**Example : 16**

**The pyrolysis of an organic ester follows a first order process and its rate can be expressed as**

$$\ln k = 78.09 - \frac{42075}{T}$$

**where k is given in the $min^{-1}$. Calculate the time required for 25 percent reaction to complete at 227°C.**

**Solution:**

$$\ln k = 78.09 - \frac{42075}{500} = -6.06$$

$$\log k = -\frac{6.06}{2.303} = -2.63\ ;$$

$k = 2.344 \times 10–3$ $min^{-1}$

When x = 0.25; $k = \frac{2.303}{t_{1/4}}\log\frac{a}{0.75\ a}$

$$t_{1/4} = \frac{2.303}{2.344\times 10^{-3}}\log 1.333 = 122.6 \text{ min}$$

**Example : 17**

**The slope of the plot of log k vs $\frac{1}{T}$ for a certain reaction was found to be $-5.4\times 10^{3}$. Calculate the energy of activation of the reaction. If the rate constant of the reaction is $1.155\times 10^{-2}$ $sec^{-1}$ at 373 K, what is its frequency factor ?**

**Solution:**

(1) slope $= \frac{-E}{2.303\ \ R} = -5.4\times 10^{3}$

$E = 5.4\times 10^{3}\times 2.303\times 1.987$

$= 24.624$ cal $mol^{-1}$

(2) $E = Ae^{-E/RT}$ ;

$$\log 1.155\times 10^{-2} = \log A - \frac{24.624}{2.303\times 1.987\times 373}$$

or $A = 3.08\times 10^{12}$ $sec^{-1}$

## 9. DERIVATION OF A SUITABLE RATE LAW WITH THE HELP OF A SUITABLE MECHANISM

- Molecularity and Order :

  The number of molecules that react in an elementary step is the molecularity of the elementary reaction. Molecularity is defined only for the elementary reactions and not for complex reactions. No elementary reactions involving more than three molecules are known, because of very low probability of near-simultaneous collision of more than three molecules.

  The rate law for the elementary reaction

  $$aA + bB \longrightarrow \text{products}$$

  rate $= k[A]^a[B]^b$, where a + b = 1, 2 or 3.

  For an elementary reaction, the orders in the rate law equal the coefficients of the reactants.

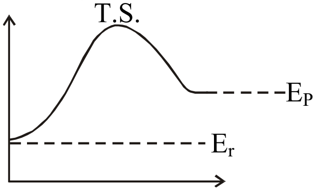
  While, the order is defined for complex as well as elementary reactions and is always experimentally calculated by the mechanism of the reaction, usually by the slowest step of the mechanism known as **rate determining step of the reaction.**

| Comparison B/W Molecularity and order of reaction | |
|---|---|
| Molecularity of Reaction | Order of Reaction |
| 1. It is defined as the no. of molicules of reactant taking part in a chemical reaction.<br>eq $NH_4NO_2 \rightarrow N_2 + 2H_2O$ m = 1 | 1. It is defined as the sum of the power of concentration terms that appear in rate law.<br>$NH_4No_2 \rightarrow N_2 + 2H_2O$.<br>Rate = K $[NH_4NO_2]$ |
| 2. It is always a whole Number It can neither be zero nor fractional | 2. It may be zero, fractional or integer. |
| 3. It is derived from RDS in the mechanism of reaction. | 3. It is derived from rate expression. |
| 4. It is theoretical value. | 4. It is experimental value. |
| 5. Reactions with molecularity ≥ 4 are rare. | 5. Reactions with O.R. ≥ are also rare. |
| 6. Molecularity is in independent of pressure and temperature. | 6. OR. depends upon Pressure and temperature. |

❖ **Mechanism of a reaction :**
Reactions can be divided into
- Elementary / simple / single step
- Complex / multi-step

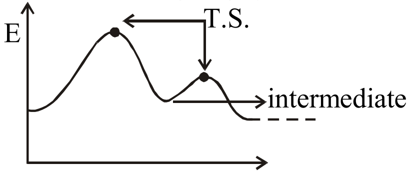
❖ **ELEMENTARY REACTION :**

- These reaction take place in single step without formation of any intermediate



- For elementary reaction we can define molecularity of the reaction which is equal to no of molecules which make transition state or activated complex because of collisions in proper orientation and with sufficient energy
- molecularity will always be a natural no
1 = unimolecular one molecule gets excited (like radioactivity)
2.= bimolecular
3 = trimolecular
- Molecularly ≤ 3 because the probabilty of simaltaneous collision between 4 or more molecules in proper orientation is very low
- For elementary reaction there is only single step and hence it is going to be rate determining step so order of an elementary reaction is its molecularity
Order of elementary reaction w.r.t. reactant = stoichiometric co-efficient of the reactant
$H_2 + I_2 \rightarrow 2HI \rightarrow$ Simple reaction
rate = k $[H_2]$ $[I_2]$
$2H_2 + 2I_2 \rightarrow 4HI$ (not elementary)
reaction obtained by multiplying an elementary reaction with some no will not be of elementary nature
$H_2 + Cl_2 \rightarrow 2HCl$ order = 0

❖ **COMPLEX REACTION :**



- Reaction which proceed in more than two steps. or having some mechanism. ( sequence of elementary reaction in which any complex reaction proceeds)
- For complex reaction each step of mechanism will be having its own molecularity but molecularity of net complex reaction will not be defined.
- Order of complex reaction can be zero fractions whole no, even negative w.r.t. some species.
- Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction generally using Rate determine step (R.D.S) if given.
- Rate law of a reaction is always written in terms of conc. of reactant, products or catalysts but never in terms of conc. of interimediates.

The mechanism of any complex reaction is always written in terms of elementary steps, so molecularity of each of these steps will be defined but net molecularity of complex reaction has no meaning.
The mechanism of most of the reaction will be calculated or predicted by using mainly the following approximations.

**Example : 18**

The thermal decomposition of $N_2O_5$ occurs in the following steps.

Step - I $N_2O_5 \xrightarrow{\text{slow}} NO_2 + NO_3$

Step - II $N_2O_5 + NO_3 \xrightarrow{\text{fast}} 3NO_2 + O_2$

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

suggest the rate expression.

**Solution:**

$N_2O_5 \longrightarrow NO_2 + NO_3$ (slow)

$N_2O_5 + NO_3 \longrightarrow 2NO_2 + O_2$ (Fast)

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

rate = k $[N_2O_5]$

## 10. COMPLICATIONS IN 1ST ORDER REACTION

❖ **PARRALLEL 1st ORDER REACTION**

Frequently a species can react in different ways to give a variety of products. For example, toluene can be nitrated at the ortho, meta, or para positions, We shall consider the simplest case, that of two competing irreversible first-order reactions :

$A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$

where the stoichiometric coefficients are taken as unity for simplicity. The rate law is

$$\frac{d\ [B]}{dt} = K_1\,[A] \quad \frac{d\ [C]}{dt} = K_2\,[A]$$

$$\frac{-d[A]}{dt} = \frac{d[B]}{dt} + \frac{d[C]}{dt}$$

$$\frac{-d[A]}{dt} = (K_1 + K_2)\,[A] = K_{eff}\,[A]$$

$$K_{eff} = K_1 + K_2$$

$$\frac{\ln 2}{T_{eff}} = \frac{\ln 2}{T_1} + \frac{\ln 2}{T_2}$$

(where T represent half life)

$$\boxed{\frac{1}{T_{eff}} = \frac{1}{T_1} + \frac{1}{T_2}} \quad \text{(remember)}$$

Now, $[A]_t = a\,e^{-K_{eff}t} = a\,e^{-(K_1+K_2)t}$

$$\frac{d[B]}{dt} = K_1\,[A] \qquad \frac{d[B]}{dt} = K_1 a\,e^{-(K_1+K_2)t}$$

$$[B] = \left(\frac{k_1 a}{k_1 + k_2}\right)(1 - e^{-(K_1+K_2)t})$$

similarly,

$$[C] = \frac{K_2\ \ a}{K_1 + K_2}\,(1 - e^{-(K_1+K_2)t})$$

$$\boxed{\frac{[B]}{[C]} = \frac{K_1}{K_2}} \quad \text{(Remember)} \qquad K_{eff} = k_1 + k_2$$

### Example: 19

For each reaction below, express the rates of change of [product] and [reactant] in the correct relationship to each other.

(1) $2O_3(g) \rightarrow 3O_2(g)$

(2) $2HOF(g) \rightarrow 2HF(g) + O_2(g)$

**Solution:**

(1) $$\frac{-d[O_3]}{2dt} = +\frac{1}{3}\frac{d[O_2]}{dt}$$

$$\frac{-d[O_3]}{dt} = \frac{2}{3}\frac{d}{dt}\,[O_2]$$

(2) $$-\frac{1}{2}\frac{d[HOF]}{dt} = +\frac{d[HF]}{2dt} = +\frac{d[O_2]}{dt}$$

$$\frac{-d[HOF]}{dt} = +\frac{d[HF]}{dt} = +\frac{2d[O_2]}{dt}$$

### Example : 20

In a catalytic experiment involving the Haber's process, $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of reaction was measured as rate = $2 \times 10^{-4}$ $M.s^{-1}$. If there were no side reactions, express the rate of reaction in terms of (1) $N_2$ (2) $H_2$?

**Solution:**

Rate of Reaction

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

(1) $$2 \times 10^{-4} = -\frac{d[N_2]}{dt}$$

(2) $$2 \times 10^{-4} \times 3 = -\frac{d[H_2]}{dt} = 6 \times 10^{-4}\ MS^{-1}.$$

### Example : 21

**Write the units of the rate constants for a (i) Zeroth order, (ii) half order, (iii) first order, (iv) 3/2 order, (v) second order, (vi) 5/2 order, (vii) third order reactions.**

**Solution:**

Unit of Rate Constant = $(Mole)^{1-n}$ $(Litre)^{n-1}$ $Sec^{-1}$

Where n is the order of Reaction

(i) For Zeroth order = $Mole^{(1-0)}$ $(Litre)^{(0-1)}$ $Sec^{-1}$

Unit of K

n = o   Mole $Litre^{(-1)}$ $Sec^{-1}$

Similarly For others

### Example : 22

**The reaction**

**$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$**

**is second order in $NO_2$ and zero order in CO at temperatures less than 500K.**

**(1) Write the rate expression for the reaction.**

**(2) How will the reaction rate change if the $NO_2$ concentration is halved?**

**Solution:**

(1) $\frac{-d}{dt}[CO] = \frac{-d}{dt}(NO_2) = K[NO_2]^2$ Order is zero w.r.t. CO but Conc will Still change

(2) Rate of Rxn = $K[NO_2]^2$ of Conc of $NO_2$ Half The Rate Becomes One fourth

### Example : 23

**For a reaction A + 3B → Product, Rate = {– d[A] / dt} = k $[A]^2$ [B] , the expression for the rate of reaction in terms of change in the concentration of B; {– d[B] / dt} will be :**

| | |
|---|---|
| **(1) k$[A]^2$ [B]** | **(2) k $[A]^2$ [3B]** |
| **(3) 3k $[A^2]$ [B]** | **(4) (1/3) k $[A^2]$ [B]** |

**Solution:**

For the given reaction

$$\frac{-d[A]}{dt} = \frac{1}{3}\frac{-d[B]}{dt} = K[A]^2[B]$$

Then $$\frac{-d[B]}{dt} = 3K[A]^2[B]$$

### Example : 24

Gaseous cyclobutene isomerizes to butadiene in a first order process which has k = $3.3 \times 10^{-4}$ $s^{-1}$ at $153^0$ C . How many minutes would it take for the isomerization to proceed 40 % to completion at this temperature .

**Solution:**

For the First order Rxn

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

$$t = \frac{2.303}{3.3\times10^{-4}}\log\left(\frac{100}{60}\right)$$

$t = 1.54 \times 10^{+3}$ Second.

= 25.66 Minute

### Example : 25

Calculate $\frac{t_{0.5}}{t_{0.25}}$ for a $1^{st}$ order reaction

**Solution:** $$\frac{t_{0.5}}{t_{0.25}} = \frac{\frac{2.303}{K}\log\frac{a}{(a-\frac{a}{2})}}{\frac{2.303}{K}\log\frac{a}{(a-\frac{a}{4})}} = \frac{\log 2}{(\log\frac{4}{3})}$$

### Example : 26

For the reaction A + B ⟶ products the following date were obtained :

| initial rate (mole/liter.sec) | [A] (mole/liter) | [B] (mole/liter) |
|---|---|---|
| 0.030 | 0.10 | 0.20 |
| 0.059 | 0.20 | 0.20 |
| 0.060 | 0.20 | 0.30 |
| 0.090 | 0.30 | 0.30 |
| 0.089 | 0.30 | 0.50 |

Write the rate equation for this reaction. Be sure to evaluate k.

**Solution:**

Rate = $K[A]^x [B]^y$

From data I.

$.030 = K [.10]^x [.20]^y$ (1) From data II.

$.059 = K [.20]^x [.20]^y$ (2) From III.

$.060 = K [.20]^x [.30]^y$ (3) divide 1 equation by (2)

$$\frac{.030}{.059} = \frac{K[.10]^x[.20]^y}{K[.20]^x[.30]^y}$$

$\Rightarrow$ x = 1

Then divide (2) equation by (3)

$$\frac{.059}{.060} = \frac{K[.20]^x[.20]^y}{K[.20]^x[.30]^y}$$

$\Rightarrow$ y = 0

Put the value of x and y in (1) equation

$.030 = K[.10]^1 [.20]^0$

$$K = \frac{.030}{.10} = .3 \text{ Sec-1}$$

**Example : 27**

Decomposition of $H_2O_2$.

$$H_2O_2 \longrightarrow H_2O\,(\ell) + \frac{1}{2}\,O_2\,(g)$$

The progress of this reaction is measured by titrating the reaction mixture with $KMnO_4$ at different time intervals. Calculate rate constant of the reaction in terms of volume of $KMnO_4$ consumed at time t = 0, $V_0$ and at time t, $V_t$.

**Solution:**

Assume the decomposetion of $H_2O_2$ is a first order reaction

$$H_2O_2 \rightarrow H_2O\,(l) + \frac{1}{2}\,O_2(g)$$

Kmno$_4$ React Only with the $H_2O_2$ them

For Ist order reaction

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

Then a$\alpha$ Vo and (a -x) $\alpha$ Vt

$$\text{Then } K = \frac{2.303}{t} \log\left(\frac{Vo}{Vt}\right)$$

**Example : 28**

**A $\xrightarrow{D}$ B + C**

| Time | 0 | t | ∞ |
|---|---|---|---|
| Volume of reagent | $V_1$ | $V_2$ | $V_3$ |

The reagent reacts with only B, C and D. Find k.

**Solution:**

A $\xrightarrow{D}$ B + C

at t = o   a   o   o

t = t   (a - x)   x   x

t = ∞   o   a   a

at t = 0 only D. React

at t = 0 after t = 0 reagent react with B.C.D.

2a $\alpha$ $(V_3 - V_1)$

$$a\ \alpha\ \frac{(V_3 - V_1)}{2}$$

2x $\alpha$ $(V_2 - V_1)$

2(a - x) $\alpha$ $(V_3 - V_1 - V_2 + V_1)$

$$(a - x)\ \ \alpha\ \frac{(V_3 - V_2)}{2}$$

$$\text{Then } K = \frac{1}{t} \ln \frac{(V_3 - V_1)}{(V_3 - V_2)}$$

**Example : 29**

A $\rightarrow$ B + C

| Time | 0 | t |
|---|---|---|
| Volume of reagent | $V_1$ | $V_2$ |

The reagent reacts with A, B and C. Find k.

**Solution:**

A $\rightarrow$ B + C

t = o   a   o   o

t = t   (a -x)   x   x

a$\alpha$ $V_1$

(a - x) + x + x $\alpha$ $V_2$

(a + x) $\alpha$ $V_2$

$$(a - x)\ \alpha\ (2V_1 - V_2)\ ; \qquad K = \frac{1}{t} \ln \frac{[A]_o}{[A]_t} = \frac{1}{t}$$

$$\ln \frac{V_1}{(2V_1 - V_2)}$$

**Example : 30**

A $\rightarrow$ B + C

| Time | T | ∞ |
|---|---|---|
| Volume of reagent | $V_2$ | $V_3$ |

Reagent reacts with all A, B and C and have ‘n’ factors in the ratio of 1 : 2 : 3 with the reagent. Find k.

**Solution:**

A $\longrightarrow$ B + C

t = o   a   o   o

t = t   (a-x)   x   x

t = ∞   o   a   a

Reagent React with all A.B.C. and have ‘n’ factor in the Ratio 1 **:** 2 **:** 3

$$2a + 3a\ \alpha\ V_3 \qquad \Rightarrow a\ \alpha\ \frac{V_3}{5}$$

(a-x) × 1 + 2x + 3x $\alpha$ $V_2$

$$(a + 4x)\ \alpha\ V_2\ \frac{V_3}{5} + 4x\ \alpha\ V_2$$

$$x\ \alpha\ \frac{1}{4}\left(V_2 - \frac{V_3}{5}\right) \Rightarrow (a\text{-}x)\ \alpha\ \frac{V_3}{5} - \frac{1}{4}\left(V_2 - \frac{V_3}{5}\right)$$

$$(a\text{-}x)\ \alpha\ \frac{V_3}{5} - \frac{1}{4}\left(V_2 - \frac{V_3}{5}\right).$$

$$(a\text{-}x)\ \alpha\ \frac{5(v_3 - v_2)}{20} \Rightarrow K = \frac{1}{t} \ln \frac{4V_3}{5(v_3 - v_2)}$$

### Example : 31

Now, let us assume that A, B and C are optically active compounds, which rotate the plane polarized light in the clockwise or anticlockwise direction.
A(soln.) B(soln.) + C(soln.)

| Time | 0 | T | ∞ |
|---|---|---|---|
| Total rotation in degrees | $r_0$ | $r_t$ | $r_\infty$ |

Calculate the expression of rate constant.

**Solution:**

The principle of the experiment is that change in the rotation is directally proportional to concentration.

$a \; \alpha \; (r_o - r_\infty)$

$(a - x) \; \alpha \; (r_t - r_\infty)$

Then Expression For rate constant

$$K = \frac{2.303}{t} \log \frac{r_o - r_\infty}{r_t - r_\infty}$$

### Example : 32

The hydrolysis of cane sugar was studied using an optical polarimeter and the following readings were taken :

**time (min.) : 0 84 min ∞**

observed rotation : 50 20 – 10

(degrees)

When will the mixture optically inactive? (log 2 = 0.3, log 3 = 0.48)

**Solution:**

From the hydrolysis

$$K = \frac{2.303}{t} \log \frac{(r_o - r_\infty)}{r_t - r_\infty} = \frac{2.303}{84} \log \frac{50+10}{20+10}$$

$$K = \frac{2.303}{84} \times .3010$$

The time taken when sample are optically Inactive is t

$$K = \frac{2.303 \times .3010}{84} = \frac{2.303}{t} \log \frac{50+10}{+10}$$

t = 217.14 minute

### Example : 33

Temperature coefficient of the rate of a reaction is 3. How many times the rate of reaction would increase if temperature is raised by 30 K :

(1) 3 (2) 9 (3) 27 (4) 81

**Solution:**

For same concentration $\frac{R_1}{R_2} = \frac{K_1}{K_2} = 3^{\frac{30}{10}} = 27$

### Example : 34

The reaction

$A + B \xrightarrow{\quad} \text{products}$

is first order with respect to both A and B has a rate constant of 6.0 ℓ $mol^{-1}$ $sec^{-1}$. at 27°C. Calculate the initial rate of the reaction at 47°C when equal volumes of A and B of concentration 0.02 moles $litre^{-1}$ in each are mixed. The activation energy of the energy of the reaction is 42 kJ $mol^{-1}$.

**Solution:**

Reaction $A + B \xrightarrow{\quad} \text{Product}$

We know $\log \left(\frac{K_2}{K_1}\right) = \frac{\Delta E}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$$\log \left(\frac{K_2}{K_1}\right) = \frac{\Delta E}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \left(\frac{K_2}{6}\right) = \frac{42 \times 10^3 [320 - 300]}{2.303 \times 8.3 \times 300 \times 320} = \frac{840}{1835.03}$$

$$\log \frac{K_2}{6} = .4577 \Rightarrow \frac{K_2}{6} = \text{anti log } (.4577)$$

$K_2 = 2.863 \times 6 = 17.178$

Rate at 47°C will be

The $Rate_2 = 17.178 \times [.01] \times [.01]$

$Rate_2 = 17.178 \times 10^{-4} = 1.7178 \times 10^{-3}$

### Example : 35

For a gaseous reaction $A \xrightarrow{\quad}$ products, the half-life of the first order decomposition at 400 K is 150 minutes and the energy of activation is 65.0 kJ $mole^{-1}$. What fraction of molecules of A at 400 K have sufficient energy to give the products ?

**Solution:**

$\frac{K}{A} = e^{\frac{-Ea}{RT}}$ =Fraction of Molecule Having Sufficient

Energy ⇒ $\frac{K}{A} = \frac{1}{e^{\frac{65 \times 10^2}{8.3 \times 400}}} = 3.13 \times 10^{-6}$

### Example : 36

**An exothermic reaction A → B has an activation energy of 17 KJ per mole of A. The heat of reaction is – 40 KJ/mole. The activation energy for the reverse reaction B → A is :**

**(1) 75KJ per mole (2) 67KJ per mole**

**(3) 57 KJ per mole (4) 17 KJ per mole**

**Solution:**

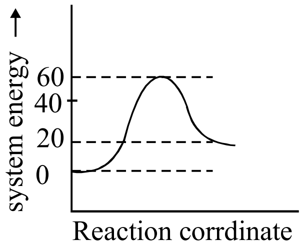
$\Delta H = E_A - E_B$

$-40 = 17 - E_B$

$E_B = 57$

### Example : 37

**Use the diagram below to answer the following questions.**



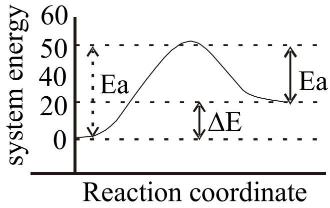
**(1) Is the forward reaction exothermic or endothermic?**

**(2) What is the approximate value of Δ *E* for the forward reaction?**

**(3) What is activation energy in each direction?**

**(4) A catalyst is found that lowers the activation energy of the reaction by about 10kJ/mol. How will this catalyst affect the rate of the reverse reaction?**

**Solution:**



(1) Forward Rxn are endothermic

(2) $\Delta E = (Ea - Ea^1) = (50-30) = 20$ KJ/Mole.

(3) Ea = 50 KJ/Mole $Ea^1 = 30$ KJ/Mole

(4) Increases

**Example : 38**

**At some temperature, the rate constant for the decomposition of HI on a gold surface is .1M.s$^{-1}$**

**$2HI \rightarrow H_2(g) + I_2(g)$**

**What is the order of the reaction? How long will it take for the concentration of HI to drop from 2M to .5M**

**Solution:**

From the unit of k given, the reaction is of zero order. As this reaction is of the type 2A → Products, we apply

$$k_0 = \frac{x}{nt} \text{ where n = 2 or } k_0 = \frac{a-(a-x)}{nt}$$

$$\text{or } .1 = \frac{(2-.5)}{2t} \text{ or t = 7.5sec}$$

**Example : 39**

**The rate of a first order reaction is 0.05 mole/L/s at 10 minutes and 0.04 mole/L/s at 30 minutes after initiation. Find the half-life of the reaction**

**Solution:**

Let the concentrations of the reactant after 10 min and 30 min be $C_1$ and $C_2$ respectively.

Rate after 10 min = $KC_1 = 0.05 \times 60$ Mmin$^{-1}$ and Rate after 30 min = $KC_2 = 0.04 \times 60$ Mmin$^{-1}$

$$\therefore \frac{c_1}{c_2} = \frac{5}{4}.$$

Supposing the reaction starting after 10 minutes

$$k = \frac{2.303}{20} \log\frac{c_1}{c_2} = \frac{2.303}{20} \log \frac{5}{4} = .011159$$

$$\therefore t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{.011159} = 62.12 \text{ min.}$$

**Example : 40**

**For a chemical reaction A+B → Product, the order is 1 with respect to each of A and B Find x and y from the given data.**

| **Rate (moles/L/s)** | **[A]** | **[B]** |
|---|---|---|
| **0.10** | **0.1 M** | **.1M** |
| **0.80** | **x** | **.1M** |
| **0.40** | **0.2 M** | **y** |

**Solution:**

The rate law may be written as

rate = k [A] [B]

Substituting the first set of data in the rate law, we get,

$0.10 = k \times .1 \times .1$

$k = 10$

Now substituting the second and third sets of data, we get,

$.8 = 10 \times x \times .1$

$x = 0.80$ M

$0.4 = 10 \times 0.2 \times y$

$y = 0.20$ M.

**Example: 41**

**In the decomposition of $H_2O_2$ at 300 K, the energy of activation was found to be 16 kcal/ mole, while it decreased to 10 kcal/ mole when the decomposition was carried out in the presence of a catalyst at 300 K, How many times is the catalysed reaction faster than the uncatalysed one?**

**Solution:**

Suppose $E_1$ and $E_2$ are the energies of activation when the reaction is carried out in the absence and presence of a catalyst respectively.

Thus,

$$k_1 = Ae^{-E_1/RT}; \quad k_2 = Ae^{-E_2/RT}$$

Taking log,

$$\text{In } k_1 = \text{In } A - \frac{E_1}{RT}$$

$$\text{In } k_2 = \text{In } A - \frac{E_2}{RT}$$

$$\therefore \text{ In } k_2 - \text{In } k_1 = -\frac{E_2}{RT} + \frac{E_1}{RT}$$

$$\text{or In } \frac{k_2}{k_1} = \frac{1}{0.002 \times 300}(16-10) = \frac{6}{0.002 \times 300}$$

$$2.303 \log \frac{k_2}{k_1} = 10$$

$$\log \frac{k_2}{k_1} = \frac{10}{2.303} = 4.342$$

$$\text{Taking antilog } \frac{k_2}{k_1} = 2.190 \times 10^4$$

**Example : 42**

In Arrhenius's equation for a certain Reaction, the value of A and E (activation energy) are $6 \times 10^{13}$ s$^{-1}$ and 98.6kJ mol-$^{1}$ respectively. If the reaction is of first order, at what temperature will its half-life period be 20 minutes?

**Solution:**

$$k = Ae^{-E/RT} = \text{In } k = \text{In } A - \frac{E}{RT}$$

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

$$\text{or } \log k = \log A - \frac{E}{2.303RT}. \quad .....(1)$$

Given that

$A = 6 \times 10^{13}\ s^{-1}$, $E = 98.6\ kJ\ mol^{-1}$

$t_{\frac{1}{2}} = 20 \times 60$ s.

For first-order reaction

$$k = \frac{0.6932}{t_{\frac{1}{2}}} = \frac{0.6932}{1200}\ s^{-1}$$

Thus (1) becomes, $\log \frac{0.6932}{1200}$

$$= \log (6 \times 10^{13}) - \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times T}$$

$[R = 8.314 \times 10^{-3}$ kJ/K/mol$] = T = 302.26$ K.

**Example : 43**

The decomposition of $N_2O_5$ according to the equation

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is a first-order reaction. After 30 minutes from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.

**Solution:**

$2N_2O_5 \rightarrow 4NO_2 + O_2$

at t = 0 a

After 30 min: a - x 2x x/2

$$\therefore\ (a - x) + 2x + \frac{x}{2} = 284.5$$

$$\text{or } a + \frac{3x}{2} = 284.5 \qquad ....(1)$$

After complete decompositon of $N_2O_5$.

$2N_2O_5 \rightarrow 4NO_2 + O_2$

0 2a a/2

$$\therefore\ 2a + \frac{a}{2} = 584.5 \text{ or } \frac{5a}{2} = 584.5 \quad ....(2)$$

From (1) and (2), we get,

a = 233.5, x = 34

Thus, for a first-order reaction of the type 2A → products

$$k = \frac{1}{2t} \log \frac{a}{a - x}$$

$$k = \frac{2.303}{2 \times 30} \log \frac{233.5}{233.5 - 34}$$

$= 2.625 \times 10^{-3}\ min^{-1}$

**Example : 44**

Nitric oxide, NO, reacts with oxygen to produce nitroen dioxide :

$\mathbf{2NO(g) + O_2(g) \longrightarrow 2NO_2(g)}$

The rate law for this reaction is

rate = k $[NO]^2[O_2]$

Propose a mechanism for the above reaction.

**Solution:**

The rate law indicate that order of reaction is 2 w.r.t. NO and 1 w.r.t. $O_2$. The possible mechanism for given reaction may be.

$NO + O_2 \xrightarrow{K_2} NO_3$ ... (fast step)

$NO_3 + NO \xrightarrow{K_2} NO_2 + NO_2$ ... (slow step)

Overall reaction, (by addition of two steps)

$2NO + O_2 \longrightarrow 2NO_2$

As slowest step of mechanism of reaction determine the rate of reaction, $\frac{2.303}{t}$

∴ Rate = $k_2 [NO_3][NO]$

But $[NO_3] = k_1 [NO][O_2]$

(∴ $NO_3$ is an intermediate species, and its formation is in equilibrium state)

∴ Rate = $k_1k_2 [NO][O_2][NO] = k[NO]^2[O_2]$

(Where k is rate constant and $k = k_1k_2$) The above expression of rate law derived from proposed mechanism is same as in given data.

**Example : 45**

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

**Solution:**

(i) Specific rate constant, k for first order reaction is given by,

$$k = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{15} \log \frac{100}{100 - 20}$$

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

$= 0.0148\ min^{-1} = 1.48 \times 10^{-2}\ min^{-1}$

(ii) When 10% of original reactant remains unreacted, 90% of reaction is complete. We are required to calculate $t_{90\%}$ of reaction.

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{100 - 90} = \frac{2.303}{0.0148} \times \log 10$$

= 155.6 minutes

(iii) After first 15 minutes. 80% of reactant is left unreacted.

∴ a = 80 a – x = 80 – 20% of 80

$$= 80 - \frac{20}{100} \times 80 = 80 - 16$$

Time for next 20% of reactant left to react is given by.

$$t = \frac{2.303}{k} \log \frac{80}{80 - 16}$$

$$= \frac{2.303}{0.0148} \times \log \frac{80}{64} = \frac{2.303}{0.0148} \times 0.0969$$

= 15 minutes

**Example : 46**

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

**Solution:**

The rate constant k for first order reaction is expressed by relation,

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

Substitute,

$$t = t_{2/3},\ k = 5.4 \times 10^{-14}\ s^{-1},\ x = \frac{2a}{3}$$

$$t_{2/3} = \frac{2.303}{5.4 \times 10^{-14} s^{-1}} \log \frac{a}{a - \frac{2}{3}\alpha}$$

$$= \frac{2.303}{5.4} \times 10^{14} (\log 3) s$$

$= 0.4265 \times 0.4771 \times 10^{14} s = 2.035 \times 10^{13}$ s Two third life of given first order reaction is $2.035 \times 10^{13}$ s.

**Example : 47**

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

**Solution:**

Use the following relation to calculate k, rate constant of first order reaction.

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

Here, t = 20 minutes, a = 100 x = 15 (for completion of 15% of reaction)

$$20 = \frac{2.303}{k} \log \frac{100}{100-15}$$

$$\therefore \text{ Rate constant, } k = \frac{2.303}{k} \log \frac{100}{85}$$

$$= \frac{2.303}{20} \times \frac{0.0706}{1} = 0.00813 \text{ min}^{-1}$$

Again use the relation for completion of 60% of reaction :

$$t_{60\%} = \frac{2.303}{k} \log \frac{a}{a-x}$$

Now, a = 100, a – x = 100 – 60

$$= \frac{2.303}{0.00813} \log \frac{100}{100-60}$$

$$= \frac{2.303}{0.00813} \log \frac{100}{40}$$

$$= \frac{2.303}{0.00813} \times \frac{(0.3979)}{1} = 112.7 \text{ minutes}$$

The 60% completion of reaction will take 112.7 minutes.

**Example : 48**

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

**Solution:**

Let initial conc. of reactant be a, then conc. after 10 minutes will be, a– x = a– 20% of a= 80% of

$$a = \frac{80}{100} \times a = \frac{4a}{5} = 0.8a$$

For the first order reaction, rate constant k can be expressed as,

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

$$= \frac{2.303}{10} \log \frac{a}{0.8a}$$

$$= \frac{2.303}{10} \log \frac{5}{4}$$

$$= \frac{2.303}{10} (\log 5 - \log 4)$$

$$\frac{2.303}{10} (0.6990 - 0.6021) = 0.02232 \text{ min}^{-1}$$

Knowing the rate constant, k we can find time for 75% completion of reaction again by using the relation.

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

$$a - x = a - 75\% \text{ of } a = \frac{a}{4},\ t = t_{75\%}$$

$$t_{75\%} = \frac{2.303}{0.2232} \times \log \frac{a}{a/4} \frac{2.303}{0.2232} \times \log 4$$

$$= \frac{2.303}{0.2232} \times \frac{0.6021}{1} = 62.125 \text{ min}$$

**Example : 49**

For a first order reaction, show that time required for completion of 99.9% of reaction is 3 times the time required for completion of 90% of the reaction. or Show that, $t_{99.9\%} = 3t_{90\%}$ for a first order reaction.

**Solution:**

For a first order reaction, we know that

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

$$\therefore t_{99.9\%} = \frac{2.303}{k} \log \frac{a}{a - .999\alpha}$$

$$= \frac{2.303}{k} \log 10^3 = \frac{3 \times 2.303}{k} \qquad \text{... (i)}$$

$$\text{and } t_{90\%} = \frac{3 \times 2.303}{k} \log \frac{a}{a - 0.90a}$$

$$= \frac{2.303}{k} \log 10 = \frac{2.303}{k} \qquad \text{... (ii)}$$

Now divide (i) by (ii)

$$\frac{t_{99.9\%}}{t_{90\%}} = \frac{3 \times 2.303}{k} \times \frac{k}{2.303} = \frac{3}{1}$$

$$t_{99.9\%} = 3t_{90\%}$$

# EXERCISE # 1

## Based On Rate of reaction

**1.** xA + yB → zC.

If $-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = 1.5 = \frac{d[C]}{dt}$ then x,y and z can be:

(1) 1,1,1 (2) 3,2,3 (3) 3,3,2 (4) 2,2,3

**2.** The rate of a reaction is expressed in different ways as follows ;
+ 1/2(d[C]/dt) = – 1/3 (d[D]/dt) = + 1/4 (d[A]/dt) = – (d[B]/dt) The reaction can be :

(1) $4A + B \longrightarrow 2C + 3D$

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

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

(4) $B + (1/2)D \longrightarrow 4A + 3C$

**3.** Consider the chemical reaction :

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

The rate of this reaction can be expressed ;in terms of time and of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongest the rate expressions.

(1) $\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$

(2) $\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{3d[H_2]}{dt} = \frac{2d[NH_3]}{dt}$

(3) $\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

(4) $\text{Rate} = -\frac{d[N_2]}{dt} = \frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

**4.** In a reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ the rate of appearance of $NH_3$ is $2.5 \times 10^{-4}$ mol $L^{-1}$ $sec^{-1}$. The rate of reaction & rate of disappearance of $H_2$ will be (in mol $L^{-1}$ $sec^{-1}$)

(1) $3.75 \times 10^{-4}$, $1.25 \times 10^{-4}$

(2) $1.25 \times 10^{-4}$, $2.5 \times 10^{-4}$

(3) $1.25 \times 10^{-4}$, $3.75 \times 10^{-4}$

(4) $5.0 \times 10^{-4}$, $3.75 \times 10^{-4}$

**5.** 3A → 2B, rate of reaction $\frac{+d\ [B]}{dt}$ is equal to :

(1) $-\frac{3}{2}\frac{d[A]}{dt}$ (2) $-\frac{2}{3}\frac{d[A]}{dt}$

(3) $-\frac{1}{3}\frac{d[A]}{dt}$ (4) $+2\frac{d\ [A]}{dt}$

**6.** ln the reaction; $A + 2B \longrightarrow 3C + D$, which of the following expression does not describe changes in the concentration of various species as a function of time :

(1) {d [C] / dt} = – {3d [A] / dt}

(2) {3d [D] / dt} = {d [C] / dt}

(3) {3d [B] / dt} = – {2d [C] / dt}

(4) {2d [B] / dt} = – {d [A] / dt}

**7.** In the following reaction :

$xA \xrightarrow{\quad} yB$

$\log\left[-\frac{d[A]}{dt}\right] = \log\left[\frac{d[B]}{dt}\right] + \log 2$

where –ve sign indicates rate of disappearance of the reactant. Thus, x : y is :

(1) 1 : 2 (2) 2 : 1 (3) 3 : 1 (4) 3 : 10

**8.** $2N_2O_5 \longrightarrow 4NO_2 + O_2$

For the above reaction which of the following is not correct above rates of reaction?

(1) $\frac{-d[N_2O_5]}{dt} = 2\frac{d[O_2]}{dt}$

(2) $\frac{-2d[N_2O_5]}{dt} = \frac{d[NO_2]}{dt}$

(3) $\frac{d[NO_5]}{dt} = 4\frac{d[O_2]}{dt}$

(4) $\frac{-2d[N_2O_5]}{dt} = 4\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$

**9.** Observe the following reaction, 2A + B → C The rate of formation of C is $2.2 \times 10^{-3}$ *mol* $L^{-1}$ min.

What is the value of $-\frac{d[A]}{dt}(\text{mol}L^{-1}\,\overset{-1}{\text{min}}\,\overset{-1}{\text{min}})$ ?

(1) $2.2 \times 10^{-3}$ (2) $1.1 \times 10^{-3}$

(3) $4.4 \times 10^{-3}$ (4) $5.5 \times 10^{-3}$

**10.** The reaction 2A + B → 3C + D

Which of the following does not express the reaction rate?

(1) $\frac{d[D]}{dt}$ (2) $-\frac{d[A]}{2dt}$

(3) $-\frac{d[C]}{3dt}$ (4) $-\frac{d[B]}{dt}$

**11.** The differential rate expression for the reaction $H_2 + I_2 \rightarrow 2HI$ is :

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

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

(3) $\frac{1}{2}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

(4) $-2\frac{d[H_2]}{dt} = -2\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

## Based On Rate law

**12.** aA + bB $\longrightarrow$ Product, dx/dt = k $[A]^a$ $[B]^b$. If conc of A is doubled, rate is four times. If conc. of B is made four times, rate is doubled. What is relation between rate of disappearance of A and that of B ?

(1) {– d [A] / dt} = {– d [B] / dtK

(2) – {d [A] / dt} = – 4 {d [B] / dt}

(3) – 4 {d [A] / dt) = {– d [B]/ dt}

(4) None of these

**13.** For a reaction pA + qB → products, the rate law expression is $r = k[A]^1 [B]^m$, then :
(1) (p+1) < (1+ m)
(2) (p + q) > (1 + m)
(3) (p + q) may or may not be equal to (1+ m)
(4) (p + q) = (1 + m)

**14.** For the reaction $H_2 + Br_2 \rightarrow 2HBr$ overall order is found to be 3/2. The rate of reaction can be expressed as:
(1) $[H_2][Br_2]^{1/2}$ (2) $[H_2]^{1/2}[Br_2]$
(3) $[H_2]^{3/2}[Br_2]^0$ (4) All of these

**15.** If concentration of reactants is increased by a factor x then the rate constant k becomes:
(1) $\ln\frac{k}{x}$ (2) $\frac{k}{x}$ (3) k + x (4) k

**16.** The rate of certain hypothetical reaction A + B + C → products is given by $r = \frac{-d\,[A]}{dt} = K\,[A]^{1/2}[B]^{1/3}[C]^{1/4}$ The order of the reaction :
(1) 1 (2) $\frac{1}{2}$ (3) 2 (4) $\frac{13}{12}$

**17.** 2A → B+C it would be a zero order reaction when:
(1) The rate of reaction is proportional to square of conc. of A
(2) The rate of reaction remains same at any conc. of A
(3) The rate remains unchanged at any conc. Of B and C
(4) The rate of reaction doubles if conc. of B is increased to double

**18.** The rate equation for the reaction 2A + B → C is found to be: rate k[A][B]. The correct statement in relation to this reaction is that the
(1) Rate of formation of C is twice the rate of disappearance of A.
(2) Half life is a constant
(3) Unit of k must be $s^{-1}$
(4) Value of k is independent of the initial concentration of A and B

**19.** The rate constant for a reaction is $10.8 \times 10^{-5}$ mol $L^{-1}$ $S^{-1}$. The reaction obeys:
(1) First order (2) Zero order
(3) Second order (4) All are wrong

**20.** For the reaction,
$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$ the rate expression can be written in the following ways: $\{dt[N_2]/dt\} = k_1[NO][H_2]$ ; $\{d[H_2O]/dt\} = k[NO][H_2]$ ; $\{-d[NO]/dt\} = k'_1[NO][H_2]$ ; $\{-d[H_2]/dt\} = k''_1[NO][H_2]$
The relationship between k, $k_1$, $k'_1$ and $k''_1$. is
(1) $k = k_1 = k'_1 = k''_1$
(2) $k = 2k_1 = k'_1 = k''_1$
(3) $k = 2k'_1 = k_1 = k''_1$
(4) $k = k_1 = k'_1 = 2k''_1$

**21.** If a reaction gets completed in finite time then its order can be :
(1) 3 (2) 2 (3) 1 (4) Zero

**22.** For the irreversible process, A + B ⟶ products, the rate is first–order w.r.t. A and second–order w.r.t. B. If 1.0 mol each of A and B introduced into a 1.0 L vessel, and the initial rate was $1.0 \times 10^{-2}$ mol $L^{-1}$ $s^{-1}$ rate when half reactants have been turned into products is :
(1) $1.25 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$
(2) $1.0 \times 10^{-2}$ mol $L^{-1}$ $s^{-1}$
(3) $2.50 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$
(4) $2.0 \times 10^{-2}$ mol $L^{-1}$ $s^{-1}$

**23.** The rate law for the single step reaction 2A + B → 2C, is given by
(1) Rate = K [A][B]
(2) Rate = K $[A]^2[B]$
(3) Rate = K [2A][B]
(4) Rate = K$[A]^2[B]^0$

**24.** For the reaction A + B → Products, it is found that the order of A is 2 and of B is 3 in the rate expression. When concentration of both is doubled the rate will increase by a factor of:
(1) 10 (2) 6 (3) 32 (4) 16

**25.** For a reaction A + B → products, the rate of the reaction was doubled when the concentration of. A was doubled, the rate was again doubled when the conc. of A & B were doubled the order of the reaction with respect to A & B are:
(1) 1,1 (2) 2,0 (3) 1,0 (4) 0,1

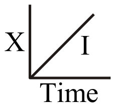
## Based On The integrated rate laws

**26.** The rate constant of reaction 2A+B ⟶ C is $2.57 \times 10^{-5}$ It $mole^{-1}$ $sec^{-1}$ after 10 sec. $2.65 \times 10^{-5}$ It. $mole^{-1}$ $sec^{-1}$ after 20 sec. and $2.55 \times 10^{-5}$ It. $mole^{-1}$ $sec^{-1}$ after 30 sec. The order of the reaction is:
(1) 0 (2) 1 (3) 2 (4) 3

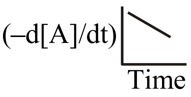
**27.** For a first order reaction, the plot of 't' against log C gives a straight line with slope equal to:
(1) (k / 2.303) (2) (– k / 2.303)
(3) (ln k / 2.303) (4) – k.

**28.** In a first order reaction the amount of reactant decayed in three half lives (let a be is initial amount) would be:
(1) 7a / 8 (2) a / 8
(3) a / 6 (4) 5a / 6

**29.** Graph between concentration of the product and time of the reaction A → B is of the type



Hence graph between – d[A]/dt and time will be of the type :

(1)


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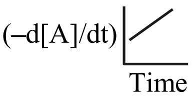

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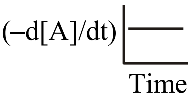

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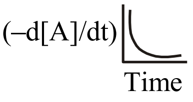
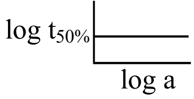


**30.** A graph plotted between log $t_{50\%}$ vs. log concentration is a straight line. What conclusion can you draw from this graph.



(1) $n = 1$ ; $t_{1/2} \propto a$
(2) $n = 2$, $t_{1/2} \propto 1/a$
(3) $n = 1$ ; $t_{1/2} = (0.693/k)$
(4) None of these

**31.** The reaction
$N_2O_5(\text{in } CCl_4) \rightarrow 2NO_2 + 1/2O_2(g)$ is first order in $N_2O_5$ with rate constant $6.2 \times 10^{-4}\ S^{-1}$. What is the value of rate of reaction when $[N_2O_5] = 1.25$ mole $L^{-1}$
(1) $7.75 \times 10^{-4}$ mol $L^{-1}$ $S^{-1}$
(2) $6.35 \times 10^{-3}$ mol $L^{-1}$ $S^{-1}$
(3) $5.15 \times 10^{-5}$ mol $L^{-1}$ $S^{-1}$
(4) $3,85 \times 10^{-4}$ mol $L^{-1}$ $S^{-1}$

**32.** K for a zero order reaction is $2 \times 10^{-2}$ mol $L^{-1}sec^{-1}$ . If the concentration of the reactant after 25 sec is 0.5 M, the initial concentration must have been.
(1) 0.5 M (2) 1.25 M
(3) 12.5 M (4) 1.0 M

**33.** Plot of log (a–x) vs time t is straight line. This indicates that the reaction is of
(1) Second order (2) First order
(3) Zero order (4) Third order

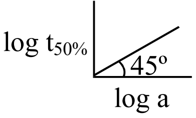
**34.** In a first order reaction the concentration of the reactant is decreased from 1.0 M to 0.25 M in 20 min. The rate constant of the reaction would be –
(1) 10 $min^{-1}$ (2) 6.931 $min^{-1}$
(3) 0.6931 $min^{-`1}$ (4) 0.06931 $min^{-1}$

**35.** In a certain reaction, 10% of the reactant decomposes in one hour, 20 % in two hours, 30% in three hours and so on the dimensions of the rate constant is:
(1) $Hour^{-1}$
(2) Mole $litre^{-1}$ $sec^{-1}$
(3) Litre $mole^{-1}$ $sec^{-1}$
(4) Mole $sec^{-1}$

**36.** If a first order reaction is completed to the extent of 75% and 50% in time intervals, $t_1$ and $t_2$, what is the ratio, $t_1 : t_2$?
(1) ln 2 (2) $\frac{\ln\ (3/4)}{\ln\ 2}$
(3) 2 (4) 1/2

**37.** The rate constant for the reaction $A \rightarrow B$ is $2 \times 10^{-4}$ It. $mol^{-1}$ $min^{-1}$. The concentration of A at which rate of the reaction is $(1/12) \times 10^{-5}$ M $sec^{-1}$ is:
(1) 0.25 M (2) $(1/20)\sqrt{5/3}$ M
(3) 0.5 M (4) None of these

**38.** What will be the order of reaction and rate constant for a chemical change having log $t_{50\%}$ vs log concentration of (1) curves as :



(1) 0, 1/2 (2) 1, 1 (3) 2, 2 (4) 3, 1

**39.** The rate constant for a reaction is $\frac{\ln 2}{10}$ $min^{-1}$. What will be the order of reaction and time taken to change concentration from 1 M to 0.25 M?
(1) One, 10 min (2) zero, 10 min
(3) One, 20 min (4) two, 20 min

**40.** In the first order reaction 75% of the reactant disappeared in 1.388 hrs. Calculate the rate constant of the reaction:
(1) 1 $s^{-1}$ (2) $2.8 \times 10^{-4}$ $s^{-1}$
(3) $17.2 \times 10^{-3}$ $s^{-1}$ (4) $1.8 \times 10^{-3}$ $s^{-1}$

**41.** In the case of zero order reaction, the ratio of time required for 75% completion to 50% completion is :
(1) ln 2 (2) 2 (3) 1.5 (4) None

**42.** In a I order reaction A $\longrightarrow$ products, the concentration of the reactant decrases to 6.25% of its initial value in 80 minutes. What is (i) the rate constant and (ii) the rate of the reaction, 100 minutes after the start, if the initial concentration is 0.2 mole/litre?
(1) $2.17 \times 10–^{2}$ $min–^{1}$, $3.47 \times 10–^{4}$ mol. $Litre–^{1}$ $min–^{1}$
(2) $3.465 \times 10–^{2}$ $min–^{1}$, $2.166 \times 10–^{4}$ mol. $Litre–^{1}$ $min–^{1}$
(3) $3.465 \times 10–^{3}$ $min–^{1}$, $2.17 \times 10–^{3}$ mol. $Litre–^{1}$ $min–^{1}$
(4) $2.166 \times 10–^{3}$$min–^{1}$, $2.667 \times 10–^{4}$ mol. $Litre–^{1}$$min–^{1}$

## Based On | Methods to determine the rate law

**43.** The data for the reaction $A + B \rightarrow C$ is

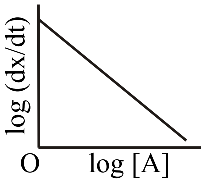
| Exp. | $[A]_0$ | $[B]_0$ | initial rate |
|---|---|---|---|
| 1 | 0.012 | 0.035 | 0.10 |
| 2 | 0.024 | 0.035 | 0.80 |
| 3 | 0.012 | 0.070 | 0.10 |
| 4 | 0.024 | 0.070 | 0.80 |

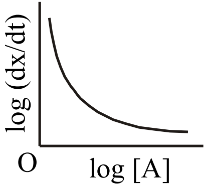
(1) $r = k\,[B]^3$ (2) $r = k\,[A]^3$
(3) $r = k\,[A]\,[B]^4$ (4) $r = k\,[A]^2\,[B]^2$.

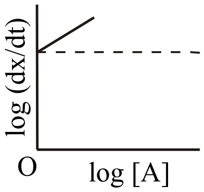
**44.** $A + B \longrightarrow$ Product, $\frac{dx}{dt} = k\,[A]^a\,[B]^b$

If $\left(\frac{dx}{dt}\right) = k$, then order is :
(1) 4 (2) 2 (3) 1 (4) 0

**45.** A → Product and $\left(\frac{dx}{dt}\right) = k[A]^2$. If $\log\left(\frac{dx}{dt}\right)$ is plotted against log [A], then graph is of the type:

(1)


(2)


(3)


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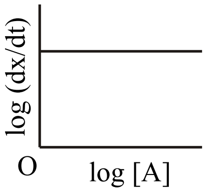


**46.** For the reaction A $\longrightarrow$ Products, $-\frac{d[A]}{dt} = k$ and at different time interval, [A] values are:

| Time | 0 | 5 min | 10 min | 15 min |
|---|---|---|---|---|
| [A] | 20 mol | 18 mol | 16 mol | 14 mol |

At 20 minute, rate will be :

(1) 12 mol /min (2) 10 mol/min

(3) 8 mol/min (4) 0.4 mol/min

**47.** The rate law for a reaction A + B → product is rate = $K[A]^1[B]^2$. Then which one of the following statement is false :

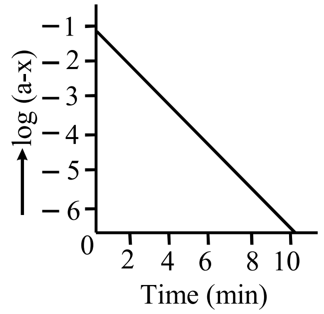
(1) If [B] is held constant while [A] is doubled, the reaction will proceed twice as fast

(2) If [A] is held constant while [B] is reduced to one quater, the rate will be halved

(3) If [A] and [B] are both doubled, the reaction will proceed 8 times as fast

(4) This is a third order reaction

**48.** The conversion of vinyl allyl ether to pent-4-enol follows a certain kinetics. The following plot is obtained for such a reaction.



The order for the reaction is

(1) Zero (2) –1 (3) 1 (4) 2

**49.** The reaction A(s) → 2 B(g) + C(g) is first order. The pressure after 20 min. and after very long time are 150 mm Hg and 225 mm Hg. The value of rate constant and pressure after 40 min. are :

(1) 0.05 In 1.5 min$^{-1}$, 200 mm

(2) 0.5 ln 2 min$^{-1}$, 300 mm

(3) 0.05 In 3 min$^{-1}$, 300 mm

(4) 0.05 In 3 min$^{-1}$, 200 mm

## **Based On** Methods to monitor the progress of the reaction

**50.** Consider the reaction

$2A(g) \longrightarrow 3B(g) + C(g)$. Starting with pure A initially, the total pressure doubled in 3 hrs. The order of the reaction might possibly be

(1) Zero (2) First

(3) Second (4) Unpredictable from this data

**51.** Let there be as first-order reaction of the type, A $\longrightarrow$ B + C. Let us assume that only A is gaseous. We are required to calculate the value of rate constant based on the following data.

| Time | 0 | t | ∞ |
|---|---|---|---|
| Partial pressure of A | $P_0$ | $P_t$ | – |

(1) $k = \frac{1}{t}\ln\left(\frac{P_0}{P_t}\right)$ (2) $k = \frac{1}{t}\ln\left(\frac{P_t}{P_0}\right)$

(3) $k = \frac{1}{t}\ln\left(\frac{2P_0}{P_t}\right)$ (4) $k = \frac{1}{t}\ln\left(\frac{P_t}{2P_0}\right)$

**52.** Let there be a first order reaction, A B + C. Let us assume all there are gases. We are required to calculate the value of rate constant based on the following data

| Time | 0 | t | ∞ |
|---|---|---|---|
| Total pressure | $P_0$ | $P_t$ | – |

Calculate the expression of rate constant.

(1) $k = \frac{1}{t}\ln\left(\frac{2P_0 - P_t}{P_0}\right)$ (2) $k = \frac{1}{t}\ln\left(\frac{P_0}{2P_0 - P_t}\right)$

(3) $k = \frac{t}{1}\ln\left(\frac{P_0}{2P_0 - P_t}\right)$ (4) $k = \frac{1}{t}\ln\left(\frac{P_t}{2P_0 - P_t}\right)$

**53.** For the first order reaction, $X_{(s)} \longrightarrow X_{(g)}$ the monitoring is done by observing the volume :

| Time | T | ∞ |
|---|---|---|
| Volume | $V_t$ | $V_\infty$ |

The rate constant is given by :

(1) $\frac{1}{t}\ln\left(\frac{V_\infty}{V_t}\right)$ (2) $\frac{1}{t}\ln\left(\frac{V_\infty}{V_\infty - V_t}\right)$

(3) $\frac{1}{t}\ln\left(\frac{V_\infty + V_t}{V_\infty}\right)$ (4) $\frac{1}{t}\ln\left(\frac{V_\infty + V_t}{V_\infty - V_t}\right)$

## **Based On** Effect of Temperature

**54.** Rate of which reactions increases with temperature:

(1) Of any

(2) Of exothermic reactions

(3) Of endothermic

(4) Of none.

**55.** For a zero order reaction. Which of the following statement is false:
(1) The rate is independent of the temperature of the reaction.
(2) The rate is independent of the concentration of the reactants.
(3) The half life depends as the concentration of the reactants.
(4) The rate constant has the unit mole $lt^{-1}$ $sec^{-1}$.

**56.** A large increase in the rate of a reaction for a rise in temperature is due to
(1) Increase in the number of collisions
(2) The increase in the number of activated molecules
(3) The shortening of mean free path
(4) The lowering of activation energy

**57.** The rate constant, the activation energy and the frequency factor of a chemical reaction at 25°C are $3.0 \times 10^{-4}$ $s^{-1}$, 104.4 KJ $mol^{-1}$ and $6.0 \times 10^{14}$ $s^{-1}$ respectively. The value of the rate constant as $T \to \infty$ is:
(1) $2.0 \times 10^{18}$ $s^{-1}$ (2) $6.0 \times 10^{14}$ $s^{-1}$
(3) $\infty$ (4) $3.6 \times 10^{30}$ $s^{-1}$

**58.** According to collision theory of reaction rates
(1) Every collision between reactant leads to chemical reaction
(2) Rate of reaction is proportional to velocity of molecules
(3) All reactions which occur in gaseous phase are zero order reaction
(4) Rate of reaction is directly proportional to collision frequency.

**59.** Activation energy of a reaction is –
(1) The energy released during the reaction
(2) The energy evolved when activated complex is formed
(3) Minimum amount of energy needed to overcome the potential barrier of reaction
(4) The energy needed to form one mole of the product.

**60.** The minimum energy for molecules to enter into chemical reaction is called.
(1) Kinetic energy
(2) Potential energy
(3) Threshold energy
(4) Activation energy

**61.** The activation energy for the forward reaction $X \rightarrow Y$ is 60 KJ $mol^{-1}$ and $\Delta H$ is –20 KJ $mol^{-1}$. The activation energy for the backard reaction $Y \rightarrow X$ is:
(1) 80 KJ $mol^{-1}$ (2) 40 KJ $mol^{-1}$
(3) 60 KJ $mol^{-1}$ (4) 20 KJ $mol^{-1}$

**62.** For producing the effective collisions, the colloiding molecules must possess :
(1) A certain minimum amount of energy
(2) Energy equal to or greater than threshold energy
(3) Proper orientation
(4) Threshold energy as well as proper orientation of collision.

**63.** In a gaseous state reaction,
$A_2(g) \longrightarrow B(g) + (1/2)C(g)$, The increase in pressure from 100 mm to 120 mm is notices in 5 minutes. The average rate of disappearance of $A_2$ in mm $min^{-1}$ is :
(1) 4 (2) 8 (3) 16 (4) 2

**64.** The first order rate constant k is related to temp. as $\log k = 15.0 - (10^6/T)$ Which of the following pair of value is correct ?
(1) $A = 10^{15}$ and $E = 1.9 \times 10^4$ KJ
(2) $A = 10^{-15}$ and E = 40 KJ
(3) $A = 10^{15}$ and E = 40 KJ
(4) $A = 10^{-15}$ and $E = 1.9 \times 10^4$ KJ.

**65.** For a given reaction, energy of activation for forward reaction ($E_{af}$) is 80kJ.mol–$^1$. $\Delta H$= 40kJ. mol–$^1$ for the reaction. A catalyst lowers $E_{af}$ to 20 kJ.mol–$^1$. The ratio of energy of activation for reverse reaction before and after addition of catalyst is :
(1) 1.0 (2) 0.5 (3) 1.2 (4) 2.0

### Based On Mechanism of reactions

**66.** For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ the experiment data suggested that $r = k[H_2][Br_2]^{1/2}$ The molecularity and order of the reaction are respectively :
(1) 2, 3/ 2 (2) 3/2 , 3/2
(3) Not defined, 3/2 (4) 1,1/2

**67.** The reaction of hydrogen, and iodine monochloride is represented by the equation :
$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$
This reaction is first–order in $H_2(g)$ and also first–order in ICl(g). Which of these proposed mechanism can be consistent with the given information about this reaction ?

**Mechanism I :**
$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$

**Mechanism II :**
$H_2(g) + ICl(g) \xrightarrow{\text{Slow}} HCl(g) + HI(g)$
$HI(g) + ICl(g) \xrightarrow{\text{fast}} HCl(g) + I_2(g)$
(1) I only (2) II only
(3) Both I and II (4) neither I nor II

**68.** Following mechanism has been proposed for a reaction.
$2A + B \rightarrow D + E$
Step -1 $A + B \rightarrow C + D$ – (slow)
Step -2 $A + C \rightarrow E$ – (fast)
The rate law expression for the reaction is :
(1) $r = K[A]^2[B]$ (2) $r = K[A][B]$
(3) $r = K[A]^2$ (4) $r = K[A][C]$

**69.** For an elementary process $2X + Y \rightarrow Z + W$, the molecularity is :
(1) 2 (2) 1
(3) 3 (4) Unpredictable

**70.** For the reaction $2NO + Cl_2 \rightarrow 2NOCl$ the following mechanism has been proposed

$NO + Cl_2 \rightarrow NOCl_2$ (fast)

$NOCl_2 + NO \rightarrow 2NOCl$ (slow)

the rate low for the reaction is :

(1) Rate = $K[NO]^2[Cl_2]$

(2) Rate = $K[NO][Cl_2]^2$

(3) Rate = $K[NOCl_2]$

(4) Rate = $K[NOCl]^2$

**71.** The reaction of $NO_2$ (g) and $O_3$ (g) is first-order in $NO_2$ (g) and $O_3$ (g)

$$2\,NO_2\,(g) + O_3\,(g) \longrightarrow N_2O_5\,(g) + O_2\,(g)$$

The reaction can take place by mechanism :

I : $NO_2 + O_3 \xrightarrow{\text{slow}} NO_3 + O_2$

$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$

II : $O_3 \underset{k_b}{\overset{k_a\ \text{fast}}{\rightleftharpoons}} O_2 + [O]$

$NO_2 + O \xrightarrow{\text{slow}} NO_3$

$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$

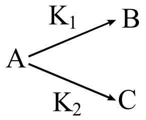
Select correct mechanism.

(1) I only (2) II only

(3) Both I and II (4) None of I and II

### Based On Complications in first order reactions

**72.** The substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :



$K_1 = 1.26 \times 10^{-4}\ sec^{-1}$ and $K_2 = 3.8 \times 10^{-5}\ sec^{-1}$

The percentage distribution of B and C

(1) 80% B and 20% C

(2) 76.83% B and 23.17%C

(3) 90% B and 10% C

(4) 60% B and 40% C

### Questions MICELLANEOUS

**73.** In the reaction

$$O_3^-(aq) + 5Br^-(aq) + 6H^+ \rightarrow 3Br_2(l) + 3H_2O(l)$$

The rate of appearance of bromine ($Br_2$) is related to rate of disappearance of bromide ions as following:

(1) $\frac{d(Br_2)}{dt} = \frac{3}{5}\frac{d(Br^-)}{dt}$

(2) $\frac{d(Br_2)}{dt} = -\frac{3}{5}\frac{d(Br^-)}{dt}$

(3) $\frac{d(Br_2)}{dt} = -\frac{5}{3}\frac{d(Br^-)}{dt}$

(4) $\frac{d(Br_2)}{dt} = \frac{5}{3}\frac{d(Br^-)}{dt}$

**74.** Which one of the following is a second order reaction?

(1) $H_2 + Br_2 \rightarrow 2HBr$

(2) $NH_4NO_3 \rightarrow N_2 + 3H_2O$

(3) $H_2 + CI \xrightarrow{\text{sunlight}} 2HCI$

(4) $CH_3COOH_3 + NaOH \rightarrow CH_3COONa + H_2O$

**75.** The temperature coefficient of most of the reactions lies between

(1) 1 and 3 (2) 2 and 3

(3) 1 and 4 (4) 2 and 4

**76.** In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the statement is correct?

(1) *R* is Rydberg constant

(2) *k* is equilibrium constant

(3) $E_a$ is energy of activation

(4) *A* is adsorption factor

**77.** The rate of chemical reaction (except zero order):

(1) Decreases from moment to moment

(2) Remains constant throughout

(3) Is independent of the order of reaction

(4) None of the above

**78.** For a zero order reaction

(1) $t_{1/2} \propto R_0$ (2) $t_{1/2} \propto 1/R_0$

(3) $t_{1/2} \propto R_0^2$ (4) $t_{1/2} \propto 1/\ R_2^0$

**79.** Effect of temperature on reaction rate is given by

(1) Claisen-Clapeyron equation

(2) Arrhenius equation

(3) Gibbs Helmholtz equation

(4) Kirchoff's equation

**80.** The Arrhenius equation expressing the effect of temperature on the rate constant of reaction is:

(1) $K = \frac{E_a}{RT}$ (2) $K = Ae^{-E_a/RT}$

(3) $K = \log_e \frac{E_a}{RT}$ (4) $K = e^{-Ea/RT}$

**81.** Find the two third life ($t_{1/2}$) of a first order reaction in which $k = 5.48\times10^{-14}$ per second

(1) $201\times10^{13}\,s$ (2) $2.01\times10^{13}\,s$

(3) $201\times10^{20}\,s$ (4) $0.201\times10^{10}\,s$

**82.** A + B → Product

If concentration of A is doubled, rate increases 4 times. If concentration of A and B are doubled, rate increases 8 times. The differential rate equation of the reaction will be

(1) $\frac{dC}{dt} = kC_A \times C_B$ (2) $\frac{dC}{dt} = kC_A^2 \times C_B^3$

(3) $\frac{dC}{dt} = kC_A^2 \times C_B$ (4) $\frac{dC}{dt} = kC_A^2 \times C_B^2$

**83.** For the reaction A → B, the rate expression is $r = k[A]^n$. When the concentration of *A* is doubled, the rate of reaction is quadrupled. The value of *n* is

(1) 1 (2) Zero (3) 3 (4) 2

**84.** The rate constant for the first order reaction is 60 $s^{-1}$. How much time will it take to reduce the concentration of the reaction to 1/16 M value ?
(1) $4.6 \times 10^{-2}$ s (2) $4.6 \times 10^{4}$ s
(3) $4.6 \times 10^{2}$ s (4) $4.6 \times 10^{-4}$ s

**85.** In the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ initial pressure is 500 atm and rate constant k is $3.38 \times 10^{-5}$ $s^{-1}$ after 10 min the final pressure of $N_2O_5$ is
(1) 490 atm (2) 250 atm
(3) 480 atm (4) 420 atm

**86.** For a chemical reaction … can never to a fraction
(1) Order (2) Half life
(3) Rate constant (4) Molecularity

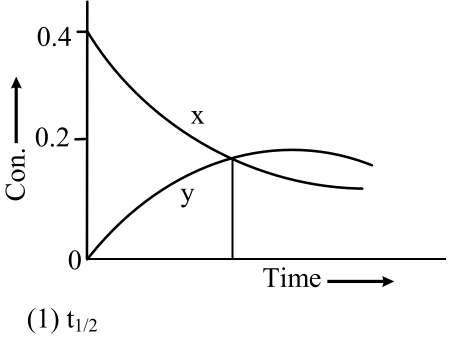
**87.** The time taken for the completion of 3/4 of a first order reaction is
(1) (2.303/k) log 3/4 (2) (2.303/k) log 4
(3) (2.303/k) log 1\4 (4) (2.303/0.75) log k

**88.** $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ What is the ratio of the rate of decomposition of $N_2O_5$ to rate of formation of $O_2$ ?
(1) 1 : 2 (2) 2 : 1 (3) 1 : 4 (4) 4 : 1

**89.** A first order reaction is 75% complete after 32 min. when was 50% of the reaction completed?
(1) 16 min (2) 8 min
(3) 4 min (4) 32 min

**90.** For a reaction, $A + 2B \rightarrow C$, rate is given by $+\frac{d[C]}{dt} = k[A][B]$, hence, the order of the reaction is
(1) 3 (2) 2 (3) 1 (4) 0

**91.** The accompanying figure depicts the change in concentration of species X and Y for the reaction $X \rightarrow Y$, as a function of time. The point of intersection of the two curves represents:



(1) $t_{1/2}$
(2) $t_{3/4}$
(3) $t_{2/3}$
(4) Data is insufficient to predict

**92.** The rate constant of a reaction at temperature 200 K is 10 times less than the rate constant at 400 K. What is the activation energy ($E_a$) of the reaction?
(1) 1842.4 R (2) 921.2 R
(3) 460.6 R (4) 230.3 R

**93.** A zero order reaction is one:
(1) In which reactants do not react
(2) In which one of the reactants is in large excess
(3) Whose rate does not change with time
(4) Whose rate increases with time

**94.** In a first order reaction the a/(a – x) was found to be 8 after 10 minute. The rate constant is:
(1) (2.303 × 3 log 2)/10
(2) (2.303 × 2 log 3)/10
(3) 10 × 2.303 × 2 log 3
(4) 10 × 2. 303 × 3 log 2

**95.** If the rate of reaction $A \rightarrow B$ doubles on increasing the concentration of A by 4 times, the order of the reaction is
(1) 2 (2) 1 (3) 1/2 (4) 4

**96.** The rate of chemical reaction
(1) Increase as the reaction proceeds
(2) Decrease the reaction proceeds
(3) May increase or decrease during reaction
(4) Remains constant as the reaction proceeds

**97.** For zero order reaction, the integrated rate equation is
(1) $kt = \frac{[A]}{[A]_0}$ (2) $kt = [A] - [A]_0$
(3) $[A] = -kt + [A]_0$ (4) $[A] = kt - [A]_0$

**98.** The half-life period of a first order reaction is 69.3 s. what is the rate constant?
(1) 0.01 $s^{-1}$ (2) 0.1 $s^{-1}$
(3) 1 $s^{-1}$ (4) 10 $s^{-1}$

**99.** A reaction has a rate constant of 0.5 $mol^{-1}$ $dm^3$ $min^{-1}$. If initial concentration of the reactant is 0.2 mol $dm^{-3}$, half-life of the reaction
(1) 1.4 min (2) 10 min
(3) 15 min (4) 20 min

**100.** The bromination of acetone that occurs in acid solution is represented by this equation.
$CH_3COCH_3(aq) + Br_2\,(aq) \rightarrow CH_3COCH_2Br(aq) \rightarrow H^+\,(aq) + Br^-\,(aq)$
These kinetic data were obtained for given reaction concentrations.
Initial concentrations,*M*

| $[CH_3COCH_3]$ | $[Br_2]$ | $[H^+]$ | Initial rate, disappearance of $Br_2$, M $s^{-1}$ |
|---|---|---|---|
| 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 |

Based on these data, the rate equation is:
(1) $\text{rate} = k[CH_3COCH_3][Br_2]$
(2) $\text{rate} = k[CH_3COCH_3][Br_2][H^+]^2$
(3) $\text{rate} = k[CH_3COCH_3][Br_2][H^+]$
(4) $\text{rate} = k[CH_3COCH_3][H^+]$

**101.** The rate constant for a chemical reaction has units L $mol^{-1}s^{-1}$, order of the reaction will be
(1) 0 (2) 1 (3) 2 (4) 3

**102.** Activation energy of a chemical reaction can be determined by
(1) Evaluating rate constant at standard temperatures
(2) Evaluating velocities of reaction at two different temperatures
(3) Evaluating rate constants at two different temperatures
(4) Changing concentration of reactants

**103.** Which statement about molecularity of a reaction is wrong?
(1) It is the number of molecules of the eactants taking part in a single step of reaction
(2) It is calculated from the reaction mechanism
(3) It may be either whole number or fractional
(4) None of the above

**104.** Arrhenius equation may not be represented as
(1) $\ln\frac{A}{k}=\frac{E_a}{RT}$
(2) $\frac{d\ln k}{dT}=\frac{E}{RT^2}$
(3) $\log A=\log k+\frac{E_a}{2.303RT}$
(4) $\log\left[-\frac{E_a}{RT}\right]=\frac{k}{A}$

**105.** The reaction $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ is carried out in a $1dm^3$ vessel and $2dm^3$ vessel separately. The ratio of the reaction velocities will be
(1) 1:8 (2) 1:4 (3) 4:1 (4) 8:1

**106.** The rate for the reaction,
$RCI + NaOH (aq) \rightarrow ROH + NaCI$ is given by rate = k [RCl], the freezing point of the reaction is
(1) Unaffected by increasing the temperature of the reaction
(2) Decreased on increasing the temperature of the reaction
(3) Halved on reducing the concentration of RCl to half
(4) Doubled on doubling the concentration of NaOh

**107.** In the sequence of reaction,
$A\xrightarrow{k_1}B\xrightarrow{k_2}C\xrightarrow{k_3}D$ $k_3 > k_2 > k_1$ then the rate determining step of reaction is
(1) A → B (2) B → C
(3) C → D (4) A → D

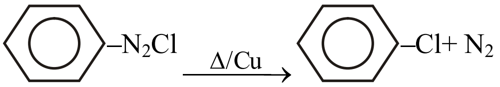
**108.** A first order reaction is 20% complete in 10 min. What is the rate constant of the reaction?
(1) 0.223 (2) 0.0223
(3) 0.322 (4) 0.0322

**109.** The activation energy of exothermic reaction A → B 80 kJ $mol^{-1}$. The heat of reaction is 200 kJ $mol^{-1}$. The activation energy for the reaction B → A (in kJ $mol^{-1}$) will be
(1) 80 (2) 120 (3) 40 (4) 280

**110.** An endothermic reaction A → B has an activation energy of 15 kcal/mol and the energy of reaction is 5 kcal/mol. The activation energy for the reaction B → A is
(1) 20 kcal/mol (2) 15 kcal/mol
(3) 10 kcal/mol (4) Zero

# EXERCISE # 2

**1.** A drop of solution (volume 0.05 mL) contains $3.0 \times 10^{-6}$ moles of $H^+$. If the rate contant of disappearance of $H^+$ is $1.0 \times 10^7$ mole litre$^{-1}$ sec$^{-1}$. How long would it take for $H^+$ in drop to disappear:
(1) $6 \times 10^{-8}$ sec (2) $6 \times 10^{-7}$ sec
(3) $6 \times 10^{-9}$ sec (4) $6 \times 10^{-10}$ sec

**2.** 

Half-life is independent of concentration of reactant. After 10 minutes volume of $N_2$ gas is 10 L and after complete reaction it is 50 L. Hence rate constant is:
(1) (2.303 /10) log 5 min$^{-1}$
(2) (2.303 /10) log 1.25 min$^{-1}$
(3) (2.303 /10) log 2 min$^{-1}$
(4) (2.303 /10) log 4 min$^{-1}$

**3.** At a given temperature, $k_1 = k_2$ for the reaction
$A + B \rightarrow C + D$
If $\left[\frac{dx}{dt}\right] = k_1[A][B] - k_2[C][D]$ in which set of the concentration reaction ceases?

| | [A] | [B] | [C] | [D] |
|---|---|---|---|---|
| (1) | 0.1 M | 0.2 M | 0.3 M | 0.4 M |
| (2) | 0.4 M | 0.25 M | 0.2 M | 0.5 M |
| (3) | 0.2 M | 0.2 M | 0.3 M | 0.2 M |
| (4) | 0.2 M | 0.2 M | 0.4 M | 0.2 M |

**4.** The rate of a reaction gets doubled when the temperature changes from 7ºC to 17ºC. By what factor will it change for the temperature change from 17ºC to 27ºC?
(1) 1.81 (2) 1.71 (3) 1.91 (4) 1.76

**5.** Two I-order reactions have half-lives in the ratio 3 : 2. Calculate the ratio of time intervals $t_1 : t_2$. Where $t_1$ is the time period for 25% completion of the first reaction and $t_2$, for 75% completion of the second reaction.
(1) 0.311 : 1 (2) 0.420 : 1
(3) 0.273 : 1 (4) 0.199 : 1

**6.** Formation of $NO_2F$ from $NO_2$ and $F_2$ as per the reaction $2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$ is a second order reaction, first order with respect to $NO_2$ and first order with respect to $F_2$. If $NO_2$ and $F_2$ are present in a closed vessel in ratio 2 :1 maintained at a constant temperature with an initial total pressure of 3 atm, what will be the total pressure in the vessel after the reaction is complete?
(1) 1atm (2) 2 atm (3) 2.5 atm (4) 3 atm

**7.** The decomposition of a gaseous substance (1) to yield gaseous products (2), (3) follows First order kinetics. If initially only (1) is present and 10 minutes after the start of the reaction the pressure of (1) is 200 mm Hg and that of over all mixture is 300 mm Hg, then the rate constant for $2A \rightarrow B + 3C$ is :
(1) (1/600) ln 1.25 sec$^{-1}$
(2) (2.303 /10) log 1.5 min$^{-1}$
(3) (1/10) ln 1.25 sec$^{-1}$
(4) None of these

**8.** In the reaction $NH_4NO_2$ (aq.) $\rightarrow N_2$ (g) + 2 $H_2O$ (*l*) the volume of $N_2$ after 20 min and after a long time is 40 ml and 70 ml respectively. The value of rate constant is :
(1) (1/20) In (7/4) min$^{-1}$
(2) (2.303 /1200) log (7/3) sec$^{-1}$
(3) (1/20) log (7/3) min$^{-1}$
(4) (2.303 / 20) log (11/7) min$^{-1}$

**9.** Catalyst increases the rate of reaction because:
(1) It decreases ΔH
(2) It increases ΔH
(3) It decreases activation energy
(4) It increases activation energy

**10.** Consider the elementary reaction sequence shown in figure. Which of the following equations are correct?

$$\begin{tikzcd} A \arrow[r, "k_1"] \arrow[d, "k_4"'] & B \arrow[d, "k_2"] \\ D & C \arrow[l, "k_3"] \end{tikzcd}$$

(1) $\frac{d[A]}{dt} = -k_1[A] + k_4[D]$
(2) $\frac{d[C]}{dt} = k_2[B] - k_3[C]$
(3) $\frac{d[D]}{dt} = k_4[D] + k_3[D]$
(4) Nothing can be said about order of reactions in this problem

**11.** For a certain reaction of order n, the time for half change, $t_{1/2}$, is given by
$t_{1/2} = \frac{(2-\sqrt{2})}{k} x C_0^{1/2}$ where k is constant and $C_0$ is the initial concentration. What is n?
(1) 1 (2) 2 (3) 0 (4) 0.5

**12.** For a reaction following n$^{th}$ order kinetics, the half life ($t_{1/2}$) would depend upon the initial concentration (1) as:
(1) $t_{1/2} \propto a^{1-n}$ (2) $t_{1/2} \propto a^{n-1}$
(3) $t_{1/2} \propto a^{n}$ (4) $t_{1/2} \propto a^{-n}$

**13.** Trimolecular reactions are uncommon because
(1) The probability of three molecules colliding at an instant is very low.
(2) The probability of three molecules colliding at an instant is high.
(3) The probability of three molecules colliding at an instant is zero.
(4) The probability of many molecules colliding at an instant is high.

**14.** For A + B → C + D, $\Delta H = -20 \text{kJ mol}^{-1}$ the activation energy of the forward reaction is 85 kJ $\text{mol}^{-1}$. The activation energy for backward reaction is … kJ $\text{mol}^{-1}$.
(1) 65 (2) 105 (3) 85 (4) 40

**15.** For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$, the rate $\frac{d[\text{NH}_3]}{dt} = 2\times10^{-4} M\text{s}^{-1}$. Therefore, the rate $-\frac{d[\text{N}_2]}{dt}$ is given as:
(1) $10^{-4} M\,s^{-1}$ (2) $10^{4} M\,s^{-1}$
(3) $10^{-2} M\,s^{-1}$ (4) $10^{-4}\,s\,M^{-1}$

**16.** The reaction L → M is started with 10.0 g of L. After 30 and 90 min, 5.0 g and 1.25 g of L respectively are left. The order of the reaction is
(1) 0 (2) 1 (3) 2 (4) 3

**17.** The rate of a reaction is expressed in different ways as follows
$$+\frac{1}{2}\frac{d[C]}{dt} = -\frac{1}{5}\frac{d[D]}{dt} = +\frac{1}{3}\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$
The reaction is
(1) $4A + B \rightarrow 2C + 3D$
(2) $B + 5D \rightarrow 3A + 2C$
(3) $4A + 2B \rightarrow 2C + 3D$
(4) $B + \frac{1}{2}D \rightarrow 4A + 2C$

**18.** The rate of elementary reaction, A → B, increases by 100 times when the concentration of A is increased ten folds. The order of the reaction with respect to A is:
(1) 1 (2) 2 (3) 10 (4) 100

**19.** The differential rate law for the reaction $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ is
(1) $-\frac{d[\text{NH}_3]}{dt} = -\frac{d[\text{O}_2]}{dt} = -\frac{d[\text{NO}]}{dt} = -\frac{d[\text{H}_2\text{O}]}{dt}$
(2) $\frac{d[\text{NH}_3]}{dt} = \frac{d[\text{O}_2]}{dt} = -\frac{1}{4}\frac{d[\text{NO}]}{dt} = -\frac{1}{6}\frac{d[\text{H}_2\text{O}]}{dt}$
(3) $\frac{1}{4}\frac{d[\text{NH}_3]}{dt} = \frac{1}{5}\frac{d[\text{O}_2]}{dt} = \frac{1}{4}\frac{d[\text{NO}]}{dt} = \frac{1}{6}\frac{d[\text{H}_2\text{O}]}{dt}$
(4) $-\frac{1}{4}\frac{d[\text{NH}_3]}{dt} = -\frac{1}{5}\frac{d[\text{O}_2]}{dt} = \frac{1}{4}\frac{d[\text{NO}]}{dt} = \frac{1}{6}\frac{d[\text{H}_2\text{O}]}{dt}$

**20.** For the reaction A → B, when concentration of A is made 1.5 times, the rate of reaction becomes 1.837 times. The order of reaction is
(1) 1 (2) 1.5 (3) 2 (4) 2.5

**21.** For the reaction, $Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$, the initial concentration of $I^-$ was 0.20 mol $L^{-1}$ and the concentration after 20 min was 0.20 mol $L^{-1}$. Then the rate of formation of $I_2$ in mol $L^{-1}$ would be
(1) $1 \times 10^{-4}$ (2) $5 \times 10^{-4}$
(3) $1 \times 10^{-3}$ (4) $5 \times 10^{-3}$

**22.** The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightarrow 2AB$ are 180 kJ $\text{mol}^{-1}$ and 200 kJ $\text{mol}^{-1}$ respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ $\text{mol}^{-1}$. The enthalpy change of the reaction ($A_2+B_2 \rightarrow 2AB$) in the presence of catalyst will be (in kJ $\text{mol}^{-1}$)
(1) 300 (2) 120 (3) 280 (4) 20

**23.** Which statement is correct?
(1) Reactions with low activation energy are usually exothermic
(2) The rate law sometimes enable to deduce the mechanism of a reaction
(3) The rate law for reaction is an algebraic expression relating the forward reaction rate to product concentration
(4) Increase in the total pressure of a gas phase reaction increase the fraction of collisions effective in producing reactions

**24.** The temperature coefficient of a reaction is:
(1) The rate constant at a fixed temperature
(2) The ratio of rate constant at two temperature
(3) The ratio of rate constant differing by 10º preferably 25º and 35ºC
(4) None of the above

**25.** The term (–*dc/dt*) in rate equation refers to:
(1) The concentration of a reactant
(2) The decrease in concentration of the reactant with time
(3) The velocity constant of reaction
(4) None of the above

**26.** For a first order reaction, the initial concentration of a reactant is 0.05 M. After 45 min it is decreased by 0.015 M. calculation half reaction time ($t_{1/2}$)
(1) 87.42 min (2) 25.90 min
(3) 78.72 min (4) 77.20 min

**27.** The order of a gaseous phase reaction for which rate becomes half if volume of container having same amount of reactant is doubled is:
(1) 1 (2) 1/2 (3) 2 (4) 1/3

**28.** For the reaction, $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$

Given, $-\frac{d[N_2O_5]}{dt} = K_1[N_2O_5]$ $\frac{d[NO_2]}{dt} = K_2[N_2O_5]$ and $\frac{d[O_2]}{dt} = K_3[N_2O_5]$ The relation in between $K_1$, $K_2$ and $K_3$ is:

(1) $2K_1 = K_2 = 4K_3$ (2) $K_1 = K_2 = K_3$
(3) $2K_1 = 4K_2 = K_3$ (4) None of these

**29.** Temperature dependent equation can be written as

(1) $\text{In}\,k = A - e^{E_a/RT}$ (2) $\text{In}\,k = A + e^{E_a/RT}$
(3) $\text{In}\,k = A - e^{RT/E_a}$ (4) None of these

**30.** A first order reaction is 50% complete in 30 min at 27ºC and in 10 min at 47ºC. The energy of activation of the reaction is

(1) 52.8 kJ (2) 23.6 kJ (3) 29.5 kJ (4) 43.8 kJ

**31.** Increase in the concentration of the reactants leads to the change in

(1) Activation energy (2) Heat of reaction
(3) Collision frequency (4) Threshold energy

**32.** When a graph is plotted between In $k$ and $1/T$ for a first order reaction, a straight line is obtained. The slope of the line is equal to

(1) $-\frac{E_a}{2.303}$ (2) $-\frac{E_a}{2.303R}$
(3) $-\frac{2.303}{E_aR}$ (4) $-\frac{E_a}{R}$

**33.** For the two gaseous reactions, following data are given

$A \rightarrow B$ ; $k_1 = 10^{10} e^{-20,000/T}$
$C \rightarrow D$ ; $k_2 = 10^{12} e^{-24,606/T}$

The temperature at which $k_1$ becomes equal to $k_2$ is

(1) 400 K (2) 1000 K
(3) 800 K (4) 1500 K

**34.** Hydrogenation of vegetable ghee at 25ºC reduces pressure of $H_2$ from 2 atm to 1.2 atm in 50 minute. The rate of reaction in terms of molarity per second is:

(1) $1.09\times10^{-6}$ (2) $1.09\times10^{-5}$
(3) $1.09\times10^{-7}$ (4) $1.09\times10^{-8}$

**35.** In the reaction $A + B \rightarrow$ products, if $B$ is taken in excess, then it is an example of

(1) Second order reaction
(2) Zero order reaction
(3) Pseudounimolecular reaction
(4) First order reaction

**36.** The rate of a chemical reaction depends upon:

(1) Time (2) Pressure
(3) Concentration (4) All of these

**37.** The rate constant for the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ is $3.0 \times 10^{-5} s^{-1}$. If the rate is $2.40 \times 10^{-5}$ then the concentration of $N_2O_5$ (in mol/L) is

(1) 1.4 (2) 1.2 (3) 0.04 (4) 0.8

**38.** The following data are for the decomposition of ammonium nitrite in aqueous Solution:

| Vol.of $N_2$ in cc | Time (min) |
|---|---|
| 6.25 | 10 |
| 9.00 | 15 |
| 11.40 | 20 |
| 13.65 | 25 |
| 33.05 | Infinity |

The order of reaction is

(1) Zero (2) One (3) Two (4) Three

**39.** For a reaction A $\rightarrow$ Product, rate law is $-\frac{d[A]}{dt} = K[A]_0$. The concentration of A left after time $t$ when $t = \frac{1}{K}$ is:

(1) $\frac{[A]_0}{e}$ (2) $[A]_0 \times e$
(3) $\frac{[A]_0}{e^2}$ (4) $\frac{1}{[A]_0}$

**40.** For a first order reaction A $\rightarrow$ P, the temperature ($T$) dependent rate constant ($k$) was found to follow the equation.

$\log k = -(2000) / T + 6.0$

The pre-exponential factor $A$ and the activation energy $E_a$, respectively, are

(1) $1.0 \times 10^6 s^{-1}$ and 9.2 kJ $mol^{-1}$
(2) 6.0 $s^{-1}$ and 16.6 kJ $mol^{-1}$
(3) $1.0 \times 10^6$ $s^{-1}$ and 16.6 kJ $mol^{-1}$
(4) $1.0 \times 10^6$ $s^{-1}$ and 38.3 kJ $mol^{-1}$

**41.** In Arrhenius equation $K = Ae^{-Ea/RT}$, the quantity $-E_a / RT$ is referred as:

(1) Boltzmann factor
(2) Frequency factor
(3) Activation factor
(4) None of these

**42.** Among the following reaction, the fastest one is:

(1) Burning of coal
(2) Rusting of iron in moist air
(3) Conversion of monoclinic sulphur to rhombic sulphur
(4) Precipitation of silver chloride by mixing silver itrate and sodium chloride solutions

**43.** The following homogeneous gaseous reactions were experimentally found to be second order overall.

1. $2NO \rightarrow N_2 + O_2$
2. $30_2 \rightarrow 20_3$
3. $N_2O_3 \rightarrow NO + NO_2$
4. $H_2 + I_2 \rightarrow 2HI$

Which of these are most likely to be elementary reaction that occur in one step?

(1) 3 only (2) 1 and 3
(3) 1 and 4 (4) 3 and 4

**44.** Consider a reaction; aG + bH → Products When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall of the reaction,
(1) 0 (2) 1 (3) 2 (4) 3

**45.** The rate constant for a zero order reaction is
(1) $k=\ln\frac{c_0-c_t}{2t}$ (2) $k=\frac{c_0-c_t}{t}$
(3) $k=\frac{c_0}{c_t}$ (4) $k=\frac{c_0}{2t}$

**46.** The ratio of the times for 99.9% of the reaction to complete and half of the reaction to complete is
(1) 2 (2) 4 (3) 8 (4) 10

**47.** The activation energy for a simple chemical reaction $A \to B$ is $E_a$ in forward direction. The activation energy for the reverse reaction
(1) Is negative of $E_a$
(2) Is always less than $E_a$
(3) Can be less than or more than $E_a$
(4) Is always double of $E_a$

**48.** After how many second will the concentration of the reactant in a first order reaction be halved if the rate constant is $1.55 \times 10^{-3}$ $s^{-1}$?
(1) 600 (2) 100 (3) 60 (4) 10

**49.** For the reaction A + 2B → C, the rate of reaction at a given instant can be given by
(1) $+\frac{d[A]}{dt}=+\frac{1}{2}\frac{d[B]}{dt}=+\frac{d[C]}{dt}$
(2) $\frac{d[A]}{dt}=-\frac{1}{2}\frac{d[B]}{dt}=-\frac{d[C]}{dt}$
(3) $-\frac{d[A]}{dt}=-\frac{1}{2}\frac{d[B]}{dt}=+\frac{d[C]}{dt}$
(4) $+\frac{d[A]}{dt}=+\frac{1}{2}\frac{d[B]}{dt}=+\frac{d[C]}{dt}$

**50.** Which of the following theory is not related to chemical kinetics?
(1) Collision theory
(2) Activated complex theory
(3) Absolute reaction rate theory
(4) VSPER theory

**51.** For the chemical change A → B it is found that the rate of reaction doubles when the concentration is increased by 4 times. The order of the reaction is
(1) One (2) Two
(3) Half (4) None of these

**52.** If a certain reaction is first order with respect to *A,* second order with respect to *B* and zero order with respect to *C* then what is the order of reaction?
(1) First (2) Second (3) Third (4) Zero

**53.** If a plot of $\log_{10} C$ versus t give a straight line for a given reaction, then the reaction is
(1) Zero order (2) First order
(3) Second order (4) Third order

**54.** The given reaction $2FeCl_3 + SnCl_2 \to 2FeCl_2 + SnCl_4$ is an example of
(1) Third order reaction
(2) Second order reaction
(3) First order reaction
(4) None of these

**55.** The order for the reaction, $H_2+Cl_2 \xrightarrow{hv} 2HCl$ over water is:
(1) 0 (2) 1 (3) 2 (4) 3

**56.** The inversion of cane sugar into glucose and fructose is:
(1) I order (2) II order
(3) III order (4) Zero order

**57.** For the reaction, $N_2 + 3H_2 \to 2NH_3$, if $\frac{d[NH_3]}{dt}$ $= 2 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$, the value of $\frac{-d[H_2]}{dt}$ would be:
(1) $1 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$
(2) $3 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$
(3) $4 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$
(4) $6 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$

**58.** For the reaction $\underset{(g)}{N_2O_5} \Rightarrow \underset{(g)(g)}{2NO_2+\frac{1}{2}O_2}$, the rate of disappearance of $N_2O_5$ is $6.25 \times 10^{-3}$ mol $L^{-1}s^{-1}$. The rate of formation of $NO_2$ and $O_2$ will be respectively.
(1) $6.25 \times 10^{-3}$ mol $L^{-1}s^{-1}$ and $6.25 \times 10^{-3}$ mol $L^{-1}s^{-1}$
(2) $1.25 \times 10^{-2}$ mol $L^{-1}s^{-1}$ and $3.125 \times 10^{-3}$ mol $L^{-1}s^{-1}$
(3) $6.25 \times 10^{-3}$ mol$L^{-1}s^{-1}$ and $3.125 \times 10^{-3}$ mol $L^{-1}s^{-1}$
(4) $1.25 \times 10^{-2}$ mol$L^{-1}s^{-1}$ and $6.25 \times 10^{-3}$ mol $L^{-1}s^{-1}$

**59.** If the concentration units are reduced by *n* times, then the value of rate constant of first order will:
(1) Increase by *n* times
(2) Decrease by factor of *n*
(3) Not change
(4) None of these

**60.** Unit of frequency factor (1) is
(1) mol/L
(2) mol/L×s
(3) Depends upon order of reaction
(4) It does not have any unit

**61.** The ionic reactions are usually very fast because:
(1) It does not involve bond breaking
(2) The energy of activation between charged ions is greater than that between neutral molecules
(3) Collision frequency is very low
(4) The reactions are highly exothermic

**62.** In the first order reaction, 75% of the reactant gets disappeared in 1.386 h. The rate constant of the reaction is

(1) $3.0 \times 10^{-3} s^{-1}$ (2) $2.8 \times 10^{-4} s^{-1}$
(3) $17.2 \times 10^{-3} s^{-1}$ (4) $1.8 \times 10^{-3} s^{-1}$

**63.** Number of mole of a substance present in 1 litre volume is known as:

(1) Activity
(2) Molar concentration
(3) Active mass
(4) None of these

**64.** The rate of a reaction is doubled when temperature increases by 10ºC. If temperature is increased by 100ºC, then rate of reaction will become

(1) 64 times (2) 256 times
(3) 512 times (4) 1024 times

**65.** For a hypothetical reaction

A + 2B → 3C + D d[C]/dt is equal to

(1) $\frac{3d[A]}{dt}$ (2) $-\frac{3}{2}\frac{d[B]}{dt}$
(3) $-\frac{d[B]}{dt}$ (4) $-\frac{d[A]}{dt}$

**66.** The half-life of two samples is 0.1 and 0.4 s. Their reactive concentration is 200 and 50 respectively. What is the order of reaction?

(1) 0 (2) 2 (3) 1 (4) 4

**67.** Consider following two reaction,

$$A \rightarrow product - \frac{d[A]}{dt} = k_1 [A]^0$$

$$B \rightarrow product - \frac{d[B]}{dt} = k_2 [B]^0$$

$k_1$ and $k_2$ are expressed in term of molarity mol $L^{-1}$) and time ($s^{-1}$) as

(1) $s^{-1}, M s^{-1} L^{-1}$ (2) $M s^{-1}, M s^{-1}$
(3) $s^{-1}, M^{-1} s^{-1}$ (4) $M s^{-1}, L s^{-1}$

**68.** The reaction, $NO + (1/2)O_2 \rightarrow NO_2$ exhibits:

(1) Small negative temperature coefficient
(2) Decrease in value of *K* with temperature
(3) Decrease in value of rate with temperature
(4) All of the above

**69.** Consider the reaction, $Cl_2(aq) + H_2S(aq) \rightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$ the rate equation for this reaction is , rate = *k* $[Cl_2]$ $[H_2S]$

Which of these mechanisms is/are consistent with this rate equation?

$Cl_2 + H_2S(aq) \rightarrow H^+Cl^- + Cl^+ + HS^-$ (slow)
$Cl^+ + HS^- \rightarrow H^+Cl^- + S$ (fast)
$H_2S \leftrightarrow H^+ + HS^-$ (fast equilibrium)
$Cl_2 + HS^- \rightarrow 2Cl^- + H^+S$ (slow)

(1) (2) only
(2) Both (1) and (2)
(3) Neither (1) nor (2)
(4) (1) Only

**70.** In a reaction 2A → Products; the concentration of A decreases from 0.5 mol $litre^{-1}$ to 0.4 mol $litre^{-1}$ in 10 minute. The rate of reaction during this interval is:

(1) 0.05 $M\,min^{-1}$ (2) 0.005 $M\,min^{-1}$
(3) 0.5 $M\,min^{-1}$ (4) 5 $M\,min^{-1}$

**71.** What is the two third life of a first order reaction having $k = 5.48 \times 10^{-14} s^{-1}$ ?

(1) $2.01 \times 10^{13}$ s (2) $2.01 \times 10^{12}$ s
(3) $4.02 \times 10^{13}$ s (4) $4.02 \times 10^{26}$ s

**72.** In a Ist order reaction the concentration of reactant decreases from 800 $mol/dm^3$ to 50 $mol/dm^3$ in $2 \times 10^4$s. The rate constant of reaction in$S^{-1}$ is

(1) $2 \times 10^4$ (2) $3.45 \times 10^{-5}$
(3) $1.386 \times 10^{-4}$ (4) $2 \times 10^{-4}$

**73.** The rate constant of a first order reaction is $6.9 \times 10^{-3} s^{-1}$. How much time will it take to reduce the initial concentration to its 1/8th value ?

(1) 100s (2) 200s (3) 300s (4) 400s

**74.** Which of the following rate laws has an overall 0.5 for reaction involving substance *x*, *y* and *z*?

(1) $\text{Rate} = k[C_x][C_y][C_z]$
(2) $\text{Rate} = k[C_x]^{0.5}[C_y]^{0.5}[C_z]^{0.5}$
(3) $\text{Rate} = k[C_x]^{1.5}[C_y]^{-1}[C_z]^{0}$
(4) $\text{Rate} = k[C_x][C_z]^2/[C_y]^2$

**75.** The rate law for the reaction,

$2H_{2(g)} + 2NO_{(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$ is

$$\frac{d[N_2]}{dt} = k[H_2][NO]^2$$

Which of the following mechanisms is consistent with the rate law?

(1) $H_{2(g)} + 2NO_{(g)} \xrightarrow{k_1} N_2O + H_2O_{(g)}$
(2) $H_{2(g)} + N_2O_{(g)} \xrightarrow{k_2} N_{2(g)} + H_2O_{(g)}$
(3) $H_2O_{(g)} + NO_{(g)} \xrightarrow{k_3} H_{2(g)} + NO_{2(g)}$
(4) $H_{2(g)} + 2NO_{(g)} \xrightarrow{k_4} N_{2(g)} + H_2O + \frac{1}{2}O_{2(g)}$

**76.** Consider the following:

| | $C_2H_5COOC_2H_5$ | $+ H_2O \xrightarrow{H^+}$ | $C_2H_5COOH$ | $+ C_2H_5OH$ |
|---|---|---|---|---|
| Init.mol | 0.02 | 10 | 0 | 0 |
| At time t | 0 | 9.8 | 0.02 | 0.02 |

What inference can be drawn from the given data?

(1) The concentration of ester changes preciably.
(2) The concentration of $H_2O$ can be taken as constant.
(3) It is a pseudo first order reaction
(4) All of these.

**77.** The reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ is a first order reaction with half life. $3.15\times10^4 s$ At 320°C. What percentage of $SO_2Cl_2$ would be decomposed on heating at 320°C for 90 minutes?
(1) 22.4% (2) 10.7 %
(3) 1.12% (4) 13.2%

**78.** The half-life for the reaction, $SO_3 \longrightarrow 2SO_2 + O_2$ is 2 hours at 30°C. Starting with 10 g of $SO_3$ how many grams of $SO_3$ will remain after a period of 48 hours?
(1) 1.25 g (2) 0.625 g
(3) 1.77 g (4) 0.5 g

**79.** The time for half life period of a certain reaction A ⟶ Products is 1 hour. When the initial concentration of the reaction A is 2.0 mol $L^{-1}$, how much time does it take for its concentration to come from 0.50 to 0.25 mol $L^{-1}$if it is a zero order reaction?
(1) 1 hr (2) 4 hr
(3) 0.5 hr (4) 0.25 hr

**80.** In a first order reaction the $a/(a–x)$ was found to be 8 after 10 minute. The rate constant is
(1) (2.303 × 3 log 2)/10
(2) (2.303 × 2 log 3)/10
(3) 10 × 2.303 × 2 log 3
(4) 10 × 2.303 × 3 log 2

**81.** The decomposition of a substance follows first order kinetic. If its concentration is reduced to $\frac{1}{8^{th}}$ of its initial value, in 24 minutes, the rate constant of decomposition process is
(1) $1/24 \min^{-1}$ (2) $\frac{0.692}{24}\min^{-1}$
(3) $\frac{2.303}{24}\log\left(\frac{1}{8}\right)\min^{-1}$ (4) $\frac{2.303}{24}\log\left(\frac{8}{1}\right)\min^{-1}$

**82.** The rate constant, $k$ of the reaction,

$$N_2O_{5(g)} \rightarrow 2NO_{2(g)} + \frac{1}{2}O_2(g) 2.3\times10^{-2} s^{-1}.$$

Which equation given below describes the change $[N_2O_5]$ with time? $[N_2O_5]_0$ and $[N_2O_5]_t$, correspond to concentration of $N_2O_5$ initially and at time $t$.
(1) $[N_2O_5]_t = [N_2O_5]_0 + kt$
(2) $\log[N_2O_5]_t = \log[N_2O_5]kt$
(3) $[N_2O_5]_0 = [N_2O_5]_t e^{kt}$
(4) $\ln\frac{[N_2O_5]_0}{[N_2O_5]} = kt$

**83.** Which one of the following is not true?
(1) For first order reaction, straight-line graph of log C versus t is obtained, slope = – k/2.303.
(2) A plot of log k vs $\frac{1}{T}$ gives a straight-line graph for which slope = – Ea/2.303 R.
(3) For third order reaction, the product of $t_{1/2}$ and initial concentration (1) is constant.
(4) Unit of k for the first order reaction are in depended of concentration units.

**84.** Which one of the following statement is incorrect?
(1) The temperature coefficient of a reaction is the ratio of the rate constants at any two temperatures.
(2) The temperature coefficient of a reaction is the ratio of the rate constants at 298 K and 308 K.
(3) The temperature coefficient of most of the reactions lies between 2 and 3.
(4) In an endothermic reaction, activation energy of reactants is more than that of the products.

**85.** According to collision theory of reaction rates
(1) Every collision between reactants leads to chemical reaction
(2) Rate of reception is proportional to velocity of molecules
(3) All reactions which occur in gaseous phase are zero order reactions
(4) Rate of reaction is directly proportional to collision frequency.

# EXERCISE # 3

**Question** **Previous Year (JEE Main)**

**1.** For the reaction A + 2B → C, rate is given by R = [A][B]2 then the order of the reaction is **[AIEEE 2002]**

(1) 3 (2) 6 (3) 5 (4) 7

**2.** For the reaction system :

$2NO_{(g)} + o_{2(g)} \rightarrow 2NO_{2(g)},$

Volume is suddenly reduced to half its Value by increasing the pressure on it. if the reaction is of first order with respect to $O_2$ and second order with respect to $NO_2$, the rate of reaction will **[AIEEE 2003]**

(1) Diminish to one – fourth of its initial value by
(2) Diminish to one- eighth of its initial value
(3) Increase to eight times of its initial value
(4) Increase to four times of its initial value.

**3.** In a first order reaction, the concentration of the reactant decreases from 0.8 M to in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is **[AIEEE 2004]**

(1) 30 minutes (2) 15 minutes
(3) 7.5 minutes (4) 60 minutes

**4.** $t_{1/4}$ con be taken as the time taken for the concentration of a reactant to drop to 3/4 of its initial value. If the rate constant for a first order reaction is $k$, the $t_{1/4}$ can be written as **[AIEEE 2005]**

(1) $0.10/k$ (2)$0.29/k$ (3) $0.69/k$ (4) $0.75/k$

**5.** A reaction was found to be second order with respect to the concentration of carbon monoxide. if the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will be **[AIEEE 2006]**

(1) Remain unchanged
(2) Tripled
(3) Increased by a factor of 4
(4) Doubled.

**6.** Consider the reaction, $2A + B \rightarrow$ products. When concentration of $B$ alone was doubled, the half-life did not change. When the concentration of $A$ alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is **[AIEEE 2007]**

(1) $s^{-1}$ (2) $L\ mol^{-1}\ s^{-1}$
(3) no unit (4) $mol\ L^{-1}\ s^{-1}$

**7.** For a reaction $\frac{1}{2}A \rightarrow 2B$ rate of disappearance of $A$ is related to the rate of appearance of $B$ by the expression **[AIEEE 2008]**

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

(3) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$ (4) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$

**8.** 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]**

(1) 230.3 minutes (2) 23.03 minutes
(3) 46.06 minutes (4) 460.6 minutes.

**9.** Consider the reaction : **[AIEEE 2010]**

$Cl_{2(aq)} + H_2S_{(aq)} \rightarrow S_{(s)} + 2H^+_{(aq)} + 2Cl^-_{(aq)}$

The rate of reaction for this reaction is

Rate = $k[Cl_2][H_2S]$

Which of these mechanism is/are consistent with this rate equation?

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

B. $H_2S \Leftrightarrow H^+ + HS^-$ (fast equilibrium)
$Cl_2 + HS^- \rightarrow 2Cl^- + H^+ + S$ (slow)

(1) A only (2) B only
(3) Both A and B (4) Neither A nor B

**10.** The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about **[AIEEE 2011]**

(1) 10 times (2) 24 times
(3) 32 times (4) 64 times

**11.** For a first order reaction, (1) → products, the concentration of $A$ changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of $A$ is 0.01 M is **[AIEEE 2012]**

(1) $3.47 \times 10^{-4}$ M/min
(2) $3.47 \times 10^{-5}$ M/min
(3) $1.73 \times 10^{-4}$ M/min
(4) $1.73 \times 10^{-5}$ M/min

**12.** The rate of a reaction doubles when its temperature changes from 300 k to 310 k. Activation energy of such a reaction will be ($R = 8.314\ J\ k^{-1}$ and log 2 = 0.301) **[JEE Main 2013]**

(1) 60.5 kJ $mol^{-1}$ (2) 53.6 kJ $mol^{-1}$
(3) 48.6 kJ $mol^{-1}$ (4) 58.5 kJ $mol^{-1}$

**13.** For the non-stoichiometeic reaction: $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

| Initial concentration [A] | Initial concentration [A] | Initial rate of formation of C (mol $L^{-1}s^{-1}$) |
|---|---|---|
| 0.1 M | 0.1 M | $1.2 \times 10^{-3}$ |
| 0.1 M | 0.2 M | $1.2 \times 10^{-3}$ |
| 0.2 M | 0.1 M | $2.4 \times 10^{-3}$ |

The rate law for the formation of $C$ is **[JEE Main 2014]**

(1) $\frac{dC}{dt} = k[A]$ (2) $\frac{dC}{dt} = k[A][B]$

(3) $\frac{dC}{dt} = k[A]^2[B]$ (4) $\frac{dC}{dt} = k[A][B]^2$

**14.** Higher order (>3) reactions are rare due to **[JEE Main 2015]**

(1) Shifting of equilibrium towards reactants due to elastic collisions
(2) Loss of active species on collision
(3) Low probability of simultaneous collision of all the reacting species
(4) Increase in entropy and activation energy as More molecules are involved.

**15.** Decomposition of $H_2O_2$ follows a first order reaction. In fifty minutes the concentration of $H_2O_2$ decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of $H_2O_2$ reaches 0.05 M. the rate of formation of $O_2$ will be **[JEE Main 2016]**

(1) $6.93 \times 10^{-2}$ mol min$^{-1}$
(2) $6.93 \times 10^{-4}$ mol L$^{-1}$min$^{-1}$
(3) 2.66 L min$^{-1}$ at STP
(4) $1.34 \times 10^{-2}$ mol min$^{-1}$

**16.** Two reactions $R_1$ and $R_2$ have identical pre-exponential factors. Activation energy of $R_1$ exceeds that of $R_2$ by 10 kJ mol$^{-1}$. If $k_1$ and $k_2$ are rate constants for reactions $R_1$ and $R_2$ respectively at 300 K. then In($k_2/k_1$) is equal to ($R = 8.314$ J mol$^{-1}$ K$^{-1}$) **[JEE Main 2017]**

(1) 6 (2) 4 (3) 8 (4) 12

**17.** At 518° C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torr s$^{-1}$ when 5% had reacted and 0.5 Torr s$^{-1}$ when 33% had reacted. The order of the reaction is : **[JEE Mains 2018]**

(1) 1 (2) 0 (3) 2 (4) 3

**18.** For the reaction 2A + B → C, the values of initial rate at different reactant concentrations are given in the table below. The rate law for the reaction is : **[JEE Main 2019]**

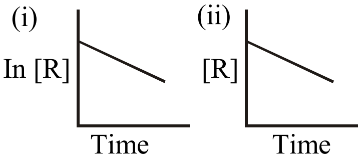
| [A] (mol L$^{-1}$) | [B] (mol L$^{-1}$) | Initial Rate (mol L$^{-1}$s$^{-1}$) |
|---|---|---|
| 0.05 | 0.05 | 0.045 |
| 0.10 | 0.05 | 0.090 |
| 0.20 | 0.10 | 0.72 |

(1) Rate = k [A][B] (2) Rate = k $[A]^2[B]^2$
(3) Rate = k $[A][B]^2$ (3) Rate = k $[A]^2[B]$

**19.** For a reaction scheme $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, if the rate of formation of B is set to be zero then the concentration of B is given by : **r[JEE Main 2019]**

(1) $(k_1 / k_2)$ [A] (2) $(k_1 + k_2)$ [A]
(3) $k_1k_2$ [A] (4) $(k_1 - k_2)$ [A]

**20.** The given plots represent the variation of the concentration of a reactant R with time for two different reactions (i) and (ii). The respective orders of the reactions are : **[JEE Main 2019]**



(1) 1, 0 (2) 1, 1 (3) 0, 1 (4) 0, 2

**21.** For the reaction of $H_2$ with $I_2$, the rate constant is $2.5 \times 10^{-4}$dm$^3$ mol$^{-1}$ s$^{-1}$ at 327°C and 1.0 dm$^3$ mol$^{-1}$ s$^{-1}$ at 527°C. The activation energy for the reaction, in kJ mol$^{-1}$ is: **[JEE Main 2019]**
($R = 8.314$ J k$^{-1}$ mol$^{-1}$)

(1) 72 (2) 166 (3) 150 (4) 59

**22.** $NO_2$ required for a reaction is produced by the decomposition of $N_2O_5$ in $CCl_4$ as per the equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$
The initial concentration of $N_2O_5$ is 3.00 mol L$^{-1}$ and it is 2.75 mol L$^{-1}$ after 30 minutes. The rate of formation of $NO_2$ is : **[JEE Main 2019]**

(1) $2.083 \times 10^{-3}$ mol L$^{-1}$ min$^{-1}$
(2) $4.167 \times 10^{-3}$ mol L$^{-1}$ min$^{-1}$
(3) $8.333 \times 10^{-3}$ mol L$^{-1}$ min$^{-1}$
(4) $1.667 \times 10^{-2}$ mol L$^{-1}$ min$^{-1}$

**23.** The following results were obtained during kinetic studies of the reaction:
2A + B → Products

| Experiment | [A] (in mol L$^{-1}$) | [B] (in mol L$^{-1}$) | Initial Rate of reaction (in mol L$^{-1}$ min$^{-1}$) |
|---|---|---|---|
| (I) | 0.10 | 0.20 | $6.93\times10^{-3}$ |
| (II) | 0.10 | 0.25 | $6.93\times10^{-3}$ |
| (III) | 0.20 | 0.30 | $1.386\times10^{-2}$ |

The time (in minutes) required to consume half of A is : **[JEE Main 2019]**

(1) 10 (2) 5 (3) 100 (4) 1

**24.** For the reaction, 2A + B → products, when the concentrations of A and B both were doubled, the rate of the reaction increased from 0.3 mol L$^{-1}$s$^{-1}$ to 2.4 mol L$^{-1}$ s$^{-1}$. When the concentration of A alone is doubled, the rate increased from 0.3 mol L$^{-1}$s$^{-1}$ to0.6 mol L$^{-1}$s$^{-1}$. Which one of the following statements is **correct?** **[JEE Main 2019]**

(1) Order of the reaction with respect to B is 2.
(2) Order of the reaction with respect to A is 2.
(3) Total order of the reaction is 4.
(4) Order of the reaction with respect to B is 1.

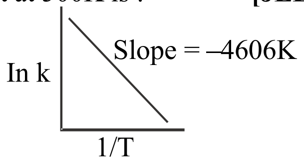
**25.** For an elementary chemical reaction, $A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$, the expression for $\frac{d[A]}{dt}$ is - **[JEE Main 2019]**

(1) $2k_1[A_2] - k_{-1}[A]^2$ (2) $k_1[A_2] - k_{-1}[A]^2$
(3) $2k_1[A_2] - 2k_{-1}[A]^2$ (4) $k_1[A_2] + k_{-1}[A]^2$

**26.** Decomposition of X exhibits a rate constant of 0.05 mg/year. How many years are required for the decomposition of 5 mg of X into 2.5 μg ? **[JEE Main 2019]**

(1) 50 (2) 25 (3) 20 (4) 40

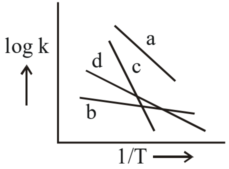
**27.** For a reaction consider the plot of ln k versus 1/T given in the figure. If the rate constant of this reaction at 400 K is $10^{-5}$ $s^{-1}$, then the rate constant at 500K is : **[JEE Main 2019]**



(1) $2 \times 10^{-4}$ $s^{-1}$ (2) $10^{-4}$ $s^{-1}$
(3) $10^{-6}$ $s^{-1}$ (4) $4 \times 10^{-4}$ $s^{-1}$

**28.** For the reaction **[JEE Main 2020]**
$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$
the observed rate expression is,
rate = $k_f [NO]^2[H2]$. The rate expression of the reverse reaction is :
(1) $k_b[N_2][H_2O]^2/[NO]$ (2) $k_b[N_2][H_2O]$
(3) $k_b[N_2][H_2O]^2$ (4) $k_b[N_2][H_2O]^2/[H_2]$

**29.** Consider the following plots of rate constant versus 1/T for four different reactions. Which of the following orders is correct for the activation energies of these reactions? **[JEE Main 2020]**



(1) $E_b > E_d > E_c > E_a$ (2) $E_a > E_c > E_d > E_b$
(3) $E_c > E_a > E_d > E_b$ (4) $E_b > E_a > E_d > E_c$

**30.** Rate of a reaction increases by $10^6$ times when a reaction is carried out in presence of enzyme catalyst at same temperature. Determine change in activation energy. **[JEE Main 2020]**
(1) –6 × 2.303 RT (2) +6 × 2.303RT
(3) + 6 RT (4) –6RT

**31.** For the following reactions **[JEE Main 2020]**

$$A \xrightarrow{700\ K} \text{Product}$$

$$B \xrightarrow[\text{catalyst}]{500\ K} \text{Product}$$

it was found that $E_a$ is decreased by 30 kJ/mol in the presence of catalyst. If the rate remains unchanged, the activation energy for catalysed reaction is (Assume pre exponential factor is same):
(1) 135 kJ/mol (2) 105 kJ/mol
(3) 198 kJ/mol (4) 75 kJ/mol

**32.** The results given in the below table were obtained during kinetic studies of the following reaction: **[JEE Main 2020]**
$2A + B \rightarrow C + D$

| Experiment | [A]/molL$^{-1}$ | [B]/molL$^{-1}$ | Initial rate/molL$^{-1}$ min$^{-1}$ |
|---|---|---|---|
| I | 0.1 | 0.1 | $6.00 \times 10^{-3}$ |
| II | 0.1 | 0.2 | $2.40 \times 10^{-2}$ |
| III | 0.2 | 0.1 | $1.20 \times 10^{-2}$ |
| IV | X | 0.2 | $7.20 \times 10^{-2}$ |
| V | 0.3 | Y | $2.88 \times 10^{-1}$ |

X and Y in the given table are respectively :
(1) 0.3, 0.4 (2) 0.4, 0.3
(3) 0.4, 0.4 (4) 0.3, 0.3

**33.** It is true that : **[JEE Main 2020]**
(1) A zero order reaction is a single step reaction
(2) A second order reaction is always a multistep reaction.
(3) A first order reaction is always a single step reaction.
(4) A zero order reaction is a multistep reaction.

**34.** For the reaction 2A + 3B + (3/2) C → 3P, which statement is correct ? **[JEE Main 2020]**

(1) $\frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dn_C}{dt}$

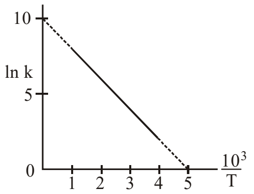
(2) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

(3) $\frac{dn_A}{dt} = \frac{3}{2}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

(4) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{4}{3}\frac{dn_C}{dt}$

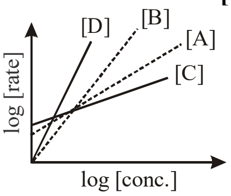
**35.** A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives for A and B are 300 s and 180 s, respectively. If the concentrations of A and B are equal initially, the time required for the concentration of A to be four times that of B(in s) : (Use ln 2 = 0.693) **[JEE Main 2020]**
(1) 180 (2) 120 (3) 300 (4) 900

**36.** The rate constant (k) of a reaction is measured at different temperatures (T), and the data are plotted in the given figure. The activation energy of the reaction in kJ mol$^{-1}$ is : (R is gas constant) **[JEE Main 2020]**



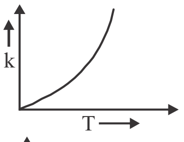
(1) 2R (2) R (3) 1/R (4) 2/R

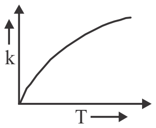
**37.** Consider the following reactions :
$A \rightarrow P_1$ ; $B \rightarrow P_2$ ; $C \rightarrow P_3$ ; $D \rightarrow P_4$
The order of the above reactions are a, b, c, and d, respectively. The following graph is obtained when log [rate] vs. log [conc] are plotted:
**[JEE Main 2020]**

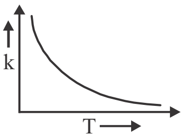


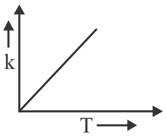
Among the following , the correct sequence for the order of the reactions is:
(1) a > b > c > d (2) c > a > b > d
(3) d > b > a > c (4) d > a > b > c

**38.** Which one of the following given graphs represents the variation of rate constant (k) with temperature (T) for an endothermic reaction?
**[JEE Main 2021]**

(1)


(2)


(3)


(4)


**39.** $2NO + 2H_2 \rightarrow N_2 + 2H_2O$
The above reaction has been studied at 800°C. The related date are given in the table below

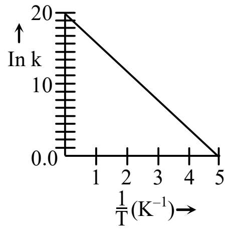
| **Reaction serial number** | **Initial Pressure of $H_2$/kPa** | **Initial Pressure of NO/kPa** | **Initial rate $\left(\frac{-dp}{dt}\right)$/(kPa/s)** |
|---|---|---|---|
| 1. | 65.6 | 40.0 | 0.135 |
| 2. | 65.6 | 20.1 | 0.033 |
| 3. | 38.6 | 65.6 | 0.214 |
| 4. | 19.2 | 65.6 | 0.106 |

The order of the reaction with respect to NO is ______.
(Nearest integer) (Given: R = 2 cal $K^{-1}$ $mol^{-1}$)
**[JEE Main 2022]**

**40.** [A] $\longrightarrow$ [B]
Reactant Product
If formation of compound [B] follows the first order of kinetics and after 70 minutes the concentration of [A] was found to be half of its initial concentration. Then the rate constant of __________ . (Nearest Integer)
**[JEE Main 2022]**

**41.** For the given first order reaction $A \rightarrow B$, the half life of the reaction is 0.3010 min. The ratio of the initial concentration of reactant to the concentration of reactant at time 2.0 min will be equal to ______. (Nearest integer)
**[JEE MAIN 2022]**

**42.** For a reaction, given below is the graph of ln k vs $\frac{1}{T}$. The activation energy for the reaction is equal to____ cal $mol^{-1}$.
**[JEE Main 2022]**



**43** For a first order reaction $A \rightarrow B$, the rate constant, $k = 5.5 \times 10^{-14}$ $s^{-1}$. The time required for 67% completion of reaction is $x \times 10^{-1}$ times the half life of reaction. The value of x is _____. (Nearest integer) **[JEE Main 2022]**

**44.** The reaction between X and Y is first order with respect to X and zero order with respect to Y.

| Experiment | [X]/mol $L^{-1}$ | [Y]/mol $L^{-1}$ | Initial rate/mol $L^{-1}$ $min^{-1}$ |
|---|---|---|---|
| I. | 0.1 | 0.1 | $2 \times 10^{-3}$ |
| II. | L | 0.2 | $4 \times 10^{-3}$ |
| III. | 0.4 | 0.4 | $M \times 10^{-3}$ |
| IV | 0.1 | 0.2 | $2 \times 10^{-3}$ |

Examine the data of table and calculate ratio of numerical values of M and L. (Nearest Integer)
**[JEE Main 2022]**

**45.** The activation energy of one of the reactions in a biochemical process is 532611 J $mol^{-1}$. When the temperature falls from 310 K to 300 K, the change in rate constant observed is $k_{300} = x \times 10^{-3}$ $k_{310}$. The value of x is ______.
[Given: ln10 = 2.3, R = 8.3 $JK^{-1}$ $mol^{-1}$]
**[JEE Main 2022]**

**46.** The number of terminal oxygen atoms present in the product B obtained from the following reaction is ________.
$FeCr_2O_4 + Na_2CO_3 + O_2 \rightarrow A + Fe_2O_3 + CO_2$
$A + H+ \rightarrow B + H_2O + Na^+$ **[JEE Main 2022]**

**47.** The equation $k = (6.5 \times 10^{12} s^{-1})e^{-26000K/T}$ is followed for the decomposition of compound A. The activation energy for the reaction is ______ kJ $mol^{-1}$. [nearest integer] **[JEE Main 2022]**
(Given : R = 8.314 J $K^{-1}$ $mol^{-1}$]

**48.** The number of correct statement/s from the following is __________.
A. Larger the activation energy, smaller is the value of the rate constant.

the reaction is $x \times 10^{-6}$ $s^{-1}$. The value of x is

B. The higher is the activation energy, higher is the value of the temperature coefficient.
C. At lower temperatures, increase in temperature causes more change in the value of k than at higher temperature.
D. A plot of ln k vs $\frac{1}{T}$ is a straight line with slope equal to $-\frac{E_a}{R}$. **[JEE Main 2023]**

**49.** A student has studied the decomposition of a gas $AB_3$ at 25°C. He obtained the following data.

**[JEE Main 2023]**

| **p (mm Hg)** | 50 | 100 | 200 | 400 |
|---|---|---|---|---|
| **Relative $t_{1/2}$ (s)** | 4 | 2 | 1 | 0.5 |

The order of the reaction is

(1) 1 (2) 0(Zero)

(3) 2 (4) 0.5

**50.** It compound A reacts with B following first order kinetics with rate constant $2.011 \times 10^{-3}\ s^{-1}$. The time taken by A (in seconds) to reduce from 7 g to 2 g will be ________ . (Nearest Integer) [log 5 = 0.698, log 7 = 0.845, log 2 = 0.301]

**[JEE Main 2023]**

**51.** $A \rightarrow B$

The rate constants of the above reaction at 200 K and 300 K are 0.03 $min^{-1}$ and 0.05 $min^{-1}$ respectively. The activation energy for the reaction is __________ J (Nearest integer)

(Given : ln 10 = 2.3

$R = 8.3\ J\ K^{-1}\ mol^{-1}$

log 5 = 0.70

log 3 = 0.48

log 2 = 0.30) **[JEE Main 2023]**

**52.** The rate constant for a first order reaction is 20 $min^{-1}$. The time required for the initial concentration of the reactant to reduce to its $\frac{1}{32}$ level is ________ $\times 10^{-2}$ min. (Nearest integer)

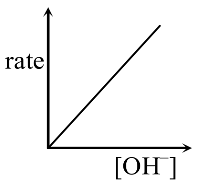
Given : ln 10 = 2.303

log 2 = 0.3010 **[JEE Main 2023]**

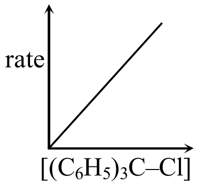
**53.** The graph which represents the following reaction is : **[JEE Main 2023]**

$$(C_6H_5)_3C\text{–}Cl \xrightarrow[\text{Pyridine}]{OH^-} (C_6H_5)_3C\text{–}OH$$

(1)



(2)



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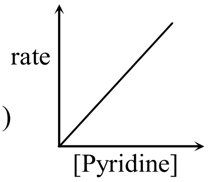
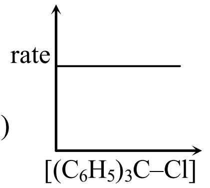


(4)



**54.** $A \rightarrow B$

The above reaction is of zero order. Half life of this reaction is 50 min. The time taken for the concentration of A to reduce to one-fourth of its initial value is _________ min. **[JEE Main 2023]**

**55.** Time required for completion of 99.9% of a First order reaction is ______ times of half life ($t_{1/2}$) of the reaction. **[JEE Main 2024]**

**56.** Consider the following first order gas phase reaction at constant temperature

$A(g) \rightarrow 2B(g) + C(g)$

If the total pressure of the gases is found to be 200 torr after 23 sec. and 300 torr upon the complete decomposition of A after a very long time, then the rate constant of the given reaction is____$\times\ 10^{-2}\ s^{-1}$ (nearest integer) [Given : $\log_{10}(2) = 0.301$] **[JEE Main 2024]**

**57.** Time required for 99.9% completion of a first order reaction is ____ time the required for completion of 90% reaction. (nearest integer).

**[JEE Main 2024]**

**58.** Consider the following transformation involving first order elementary reaction in each step at constant temperature as shown below.

$$A + B \underset{\text{Step3}}{\overset{\text{Step I}}{\rightleftharpoons}} C \xrightarrow{\text{Step 2}} P$$

Some details of the above reaction are listed below.

| **Step** | **Rate constant ($sec^{-1}$)** | **Activation energy (kJ $mol^{-1}$)** |
|---|---|---|
| 1 | $k_1$ | 300 |
| 2 | $k_2$ | 200 |
| 3 | $k_3$ | $Ea_3$ |

If the overall rate constant of the above transformation (k) is given as $k = \frac{k_1k_2}{k_3}$ and the overall activation energy ($E_a$) is 400 kJ $mol^{-1}$, then the value of $Ea_3$ is ______ kJ $mol^{-1}$ (nearest integer) **[JEE Main 2024]**

**59.** The reaction $A_2 + B_2 \rightarrow 2\ AB$ follows the mechanism

$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + A \text{ (fast)}$$

$$A + B_2 \xrightarrow{k_2} AB + B \text{ (slow)}$$

$$A + B \rightarrow AB \text{ (fast)}$$

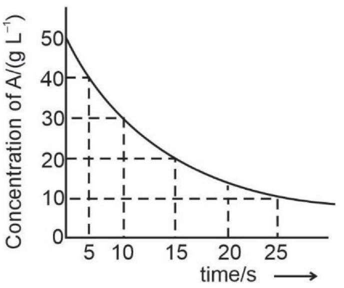
The overall order of the reaction is :

**[JEE Main 2025]**

(1) 1.5 (2) 3 (3) 2.5 (4) 2

**60.** For the reaction $A \rightarrow B$ the following graph was obtained. The time required (in seconds) for the concentration of A to reduce to 2.5 g $L^{-1}$ (if the initial concentration of A was 50 g $L^{-1}$) is _______. (Nearest integer) Given: log 2 = 0.3010

**[JEE Main 2025]**



# EXERCISE # 4

**Questions** **Previous Year (AIPMT & NEET)**

**1.** 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 **[AIPMT 2008]**

(1) $\frac{1000}{2.303}$ K (2) 1000 K

(3) $\frac{2000}{2.303}$ K (4) 2000 K

**2.** For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$,

If $\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol $L^{-1}s^{-1}$, The value of $\frac{-d[H_2]}{dt}$ would be - **[AIPMT 2009]**

(1) $1 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$

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

(3) $4 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$

(4) $6 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$

**3.** For the reaction A + B → products, it is observed that : **[AIPMT 2009]**

(1) On doubling the initial concentration of A only, the rate of reaction is also doubled and

(2) On doubling the initial concentration of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is given by :

(1) rate = k[A] [B]

(2) rate = $k[A]^2[B]$

(3) rate = $k[A][B]^2$

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

**4.** In the reaction

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \rightarrow 3Br_2(l) + 3H_2O(l)$

The rate of appearance of bromine ($Br_2$) is related to rate of disappearance of bromide ions as following **[AIPMT 2009]**

(1) $\frac{d(Br_2)}{dt} = \frac{3}{5}\frac{d(Br^-)}{dt}$

(2) $\frac{d(Br_2)}{dt} = -\frac{3}{5}\frac{d(Br^-)}{dt}$

(3) $\frac{d(Br_2)}{dt} = -\frac{5}{3}\frac{d(Br^-)}{dt}$

(4) $\frac{d(Br_2)}{dt} = \frac{5}{3}\frac{d(Br^-)}{dt}$

**5.** Half-life period of a first-order reaction is 1386 seconds. The specific rate constant of the reaction is : **[AIPMT 2009]**

(1) $5.0 \times 10^{-2}$ $s^{-1}$ (2) $5.0 \times 10^{-3}$ $s^{-1}$

(3) $0.5 \times 10^{-2}$ $s^{-1}$ (4) $0.5 \times 10^{-3}$ $s^{-1}$

**6.** For the reaction $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2$ (g) the value of rate of disappearance of $N_2O_5$ is given as $6.25 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$. The rate of formation of $NO_2$ and $O_2$ is given respectively as: **[AIPMT 2010]**

(1) $6.25 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$ and
$6.25 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$

(2) $1.25 \times 10^{-2}$ mol $L^{-1}$ $s^{-1}$ and
$3.125 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$ and

(3) $6.25 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$ and
$3.125 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$

(4) $1.25 \times 10^{-2}$ mol $L^{-1}$ $s^{-1}$ and
$6.25 \times 10^{-3}$ mol $L^{-1}$ $s^{-1}$

**7.** During the kinetic study of the reaction, 2A + B → C + D, following results were obtained:

| Run | [A]/mol $L^{-1}$ | [B]/mol $L^{-1}$ | Initial rate of formation of D/mol $L^{-1}$ $min^{-1}$ |
|---|---|---|---|
| I | 0.1 | 0.1 | $6.0 \times 10^{-3}$ |
| II | 0.3 | 0.2 | $7.2 \times 10^{-2}$ |
| III | 0.3 | 0.4 | $2.88 \times 10^{-1}$ |
| IV | 0.4 | 0.1 | $2.40 \times 10^{-2}$ |

Based on the above data which one of the following is correct? **[AIPMT 2010]**

(1) rate = k $[A]^2$ [B] (2) rate = k [A] [B]

(3) rate = k $[A]^2$ $[B]^2$ (4) rate = k [A] $[B]^2$

**8.** Which one of the following statements for the order of a reaction is incorrect? **[AIPMT 2011]**

(1) Order of reaction is always whole number

(2) Order can be determined only experimentally

(3) Order is not influenced by stoichiometic coefficient of the reactants.

(4) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction

**9.** The unit of rate constant for a zero order reaction is - **[AIPMT 2011]**

(1) $s^{-1}$ (2) mol $L^{-1}s^{-1}$

(3) L $mol^{-1}$ $s^{-1}$ (4) $L^2$ $mol^{-2}$ $s^{-1}$

**10.** The half life of a substance in a certain enzyme-catalysed reaction is 138 s. The time required for the concentration of to fall from 1.28 mg $L^{-1}$ to 0.04 mg $L^{-1}$, is- **[AIPMT 2011]**

(1) 276 s (2) 414 s

(3) 552 s (4) 690 s

**11.** The rate of the reaction

$2N_2O_5 \rightarrow 4NO_2 + O_2$

can be written in three ways: **[AIPMT 2011]**

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

$$\frac{d[NO_2]}{dt} = k'[N_2O_5]$$

$$\frac{d[O_2]}{dt} = k''[N_2O_5]$$

The relationship between k and k′ and between k and k″ are-

(1) $k' = k, k'' = k$ (2) $k' = 2k; k'' = k$

(3) $k' = 2k, k'' = k/2$ (4) $k' = 2k; k'' = 2k$

**12.** In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become: **[AIPMT 2012]**

(1) 64 times (2) 128 times

(3) 256 times (4) 512 times

**13.** In a reaction, $A + B \rightarrow \text{Product}$, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentrations of both the reactants (A and B) are doubled, rate law for the reaction can be written as **[AIPMT 2012]**

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

(3) $\text{Rate} = k[A][B]^2$ (4) $\text{Rate} = k[A]^2[B]^2$

**14.** Activation energy ($E_a$) and rate constant ($k_1$ and $k_2$) of a chemical reaction at two different temperatures ($T_1$ and $T_2$) are related by – **[AIPMT 2012]**

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

(2) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} + \frac{1}{T_1}\right)$

(3) $\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

(4) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

**15.** What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20ºC to 35ºC ? ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) **[NEET 2013]**

(1) 342 kJ $mol^{-1}$ (2) 269 kJ $mol^{-1}$

(3) 34.7 kJ $mol^{-1}$ (4) 15.1 kJ $mol^{-1}$

**16.** Energies of activation for forward and reverse reactions has - **[NEET 2013]**

(1) $\Delta S = 0$ (2) $\Delta G = 0$

(3) $\Delta H = 0$ (4) $\Delta H = \Delta G = \Delta S = 0$

**17.** The activation energy of a reaction can be determined from the slope of which of the following graphs ? **[AIPMT 2015]**

(1) $\ell n$ K vs. T (2) $\frac{\ell n K}{T}$ vs. T

(3) $\ell n$ K vs. $\frac{1}{T}$ (4) $\frac{T}{\ell n K}$ vs. $\frac{1}{T}$

**18.** When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is: **[NEET 2015]**

(1) Zero

(2) First

(3) Second

(4) More than zero but less than first

**19.** If the value of an equilibrium constant for a particular reaction is $1.6 \times 10^{12}$ then at equilibrium the system will contain: **[NEET 2015]**

(1) All reactants

(2) Mostly reactants

(3) Mostly products

(4) Similar amounts of reactants and products

**20.** The rate constant of the reaction $A \rightarrow B$ is $0.6 \times 10^{-3}$ mole per second. If the concentration of A is 5 M, then concentration of B after 20 minutes is - **[NEET 2015]**

(1) 0.36 M (2) 0.72 M

(3) 1.08 M (4) 3.60 M

**21.** The addition of a catalyst during a chemical reaction alters which of the following quantities ? **[NEET 2016]**

(1) Internal energy (2) Enthalpy

(3) Activation energy (4) Entropy

**22.** The rate of a first order reaction is 0.04 mol $l^{-1}$ $s^{-1}$ at 10 seconds and 0.03 mol $l^{-1}$ $s^{-1}$ at 20 seconds after initiation of the reaction. The half-life period of the reaction is : **[NEET 2016]**

(1) 34.1 s (2) 44.1 s

(3) 54.1 s (4) 24.1 s

**23.** A first order reaction has a specific reaction rate of $10^{-2}$ $sec^{-1}$. How much time will it take for 20 g of the reactant to reduce to 5g ? **[NEET 2017]**

(1) 693.0 sec (2) 238.6 sec

(3) 138.6 sec (4) 346.5 sec

**24.** Mechanism of a hypothetical reaction

$X_2 + Y_2 \rightarrow 2XY$ is given below.

(i) $X_2 \rightarrow X + X$ (fast)

(ii) $X + Y_2 \rightleftharpoons XY + Y$ (slow)

(iii) $X + Y \rightarrow XY$ (fast)

The overall order of the reaction will be– **[NEET 2017]**

(1) 1.5 (2) 1 (3) 2 (4) 0

**25.** The correct difference between first and second order reactions is that **[NEET 2018]**

(1) The rate of a first-order reactions does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations

(2) The half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$

(3) A first-order reaction can be catalyzed; a second-order reaction cannot be catalyzed

(4) The rate of a first-order reaction does depend on reactant concentrations; the rate second- order reaction does not depend on reactant concentrations

**26.** When initial concentration of the reactant is doubled, the half-life period of a zero order reaction **[NEET 2018]**

(1) is halved (2) is doubled

(3) is tripled (4) remains unchanged

**27.** For the chemical reaction **[NEET 2019]**

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(1) $-\frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

(2) $3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$

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

(4) $-\frac{d[N_2]}{dt} = 2\frac{d[NH_3]}{dt}$

**28.** If the rate constant for a first order reaction is k, the time (t) required for the completion of 99 % of the reaction is given by - **[NEET 2019]**

(1) t = 4.606/k (2) t = 2.303/k

(3) t = 0.693/k (4) t = 6.909/k

**29.** The rate constant for a first order reaction is $4.606 \times 10^{-3}\ s^{-1}$. The time required to reduce 2.0g of the reactant to 0.2 g is: **[NEET 2020]**

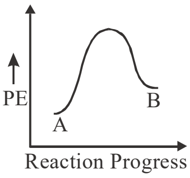
(1) 1000 s (2) 100 s (3) 200 s (4) 500 s

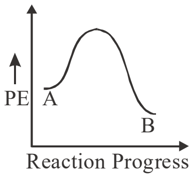
**30.** An increase in the concentration of the reactants of a reaction leads to change in : **[NEET 2020]**

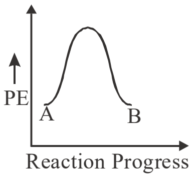
(1) collision frequency (2) activation energy

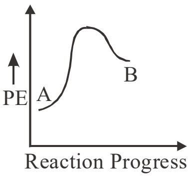
(3) heat of reaction (4) threshold energy

**31.** For a reaction A → B, enthalpy of reaction is –4.2 kJ/mol and enthalpy of activation is 9.6 kJ $mol^{-1}$. The correct potential energy profile for the reaction is shown in option. **[NEET 2021]**

(1) 

(2) 

(3) 

(4) 

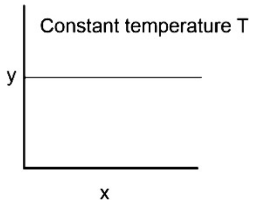
**32.** The slope of Arrhenius Plot (ln k v /s 1/T) of first order reaction is $-5 \times 10^3$ K. The value of $E_a$ of the reaction is. Choose the correct option for your answer. **[NEET-2021]**

[Given R = 8.314 $JK^{-1}\ mol^{-1}$]

(1) 41.5 kJ $mol^{-1}$ (2) 83.0 kJ $mol^{-1}$

(3) 166 kJ $mol^{-1}$ (4) –83 kJ $mol^{-1}$

**33.** The given graph is a representation of kinetics of a reaction. **[NEET 2022]**



The y and x axes for zero and first order reactions, respectively are

(1) zero order (y = concentration and x = time), first order (y = rate constant and x = concentration)

(2) zero order (y = rate and x = concentration), first order ($y = t_{1/2}$ and x = concentration)

(3) zero order (y = rate and x = concentration), first order (y = rate and $x = t_{1/2}$)

(4) zero order (y = concentration and x = time), first order ($y = t_{1/2}$ and x = concentration)

**34.** For a first order reaction A → Products, initial concentration of A is 0.1 M, which becomes 0.001 M after 5 minutes. Rate constant for the reaction in $min^{-1}$ is **[NEET 2022]**

(1) 0.9212 (2) 0.4606

(3) 0.2303 (4) 1.3818

**35.** For a certain reaction, the rate = $k[A]^2[B]$, when the initial concentration of A is tripled keeping concentration of B constant, the initial rate would **[NEET 2023]**

(1) increase by a factor of three

(2) decrease by a factor of nine

(3) increase by a factor of six

(4) increase by a factor of nine

**36.** Activation energy of any chemical reaction can be calculated if one knows the value of **[NEET 2024]**

(1) orientation of reactant molecules during collision.

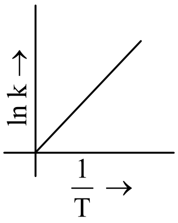
(2) rate constant at two different temperatures.

(3) rate constant at standard temperature.

(4) probability of collision.

**37.** Which plot of ln k vs $\frac{1}{T}$ is consistent with Arrhenius equation ? **[NEET 2024]**

(1)



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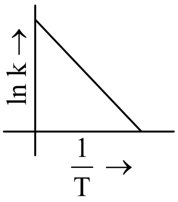

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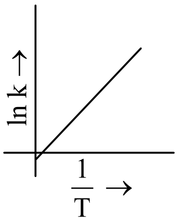
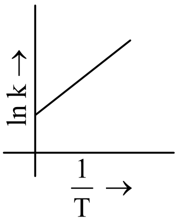


(4)



**38.** The rate of a reaction quadruples when temperature changes from 27ºC to 57ºC. Calculate the energy of activation.
Given R = 8.314 J $K^{-1}$ $mol^{-1}$, log 4 = 0.6021 **[NEET 2024]**

(1) 3.80 kJ/mol (2) 3804 kJ/mol

(3) 38.04 kJ/mol (4) 380.4 kJ/mol

**39.** If the rate constant of a reaction is 0.03 $s^{-1}$, how much time does it take for 7.2 mol $L^{-1}$ concentration of the reactant to get reduced to 0.9 mol $L^{-1}$? (Given: log 2 = 0.301) **[NEET-2025]**

(1) 210 s (2) 21.0 s (3) 69.3 s (4) 23.1 s

**40.** If the half-life ($t_{1/2}$) for a first order reaction is 1 minute, then the time required for 99.9% completion of the reaction is closest to : **[NEET-2025]**

(1) 5 minutes (2) 10 minutes

(3) 2 minutes (4) 4 minutes

# ANSWER KEY

## EXERCISE-1

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | 3 | 2 | 1 | 3 | 2 | 4 | 2 | 4 | 3 | 3 | 4 | 2 | 3 | 4 | 4 | 4 | 2 | 4 | 2 | 2 |
| Que. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| Ans. | 4 | 1 | 2 | 3 | 3 | 3 | 2 | 1 | 3 | 3 | 1 | 4 | 2 | 4 | 2 | 3 | 3 | 1 | 3 | 2 |
| Que. | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 |
| Ans. | 3 | 2 | 2 | 4 | 3 | 4 | 2 | 3 | 4 | 1 | 1 | 2 | 2 | 1 | 1 | 2 | 2 | 4 | 3 | 3 |
| Que. | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 |
| Ans. | 1 | 4 | 2 | 1 | 4 | 3 | 2 | 2 | 3 | 1 | 3 | 2 | 2 | 4 | 2 | 3 | 1 | 1 | 2 | 2 |
| Que. | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
| Ans. | 2 | 3 | 4 | 1 | 1 | 4 | 2 | 2 | 1 | 2 | 1 | 2 | 3 | 1 | 3 | 2 | 3 | 1 | 2 | 4 |
| Que. | 101 | 102 | 103 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | | | | | | | | | | |
| Ans. | 3 | 3 | 3 | 4 | 4 | 3 | 1 | 2 | 4 | 3 | | | | | | | | | | |

## EXERCISE-2

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | 3 | 2 | 2 | 3 | 1 | 2 | 1 | 2 | 3 | 2 | 4 | 1 | 1 | 2 | 1 | 2 | 2 | 2 | 4 | 2 |
| Que. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| Ans. | 2 | 4 | 4 | 3 | 2 | 1 | 1 | 4 | 4 | 4 | 3 | 4 | 2 | 2 | 4 | 4 | 4 | 2 | 1 | 4 |
| Que. | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 |
| Ans. | 1 | 4 | 3 | 4 | 2 | 4 | 3 | 1 | 3 | 4 | 3 | 3 | 2 | 1 | 1 | 1 | 2 | 2 | 3 | 3 |
| Que. | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 |
| Ans. | 1 | 2 | 2 | 4 | 2 | 2 | 4 | 4 | 4 | 2 | 1 | 3 | 3 | 3 | 4 | 4 | 2 | 2 | 4 | 1 |
| Que. | 81 | 82 | 83 | 84 | 85 | | | | | | | | | | | | | | | |
| Ans. | 4 | 4 | 3 | 1 | 4 | | | | | | | | | | | | | | | |

## EXERCISE-3

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | 1 | 3 | 1 | 2 | 3 | 2 | 3 | 3 | 3 | 3 | 1 | 2 | 1 | 3 | 2 | 2 | 3 | 3 | 1 | 1 |
| Que. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| Ans. | 2 | 4 | 2 | 1 | 3 | 1 | 2 | 4 | 3 | 1 | 4 | 1 | 4 | 4 | 4 | 1 | 3 | 1 | 2 | 165 |
| Que. | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 |
| Ans. | 100 | 8 | 16 | 40 | 1 | 6 | 216 | 3 | 3 | 623 | 2520 | 17 | 2 | 75 | 10 | 3 | 3 | 100 | 1 | 47.00 |

## EXERCISE-4

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ans. | 1 | 2 | 3 | 2 | 4 | 2 | 4 | 1 | 2 | 4 | 3 | 4 | 2 | 1 | 3 | 3 | 3 | 2 | 3 | 2 |
| Que. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| Ans. | 3 | 4 | 3 | 1 | 2 | 2 | 1 | 1 | 4 | 1 | 2 | 1 | 2 | 1 | 4 | 2 | 2 | 3 | 3 | 2 |