

CHEMICAL KINETICS



Investigation Report

TARGET EXAM	PREDICTED NO. OF MCQs	CRITICAL CONCEPTS
NEET	3-4	• Rate of Reaction, Effect of Temperature, Order of Reaction, Collision.

Perfect Practice Plan

Topicwise Questions	Learning Plus	Multiconcept MCQs NEET Past 10 Years Questions T		Total MCQs
108	32	26	26	192

INTRODUCTION

Chemical Kinetics is the branch of chemistry that deals with

- Rates of reactions
- · Factors influencing the rates of reaction
- Reaction mechanism

Kinetics studies help us to determine the speed or rate of a chemical reaction and also describe the conditions by which the reaction rates can be altered.

Based on the velocity of chemical reactions, the reactions are classified into three types:

(*a*) Very fast (or) instantaneous reactions: The chemical reactions which are completed within the fraction of seconds are called as very fast reactions.

Example:

- 1. Neutralization between strong acids and strong bases.
 - $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
- 2. Precipitation reactions

$$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

3. Explosive reactions : Explosion of T.N.T

(b) Moderate reactions: The chemical reactions which are completed within hours (or) minutes are called as moderate reactions.

Example:

1. Inversion of cane sugar

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \to C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$

2. Combustion of hydrogen (or) coal [under normal conditions].

$$H_2(g) + \frac{1}{2}O_2(g) \to H_2O(g)$$

(c) Very slow reactions: The chemical reactions which complete in very long time are called very slow reactions.

Example:

- 1. Rusting of Iron in presence of air and moisture $4Fe + 3O_2 + xH_2O \rightarrow 2Fe_2O_3.xH_2O.$
- 2. $2H_2(g) + O_2(g) 2H_2O(l)$

🖉 KEY NOTE

It is not possible to determine the rates of very fast and very slow reactions by conventional methods.But the rates of reactions with moderate speed can be determined.

RATE OF REACTION

The decrease in the concentration of the reactant per unit time or increase in the concentration of the product per unit time is called rate of a reaction.

Rate = $\frac{\Delta c}{\Delta t} = \frac{mol / lit.}{sec}$ = 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.

For a reaction $R \rightarrow P$

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

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

$$r_{inst} = \frac{d[P]}{dt} = slope$$

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

$$r_{av} = \frac{\Delta[P]}{\Delta t} = \frac{[P_2] - [P_1]}{(t_2 - t_1)}$$

Fig.: Average rate of reaction

Instantaneous rate : rate of reaction at a particular instant.



Fig.: Instantaneous rate of reaction

Example:

1.
$$A \rightarrow B$$

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

2.
$$pP + qQ \rightarrow rR + sS$$

rate =
$$-\frac{1}{p}\frac{d[P]}{dt} = -\frac{1}{q}\frac{d[Q]}{dt} = +\frac{1}{r}\frac{d[R]}{dt} =$$

= $+\frac{1}{s}\frac{d[S]}{dt}$

3.
$$5Br^{-}(aq)+BrO_{3}^{-}(aq)+6H^{+}(aq) \rightarrow 3Br_{2}(aq)+3H_{2}O(1)$$

$$Rate = -\frac{1}{5} \frac{\Delta \left[Br^{-}\right]}{\Delta t} = -\frac{\Delta \left[BrO_{3}^{-}\right]}{\Delta t}$$
$$= -\frac{1}{6} \frac{\Delta \left[H^{+}\right]}{\Delta t} = \frac{1}{3} \frac{\Delta \left[Br_{2}\right]}{\Delta t} = \frac{1}{3} \frac{\Delta \left[H_{2}O\right]}{\Delta t}$$

Relation between reaction rates of different species involved in a reaction

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

Rate of reaction of N₂ = $-\frac{d[N_2]}{dt}$

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

🖉 KEY NOTE

Rate of reaction value is dependent on the stoichiometric coefficients used in the reaction while rate of any species will be fixed value under given conditions.

The rate of a reaction varies exponentially with time of the reaction.

The concentration of the reactants in a reaction varies exponentially with time.

No reaction takes place with uniform rate throughout the course of the reaction.

The rates of chemical reactions differ from one another, since the number and the nature of the bonds are different in the different substances (reactants or products or both)

FACTORS AFFECTING THE RATE OF REACTION

Factors affecting rate of chemical reaction :

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

1. Nature of the Reactants

(a) Physical state of reactants : Gaseous state > Liquid state > Solid state

Decreasing order of rate of reaction.

(b) **Physical size of reactants :** As the particle size decreases, rate of reaction increases since surface area increases.

(c) 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.

• Reactions between ionic substances take place much faster than the reactions occuring between covalent substances. Because in ionic reactions there is no breaking and forming of bonds.

 $NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) \downarrow + NaNO_3(aq)$

• But covalent molecules involve the breaking (cleavage) and the making (formation) of covalent bonds.

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

2. Concentration of the reactants

Except zero order reactions, for all other reactions the rate depends on the concentration of the reactants.

Rate ∞ (concentration of the reactants)ⁿ or

$$-\frac{dc}{dt} \propto C^n (\text{or}) - \frac{dc}{dt} = kC^n$$

'n' may be any simple value including zero.

For gaseous reactants, rate \propto (pressure of the reactants)ⁿ

Chemical reactions occur due to the collisions between the reacting molecules. Hence greater the number of these molecules in unit volume, greater will be the possibility of their collisions and higher will be the rate of reaction.

Eg: When zinc pieces are added to dilute HCl, chemical reaction takes place slowly liberating H_2 gas. But the same reaction is rapid by taking concentrated HCl.



From this graph it is clear that, the rate of reaction gradually decreases with time because of the decrease in the concentration of reacting substances with time.

3. Effect of temperature on the reaction rate

The rate of a reaction increases with increase in temperature.

In most cases, a rise of 10°C in temperature generally doubles the specific rate of the reaction.

Increase of temperature increases the number of collisions between the molecules and increases the internal energy of the molecules and hence increases the rate of reaction.

The ratio of two specific rates measured at temperature that differ by 10°C is called the Temperature co-efficient.

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

Arrhenius equation for temperature dependence of a rate constant is $k = Ae^{-E_a/RT}$

TRAIN YOUR BRAIN

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

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

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

- (i) 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).
- (*ii*) Every collision does not bring a chemical change. The collisions that actually produce the products are effective collisions. For a collision to be effective the following two barriers are to be effective:
- (a) Energy barrier- The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur is known as threshold energy."The minimum amount of extra energy required by reactant"

molecules to participate in a reaction is called activation energy (E_a) "

(b) Orientation barrier- Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper direction to make collision effective.

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

k = Rate constant,

A = Arrhenius frequency constant/pre-exponential factor

 $E_a =$ Activation energy,

R= Gas constant

- T = absolute temperature
- For the different temperatures (T₁ & T₂) the equation is written as



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For Example:

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



Fig.: Formation of HI through intermediale







Fig.: Distribution curves showing energies gaseous molecule



Fig.: Distribution curve showing dependence of rate of reaction

TRAIN YOUR BRAIN

Q. For the reaction CO(g) + Cl₂(g) → COCl₂(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 × 10¹⁰ M⁻¹ sec⁻¹, calculate the rate constant of the reaction at 150°C.

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

 $\log 1500 = \frac{E_a}{2.303 \times 2} \times \frac{100}{523 \times 423}$
 $E_a = \frac{3.1761 \times 2.303 \times 2 \times 523 \times 423}{100} = 32.36 \text{ kcal mol}^{-1}$

$$\log k = \log A - \frac{E_a}{2.303 \ RT} = \log (2.0 \times 1010) - \frac{32360}{2.303 \times 2 \times 423}$$
$$= 10.301 - 16.609 = -6.308$$

 $k = 4.92 \times 10^{-7}$ litres mol⁻¹ sec⁻¹

Q. 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 min⁻¹. Calculate the time required for 25 percent reaction to complete at 227°C.

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

 $\log k = -\frac{6.06}{2.303} = -2.63$; $k = 2.344 \times 10^{-3} \text{ min}^{-1}$
when $x = 0.25$; $k = \frac{2.303}{t_{1/4}} \log \frac{a}{0.75 a}$
 $t_{1/4} = \frac{2.303}{2.344 \times 10^{-3}} \log 1.333 = 122.6 \text{ min}$

4. Effect of Catalyst

A catalyst increases the rate of the reaction without undergoing any chemical change till the end of the reaction.



Fig.: Effect of catalyst an activation energy

4. Threshold energy

Catalyst alters

- 1. Rate of reaction 2. Path of reaction
- 3. Activation energy
- 5. Rate constant

Catalyst does not alter

- 1. ΔG of reaction
- 2. Energy of reactants and energy of products
- 3. ΔH
- 4. ΔS
- 5. K_C

In some reactions, the rate of the reaction is directly proportional to the concentration of the catalyst.

Eg : In Acid catalysed hydrolysis reactions of esters, the rate is proportional to the concentration of the acid catalyst.

🖉 KEY NOTE

Catalyst increases the rate of reaction by making an alternate path of low activation energy for reactant molecules.

RATE LAW

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

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let nA + mB \rightarrow Products
rate, r \propto [A]^n [B]^m
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$$r = k[A]^n[B]^n$$

Rate equation is obtained experimentally.

Rate Constant

The rate constant of reaction becomes equal to the rate of the reaction when the concentration of all the reactants are unity, hence the rate constant is also known as the **specific reaction rate**.

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

'k' is called rate constant or specific rate or rate per unit concentrations of the reactants.

$$k = \frac{Rate}{\left[reactants\right]^n}$$

Examples: units of $k = mole^{1-n} L^{n-1}sec^{-1}$ (a) $CH_3COOC_2H_5(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) +$ $C_{2}H_{2}OH(aq)$ Rate = $k[CH_3COOC_2H_5]^1[NaOH]^1$ (b) $\operatorname{CHCl}_3 + \operatorname{Cl}_2 \rightarrow \operatorname{CCl}_4 + \operatorname{HCl}$ Rate = $k[CHCl_3][Cl_3]^{1/2}$ (c) $CH_{3}COOC_{2}H_{5} + H_{2}O \rightarrow CH_{3}COOH + C_{2}H_{5}OH$ $Rate = k[CH_3COOC_2H_5]^{1}[H_2O]^{0}$ • Rate law equation for reversible reaction $H_2 + I_2 \xrightarrow{K_1} 2HI$ Rate = $\frac{1}{2} \frac{d[HI]}{dt} = k_1 [H_2] [I_2] - k_2 [HI]^2$ $Rate = \begin{bmatrix} Rate \ of \ forward \\ reaction \end{bmatrix} - \begin{bmatrix} Rate \ of \ backward \\ reaction \end{bmatrix}$ • Rate law equation involving side reactions. Ac²²⁷ k_1 Th²²⁷ h_2 Th²²⁷ k_2 Fr²²³ Rate of formation of $Th^{227} = k_1 [Ac^{227}]$ Rate of formation of $Fr^{223} = k_2[Ac^{227}]$

:. Rate = $(k_1 + k_2)[Ac^{227}]$

Characteristics of Rate Constant

Rate constant is a measure of the rate of the reaction. Greater the value of k, faster is the reaction. Similarly, smaller value of rate constant indicates slow reaction.

The value of k depends on the nature of the reactants. It is a characteristic constant for a particular reaction at a fixed temperature. Different reactions have different values of k.

Value of k is a constant for a given reaction, depends only on **temperature.**

The units of rate constant depend on the order of reaction.

ORDER OF THE REACTION

Let there be a reaction: $m_1A + m_2B \rightarrow$ 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.

🖉 KEY NOTE

Order of the reaction can be determined by experimental method only.

For elementary reactions order can be obtained from stoichiometric equation.

But for complex reactions order is to be experimentally calculated.

E.g. $xA + yB + zC \rightarrow \text{products}$ $R = k[A]^{x}[B]^{y}[C]^{z}$ order = x + y + zE.g. Rate = $k[A]^{3/2}[B]^{-1}$ order = $\frac{3}{2} + (-1) = \frac{1}{2}$

Zero Order Reactions

The reaction rate is independent of the concentration of the reactants

Some examples of zero order reactions are

eg: (I)
$$H_2(g) + Cl_2(g) \xrightarrow{hv} 2HCl(g)$$

(II) $2NH_3(g) \xrightarrow{M_a} N_2(g) + 3H_2(g)$
(III) $2HI \xrightarrow{Au} H_2 + I_2$
 $A \rightarrow \text{product}$
Rate = k[A]⁰
 $k = \frac{C_0 - C}{t} = \frac{x}{t}$

Where $C_0 =$ Initial concentration of reactant

C = Concentration of reactant at 't' time

x = Concentration of product at 't' time

Half-life period $(t_{1/2}) = \frac{a}{2k} \Rightarrow t_{1/2} \propto a$ Where a = initial concentration Unit of rate constant : mol L⁻¹S⁻¹

First Order Reactions

A \rightarrow Products $r = k_1 [A]^1$ Equation for rate: $\frac{dx}{dt} = k_1 (a - x)$ Equation for rate constant :

$$k_1 = \frac{2.303}{t} \log \frac{a}{a - x}$$

Units for rate constant: sec⁻¹ Half life time: $t_{1/2} \propto a^0$

$$t_{\frac{1}{2}} = \frac{0.693}{k_1}$$

Wilhemy formula:
$$C_{.} = C_{0}e^{-kt}$$

Let us consider a typical first order gas phase reaction $A(g) \to B(g) + C(g)$

Let P_i be the initial pressure of A and P_t the total pressure of the reaction mixture at time 't' then

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

Examples: Acid Hydrolysis of ester.

$$CH_{3}COOC_{2}H_{5} + H_{2}O \xrightarrow{H^{+}} CH_{3}COOH + C_{2}H_{5}OH$$

 $NH_4NO_2(aq) \rightarrow N_2(g) + 2H_2O(l)$ Disintegration of radioactive elements Hydrogenation of ethene is an example of first order reaction. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ Rate = k[C_2H_4] $^{226}_{88}Ra \rightarrow ^4_2He + ^{222}_{86}Rn$ Rate = k[Ra]

____ TRAIN YOUR BRAIN __

Q. Calculate
$$t_{3/4}$$
: $t_{1/2}$ for a 1st order reaction

Ans
$$k = \frac{2.303}{t_{3/4}} \log \frac{C_0}{\frac{1}{4}C_0} = \frac{2.303}{t_{1/2}} \log \frac{C_0}{\frac{C_0}{2}}$$

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

Q. At least how many half-lives should elapse for a 1st order reaction so that the reaction is at least 96.8% completed ? $(\log 2 = 0.3)$

5

(c) 6
(d) 7
Ans. (b)
$$100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5 \xrightarrow{t_{1/2}} 6.25 \xrightarrow{t_{1/2}} 3.125 93.75\%$$

Second Order Reactions

$$2A \rightarrow A \rightarrow \text{ products}$$

$$r = k_2[A]^2$$

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

$$r = k_2[A][B]$$
Units for rate constant: lit. mole⁻¹.sec⁻¹
Half life time: $t_{\frac{1}{2}} \propto \frac{1}{a}$ (or) $t_{\frac{1}{2}} = \frac{1}{k_2 a}$

$$A \qquad B \rightarrow \text{ products.}$$
a b 0
at time t: $a - x \qquad b - x$

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

Examples :

1.
$$2N_2O \rightarrow 2N_2 + O_2$$

- 2. $2Cl_2O \rightarrow 2Cl_2 + O_2$
- 3. $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$
- 4. $2NO_2 \rightarrow 2NO + O_2$

5.
$$C_2H_4 + H_2 \xrightarrow{Ni} C_2H_6$$

6. $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$

For first order Growth Kinetics

It it used in population growth and bacteria multiplication

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

When 'a' is initial population and (a+x) is population after time 't'

nth Order Reactions

Units for rate constant : $lit^{n-1}.mole^{1-n}.sec^{-1}. or (atm)^{n-1} sec^{-1}$ When the order of reaction is n

$$t_{1/2} = \frac{1}{k(n-1)} \left[\frac{2^{n-1}-1}{a^{n-1}} \right]$$

Half life: $t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}$

TRAIN YOUR BRAIN

Q. The reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ is second order in NO and first order in Cl_2 . In a volume of 2 dm³, 5 mole of nitric oxide and 2 mol of Cl_2 were brought together, and the initial rate was 2.4×10^{-3} mole dm⁻³ s⁻¹. What will be the rate when half of the chlorine has reacted ?

Ans. 4.32×10^{-4} M sec⁻¹

$$2NO + Cl_{2} \rightarrow 2NOCl$$

$$t= 0 \quad 5 \text{ mol} \quad 2 \text{ mol}$$

$$C : \quad 5/2 \quad 2/2$$

$$R = K [NO]^{2} [CI]^{1}$$

$$R = k \left(\frac{5}{2}\right)^{2} (1)$$

$$2.4 \times 10^{-3} = k \left(\frac{25}{4}\right)$$

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

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

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

Pseudo Unimolecular Reactions

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 pseudo first order reactions.

 $\therefore \text{ For } A + B \rightarrow \text{Products} \qquad [\text{Rate} = k [A]^1 [B]^1]$ $k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$

Characteristics of First-and Second-Order Reactions of the Type $A \rightarrow$ Products

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

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

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

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

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

k is pseudo first order rate constant k' will have units of first order.

k will have units of second order.

Examples of Pseudo 1st order reactions :

(a) Hydrolysis of canesugar

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

(b) Hydrolysis of esters

$$CH_{3}COOCH_{3} + H_{2}O \xrightarrow{H^{+}} CH_{3}COOH + CH_{3}OH$$

excess

TRAIN YOUR BRAIN

Q. 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 200 mm. In a second experiment the time of half reaction was 140 seconds when the initial pressure was 300 mm. Calculate the total order of the reaction.

Ans. For a nth order reaction
$$(n \neq 1)$$
, $t_{1/2} \propto \frac{1}{c_0^{n-1}}$

-1

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

n = 2

🖉 KEY NOTE

- If a reactant is present in excess, order w.r.t. this reactant is zero.
- In the presence of an acid, hydrolysis of ethyl acetate is a pseudo-unimolecular reaction but the actual value of the rate constant depends upon the concentration of H⁺ ions.

	Zero Order	First-Order	Second-Order	n th order
Differential Rate law	$\frac{-\Delta A}{\Delta t} = k \left[A \right]^{\circ}$	$-\frac{\Delta[A]}{\Delta t} = k \left[A \right]$	$-\frac{\Delta[A]}{\Delta t} = k \left[A \right]^2$	$-\frac{\Delta A}{\Delta t} = k \left[A \right]^n$
(Integrated Rate law)	$[A]_t = [A]_0 - kt$	$\ln [A]_t = -kt + \ln[A]_0$	$\frac{1}{\left[A\right]_{t}} = kt + \frac{1}{\left[A\right]_{0}}$	$\frac{1}{\left[A_{t}\right]^{n-1}} - \frac{1}{\left[A_{0}\right]^{n-1}} = (n-1)kt$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$ (depends on [A]_0)	$t_{1/2} = \frac{0.693}{k}$ (Independent of [A] ₀)	$t_{1/2} = \frac{1}{k[A]_0}$ (depends on [A]_0)	$t_{1/2} \propto \frac{1}{\left[A_0\right]^{n-1}}$

MOLECULARITY OF THE REACTIONS

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

 $aA + bB \rightarrow products$ rate = k[A]^a[B]^b, where a + b = 1, 2 or 3.

Difference Between Molecularity and order of Reaction

	Molecularity of Reaction		Order of Reaction
1.	It is defined as the no. of molecules or reactant tak- ing part eg: $NH_4NO_2 \rightarrow N_2$ $+ 2H_2O; m=1$	1.	It is defined as the sum of the power of concentration terms that appear in rate law. $NH_4NO_2 \rightarrow N_2+2H_2O.$ Rate = k[NH_4NO_2]
2.	It is always a whole num- ber it can neither be zero nor fractional.	2.	It may be zero, fractional or even negative w.r.t a particu- lar reaction
3.	It is derived from RDS in the mechanism of reacation.	3.	It is derived from rate expression.
4.	It is theoretical value.	4.	It is experimental value.
5.	Reactions with molecularity \geq 4 are rare.	5.	Reactions with order ≥ 4 are also rare.
6.	Molecularity is independent of pressure and temperature.	6.	order of reaction depends upon pressure and temperature

METHODS OF DETERMINATION OF ORDER OF REACTION

1. Trial and Error method or Integrated form of rate equation method



$$x = kt$$
 (or) $k = \frac{x}{t} = \frac{a - (a - t)}{t}$

First order : $\mathbf{R} \rightarrow \mathbf{P}$





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

Second order: $2R \rightarrow P$

$$k = \frac{1}{at} \times \frac{x}{(a-x)}$$

Second order $R_1 + R_2 \rightarrow P$

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

2. Half-time $(t_{1/2})$ method

The half lives of each order is unique so by comparing half lives we can determine order for n^{th} order reaction

$$t_{1/2} \propto \frac{1}{a^{n-1}} \\ \left(\frac{t_{1/2}}{t_{1/2}}\right) = \left(\frac{a}{a}\right)^{n-1}$$

where n = order of reaction

3. Van't Hoff Differential method

$$\frac{-dC}{dt} = kC$$

For two initial concentrations C_1, C_2 we have

$$\frac{-dC_1}{dt} = kC_1^n; \qquad \frac{-dC_2}{dt} = kC_2^n$$
$$\therefore n = \frac{\log\left(\frac{-dC_1}{dt}\right) - \log\left(\frac{-dC_2}{dt}\right)}{(\log C_1 - \log C_2)}$$

4. Ostwald's Isolation method

This method is useful for reaction which involve a large number of reactants. In this method, the concentration of all the reactants are taken in large excess exception that of one, so if rate = k [A] a [B] b [C] c = k₀ [A] a

Then value of 'a' can be calculated by previous methods and similarly 'b' and 'c' can also be calculated.

COLLISION THEORY OF REACTION RATES OR KINETIC MOLECULAR THEORY

The reactant molecules collide with each other and exchange their bonds to convert into products. Without collision there is no reaction. This is called **collision theory**.

Collision theory is applicable only for gaseous covalent molecular reactions, not for ionic reactions.

The rate of the reaction at any given temperature is expected to be proportional to the number of collisions taking place between the reactant molecules in unit time at that temperature.

The actual rate of the reaction is much smaller than the rate calculated from the number of binary collisions of the reacting molecules taking place in unit time.

The number of collisions taking place in one second in one litre of an equimolar mixture of $H_2(g)$ and $I_2(g)$ at STP is around 10^{30} .

Collision theory was proposed by Arrhenius.

The main postulates of collision theory are



All collisions do not lead to the formation of products. (Only fruitful collisions leads to formation of products)

The minimum amount of energy possessed by the colliding molecules to the formation of products or reaction to occur is known as threshold energy.

The energy possessed by the molecules at STP is known as normal energy or internal energy.

Normal energy possessed by molecules is always less than threshold energy.

The energy to be gained by the molecules during the collision to convert into products is known as activation energy or energy of activation.

Activation energy = Threshold energy - energy of colliding molecules.

Activation energy increases, the rate of the reaction decreases.

No. of binary collisions per unit time (Z) is

$$Z = \pi \sigma_{AB}^2 \sqrt{\frac{8kT}{\pi\mu}} n_A n_B$$

 σ_{AB} = collision diameter ;

 μ = reduced mass

Specific rate, $k = \rho . Ze^{-E_a/RT}$

$$\rho.Ze^{-E_a/RT}$$
 or $k = Ae^{-E_a/RT}$

The collisions in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions. Whereas improper orientation makes them simply bounce back and no products are formed. For example, formation of methanol from bromo methane. $CH_3Br + OH \rightarrow CH_3OH + Br$



Fig.: Diagram showing molecules having proper and improper orientantion

The fraction of activated collisions is smaller than the total number of collisions.

Actual rate of reaction is much smaller than the rate of the reaction calculated on the basis of the normal collisions.

Collision Frequency (Z)

Total number of collisions which occur among the reacting molecules per second per unit volume is called collision frequency.

Its value is given by $Z = \sqrt{2}\pi v \sigma^2 n^2$

- v = average velocity
- σ = molecular diameter in cm
- n = number of molecules per cc.
- \therefore Rate (k) = Ze^{-E_a/RT}

CONCEPT OF ACTIVATION ENERGY

The difference between the energy barrier (i.e., threshold energy) E_T and the energy of normal molecules E_R is called activation energy E_a .





 $E_T - E_R = E_a$ = activation energy of the forward reaction $E_T - E_P = E'_a$ = activation energy of the backward reaction

TRANSITION STATE THEORY

According to this theory, the bimolecular reaction between two molecules passes through the formation of activated complex which then decomposes to yield the product AB, as shown below

$$\begin{array}{ccc} A_2 + B_2 \rightarrow \left(A_2 B_2\right) \\ & \xrightarrow{Reactants} & (Activated Complex) \end{array} \rightarrow \begin{array}{c} 2AB \\ & \xrightarrow{Product} \end{array}$$

The constant 'A' has unit of time $^{-1}$ and is constant for a given reaction.

🗷 KEY NOTE

At very high temperature rate becomes equal to frequency factor, i.e., k = A.

PHOTOCHEMICAL REACTION

Reactions which take place by the absorption of radiations of suitable wavelength

Eg:
$$H_2(g) + Cl_2(g) \xrightarrow{light} 2HCl(g)$$

Photosynthesis of carbohydrates in plants takes place in presence of chlorophyll and sunlight

$$6CO_2 + 6H_2O \xrightarrow{light} C_6H_{12}O_6 + 6O_2$$

The free energy change of a photochemical reaction may not be negative. In the synthesis of carbohydrates and formation of HCl, ΔG is +ve.

OTHER IMPORTANT RELATIONS

Zero order reactions

(i)
$$\frac{x_1}{t_1} = \frac{x_2}{t_2}$$

(ii) $t_{75\%} = \frac{3}{2}t_{50\%}$

(*iii*)
$$t_{100\%} = 2 \times t_{50\%}$$

First Order Reactions

(*i*)
$$t_{75\%} = 2t_{50\%}$$

(*ii*) $t_{87,5\%} = 3t_{50\%}$
(*iii*) $t_{93,75\%} = 4t_{50\%}$
(*iv*) $t_{99,9\%} = 10t_{50\%}$

(v)
$$t_{90\%} = \frac{10}{3} t_{50\%}$$

(*vi*)
$$t_{99\%} = 2t_{90\%}$$

(*vii*)
$$t_{99.9\%} = 3t_{90\%}$$

(*viii*)
$$t_{99.99\%} = 4t_{90\%}$$

Second Order Reactions

(i)
$$t_{2/3} = 2 \times t_{1/2}$$

(ii) $t_{3/4} = 3 \times t_{1/2}$
(iii) $t_{4/5} = 4 \times t_{1/2}$

Topicwise Questions

RATE OF REACTION & INTEGRATED RATE EQUATION

1. $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$ (excess) (glucose) (fructose)

Rate law is expressed as

(a)
$$r = k[C_{12}H_{22}O_{11}][H_2O]$$

(b) $r = k[C_{12}H_{22}O_{11}]$

(c)
$$r = k[H_2O]$$

(d)
$$r = k[C_{12}H_{22}O_{11}][H_2O]^2$$

- **2.** The term $-\frac{d[C]}{dt}$ refers to
 - (a) Rate of reaction
 - (b) Decrease in conc. of reactants with time
 - (c) Increase in conc. of reactants
 - (d) Decrease in the conc. of products with time
- **3.** When a chemical reaction takes place, during the course of the reaction the rate of reaction:(excluding zero order)
 - (a) Keeps on increasing with time
 - (b) Remains constant with time
 - (c) Keeps on decreasing with time
 - (d) Shows irregular trend with time
- 4. For the reaction $2NH_3 \rightarrow N_2 + 3H_2$,

If
$$\frac{-d[NH_3]}{dt} = k_1[NH_3]$$
, $\frac{d[N_2]}{dt} = k_2[NH_3]$,
 $\frac{d[H_2]}{dt} = k_3[NH_3]$

$$\frac{-2}{dt} = k$$

then the relation between k_1 , k_2 and k_3 is:

- (a) $k_1 = k_2 = k_2$ (b) $k_1 = 3 k_2 = 2 k_3$ (c) $1.5 k_1 = 3 k_2 = k_3$ (d) $2 k_1 = k_2 = 3 k_3$
- 5. In a reaction $2X \rightarrow Y$, the concentration of X decreases from 3.0 moles/litre to 2.0 moles/litre in 5 minutes. The rate of reaction is:
 - (a) $0.1 \mod L^{-1} \min^{-1}$ (b) $5 \mod L^{-1} \min^{-1}$
 - (c) $1 \mod L^{-1} \min^{-1}$ (d) $0.5 \mod L^{-1} \min^{-1}$
- 6. Consider the reaction, 2N₂O₅ → 4NO₂ + O₂
 In the reaction NO₂ is being formed at the rate of 0.0125 mol L⁻¹ S⁻¹. What is the rate of reaction at this time?
 - (a) $0.0018 \text{ mol}^{-1} \text{ L S}^{-1}$ (b) $0.0031 \text{ mol}^{-1} \text{ L}^{-1} \text{ sec}^{-1}$
 - (c) $0.0041 \text{ mol}^{-1} \text{ L S}^{-1}$ (d) $0.050 \text{ mol} \text{ L}^{-1} \text{ S}^{-1}$

- 7. Under a given set of experimental conditions with increase in the concentration of the reactants, the rate of chemical reaction
 - (a) Decreases
 - (b) Increases
 - (c) Remains constant
 - (d) First decreases and increases
- 8. In a chemical reaction, rate of a chemical reaction increases with temperature. The reason is due to
 - (a) Number of collisions between molecules increases
 - (b) Decreases in activation energy
 - (c) Increase in the number of the molecules with activation energy
 - (*d*) Kinetic energy of reactants increases
- 9. The half-life period for a first order reaction is:
 - (a) Independent of concentration
 - (b) Proportional to concentration
 - (c) Inversely proportional to concentration
 - (d) Inversely proportional to the square of the concentration
- **10.** 75% of a first order reaction is completed in 30 minutes, what is the time required for 93.75% of the reaction in minutes?
 - (a) 45 (b) 120
 - (c) 90 (d) 60
- **11.** If 60% of first order reaction was completed in 60min, 50% of the same reaction would be completed in approximately:
 - (a) 45 min (b) 60 min
 - (c) $40 \min$ (d) $50 \min$
- **12.** On increasing the pressure three fold, the rate of reaction of

 $2H_2S + O_2 \rightarrow products$, would increase

- (a) 3 times (b) 9 times
- (c)12 times (d) 27 times
- 13. The value of rate constant for a first order is $2.303 \times 10^{-2} \text{ sec}^{-1}$. What will be the time required to reduce the concentration
 - to $\frac{1}{10}$ th of the initial concentration?
 - (a) 100 sec (b) 10 sec
 - (c) 2303 sec (d) 23.03 sec
- 14. Units of specific reaction rate for second order reaction: (a) s^{-1} (b) mol $L^{-1} s^{-1}$
 - (c) $L \mod^{-2} s^{-1}$ (d) $L \mod^{-1} s^{-1}$
- **15.** For which order half-life period is independent of initial concentration?
 - (a) Zero (b) First
 - (c) Second (d) Third

16. k represents the rate constant of a reaction when log k is plotted against 1/T (T = temperature) the graph obtained is a

(a) Curve

- (b) A straight line with a constant positive slope
- (c) A straight line with constant negative slope
- (d) A straight line with no slope
- **17.** Slowest reaction among the following under identical conditions is
 - (a) $NaOH + HCl \rightarrow NaCl + H_2O$
 - (b) $\mathrm{H^{+} + OH^{-} \rightarrow H_{2}O}$
 - (c) $2NO + O_2 \rightarrow 2NO_2$
 - (d) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
- **18.** For a reaction, $I^- + OCI^- \rightarrow IO^- + CI^-$ in an aqueous medium, the rate of reaction is given by

 $\frac{\mathrm{d}[\mathrm{IO}^-]}{\mathrm{dt}} = \frac{\mathrm{k}[\mathrm{I}^-][\mathrm{OCI}^-]}{[\mathrm{OH}^-]}$

The overall order of reaction is:

(<i>a</i>) 1	<i>(b)</i> 0
(c) 3	(<i>d</i>) 2

- **19.** The order of reaction is decided by:
 - (a) Temperature
 - (b) Molecularity
 - (c) Pressure
 - (*d*) Mechanism of reaction as well as relative concentration of reactants
- 20. The unit of rate and rate constant are same for a:
 - (a) Zero order reaction
 - (b) First order reaction
 - (c) Second order reaction
 - (d) Third order reaction
- **21.** The number of molecules of the reactants taking part in a single step of the reaction is indicative of:
 - (a) Order of a reaction
 - (b) Molecularity of a reaction
 - (c) Fast step of the mechanism of a reaction
 - (*d*) Half-life of the reaction
- **22.** In reactions involving gaseous reactants and gaseous products the units of rate are
 - (a) Atm (b) Atm-sec
 - (c) Atm.sec⁻¹ (d) Atm² sec²
- 23. 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 the reaction is

(a) $A \rightarrow B$	(b) $C \rightarrow D$
(c) $B \rightarrow C$	(d) $A \rightarrow D$

24. The rate law for the reaction, $xA + yB \rightarrow mP + nQ$ is rate $= k [A]^{c} [B]^{d}$ what is the total order of the reaction?

<i>(a)</i>	x + y	<i>(b)</i>	m + n
())	(~)	

(c) c + d (d) Two

25. The rate equation for a reaction, $A \rightarrow B$ is $r = k[A]^0$ if the initial concentration of the reactant is a mol dm⁻³, the half period of the reaction is:

(a)
$$\frac{k}{a}$$
 (b) $\frac{a}{k}$
(c) $\frac{2a}{k}$ (d) $\frac{a}{2k}$

- **26.** Which of the following does not effect half-life of first order reaction?
 - (a) Initial concentration (b) Catalyst
 - (c) Temperature (d) Pressure
- **27.** For a first order reaction, the time taken to reduce the initial concentration by a factor of 1/4 is 20 min. the time required to reduce initial concentration by a factor of 1/16 is:
 - (a) 20 min (b) 10 min
 - (c) $80 \min$ (d) $40 \min$
- **28.** Chemical reactions of the type $X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$ are called
 - (a) Consecutive reactions (b) Parallel reactions
 - (c) Reversible reactions (d) Chain reactions
- **29.** The rate of chemical reaction depends on the nature of reactants because
 - (*a*) The number of bonds broken in the reactant molecules and the number of bonds formed in product molecules changes
 - (b) Some of the reactants are solids at the room temperature
 - (c) Some of the reactants are coloured
 - (d) Some of reactants are liquids at room temperature
- 30. Half-life period of a first order reaction is 10min. What percentage of the reaction will be completed in 100 min?
 (a) 25%
 (b) 50%
 - (c) 99.9% (d) 75%
- **31.** The expression to calculate time required for completion of zero order reaction is:

(a)
$$t = \frac{[R_o]}{k}$$

(b) $t = [R] - [R_o]$
(c) $t = \frac{k}{[R_o]}$
(d) $t = \frac{[R_o] - [R]}{[R_o]}$

- 32. Dimensions of rate of reaction involves
 - (a) Concentration only
 - (b) Time only
 - (c) Both concentration and time
 - (*d*) Neither time nor concentration
- **33.** Which of the following about the rate constant k of a reaction is wrong ?
 - (a) It remains unchanged throughout the course of reaction
 - (b) It provides a convenient measure of reaction rate
 - (c) It is expressed in the same $unit(sec)^{-1}$ for all reactions
 - (*d*) The more rapid the reaction, the larger is the value of k, the slower the reaction the smaller is its value

34. A first order reaction is 20% complete in 10 minutes. What is the specific rate constant for the reaction?

<i>(a)</i>	0.0970 min ⁻¹	<i>(b)</i>	0.009 min ⁻¹
(<i>c</i>)	0.0223 min ⁻¹	<i>(d)</i>	2.223 min ⁻¹

- **35.** In a first order reaction the concentration of reactants decreases from 400mol L^{-1} to 25 mol L^{-1} in 200 seconds. The rate constant for the reaction is:
 - (a) 1.01386 s⁻¹ (b) 2×10 s⁻¹
 - (c) $1.386 \times 10^{-2} \,\mathrm{s}^{-1}$ (d) $3.4 \times 10 \,\mathrm{s}^{-1}$
- **36.** $t_{1/2}$ for a first order reaction is 10 min. Starting with 10 M, the rate after 20 min is:
 - (a) 0.0693 M min⁻¹
 - (b) $0.0693 \times 5 \text{ M min}^{-1}$
 - (c) $0.0693 \times 2.5 \text{ M min}^{-1}$
 - (d) $0.0693 \times 10 \text{ M min}^{-1}$
- **37.** For a first order reaction the rate constant is 6.909 min⁻¹. The time taken for 75% conversion in minutes is:

(a)
$$\frac{3}{2}\log 2$$
 (b) $\frac{2}{3}\log 3$
(c) $\frac{2}{3}\log 2$ (d) $\frac{3}{2}\log \frac{3}{4}$

- **38.** The value of the rate constant of a reaction depends on
 - (a) Time (b) Activation energy
- (c) Temperature (d) Half-life value
- **39.** A catalyst
 - (a) Increases the heat of reaction
 - (b) Decreases the rate of the reaction
 - (c) Does not alter the rate of the reaction
 - (d) Increases the number of collisions
- **40.** In the first order reaction the relation between the velocity constant (K_1) and half-life period ($t_{1/2}$) is:

(a)
$$t_{\frac{1}{2}} = \frac{0.693}{k_1}$$
 (b) $k_1 = \frac{t_{\frac{1}{2}}}{0.693}$
(c) $t_{\frac{1}{2}} = 0.693 + k_1$ (d) $t_{\frac{1}{2}} = \frac{k_1}{0.693}$

41. The first order integrated rate equation is:

(a)
$$k = \frac{x}{t}$$
 (b) $k = \frac{-2.303}{t} \log \frac{a}{a-x}$
(c) $k = \frac{1}{t} ln \frac{a}{a-x}$ (d) $k = \frac{1}{t} - \frac{x}{a(a-x)}$

42. For the first order reaction half-life is 14 sec, the time required for the initial concentration to reduce to 1/8 of its value is:

(a) $(14)^3$ sec	(b) 28 sec
/	

(c) 42 sec (d) $(14)^2$ sec

- **43.** A \rightarrow B is a first order reaction. The initial concentration of A is 0.2 mol L⁻¹. After 10 min, the concentration of B is found to be 0.18 mol L⁻¹. The rate constant (in min⁻¹) for the reaction is:
 - (*a*) 0.2303 (*b*) 2.303
 - $(c) \ 0.693 \qquad \qquad (d) \ 0.01$
- 44. Arrhenius equation may be written as

(a)
$$\frac{d \ln k}{dT} = \frac{E_a}{RT}$$
 (b) $\frac{d \ln k}{dT} = +\frac{E_a}{RT^2}$
(c) $\frac{d \ln k}{dT} = -\frac{E_a}{RT}$ (d) $\frac{d \ln k}{dT} = -\frac{E_a}{RT^2}$

TEMPERATURE DEPENDENCE OF THE RATE OF A REACTION

- **45.** The activation energy in a chemical reaction is defined as: *(a)* The difference in energy of reactants and products
 - (b) The sum of energies of reactant and products
 - (c) The difference in energy of intermediate complex with the average energy of reactants and products
 - (*d*) The difference in energy of intermediate complex and the average energy of reactants
- 46. The temperature dependence of the rate of a chemical reaction can be explained by Arrhenius equation which is:
 (a) k = Ae^{-E}a^{/RT}

(b)
$$\mathbf{k} = \mathbf{A}\mathbf{e}^{\mathrm{E}_{\mathrm{a}}/\mathrm{RT}}$$

(c)
$$k = Ae \times \frac{E_a}{RT}$$

(d) $k = Ae \times \frac{RT}{RT}$

d)
$$k = Ae \times \frac{RT}{E_a}$$

- **47.** When a catalyst is used in an equilibrium process:
 - (*a*) It increases the rate of forward reaction
 - (b) It decreases the rate of backward reaction
 - (c) It decreases activation energy of forward process and decreases activation energy of backward process
 - (*d*) It fastens the attainment of equilibrium by lowering activation energy
- **48.** The rate constant for a first order reaction at 300°C for which E_a is 35 Kcal mol⁻¹ and frequency constant 'A' is 1.45×10^{11} sec⁻¹ is:
 - (a) $10 \times 10^{-2} \,\mathrm{S}^{-1}$ (b) $5.37 \times 10^{10} \,\mathrm{S}^{-1}$
 - (c) $5 \times 10^{-4} \text{ S}^{-1}$ (d) $7.94 \times 10^{-3} \text{ S}^{-1}$
- **49.** Which of the following statements about the catalyst is true?
 - (a) A catalyst makes the reaction feasible by making ΔG more negative
 - (*b*) A catalyst makes equilibrium constant more favorable for forward reaction
 - (c) A catalyst accelerate rate of reaction by bringing down the activation energy
 - (d) A catalyst always increases the rate of reaction

50. In a zero order reaction for every 10°C rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, rate of reaction will becomes:

(a)	256 times	<i>(b)</i>	512 times
(<i>c</i>)	64 times	(d)	128 times

- **51.** The rate constant 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:
 - (b) $\frac{2000}{2.303}$ K (a) 1000K (d) $\frac{1000}{2.303}$ K (c) 2000K
- 52. The potential energy diagram for a reaction $R \rightarrow P$ is given below.



 ΔH^0 of the reaction corresponding to the energy:

(a) a (b) b
(c) c (d)
$$a + b$$

53. According to arrhenius equation, the slope of log k vs $\frac{1}{T}$ plot is:

(a)
$$\frac{-E_{a}}{2.303R}$$
 (b) $\frac{-E_{a}}{2.303}$
(c) $\frac{-E_{a}}{2.303RT}$ (d) $\frac{E_{a}}{2.303RT}$

- 54. According to arrhenius hypothesis, rate of reaction increases with:
 - (a) Rise in temperature
 - (b) Decrease in temperature
 - (c) Rise in pressure
 - (d) Decrease in pressure
- 55. A reaction having equal energies of activation for forward and reverse reaction has:
 - (a) $\Delta S = 0$
 - (b) $\Delta G = 0$
 - (c) $\Delta H = 0$
 - (d) $\Delta H = \Delta G = \Delta S = 0$
- **56.** The effect of temperature on reaction rate is shown by:
 - (a) Kirchoff's equation
 - (b) Arrhenius equation
 - (c) Gibb's-Helmhoitz equation
 - (d) Clausius- Clapeyron equation

- 57. The rate constant of a first order reaction at 27°C is 10⁻³ min⁻¹. The rate constant (in min⁻¹) at 17°C for this reaction?
 - (a) 10^{-3} (b) 5×10^{-4} (c) 2×10^{-3} (*d*) 10^2

58. $N_2(g) + 3H_2(g) \implies 2NH_3(g) + 22 \text{ kcal}$

the activation energy for forward reaction is 50kcal. What is the activation energy for the backward reaction?

- (a) -72 kcal (b) -28 kcal
- (d) +72 kcal (c) + 28 kcal
- **59.** Chemical reaction with high E_a values are generally:
 - (*a*) Very fast (b) Very slow
 - (c) Moderately fast (d) Spontaneous
- 60. In the presence of a catalyst, activation energy of a reaction is lowered by 2 kcal at 27°C.Hence, rate will be:
 - (a) 20 times (b) 28 times
 - (c) 14 times (d) Remain same
- 61. The activation energy of a reaction at a given temperature is found to be 2.303 RTJmol⁻¹. The ratio of rate constant (k) to the arrhenius factor (A) is:

(<i>a</i>) 0.01	<i>(b)</i>	0.1
(c) 0.02	(d)	0.001

ORDER & MOLECULARITY OF REACTION

- 62. In the reaction $A+B \rightarrow Products$, if B is taken in excess. then it is an example of
 - (a) Second order reaction
 - (b) Zero order reaction
 - (c) Fractional order reaction
 - (d) First order reaction

63. The unit of rate constant for a second order reaction is

- (b) lit. mole sec. (a) sec.
- (c) Mole⁻¹. Lit. sec⁻¹ (d) mole. sec
- 64. The reaction that obeys the expression $t_{1/2} = \frac{1}{k \cdot a}$ in chemical kinetics is of _____ order reaction

- (c) 2(d) 3
- 65. When molecules of type A react with molecules of type B in one-step process to give AB2, the rate law is
 - (*a*) rate = $k[A]^1 [B]^2$ (b) rate= $k[A]^2 [B]^1$
 - (c) rate=k[2A][B](d) rate=k[A][B]
- 66. The units of rate of reaction and rate constant are identical for
 - (a) Fraction-order reaction
 - (b) Zero-order reaction
 - (c) First-order reaction
 - (d) Second-order reaction

- 67. A zero order reaction is one whose rate is independent of
 - (a) Temperature of the reaction
 - (b) The concentration of the reactants
 - (c) The concentration of the products
 - (d) Activation energy
- 68. The order of a reaction
 - (a) Can never be zero
 - (b) Can never be fraction
 - (c) Must be a whole number
 - (d) Can be an integer or a fraction or zero
- 69. The order of a reaction can be predicted with the help of
 - (a) Molecularity of the reaction
 - (b) Activation energy of the reaction
 - (c) Rate equation of the reaction
 - (d) Reaction rate
- **70.** The decomposition of Cl_2O is
 - (a) Explosive reactions
 - (b) Second order reactions
 - (c) First order reactions
 - (d) Thermal reactions
- 71. The molecularity of a reaction will be
 - (a) Fractional (b) Zero
 - (c) Positive whole number(d) Negative
- 72. Collision theory is applicable to
 - (a) Unimolecular reactions(b) Bimolecular reactions
 - (c) Trimolecular reactions (d) Tetra molecular reactions
- 73. Radioactive decay follows which order kinetics?

<i>(a)</i>	Zero	(<i>b</i>)	1
(<i>c</i>)	2	(d)	3

- 74. A reaction involving two different reactants can never be
 - (a) Unimolecular reaction (b) First order reaction
 - (c) Second order reaction (d) Bimolecular reaction
- **75.** The rate constant of a reaction is 175 lit²mol⁻²sec⁻¹. What is the order of reaction?

(a) First	<i>(b)</i>	Second
() = 1 : 1	(*	-

- (c) Third (d) Zero
- 76. The unit of rate constant obeying the rate expression $r = k[A]^{1}[B]^{2/3}$ is
 - (a) mole^{-2/3} lit^{2/3} time⁻¹ (b) mole^{2/3} lit^{-2/3} time⁻¹
 - (c) mole^{-2/3} lit^{-2/3} time⁻¹ (d) mole^{2/3} lit^{2/3} time⁻¹
- 77. What is the order of a reaction which has a rate expression: rate = $k[A]^{3/2}[B]^{-1}$

(a) $\frac{3}{2}$	<i>(b)</i>	$\frac{1}{2}$
(c) Zero	(d)	None

- **78.** Which of the following cannot be determined experimentally?
 - (a) Order
 - (b) Rate
 - (c) Rate constnat
 - (d) Molecularity
- **79.** Which of the following is first order ?
 - (*i*) Decomposition of NH_4NO_2 in aqueous solution.
 - (ii) Inversion of cane sugar in the presence of an acid
 - (iii) Base hydrolysis of ethyl acetate.
 - (iv) All radioactive decays.

The correct combination is

- (a) i, ii, iv (b) All are correct
- (c) ii, iv (d) ii, iii, iv
- 80. Which of the following statement is not correct?
 - (*a*) In zero order reaction, the rate of the reaction remains constant throughout
 - (b) A second order reaction would become a pseudo first order reaction, when one of the reactants is taken in large excess
 - (c) The units of first order rate constant depends on the units of the concentration terms used
 - (*d*) In the first order reaction, the plot of log (a-x) v/s time follows straight line equation
- **81.** Which one of the following statements for the order of a reaction is incorrect?
 - (a) Order of reaction is always whole number
 - (b) Order can be determined only experimentally
 - (c) Order is not influenced by stoichiometric coefficient of the reactants
 - (*d*) Order of reaction is sum of power to the concentration terms of reactant to express the rate of reaction while writing the rate law.

PSEUDO FIRST ORDER REACTION

82. The hydrolysis of ethyl acetate

 $CH_3OOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

is the reaction of:

- (a) Zero order
- (b) Pseudo first order
- (c) Second order
- (d) Third order
- 83. Which one of the following is wrongly matched?
 - (a) Saponification of $CH_3COOC_2H_5$ second order reaction
 - (b) Hydrolysis of CH₃COOCH₃ Pseudo unimolecular reaction
 - (c) Decomposition of H_2O_2 first order reaction
 - (d) Combination of H_2 and Br_2 to give HBr zero order reaction

- **84.** Under what conditions a biomolecular reaction may be kinetically of first order?
 - (a) When both reactants have same concentration.
 - (b) When one of the reacting species is in large excess
 - (*c*) When the reaction is at equilibrium
 - (*d*) When the activation energy of reaction is less
- 85. The order of a reaction for an esterification process is :
 - (a) Zero (b) First
 - (*d*) Pseudo first order
- **86.** Consider the following statements.

(c) Second

The rate law for the acid catalysed hydrolysis of an ester being given is-

rate = $k[H^+][ester] = k'[ester]$, if the acid concentration is doubled at constant ester concentration.

I. The second order rate constant, k is doubled

II. The pseudo first order rate constant, k' is doubled

III. The rate of the reaction is doubled

Which of the above statement are correct?

(a) I and II (b) II and III

(c) I and III (d) I, II and III

COLLISION THEORY OF CHEMICAL REACTION

- 87. On increasing the temperature by 10°C,
 - (*a*) Number of collisions get doubled
 - (b) Value of rate constant does not change
 - (c) Energy of activation increases
 - (*d*) Specific rate of the reaction gets doubled
- **88.** The rate of a reaction can be increased in general by all the factors except
 - (a) Using a catalyst
 - (*b*) Increasing the temperature
 - (c) Increasing the activation energy
 - (d) Increasing the concentration of reactants
- 89. The threshold energy of a chemical reaction depends upon
 - (a) Nature of reacting species
 - (b) Temperature
 - (c) Concentration of species
 - (d) Number of collisions
- **90.** Activation energy is ______ to rate of reaction
 - (*a*) Directly proportional
 - (*b*) Inversely proportional
 - (c) Equal
 - (d) Not related
- **91.** The rate of a reaction can be increased in general by all the factors except
 - (a) Using a catalyst
 - (b) Increasing the temperature
 - (c) Increasing the activation energy
 - (d) Increasing the concentration of reactants

- 92. To increase the rate of a chemical reaction, catalyst
 - (a) Increases the activation energy
 - (*b*) Decreases activation energy
 - (c) Reacts with products
 - (d) Does not change the activation energy
- 93. The energy of activation of a reaction is dependent on
 - (a) Temperature (b) Pressure
 - (c) Concentration (d) Nature of reactants
- **94.** The energy of activation of positive catalyzed reaction as compared to that of an uncatalyzed reaction is
 - (a) More (b) Less
 - (c) Same (d) May be more or less
- **95.** The increase in concentration of the reactants lead to change in:
 - (a) ΔH (b) Collision frequency
 - (c) Activation energy (d) Equilibrium constant
- **96.** Which of the following statement is incorrect about the collision theory of chemical reaction?
 - (*a*) It considers reacting molecules or atoms to be hard spheres and ignores their structure features.
 - (b) Number of effective collisions determine the rate of reaction
 - (c) Collision of atoms or molecules possessing sufficient threshold energy result into the product formation
 - (*d*) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective
- 97. Threshold energy is equal to:
 - (a) Activation energy
 - (b) Activation energy energy of molecules
 - (c) Activation energy + energy of molecules
 - (d) None of these
- **98.** Which of the following statement is not correct for the catalyst?
 - (*a*) It catalyses the forward and backward reaction to the same extent.
 - (b) It alters ΔG of the reaction
 - (c) It does not change the equilibrium constant of a reaction
 - (*d*) It provides an alternate mechanism by reducing activation energy between reactants and products.
- **99.** The excess of energy required for the reactant molecules to undergo a reaction is
 - (a) Potential energy (b) Kinetic energy
 - (c) Thermal energy (d) Activation energy
- **100.** The energy to be possessed by the molecule participating in the reaction to give the products
 - (a) < activation energy
 - (b) Threshold energy
 - (c) < average energy
 - (d) Threshold energy + average energy

101. The rate constant is given by the equation $k = PZe^{-E_a/RT}$ which factor should register a decrease for the reaction to proceed more rapidly?

(<i>a</i>)	Т	<i>(b)</i>	Ζ
(c)	E _a	(d)	Р

- **102.** For a certain reaction a large fraction of molecules has energy more than the threshold energy, still the rate of reaction is very slow. The possible reason for this could be that:
 - (a) The colliding molecules could be large in size
 - (*b*) The colliding molecules must not be properly oriented for effective collisions.
 - (c) The rate of reaction could be independent of the energy
 - (*d*) One of the reactant could be in excess
- **103.** For a given reaction which one is higher than the rest among the following
 - (a) Average energy (b) Threshold energy
 - (c) Activation energy (d) Normal energy
- 104. The value of energy of activation for radioactive decay is
 - (a) High (b) Low
 - (c) Zero (d) Moderate
- **105.** Rate of a general reaction $A + B \rightarrow$ Products can be expressed as follows on the basis of collision theory.

Rate = $Z_{AB}e^{-E_a/RT}$

Which of the following statement is not correct for the above expression?

- (*a*) Z is collision frequency and is equal to number of collisions per second per unit volume of the reaction mixture
- (b) $e^{-E_a/RT}$ is the fraction of molecules with kinetic energy equal to or greater than E_a .
- (c) E_a is activation energy of the reaction
- (*d*) All the molecules which collide with one other are effective collisions
- **106.** The role of a catalyst is to change:
 - (a) Gibbs energy
 - (b) Enthalpy of reaction
 - (c) Activation energy of reaction
 - (d) Equilibrium constant
- **107.** The rate constant, activation energy and Arrhenius parameter of a chemical reaction at 25 °C are 3.0×10^{-4} s⁻¹, 104.4 kJ mol⁻¹ and 6.0×10^{14} s⁻¹ respectively. The value of the rate constant as T $\rightarrow \infty$ is
 - (a) $2.0 \times 10^{18} \text{ s}^{-1}$ (b) $6.0 \times 10^{14} \text{ s}^{-1}$
 - (c) Infinity (d) $3.6 \times 10^{30} \text{ s}^{-1}$
- **108.** In arrhenius equation, the fraction of effective collisions is given by
 - (a) $k = Ae^{-E_a/RT}$ (b) A (c) $e^{-E_a/RT}$ (d) RT

Learning Plus

- 1. A chemical reaction was carried out of 300 K and 280 K. The rate constants were found to be k_1 and k_2 respectively then
 - (a) $k_2 = 4k_1$ (b) $k_2 = 2k_1$ (c) $k_2 = 0.25k_1$ (d) $k_2 = 0.5k_1$
- 2. AT 300 K rate constant for $A \rightarrow$ products at t = 50 min is $0.02s^{-1}$, then rate constant at t = 75 min and 310 K will be (in s⁻¹).

(a)
$$\frac{0.04}{25}$$
 (b) 0.04×25

3. The rate expression for the reaction $A(g) + B(g) \rightarrow C(g)$ is rate = $kC_A^2 C_B^{1/2}$. What changes in the initial cocentations of A and B will cause the rate of reaction to increase by a factor of eight?

- 4. 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, the rate of reaction will
 - (a) Diminish to one eight of its initial value
 - (b) Increase to eight times of its initial value
 - (c) Increase to four times of its initial value
 - (*d*) Diminish to one fourth of its initial value
- **5.** Which is not the graphical representation for the zeroth order reaction



6. Half life of a zero order reaction is 250sec. $t_{75\%}$, $t_{100\%}$ of the reaction respectively in sec. are

<i>(a)</i>	500, 375	<i>(b)</i>	375, 500
(<i>c</i>)	300, 575	(d)	575, 300

7. The amount left after completion of average life period in a first order reaction.

(a)
$$\frac{a(e-1)}{(e+1)}$$
 (b) $\frac{a}{e-1}$
(c) $\frac{a(e-1)}{e}$ (d) $\frac{a}{e}$

8. The following figure denotes the energy diagram for a reaction



Then the activation energy of the reverse reaction is

(a) 2x (b) 2y

- $(c) x + y \qquad (d) y x$
- **9.** For the elementary reaction $2A \rightarrow C$ the concentration of A after 30 minutes was found to be 0.01 mole/lit. If the rate constant of the reaction is 2.5×10^{-2} lit mole⁻¹ sec⁻¹, the rate of the reaction at 30 minutes is
 - (a) 2.5×10^{-4} mole lit⁻¹ sec⁻¹
 - (b) 2.5×10^{-6} mole lit⁻¹ sec⁻¹
 - (c) 2.5×10^{-2} mole lit⁻¹ sec⁻¹
 - (d) 2.5×10^{-8} mole lit⁻¹ sec⁻¹
- **10.** For the process $2A \rightarrow$ products, rate of reaction w.r.t A at 10 second is 2×10^{-2} Ms⁻¹ then rates of same process at 5 and 15 seconds (order \neq 0) respectively are (in M/s)
 - (a) 10^{-1} & 4×10^{-2}
 - (b) 2.7×10^{-2} & 1.6×10^{-2}
 - (c) 1.6×10^{-2} & 2.7×10^{-2}
 - (d) 2×10^{-2} & 2×10^{-2}
- 11. In the process $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ at t = 10 min rate of reaction w.r.t N_2O_5 , $NO_2 & O_2$ respectively are

	N ₂ O ₅	NO ₂	O ₂
<i>(a)</i>	500mm/min	400mm/min	200mm/min
(<i>b</i>)	1000mm/min	1000mm/min	500mm/min
(c)	1000mm/min	2000mm/min	4000mm/min
(d)	400mm/min	400mm/min	400mm/min

12. The concentration of reaction decreases from 0.2M to 0.05M in 5 minutes. The rate of reaction in moles $lit^{-1} sec^{-1}$ is

<i>(a)</i>	8.3×10^{-4}	<i>(b)</i>	0.05
(c)	0.0005	(d)	0.15

- 13. For a reaction $E_a = 0$ and $k = 3.2 \times 10^4 s^{-1}$ at 300 K. The value of k at 310 K would be
 - (a) $6.4 \times 10^4 \,\mathrm{s}^{-1}$ (b) $3.2 \times 10^4 \,\mathrm{s}^{-1}$ (c) $3.2 \times 10^8 \,\mathrm{s}^{-1}$ (d) $3.2 \times 10^5 \,\mathrm{s}^{-1}$
- 14. For a reaction, the rate constant is expressed as, $k = Ae^{-40000/T}$
 - The energy of the activation is
 - (a) 40000 cal (b) 88000 cal
 - (c) 80000 cal (d) 8000 cal
- 15. A gaseous reaction $A_2(g) \rightarrow B(g) + \frac{1}{2}C(g)$ shows increase of pressure from 100mm to 120mm in 5 min. The

rate of disappearance of A_2 is

- (a) 4mm min^{-1} (b) 40 mm min
- (c) 8mm min^{-1} (d) 20mm min^{-1}
- 16. Rate expression for xA + y B → products is Rate = k[A]^m[B]ⁿ. Units of k w.r.t A and B respectively are s⁻¹ and M⁻¹s⁻¹, when concentrations of A and B are increased by 4 times, then
 - (a) $R_f = 16R_i$ (b) $R_i = 16R_f$ (c) $R_f = 8R_i$ (d) $R_f = 64R_i$
- 17. For a given reaction of first order, it takes 20 minutes for the concentration to drop from 1.0M to 0.6M. The time required for the concentration to drop from 0.6M to 0.36M will be
 - (a) More than 20 minutes (b) Less than 20 minutes
 - (c) Equal to 20 minutes (d) Infinity
- **18.** For A+B \rightarrow C+D, Δ H =-20 kJ mole⁻¹. The activation energy for the forward reaction is 85 kJ. Then the activation energy for the backward reaction is ____
 - (*a*) 65 kJ (*b*) 105 kJ
 - (c) 85 kJ (d) 40 kJ
- **19.** In the presence of a catalyst, the heat evolved or absorbed during the reaction:
 - (a) Increases (b) Decreases
 - (c) Remains unchanged (d) May increase or decrease
- 20. Consider figure and mark the correct option:



(a) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant

- (b) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant
- (c) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product
- (d) Activation energy of backward reaction is E_1 and product is more stable than reactant
- **21.** Consider a first order gas phase decomposition reaction given below:

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

The initial pressure of the system before decomposition of A was p_i . After lapse of time 't' total pressure of the system increased by x units and became ' p_t '. The rate constant k for the reaction is given as:

(a)
$$k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$$
 (b) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$
(c) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t}$ (d) $k = \frac{2.303}{t} \log \frac{p_i}{p_i + x}$

22. According to Arrhenius equation rate constant k is equal to $Ae^{-E_a/RT}$.

Which of the following options represents the graph of



- **23.** Which of the following statements is not correct about order of a reaction?
 - (a) The order of a reaction can be a fractional number
 - (b) Order of a reaction is experimentally determined quantity
 - (c) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction
 - (d) The order of a reaction is the sum of the powers of molar concentration of the reactants in rate law expression
- 24. Which of the following statements is correct?
 - (*a*) The rate of a reaction decreases with passage of time as the concentration of reactants decreases
 - (b) The rate of a reaction is same at any time during the reaction
 - (c) The rate of a reaction is independent of temperature change
 - (*d*) The rate of a reaction decreases with increase in concentration of reactant(s)

25. Which of the following graphs represents exothermic reaction?



26. Rate law for the reaction $A + 2B \rightarrow C$ is found to be

Rate = k[A][B]

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate of reaction will be:

- (a) The same (b) Doubled
- (c) Quadrupled (d) Halved
- **27.** Which of the following statements is incorrect about the collision theory of chemical reaction?
 - (*a*) It considers reacting molecules or atoms to be hard spheres and ignores their structural features
 - (b) Number of effective collisions determines the rate of reaction
 - (c) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation
 - (*d*) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective
- **28.** A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?
 - (a) 1.26 ×10¹⁵ s
 - (b) 2.52×10^{14} s
 - (c) 2.52×10^{28} s
 - (d) Infinite

- **29.** Which of the following statement is not correct for the catalyst?
 - (*a*) It catalyses the forward and backward reactions to the same extent
 - (b) It alters ΔG of the reaction
 - (c) It is a substance that does not change the equilibrium constant of a reaction
 - (*d*) It provides an alternate mechanism by reducing activation energy between reactants and products
- **30.** The value of rate constant of a pseudo first order reaction:
 - (*a*) Depends on the concentration of reactants presents in small amount
 - (b) Depends on the concentration of reactants present in excess
 - (c) Is independent of the concentration of reactants
 - (d) Depends only on temperature
- **31.** Consider the reaction $A \rightarrow B$. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time:





- **32.** Mark the incorrect statements:
 - (a) Catalyst provides an alternative pathway to reaction mechanism
 - (b) Catalyst raises the activation energy
 - (c) Catalyst lowers the activation energy
 - (d) Catalyst alters enthalpy change of the reaction

Multiconcept MCQs

1. For an exothermic chemical process, occuring in two steps as



2. The energy profile diagrams of two reactions are shown in the figure. Then



- (a) Reaction $A \rightarrow B$ is faster and more exothermic than reaction $C \rightarrow D$
- (b) Reaction $C \rightarrow D$ is faster than reaction $A \rightarrow B$ but less exothermic
- (c) Reaction $C \rightarrow D$ is faster and more exothermic than the reaction $A \rightarrow B$.
- (d) Reaction $C \rightarrow D$ is faster than reaction $A \rightarrow B$ at the same temperature

3. Consider the energy profile, for the reaction X + Y → R, which of the following deduction about reaction is not correct?



- (*a*) The energy of activation for the backward reaction is 80 kJ
- (b) The forward reaction is Endothermic
- (c) ΔH for the forward reaction is 20 kJ
- (d) The energy of activation for forward reaction is 60 kJ
- 4. For $2NH_3 \xrightarrow{Au} N_2 + 3H_2$, rate w.r.t N_2 is 2×10^{-3} M min⁻¹, then rate w.r.t N_2 after 20 min will be (in M min⁻¹).

(a) 2×10^{-3} (b) $> 2 \times 10^{-3}$

- (c) 10^{-4} (d) $< 2 \times 10^{-3}$
- 5. The rate of the reaction

 $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$ is given as rate =k.[CH₃ COOC₂H₅] [NaOH]. If three times water is added to the reaction mixture, the rate of the reaction compared to the original rate will be

(a)
$$\frac{1}{3}$$
rd (b) $\frac{1}{9}$ th
(c) $\frac{1}{16}$ th (d) 16 times

6. Consider a system containing NO₂ and SO₂ in which NO₂ is consumed in the following two parallel reactions

$$2NO_2 \xrightarrow{k_1} N_2O_4; NO_2 + SO_2 \xrightarrow{k_2} NO + SO_3$$

The rate of disappearance of NO2 will be equal to

(a)
$$k_1[NO_2]^2 + k_2[NO_2]^2$$

(b)
$$k_1[NO_2]^2 + k_2[NO_2][SO_2]$$

(c)
$$2k_1[NO_2]^2$$

(d)
$$2k_1[NO_2]^2 + k_2[NO_2][SO_2]$$

- 7. The rate of reaction for 2A+B→C is found to be rate = k[A] [B]. The correct statement is
 - (a) Unit of k must be s^{-1}
 - (b) Value of k is independent of the initial concentration of A and B
 - (c) Rate of formation of C is twice the rate of disappearance of A.
 - (d) $t_{1/2}$ is a constant

8. The rate law for a reaction between the substances A and B is given by

Rate = $k[A]^n[B]^m$, on doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as

(a)
$$\frac{1}{2^{(m+n)}}$$
 (b) $(m+n)$
(c) $(n-m)$ (d) $2^{(n-m)}$

9. Hydrogenation of vegetable ghee at 25°C reduces pressure of H₂ from 2 atmosphere to 1.2 atmosphere in 50 minutes. The rate of reaction in terms of molarity per second is (a) 1.09×10^{-6} (b) 1.09×10^{-5}

(a)
$$1.09 \times 10^{-5}$$
 (b) 1.09×10^{-5}
(c) 4×10^{-3} (d) 1.09×10^{-6}

10. The decomposition of CH_3CHO occurs as $CH_3CHO_{(g)} \rightarrow CH_{4(g)} + CO_{(g)}$, the kinetic data provided are [CH_CHO] rate (moles lit⁻¹ sec⁻¹)

$$1.75 \times 10^{-3}$$
 2.06×10^{-11}
 3.5×10^{-3}
 8.25×10^{-11}
 7.0×10^{-3}
 3.30×10^{-10}

 The rate expression thus can be given as

 (a) K[CH₃CHO]
 (b) K[CH₃CHO]²

- (c) $K[CH_3CHO]^3$ (d) $K[CH_3CHO]^{1/2}$
- 11. For N₂O₅ \rightarrow 2NO₂ + 1/2O₂, it is found that $\frac{-d}{dt}[N_2O_5] = k_1[N_2O_5],$

$$\frac{d}{dt}[NO_2] = k_2[N_2O_5]; \frac{d}{dt}[O_2] = k_3[N_2O_5] \text{ then}$$
(a) $k_1 = 2k_2 = 3k_3$ (b) $2k_1 = 4k_2 = k_3$
(c) $2k_1 = k_2 = 4k_3$ (d) $k_1 = k_2 = k_3$

12. The experimental data for the reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ are given below

Expt	$[Cl_2]$	[NO]	Initial rate
1.	0.020	0.010	2.4×10 ⁻⁴
2.	0.020	0.030	2.16×10 ⁻³
3.	0.040	0.030	4.32×10 ⁻³

What is the order of the reaction?

(<i>a</i>) 1	<i>(b)</i>	2
(c) 3	(d)	0

13. The decomposition of ozone proceeds as

 $O_3 = O_2 + O$ (fast)

 $O + O_3 \rightarrow 2O_2$ (slow) the rate expression should be

(*a*) Rate =
$$K[O_3]^2$$

(b) Rate =
$$K[O_3]^2[O_2]^{-1}$$

(c) Rate = $K[O_3][O_2]$

(*d*) Rate =
$$K[O_3][O_2]^{-1}$$

- 14. For a process, A+B→ products, the rate of the reaction is second order with respect to A and zero order with respect to B.when 1.0 mole each of A and B are taken in a one litre vessel, the initial rate is 1×10⁻²mol L⁻¹s⁻¹. The rate of the reaction, when 50% of the reactants have been converted to products would be
 - (a) 1×10^{-2} mol L⁻¹s⁻¹
 - (b) $2.5 \times 10^{-3} \text{ mol } \text{L}^{-1} \text{s}^{-1}$
 - (c) 5.0×10^{-2} mol L⁻¹s⁻¹
 - (d) $0.5 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{s}^{-1}$
- **15.** $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ is a first order reaction with $k = 2.2 \times 10^{-5} \text{ sec}^{-1}$ at 320°C. The percentage of SO_2Cl_2 decomposed on heating for 90 minutes is:
 - (a) 1.118 (b) 0.1118
 - (c) 18.11 (d) 11.18
- 16. For the reaction $aA \rightarrow xP$ when [A] = 2.2 mM the rate was found to be 2.4 mMs⁻¹. On reducing concentration of A to half, the rate changes to 0.6 mMs⁻¹. The order of reaction with respect to A is

<i>(a)</i>	1.5	(b)	2.0)
(<i>c</i>)	2.5	(d)	3.0)

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

<i>(a)</i>	30 min	<i>(b)</i>	60 min
(<i>c</i>)	7.5 min	(d)	15 min

18. The rates of a reaction at different times are given below

Rate
2.8×10^{-2}
$2.8 imes 10^{-2}$
$2.8 imes 10^{-2}$
$2.8 imes 10^{-2}$

The order of the reaction is

<i>(a)</i>	2 nd order	<i>(b)</i>	Zero order
(<i>c</i>)	3 rd order	(d)	1 st order

- 19. The isomerization of cyclopropane to form propene $(CH_3 CH = CH_2)$ is a first order reaction. At 760K, 85% of a sample of cyclopropane changes to propene in 79 min. Calculate the value of the rate constant.
 - (a) 2.42 min^{-1} (b) $3.66 \times 10^{-2} \text{ min}^{-1}$
 - (c) $2.40 \times 10^{-2} \min^{-1}$ (d) $1.04 \times 10^{-2} \min^{-1}$
- **20.** For a reaction following first-order kinetics, which of the following statements are correct ?
 - (*a*) The time taken for the completion of 75% of the reaction is twice $t_{1/2}$.
 - (*b*) A plot of the reciprocal of the concentration of the reactants against time gives a straight line
 - (c) The degree of dissociation is equal to $1-e^{-kt}$
 - (d) A plot of $[A]_0/[A]$ versus time gives a straight line.

21. Using the data given below the order and rate constant for the reaction :

 $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ would be

Experiment No.	Initial conc.	Initial rate		
	(mol/l)	(mol/l)		
<i>(a)</i>	0.10	0.020		
(b)	0.20	0.080		
(C)	0.30	0.180		
(<i>d</i>)	0.40	0.320		

(a) $2,[k = 2.0 \text{ l/mol sec}]$	(b) $0, [k = 2.0 \text{ mol}/1 \text{ sec}]$
-------------------------------------	----------------------------------------------

(c) 2,[k = 1.5 l/mol sec] (d) $1,[k = 1.5 \text{ sec}^{-1}]$

22. For the reaction of the zeroth order, variation of log T_{50} with log a (where T_{50} is half-life period and a is the initial concentration) is given by



- **23.** In a first order reaction, 50 minutes time is taken for the completion of 93.75% of a reaction. Half life of the reaction is
 - (a) 25 min (b) 12.5 min
 - (c) $20 \min$ (d) $10 \min$
- 24. 75% of a first order reaction is completed in 32 minutes.50% of the reaction would have been completed in
 - (a) 24 mins
 - (b) 16 mins
 - (c) 18 mins
 - (d) 23 mins

- **25.** The reaction $A \rightarrow C$ has activation energy for the forward and the backwad reaction has 25kJ and 32kJ respectively. The ΔH for the reaction is
 - (a) 57 kJ
 - (b) -57 kJ
 - (c) 7 kJ
 - $(d)\,$ -7 kJ

- **26.** Consider an endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for the backward and forward reactions respectively. In general.
 - $(a) \ \mathrm{E}_{\mathrm{b}} < \mathrm{E}_{\mathrm{f}}$
 - (b) $E_b > E_f$
 - $(c) E_b = E_f$
 - (d) There is no definite relation between E_b and E_f

NEET Past 10 Years Questions

1. For a reaction $A \rightarrow B$, enthalpy of reaction is -4.2 kJ mol⁻¹ and enthalpy of activation is 9.6 kJ mol⁻¹. The correct potential energy profile for the reaction is shown in option. (2021)



2. The slope of Arrhenius Plot (ln K v/s 1/T) of first order reaction is -5×10^3 K. The value of E_a of the reaction is. Choose the correct option for your answer.

 $[\text{Given } R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}]$ (2021)

(a) 83.0 kJ mol⁻¹ (b) 166 kJ mol⁻¹

- (c) -83 kJ mol^{-1} (d) 41.5 kJ mol^{-1}
- **3.** An increase in the concentration of the reactants of a reaction leads to change in: (2020)
 - (a) Heat of reaction (b) Threshold energy
 - (c) Collision frequency (d) Activation energy
- 4. The rate contant for a first order reaction is $4.606 \times 10^{-3} \text{ s}^{-1}$. The time required to reduce 2.0 g of the reactant to 0.2 g is: (2020)
 - (a) 200 s (b) 500 s (c) 1000 s (d) 100 s
- 5. In collision theory of chemical reaction, Z_{AB} represents (2020 Covid Re-NEET)
 - (a) The collision frequency of reactants, A and B
 - (b) Steric factor
 - (c) The fraction of molecules with energies equal to E_a
 - (d) The fraction of molecules with energies greater than E_a

6. The half-life for a zero order reaction having 0.02 M initial concentration of reactant is 100 s. The rate constant (in mol L^{-1} s⁻¹) for the reaction is

(2020 Covid Re-NEET)

(2019)

- (a) 2.0×10^{-4} (b) 2.0×10^{-3} (c) 1.0×10^{-2} (d) 1.0×10^{-4}
- 7. 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: (2019)
 - (a) t = 0.693/k
 - (b) t = 6.909/k
 - (c) t = 4.606/k
 - (*d*) t = 2.303/k
- 8. For the chemical reaction $N_2(g) + 3H_2(g) \implies 2NH_3(g)$

The correct option is:

(b)
$$-\frac{d[N_2]}{dt} = 2\frac{d[NH_3]}{dt}$$

 $(a) = \frac{1}{2} d[H_2] = 1 d[NH_3]$

(c)
$$-\frac{d[N_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

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

- 9. When initial concentration of the reactant is doubled, the half-life period of a zero order reaction (2018)(a) Is halved
 - (*a*) is harved
 - (b) Is doubled
 - (c) Is tripled
 - (d) Remains unchanged
- The correct difference between first and second order reactions is that: (2018)
 - (a) The rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations

- (b) 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
- (c) The rate of a first-order reaction does depend on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations
- (*d*) A first-order reaction can catalyzed; a second-order reaction cannot be catalyzed
- 11. Mechanism of a hypothetical reaction (2017-Delhi) $X_2 + Y_2 \rightarrow 2XY$ 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

(<i>a</i>) 1.5	(<i>b</i>) 1
(<i>c</i>) 2	(<i>d</i>) 0

12. A first order reaction has a specific reaction rate of 10^{-2} s^{-1} . How much time will it take for 20 g of the reactant to reduce to 5 g? (2017-Delhi)

(c) 138.6 second (d) 346.5 second

13. Consider the reaction between chlorine and nitric oxide $Cl_2(g) + 2NO(g) \rightarrow 2NOCl(g)$

On doubling the concentration of both reactants the rate of the reaction increases by a factor of 8. However, if only the concentration of Cl_2 is doubled, the rate is increased by a factor of 2. The order of this reaction with respect to NO is: (2017-Gujarat)

<i>(a)</i>	3	<i>(b)</i>	0
(c)	1	(d)	2

14. For the reaction, $XA + YB \rightarrow ZC$,

if $\frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{1.5d[C]}{dt}$, then the correct statement among the following is: (2017-Gujarat)

- (a) The value of Y = 2
- (b) The value of X = Y = Z = 3
- (c) The value of X = Y = 3
- (d) The value of X = 2
- 15. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first-order reaction. It is because the: (2016-II)
 - (a) Rate is proportional to the surface coverage
 - (b) Rate is inversely proportional to the surface coverage
 - (c) Rate is independent of the surface coverage
 - (*d*) Rate of decomposition is very low
- 16. 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:

(2016 - I)

(a)	54.1 s	(<i>b</i>)	24.1 s
(<i>c</i>)	34.1 s	(d)	44.1 s

- 17. The addition of a catalyst during a chemical reaction alters which of the following quantities? (2016 I)(a) Activation energy (b) Entropy
 - (c) Internal energy (d) Enthalpy
- **18.** The rate constant of the reaction $A \rightarrow B$ is 0.6×10^{-3} mole / second. If the concentration of A is 5 M, then concentration of B after 20 minutes is: (2015 Re) (a) 0.72 M (b) 1.08 M (c) 3.60 M (d) 0.36 M
- **19.** When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is: (2015)
 - (a) First
 - (b) Second
 - (c) More than zero but less than first
 - (d) Zero
- **20.** The activation energy of a reaction can be determined from the slope of which of the following graphs? (2015)

(a)
$$\frac{\ln k}{T}$$
 vs. T
(b) $\ln k$ vs. $\frac{1}{T}$
(c) $\frac{T}{\ln k}$ vs. $\frac{1}{T}$
(d) $\ln k$ vs. T

21. For a given exothermic reaction, k_p and k'_p are the equilibrium constants at temperatures T_1 and T_2 , respectively. Assuming that heat of reaction is constant in temperature range between T_1 and T_2 , it is readily observed that: (2014)

(a)
$$\mathbf{k}_{\mathbf{p}} < \mathbf{k'}_{\mathbf{p}}$$
 (b) $\mathbf{k}_{\mathbf{p}} = \mathbf{k'}_{\mathbf{p}}$

(c)
$$k_{p} < \frac{1}{k'_{p}}$$
 (d) $k_{p} > k'_{p}$

- **22.** A reaction having equal energies of activation for forward and reverse reactions has: (2013)
 - (a) $\Delta S = 0$ (b) $\Delta G = 0$ (c) $\Delta H = 0$ (d) $\Delta H = \Delta G = \Delta S = 0$
- 23. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C? ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) (2013)
 - (a) 342 kJ mol^{-1} (b) 269 kJ mol^{-1}
 - (c) 34.7 kJ mol^{-1} (d) 15.1 kJ mol^{-1}
- 24. Activation energy (E_a) and rate constants $(K_1 \text{ and } K_2)$ of a chemical reaction of two different temperatures $(T_1 \text{ and } T_2)$ are related by: (2012 Mains)

(a)
$$\ln \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

 $K = F \left(1 - 1 \right)$

(b)
$$\log \frac{\mathbf{K}_2}{\mathbf{K}_1} = \frac{\mathbf{L}_a}{\mathbf{R}} \left(\frac{1}{\mathbf{T}_1} - \frac{1}{\mathbf{T}_2} \right)$$

(c)
$$\ln \frac{K_2}{K_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

(d)
$$\ln \frac{K_2}{K_1} = \frac{E_a}{R} \left(\frac{1}{T_2} + \frac{1}{T_1} \right)$$

- **25.** In a zero-order reaction for every 10° C 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: (2012 Pre)
 - (*a*) 128 times
 - (*b*) 256 times
 - (c) 512 times
 - (*d*) 64 times

26. In a reaction, $A + B \rightarrow$ 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: (2012 Pre)

<i>(a)</i>	Rate = $k[A]^2 [B]$	(<i>b</i>)	Rate = $k[A] [B]^2$
(c)	Rate = $k[A]^2 [B]^2$	(d)	Rate = $k[A][B]$

ANSWER KEYS

				Topicwis	e Questio	ns			
1. (<i>b</i>)	2. (<i>b</i>)	3. (<i>c</i>)	4. (<i>c</i>)	5. (<i>a</i>)	6. (<i>b</i>)	7. (<i>b</i>)	8. (c)	9. (<i>a</i>)	10. (<i>d</i>)
11. (<i>a</i>)	12. (<i>d</i>)	13. (<i>a</i>)	14. (<i>d</i>)	15. (<i>b</i>)	16. (<i>c</i>)	17. (<i>d</i>)	18. (<i>a</i>)	19. (<i>d</i>)	20. (<i>a</i>)
21. (<i>b</i>)	22. (<i>c</i>)	23. (<i>a</i>)	24. (<i>c</i>)	25. (<i>d</i>)	26. (<i>a</i>)	27. (<i>d</i>)	28. (<i>a</i>)	29. (<i>a</i>)	30. (<i>c</i>)
31. (<i>a</i>)	32. (<i>c</i>)	33. (<i>c</i>)	34. (<i>c</i>)	35. (<i>c</i>)	36. (<i>c</i>)	37. (<i>c</i>)	38. (<i>c</i>)	39. (<i>a</i>)	40. (<i>a</i>)
41. (<i>c</i>)	42. (<i>c</i>)	43. (<i>a</i>)	44. (<i>b</i>)	45. (<i>d</i>)	46. (<i>a</i>)	47. (<i>d</i>)	48. (<i>d</i>)	49. (<i>c</i>)	50. (<i>b</i>)
51. (<i>d</i>)	52. (<i>c</i>)	53. (<i>a</i>)	54. (<i>a</i>)	55. (<i>c</i>)	56. (<i>b</i>)	57. (<i>b</i>)	58. (<i>d</i>)	59. (<i>b</i>)	60. (<i>b</i>)
61. (<i>b</i>)	62. (<i>d</i>)	63. (<i>c</i>)	64. (<i>c</i>)	65. (<i>a</i>)	66. (<i>b</i>)	67. (<i>b</i>)	68. (<i>d</i>)	69. (<i>c</i>)	70. (<i>b</i>)
71. (<i>c</i>)	72. (<i>b</i>)	73. (<i>b</i>)	74. (<i>a</i>)	75. (<i>c</i>)	76. (<i>a</i>)	77. (<i>b</i>)	78. (<i>d</i>)	79. (<i>a</i>)	80. (<i>c</i>)
81. (<i>a</i>)	82. (<i>b</i>)	83. (<i>d</i>)	84. (<i>b</i>)	85. (<i>c</i>)	86. (<i>b</i>)	87. (<i>d</i>)	88. (c)	89. (<i>a</i>)	90. (<i>b</i>)
91. (<i>c</i>)	92. (<i>b</i>)	93. (<i>d</i>)	94. (<i>b</i>)	95. (<i>b</i>)	96. (<i>c</i>)	97. (<i>c</i>)	98. (<i>b</i>)	99. (<i>d</i>)	100. (<i>b</i>)
101. (<i>c</i>)	102. (<i>b</i>)	103. (<i>b</i>)	104. (<i>c</i>)	105. (<i>d</i>)	106. (<i>c</i>)	107. (<i>b</i>)	108. (<i>c</i>)		
				Learr	ning Plus				
1. (<i>c</i>)	2. (<i>c</i>)	3. (<i>b</i>)	4. (<i>b</i>)	5. (<i>c</i>)	6. (<i>b</i>)	7. (<i>d</i>)	8. (c)	9. (<i>b</i>)	10. (<i>b</i>)
11. (<i>d</i>)	12. (<i>c</i>)	13. (<i>b</i>)	14. (<i>c</i>)	15. (<i>c</i>)	16. (<i>d</i>)	17. (<i>c</i>)	18. (<i>b</i>)	19. (<i>c</i>)	20. (<i>a</i>)
21. (<i>b</i>)	22. (<i>a</i>)	23. (<i>c</i>)	24. (<i>a</i>)	25. (<i>a</i>)	26. (<i>b</i>)	27. (<i>c</i>)	28. (<i>d</i>)	29. (<i>b</i>)	30. (<i>b</i>)
31. (<i>b</i>)	32. (<i>d</i>)								
				Multicon	cept MCC	Qs			
1. (<i>b</i>)	2. (<i>c</i>)	3. (<i>a</i>)	4. (<i>a</i>)	5. (<i>c</i>)	6. (<i>d</i>)	7. (<i>b</i>)	8. (<i>d</i>)	9. (<i>b</i>)	10. (<i>b</i>)
11. (<i>c</i>)	12. (<i>c</i>)	13. (<i>b</i>)	14. (<i>b</i>)	15. (<i>d</i>)	16. (<i>b</i>)	17. (<i>a</i>)	18. (<i>b</i>)	19. (<i>c</i>)	20. (<i>a</i>)
21. (<i>a</i>)	22. (<i>a</i>)	23. (<i>b</i>)	24. (<i>b</i>)	25. (<i>d</i>)	26. (<i>a</i>)				
			NE	ET Past 10	Years Qu	lestions			
1. (<i>a</i>)	2. (<i>d</i>)	3. (<i>c</i>)	4. (<i>b</i>)	5. (<i>a</i>)	6. (<i>d</i>)	7. (<i>c</i>)	8. (c)	9. (<i>b</i>)	10. (<i>b</i>)
11. (<i>a</i>)	12. (<i>c</i>)	13. (<i>d</i>)	14. (<i>c</i>)	15. (<i>a</i>)	16. (<i>b</i>)	17. (<i>a</i>)	18. (<i>a</i>)	19. (<i>a</i>)	20. (<i>b</i>)
21. (<i>d</i>)	22. (<i>c</i>)	23. (<i>c</i>)	24. (<i>c</i>)	25. (<i>c</i>)	26. (<i>a</i>)				

Solution

Topicwise Questions

11.

1. (b) Rate does not depend on excess quantity

2. (*b*) $\frac{dC}{dC}$ dt

> -ve sign represents decrease in the concentration of the reactants with time

3. (c) Rate = $\frac{\Delta x}{\Delta t}$ \Rightarrow Rate $\propto \frac{1}{\text{time}}$

: As the reaction proceeds with time, rate decreases.

- 4. (c) 2 $NH_3 \rightarrow N_2 + 3H_2$ $-\frac{1}{2}\frac{d[NH_{3}]}{dt} = \frac{d[N_{2}]}{dt} = \frac{1}{3}\frac{d[H_{2}]}{dt}$ $\frac{1}{2} \times k_1 = k_2 = \frac{k_3}{3}$ $\frac{3}{2}k_1 = 3k_2 = k_3 \Longrightarrow 1.5k_1 = 3k_2 = k_3$
- 5. (a) Rate $=\frac{-1}{2}\frac{d[x]}{dt} = \frac{-1}{2}\frac{[2-3]}{5} = 0.1 \text{ mol}^{-1} \text{ L}^{-1} \text{ min}^{-1}$
- **6.** (b) Rate = $\frac{1}{4} \frac{d[NO_2]}{dt} = \frac{0.0125}{4} = 0.0031 \text{ mol } \text{L}^{-1} \text{s}^{-1}$
- 7. (b) With increase in the concentration of the reactants, the rate of the chemical reactions increases due to more number of effective collision.
- **8.** (*c*)
- 9. (a) Integrated rate law for a first order reaction is

$$k = \frac{2.303}{t} \log \frac{R_o}{R}$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$
For half-life, $t = t_{1/2}$, $x = \frac{a}{2}$

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

$$k = \frac{2.303 \times 0.301}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

10. (d)
$$k = \frac{2.303}{t} \log \frac{R_o}{R_o - x}$$

 $k = \frac{2.303}{30} \log \frac{100R_o}{25R_o}$

$$k = \frac{2.303}{30} \times 0.602$$

For 93.75% reaction, t is given by

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

$$t = \frac{2.303 \times 30}{2.303 \times 0.602} \log \frac{100}{100 - 93.75}$$

$$t = \frac{30}{0.602} \log 16 = \frac{30 \times 1.20}{0.602} = 59.8 \approx 60 \text{ min}$$

11. (a) $k = \frac{2.303}{t} \log \frac{a}{a - x}$
 $k = \frac{2.303}{60} \log \frac{100}{100 - 60} = \frac{2.303}{60} \log \frac{100}{40}$
 $k = \frac{2.303}{60} \log 2.5 = \frac{2.303 \times 0.397}{60}$
 $t = \frac{2.303}{k} \log \frac{a}{a - x}$
 $t = \frac{2.303 \times 60}{2.303 \times 0.39} \log \frac{100}{50}$
46.15 \approx 45 min
12. (d) $2H_2S + O_2 \rightarrow \text{ products}$

Rate =
$$[pH_2S]^2(pO_2)$$

= $[3pH_2S]^2(3pO_2) = 27[pH_2S](pO_2)$

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

 $t = \frac{2.303}{2.303 \times 10^{-2}} \log \frac{x}{\frac{x}{10}} = 100 \log \frac{10x}{x}$
 $t = 100 \times [\log 10] = 100[1]$
 $t = 100 \times 1 = 100 \sec$
14. (d) Rate $= \frac{Conc}{t} \times \frac{1}{(Conc)^2} = \frac{mol L^{-1}}{s} \times \frac{1}{mol^2 L^{-2}}$
 $= mol^{-1}L s^{-1}$
15. (b) $K = \frac{2.303}{t} \log \frac{a}{a-x}$
 $t = t_{\frac{1}{2}}$, 50% reaction completed
 $k = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{a}{a-\frac{a}{2}} = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{2a}{a}$
 $k = \frac{2.303 \times 0.30}{t_{\frac{1}{2}}} = \frac{0.693}{t_{\frac{1}{2}}}$
 $\therefore t_{-1}$ is independent of initial concentration

 $\therefore t_{1/2}$ is independent of initial concentration in first order reaction.



17. (d) Due to more number of bond rearrangements.

18. (a) Rate =
$$\frac{k[I^-][OCI^-]}{[OH^-]}$$

order: 1 + 1 - 1 = 1

19. (*d*)

- **20.** (*a*) For a zero order reaction, rate = $k [A]^0 = k$ Unit = mol L^{-1} time⁻¹
- 21. (b) Molecularity of a reaction is the number of molecules of the reactants taking part in a single step of a reaction.
- **22.** (*c*)
- **23.** (*a*) Slowest step is the rate determining step for which ' k_1 ' is least.
- 24. (c) Sum of power of concentration in terms of the rate law is the order of reaction. Rate = K [A]^c[B]^d \Rightarrow order = c + d
- 25. (d) According to the rate equation given, the reaction is of zero order reaction,

 \therefore General eqⁿ for zero order reaction,

$$A = a - kt \qquad \dots (1)$$

When
$$t = t_{\frac{1}{2}}$$
 & $A = \frac{a}{2}$
eqⁿ (1) becomes
 $\frac{a}{2} = a - kt_{\frac{1}{2}}$
 $\Rightarrow t_{\frac{1}{2}} = \frac{a}{2k}$

26. (a) It is independent of initial concentration as $t_{\frac{1}{2}} = \frac{0.0693}{k}$ for first order reaction.

27. (d)
$$k = \frac{2.303}{20} \log \frac{a}{\frac{a}{4}} = \frac{2.303}{20} \log \frac{4a}{a}$$

 $k = \frac{2.303}{20} [\log 4] = \frac{2.303}{20} [0.60 - 0.47]$
 $k = \frac{2.303 \times 0.60}{20}$
 $t = \frac{2.303 \times 20}{2.303 \times 0.60} \log \frac{a}{a - \frac{a}{16}} = \frac{20}{0.60} \log \frac{16a}{a}$
 $t = \frac{20}{0.13} [\log 16] = \frac{20}{0.60} [1.20]$

$$t = 40 \min$$

30.

28. (a)
29. (a)
30. (c)
$$t_{\frac{1}{2}} = 10 \min R = ?$$

 $k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{10}$
 $k = \frac{2.303}{t} \log \frac{R_o}{R}$
 $\frac{0.693}{10} = \frac{2.303}{100} \log \frac{R_o}{R_o - x}$
 $\log \frac{R_o}{R_o - x} = \frac{0.693 \times 10}{2.303}$
 $\log \frac{R_o}{R_o - x} = 3.00$
Say $R_0 - x = R$
 $\Rightarrow \log \frac{R_0}{R} = 3 \Rightarrow R_0 = 10^3 R$...(1)
Now, % of reactant left after 100 min = $\frac{R}{R_0} \times 100$
 $= \frac{R}{10^3 R} \times 100$ (from(1))
 $= 0.1 \%$

:. % of reaction completed = 100 - 0.1

31. (a) For zero order reaction,

$$\frac{dx}{dt} = k \Rightarrow x = kt \quad (\because x = prdt)$$
for completion of reaction,

$$x = R_0 \& r = t$$
eqⁿ (1) becomes,
$$t = \frac{\left[\frac{R_0}{\right]}{k}$$
32. (c) mol¹⁻ⁿ.litⁿ⁻¹.sec⁻¹
33. (c)
34. (c)
$$k = \frac{2.303}{10} \log \frac{100}{100 - 20}$$

$$k = \frac{2.303}{10} \log \frac{10}{80} = \frac{2.303}{10} [\log 10 - \log 8]$$

$$k = \frac{2.303}{10} \log \frac{10}{8} = \frac{2.303}{10} [\log 10 - \log 8]$$

$$k = \frac{2.303}{10} \log \frac{10}{8} = 0.0223 \min^{-1}$$
35. (c)
$$k = \frac{2.303}{t} \log \frac{R_0}{R}$$

$$k = \frac{2.303}{200} \log \frac{400}{25}$$

$$= 0.01386 s^{-1} = 1.386 \times 10^{-2} s^{-1}$$
36. (c)
$$t_{1/2} = 10 \min, t = 20 \min, N_0 = 10 M$$

$$t = nt_{\frac{1}{2}} \Rightarrow n = \frac{t}{t_{\frac{1}{2}}} = \frac{20}{10} = 2$$

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n \Rightarrow \frac{N}{10} = \left(\frac{1}{2}\right)^2 \Rightarrow \frac{N}{10} = \frac{1}{4} \Rightarrow N = \frac{10}{4}$$
Rate = k[A]

$$= \frac{0.693}{t_{\frac{1}{2}}} \times [A] = \frac{0.693}{10} \times 2.5 = 0.0693 \times 2.5 M \min^{-1}$$
37. (c)
$$k = \frac{2.303}{6.909} \log \frac{100}{25} = \frac{1}{3} \log 4$$

38. (c) Rate constant does not depend an activation energy

 $t = \frac{1}{3}\log 2^2 \Longrightarrow \frac{2}{3}\log 2$

39. (*a*) A catalyst is a substance which alter the rate of reaction without being consumed in the reaction.

40. (a) $t_{\frac{1}{2}} = \frac{0.693}{k_1}$

41. (c)
$$\mathbb{R} \rightarrow \operatorname{prdt}$$
 $\operatorname{Rate} = \frac{-d[\mathbb{R}]}{dt} = k[\mathbb{R}]$
or $\frac{-d[\mathbb{R}]}{[\mathbb{R}]} = \operatorname{kdt}$ (i)
 $\int \frac{d[\mathbb{R}]}{[\mathbb{R}]} = -k\int dt$
 $ln[\mathbb{R}] = -kt + C$
At $t = 0$, $[\mathbb{R}] = [\mathbb{R}]_0$
 $ln[\mathbb{R}_0] = C$
 $ln[\mathbb{R}] = -kt + ln[\mathbb{R}_0]$
 $kt = ln[\mathbb{R}_0] - ln[\mathbb{R}]$
 $k = \frac{1}{t}ln\left[\frac{\mathbb{R}_0}{\mathbb{R}}\right]$
 $k = \frac{1}{t}ln\left[\frac{\mathbb{R}_0}{\mathbb{R}}\right]$
 $k = \frac{1}{t}\left[ln\frac{a}{a-x}\right]$
42. (c) $t_{1/2} = 14 \sec$, $\mathbb{N} = \frac{\mathbb{N}_0}{8}$
 $\frac{\mathbb{N}_0}{\mathbb{N}_0} = \left(\frac{1}{2}\right)^n \Rightarrow \left(\frac{1}{2}\right)^3 = \left(\frac{1}{2}\right)^n \Rightarrow n = 3$
 $t = n t_{1/2} = 3 \times 14 = 42 \sec$
43. (a) $k = \frac{2.303}{t} \log \frac{\mathbb{R}_0}{\mathbb{R}}$ [$\because \mathbb{R} = [\mathbb{A}] - [\mathbb{B}]$]
 $k = \frac{2.303}{10} \log \frac{0.2}{0.2 - 0.18}$
 $k = \frac{2.303}{10} \log \frac{0.2}{0.02} = \frac{2.0303}{10} \times 1 = 0.2303$
44. (b) $k = \operatorname{Ae}^{-\operatorname{Ea}/\mathbb{RT}}$
 $\ln k = \ln A - \frac{\mathbb{E}_a}{\mathbb{RT}}$
 $\frac{d\ln k}{dT} = + \frac{\mathbb{E}_a}{\mathbb{RT}^2}$

- **45.** (*d*) The difference in energy of intermediate complex and the average energy of reactants.
- **46.** (*a*) K = Ae^{-E_a/RT} gives Arrhenius equation.
- **47.** (*d*) The equilibrium is attained faster in case of reaction in which it lowers the activation energy by the use of catalyst.

48. (*d*)
$$k = Ae^{-E_a/RT}$$

$$\log k = \log(1.45 \times 10^{11}) - \frac{35 \times 10^{3}}{2 \times 2.303 \times 573} \left[\because R = 2 \text{ cal mol}^{-1} \text{k}^{-1} \right]$$
$$\log k = 11.16 - 13.26 = -2.1$$
$$\text{Taking antilog,} \quad k = 7.94 \times 10^{-3} \text{ S}^{-1}$$

49. (c) 50. (b) For 10° rise in temperature n = 1So; rate = $(2)^n = (2)^1 = 2$ When temperature is increased from 10°C to 100°C, change is = $100 - 10 = 90^{0}$ C n = 9rate = $(2)^9 = 512$ times 51. (d) $k_1 = 10^{16} e^{-2000/T}$ $k_2 = 10^{15} e^{-1000/T}$ $k_1 = k_2$ $10^{16} e^{-2000/T} = 10^{15} e^{-1000/T}$ $\log 10 - \frac{2000}{2.303T} = \frac{-1000}{2.303T}$ $1 = \frac{-1000}{2.303T} + \frac{2000}{2.303T}$ $1 = \frac{1000}{2.303T} \Rightarrow T = \frac{1000}{2.303} k$

- **52.** (*c*) Activation energy of forward reaction = a Threshold energy = b
 - \therefore Heat of reaction, $\Delta H_r = c$
 - : Reaction is exothermic
- **53.** (*a*) Arrhenius equation is $k = Ae^{-Ea/RT}$ on taking log on both sides,

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

When log k is plotted with 1/T, the slope of the reaction will be $\frac{-E_a}{2.303R}$ and intercept is given by logA

54. (*a*) According to Arrhenius, with rise in temperature the rate of reaction also increases because by the rise in temperature, the number of activated reactant molecules increase.



Energy profile diagram for a reaction para change. As from the figure, it is clear that

$$(\mathbf{E}_{\mathbf{a}})_{\mathbf{f}} = (\mathbf{E}_{\mathbf{a}})_{\mathbf{b}}$$
$$\therefore \Delta \mathbf{H} = \mathbf{0}$$

56. (*b*) The effect of temperature on reaction rate is shown by Arrhenius equation: $k = Ae^{-E_a/RT}$ 57. (b) Temperature Coefficient = $\frac{k_t + 10}{k_t}$

$$2 = \frac{10^{-3}}{K_t} \Longrightarrow k_t = \frac{10^{-3}}{2} = \frac{10^{-4} \times 10}{2}$$
$$k_t = 5 \times 10^{-4}$$

58. (d) $N_2(g) + 3H_2(g) \implies 2NH_3(g) + 22 \text{ Kcal}$

 \therefore The activation energy for the forward reaction = 50 kcal

:. The activation energy for the backward reaction = 50 + 22 = 72 kcal

59. (b) Reaction having high E_a are slow reactions and reactions having low E_a are fast reactions.

If E_a is high, then the number of effective collisions will be small and the reaction will be slow.

60. (b) Arrhenius equation is $k = Ae^{-Ea/RT}$ In the presence of catalyst,

> Rate constant $k' = Ae^{-Ea/RT}$ On dividing eg (ii) by eq (i), we get

$$\frac{k^{1}}{k} = e^{(Ea - Ea^{\prime})} / RT$$
$$\frac{k^{1}}{k} = e\left(\frac{2000}{2 \times 300}\right) = e^{3.33}$$

.: on taking log both sides,

$$\log \frac{k^{1}}{k} = \frac{3.33}{2.303}$$
$$\frac{k^{1}}{k} = \text{anti} \log 1.446 = 27.92 \approx 28$$
we know that, rate (R) α K

$$\therefore \frac{R^{\prime}}{R} = \frac{k^{\prime}}{k} = 28$$
$$\therefore R^{1} = 28R$$

61. (b) k = Ae^{-Ea/RT}

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

 $\log k - \log A = \frac{-Ea}{RT}$
 $\log \frac{k}{A} = \frac{-Ea}{2.303 RT} = \frac{-2.303 RT}{2.303 RT}$
 $\frac{k}{A} = \operatorname{antilog} - 1 = 1 \times 10^{-1} = 0.1$

62. (*d*)

63. (c) mol¹⁻ⁿ litⁿ⁻¹ sec⁻¹ for n = 2, it becomes mol⁻¹ lit sec⁻¹. **64.** (c) $t_{1/2} = \frac{1}{ka^{n-1}}$ for n = 2, the expression becomes $t_{1/2} = \frac{1}{k \cdot a}$ **65.** (a) $A + 2B \rightarrow AB_2$

- **66.** (*b*) Unit of rate constant for zero order reaction and unit of rate of the reaction are same: mol. lit⁻¹.sec⁻¹
- **67.** (*b*) For zero order reactions, the rate of the reaction is independent of the concentration of the reactants.
- **68.** (*d*) Conceptual.
- **69.** (*c*) Order of the reaction can be known by the rate equation of the reaction
- **70.** (*b*) Decomposition of Cl₂O is an example of second order reaction.
- **71.** (*c*) Molecularity of the reaction is always positive whole number but can not be zero, fractional or negative.
- 72. (b) Collision theory is applicable for bimolecular reactions.
- **73.** (*b*) All radioactive disintegration reactions are examples of first order kinetics.
- **74.** (*a*)
- **75.** (*c*) From units of rate constant, the reaction is third order.
- **76.** (*a*)

77. (b) order $=\frac{3}{2}-1=\frac{1}{2}$

- **78.** (*d*) Molecularity is derived theoretically from reaction mechanism.
- **79.** (*a*) Except base hydrolysis of ester remaining are first order reactions.
- **80.** (*c*) In actual, unit of rate constant is independent of unit of concentration. The unit of K is s⁻¹
- **81.** (*a*) Order of reaction can be 0, 1, 2, 3, or even a fractional number.
- 82. (b) Hydrolysis of an ester is pseudo first order reaction.
- **83.** (d) Combination of H_2 and Br_2 is a second order reaction
- **84.** (*b*) Pseudo first order reaction is when one of the reacting species in biomolecular reaction is in large excess, then the reaction becomes first order.

85. (c)
$$R - C - OH + HO - R^{1} - H^{+} \Rightarrow R - C - OR^{1} + H_{2}O$$

Carboxylic Alcohol Ester
acid
Rate of reaction = leforthomalic acid leleghold

Rate of reaction = k[carboxylic acid] [alcohol] So; order of reaction = 2

- **86.** (*b*) As rate of reaction is doubled then pseudo first order rate constant is doubled as well. It may be noted that in presence of acid hydrolysis of ethyl acetate, a pseudo-unimolecular reaction by the actual value of k depends upon the concentration of H^+ ions, otherwise rate constant of a reaction is constant at constant temperature.
- **87.** (*d*) For every 10°C rise in temperature, the rate of the reaction generally gets doubled.

- **88.** (*c*) Activation energy is inversely proportional to rate of the reaction.
- **89.** (*a*) Threshold and activation energies depend on the nature of the reactants.
- **90.** (*b*) Lesser the activation energy, more will be the rate of the reaction.
- **91.** (*c*) Activation energy is inversely proportional to rate of the reaction.
- **92.** (*b*) A catalyst increases the rate of the reaction by decreasing the activation energy
- 93. (d) Activation energy depends on the nature of the reactants.
- **94.** (*b*) A positive catalyst increases the rate of the reaction by decreasing the activation energy
- **95.** (*b*) Collision frequency increases as the concentration of reactants increase, the probability of collisions increases.
- **96.** (*c*) Not only sufficient threshold energy of colliding atoms or molecules but also the proper orientation for the collision is required for the formation of products.
- 97. (c) According to the collision theory, only a small fraction of collisions is effective in bringing about the chemical reaction and the rest of the collisions are ineffective. For effective collision (to yield product) the colliding molecules must have more than or equal to certain minimum amount of energy called threshold energy. Threshold energy = Activation energy + average K.E. of molecules.
- **98.** (b) Gibbs energy does not get altered by catalyst (ΔG) of a reaction .
- 99. (d) Definition.
- 100.(b) Definition.
- 101. (c) Lower the activation energy, faster is the reaction
- **102.** (*b*) Apart from energy considerations, the colliding molecules should have proper orientation for effective collisions.
- **103.** (*b*) Threshold energy = Activation energy + Internal energy
- **104.** (*c*) Because $\Delta H = 0$
- **105.** (*d*) Threshold energy is only those collisions in which molecules collide with sufficient energy and proper orientation resulting in effective collisions. Rest of the molecule collide and bounce back.
- **106.** (*c*) Catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence, lowering the potential energy barrier.

108.(*c*)

Learning Plus

1. (c) The rate constant doubles for 10°C rise in temperature. For 20°C rise, the rate constant will be 4 times $\therefore k_1 = 4k_2$ or $k_2 = 0.25k_1$

3. (*b*)

- **2.** (*c*)
- **4.** (b)
- 5. (c) For zero order rate remains constant with time.

6. (b) (i)
$$t_{75\%} = \frac{3}{2} t_{50\%}$$

(ii) $t_{100\%} = 2 t_{50\%}$

- **7.** (*d*)
- **8.** (c) Activation energy for backward reaction=x+y
- 9. (b) Given $2A \rightarrow C$ Rate = k [A]ⁿ mol/litre sec = (litre / mole sec) × (mole/litre)ⁿ \therefore n = 2 Rate = k × (a)² = 2.5 × 10⁻² × (10⁻²)² = 2.5 × 10⁻⁶ mol/L sec 10. (b) 11. (d)
- **12.** (c) Rate = $\frac{\text{change in conc.}}{\text{time interval}}$
- **13.** (*b*) If $E_a = 0$, then k = A = constant**14.** (*c*) use, $k = Ae^{-E_a/RT}$

15. (c)

$$\frac{-d[A]_2}{dt} = \frac{2d[c]}{dt}$$
Thus $\frac{d[Cc]}{dt} = \frac{120 - 100}{5} = 4 \text{ mm min}^{-1}$

$$\therefore \quad \frac{-d[A_2]}{dt} = 2 \times 4 = 8 \text{ mm min}^{-1}$$

16. (*d*)

- 17. (c) $1.0 \text{ M} \rightarrow 0.6 \text{ M}$ (40%) $0.6\text{M} \rightarrow 0.36 \text{ M}$ (40%) For particular fraction of reaction , time taken is same in first order
- **18.** (b) Activation energy for backward reaction = $\Delta H + activation$ energy for forward reaction.
- **19.** (*c*) In the presence of catalyst, the heat absorbed, or evolved during the reaction remains unchanged as there is no change in stability of reactant and product.
- **20.** (*a*) Activation energy is the minimum energy required to convert reactant molecules to product molecules. Here, the energy gap between reactants and activated complex is sum of E_1 and E_2 .

 \therefore Activation energy = $E_1 + E_2$

Product is less stable than reactant as energy of product is greater than the reactant.

21. (b) $A(g) \rightarrow B(g) + C(g)$ Initially $p_i \quad 0 \quad 0$ At time t $p_{i-x} \quad x \quad x$ $P_t = p_i - x + x + x = p_i + x$ For first order reaction $x = p_t - p_i$ $k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$ $k = \frac{2.303}{t} \log \frac{p_i}{p_i - (p_t - p_i)}$

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

22. (*a*) According to Arrhenius equation, $k = A e^{-E_a/RT}$

Taking log on both side
$$\ln k = \ln \left(A \cdot e \frac{-E_a}{RT} \right)$$

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

This equation can be related to equation of straight line as shown above.

From the graph, it is very clear that slope of the plot

$$= -\frac{E_a}{R}$$
 and intercept = ln A.

23. (*c*) Out of the given four statements, option (*c*) is not correct. Order of reaction is equal to the sum of powers of concentration of the reactants in rate law expression.

For any chemical reaction

$$xA + yB \rightarrow Product$$

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

Order = x + y

Order of reaction can be a fraction also. Order of reaction is not always equal to sum of the stoichiometric coefficients of reactants in the balanced chemical equation. For of reaction it may or may not be equal to sum of stoichiometric coefficient of reactants.

24. (*a*) Rate of reaction is defined as rate of decrease of concentration of any one of reactants with passage of time

Rate of reaction = $\frac{\text{Rate of disappearance of reactant}}{\text{Time taken}}$

$$r = \frac{-dx}{dt}$$

Thus, as the concentration of reactant decreases with passage of time, rate of reaction decreases.

25. (*a*) The chemical reaction in which energy is evolved during the reaction is known as exothermic reaction i.e., activation energy of product is greater than activation energy of reactants.

Here, only (i) denotes correct picture of exothermic reaction.

26. (*b*) Rate law can be written as

Rate = k[A][B]

Rate of reaction *w.r.t* B is of first order.

 $R_1 = k [A] [B]$

when concentration of reactant `B' is doubled then rate (R_2)

 $R_2 = k [A] [2B]$

 $R_2 = 2k [A] [B]$

 $R_{2} = 2 R_{1}$

Therefore; as concentration of B is doubled keeping the concentration of A constant, rate of reaction doubles.

- 27. (c) According the postulates of collision theory there are following necessary conditions for any reaction to occur (i) Molecule should collide with sufficient threshold energy.
 - (ii) Their orientation must be proper.
 - (iii) The collision must be effective.
- 28. (d) The time taken for half the reaction to complete. *i.e.*, the time the concentration of a reactant is reduced to half of its original value is called half-life period of the reaction. But it is impossible to perform 100% of the reaction. Whole of the substance never reacts because in every half-life, 50% of the substance reacts. Hence, time taken for 100% completion of a reaction is infinite.

29. (b) Characteristics of catalyst

(*a*) It catalyses the forward and backward reaction to the same extent as it decreases energy of activation hence, increases the rate of both the reactions.

(b) Since, reaction quotient is the relation between concentration of reactants and products. Hence, catalyst does not alter reaction quotient. Thus, Gibbs free energy does not change during the reaction when catalyst is added to it.

 $\Delta G = -RT \ln Q$

where, Q = reaction quotient

(*c*) It doesn't alter equilibrium of reaction as equilibrium constant is also concentration dependent term.

(d) It provides an alternate mechanism by reducing activation energy between reactants and products.

30. (*b*) Pseudo first order reaction is a chemical reaction in which rate of reaction depends upon concentration of only one reactant (present in small amount) while concentration of another reactant (present in excess) has no effect on rate of reaction.

e.g., hydrolysis of ethyl acetate in presence of excess of water

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

excess

 $r = k [CH_3COOC_2H_5]$

where $k = k'[H_2O]$

 \therefore rate constant of pseudo 1st order reaction depends on conc. of reactant present in excess.

31. $(b) \mathbf{A} \rightarrow \mathbf{B}$

Concentration of reactants and products varies exponentially w.r.t time.

- (i) Concentration of reactant (here. A) decreases exponentially w.r.t time.
- (ii) Concentration of product (here. B) increases exponentially w.r.t time. Correct graph representing the above reaction is (b).
- **32.** (*d*) Function of Catalyst: as the catalyst is added to the reaction medium rate of reaction increases or decreased by decreasing or increasing activation energy of molecule respectively. As there are +ve & -ve catalysts Hence, it follows an alternative pathway.

Catalyst does not change the enthalpy change of reaction. Energy of reactant and product remain same in both catalysed and uncatalysed reaction.

Hence, (d) is incorrect statements.

Multiconcept MCQs

- (b) In this graph, activation energy for the formation of AB' is small, so reaction from X→AB takes place fastly.
- (c) From C→D, activation energy is lesser than that of activation energy from A→B
- **3.** (*a*) For backward reaction , activation energy = 80 40 = 40K
- **4.** (*a*)
- **5.** (*c*) r = k[CH₃COOC₂H₅][NaOH] on adding , three times of water the resultant volume becomes four times that of initial volume.
- **6.** (*d*)
- **7.** (*b*)

8. (d) $\mathbf{r} = \mathbf{k}[\mathbf{A}]^{\mathbf{n}}[\mathbf{B}]^{\mathbf{m}}$...(1) $\mathbf{r}_{\mathbf{l}} = \mathbf{k}[\mathbf{2}\mathbf{A}]^{\mathbf{n}}\left[\frac{1}{2}\mathbf{B}\right]^{\mathbf{m}}$...(2) $\frac{(2)}{(1)} \Rightarrow \frac{\mathbf{r}_{\mathbf{l}}}{\mathbf{r}} = 2^{\mathbf{n}-\mathbf{m}}$ $\mathbf{r}_{\mathbf{l}} = 2^{\mathbf{n}-\mathbf{m}}.\mathbf{r}$

9. (*b*)

- **10.** (*b*) From result (1) & (2), as the concentration increases by 2 times, rate becomes 4 times. so it is second order.
- **11.** (*c*)

12. (*c*)

13. (b)
$$O + O_3 \xrightarrow{\text{slow}} 2O_2$$

 $r = k_1[O][O_3]$ $O_3 \rightleftharpoons O_2 + O$
 $= k_1 \frac{k_c[O_3][O_3]}{[O_2]}$ $k_c = \frac{[O_2][O]}{[O_3]}$
 $= k[O_3]^2[O_2]^{-1}$
14. (b) $k = 1 \times 10^{-2} \text{L mol } \text{L}^{-1}\text{s}^{-1}$
rate $= k[A]^2[B]^0$
When 50% of the reactants are converted into products
rate $= 1 \times 10^{-2} (0.5)^2 = 2.5 \times 10^{-3} \text{ mol } \text{L}^{-1}\text{s}^{-1}$
15. (d) Use $k = \frac{2.303}{t} \log \frac{a}{a - x}$, with the help of this calculate
 $\frac{x}{a}$
16. (b) $r = k[A]^a$ (1)
 $\frac{r}{4} = k[\frac{A}{2}]^a$...(2)
 $\frac{(2)}{(1)} \Rightarrow 4 = 2^a$
 $a = 2$

17. (a) i) 0.8 to
$$0.4 \Rightarrow 50\%$$
 reaction takes 15 min
ii) 0.1 to $0.05 \Rightarrow 50\%$ reaction takes 15 min
 0.05 to $0.025 \Rightarrow 50\%$ reaction takes 15 min

18. (*b*) For zero order reactions, the rate of the reacion does not change with time.

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

 $= \frac{2.303}{79} \log_{10} \frac{100}{100-85}$
 $k = 2.4 \times 10^{-2} \text{ min}^{-1}$
20. (a)
21. (a) $r = k[CH_3CHO]^n \rightarrow (1)$
 $4r = k[2CH_3CHO]^n \rightarrow (2)$
 $\frac{(2)}{(1)} \Rightarrow n = 2$ use $k = \frac{1}{at} \frac{x}{(a-x)}$ to calculate rate constant
22. (a) Conceptual
23. (b) $t = \frac{2.303}{k} \log \frac{a}{a-x}$

 24. (b) t_{75%} = 2t_{50%}
 25. (d) Reaction from A→C is exothermic ΔH = -7kJ

26. (*a*)

NEET Past 10 Years Questions

1. (a) For a given ΔH is negative. Hence potential energy profile is an exothermic reaction.

2. (d) $\ln k = \ln A - \frac{Ea}{R} \left(\frac{1}{T}\right)$

In lnk v/s 1/T graph

Slope = -Ea/R

 $-5 \times 10^3 = -Ea/8.313$

$$Ea = 5 \times 10^{3} \times 8.314$$

= 41500J mol⁻¹
= 41.5KJ/mol

3. (*c*) When the concentrations of the reactants are raised, the reaction proceeds more quickly. This is due to an increase in the number of molecules that have the minimum required energy.

Collision frequency ∞ no. of reacting molecules or atoms.

Higher the concentration of reactant molecules higher is the probability of collision and so the collision frequency. **4.** (*b*) For first order reaction:

$$k = \frac{2.303}{t} \log \frac{[R_o]}{[R_t]}$$

$$4.606 \times 10^{-3} = \frac{2.303}{t} \log \frac{[2]}{[0.2]}$$

$$t = \frac{2.303}{4.606 \times 10^{-3}} \log 10$$

$$t = \frac{10^3}{2} = 500 \text{ s}$$

5. (*a*) Rate of reaction according to collision theory can be expressed as

Rate =
$$Z_{AB} e^{-E_a/RT}$$

Where, Z_{AB} represents the collision frequency of the reactants, A & B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a

The number of collisions per second per unit volume of the reaction mixture (A and B) is known as collision frequency Z_{AB} .

6. (d) For zero order reaction

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

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

$$k = \frac{0.02}{2 \times 100}$$

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

7. (c) First order rate constant is given as,

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]_t}$$

99% completion of reaction,

$$k = \frac{2.303}{t} \log \frac{100}{1}$$
$$k = \frac{2.303}{t} \times 2\log 10$$
$$t = \frac{2.303}{k} \times 2$$
$$t = \frac{4.606}{k}$$

8. (c) $N_2 + 3H_2 \implies 2NH_3$

Rate of reaction is given as

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

9. (b)
$$(t_{1/2})_{zero} = \frac{[A]_0}{2K}$$

 \therefore If $[A]_0 =$ doubled, $t_{1/2} =$ doubled

- **10.** (b) For first order reaction, $t_{1/2} = \frac{0.693}{k}$ which is independent of initial concentration of reactant.
 - For second order reaction, $t_{1/2} = \frac{1}{k[A_0]}$, which

depends on initial concentration of reactant.

- **11.** (*a*) In the slowest step.
 - $X + Y_2 \implies XY + Y$

half molecule of Y2 reacts with the one molecule of X $\therefore 1 + 0.5 = 1.5$

12. (c)
$$k = 10^{-2} s^{-1}$$
, $t = ? [R_0] = 20 g$

$$[R] = 5 g$$

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

$$t = \frac{2.303}{10^{-2}} \log \frac{20}{5}$$

$$t = 138.6 \sec$$

14. (c)
$$\frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{1.5d[C]}{dt}$$
 ...(i)
For the reaction
 $xA + yB \rightleftharpoons Zc$
 $\frac{-d[A]}{Xdt} = \frac{-d[B]}{Ydt} = \frac{d[C]}{Zdt}$...(ii)

Comparing equation 1st and 2nd

$$X:Y:Z=1:1:\frac{1}{1.5}$$
$$=1:1:\frac{2}{3}=3:3:2$$
$$X=Y=3, Z=2$$

- 15. (a) At Low P, rate is proportional to the surface coverage and is of Ist order while at high P, it follows zero order due to complete coverage of surface area.
- 16. (b) For a first order reaction, $A \rightarrow$ products and for concentration of the reactant at two different times.

$$k = \frac{2.303}{t_2 - t_1} \log \frac{[A]_1}{[A]_2}$$

$$k = \frac{2.303}{t_2 - t_1} \log \frac{(\text{rate})_1}{(\text{rate})_2} (\because \text{ rate } \propto [A])$$

$$k = \frac{2.303}{(20 - 10)} \log \left(\frac{0.04}{0.03}\right) = 0.0287 \text{ sec}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287 \text{ sec}^{-1}} = 24.14 \text{ sec}$$

- 17. (a) When we add catalysts to any chemical reaction. It provides an alternative pathway for the reaction and lowers the activation energy. So the reaction becomes fast. As E_f and E_h (activation energy for forward and backward reaction) is reduced to same extent, so there is no change in enthalpy of reaction.
- 18. (a) Reaction is of zero order as the unit of rate constant is mol L^{-1} s⁻¹.
 - \therefore Concentration of B = k × t = 0.6 × 10⁻³ × 20 × 60 = 0.72 M

19. (a)
$$t_{1/2} = \frac{0.693}{k} \sec^{-1}{k}$$

Ist order reaction is independent of concentration of reactant.

20. (*b*) According to Arrhenius equation:

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

 $e^{-E_a/RT}$

Comparing with y = c + mx

Slope will be ln k

- **21.** (d) $k_p > k_p'$ that is the previous pressure constant was higher as the reaction being exothermic $T_2 > T_1$.
- **22.** (c) Enthalpy(ΔH) = E_f activation energy of forward E_b activation energy of backward reaction

When
$$E_f = E_b$$

 $\Delta H = 0$

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

 $k_2 = 2k_1, T_1 = 20 + 273 = 293 \text{ K}$
or $T_2 = 35 + 273 = 308 \text{ K}$
 $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
 $\log 2 = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{293} - \frac{1}{308} \right)$
 $0.3010 = \frac{E_a}{19.147} \times \frac{15}{293 \times 308}$
 $E_a = 34673 \text{ J mol}^{-1} \text{ or } 34.7 \text{ kJ mol}^{-1}$
24. (c) $k_1 = \text{Ae}^{-E_a/RT_1}, k_2 = \text{Ae}^{-E_a/RT_2}$
 $\ln k_1 = \ln \text{A} - E_a/RT_1$ (*i*)
 $\ln k_2 = \ln \text{A} - E_a/RT_2$ (*i*)
From eq. (*i*) and (*ii*), we have
 $\ln k_2 - \ln k_1 = \ln \text{A} - \frac{E_a}{RT_2} - \ln \text{A} + \frac{E_a}{RT_1}$

$$\Rightarrow \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$
$$\Rightarrow \ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$
) For 10° rise is temperature, n

25. (c) For 10° rise is temperature, n = 1 So rate = 2ⁿ = 2¹ = 2 When temperature is increased from 10° to 100°C change in temperature = 100 - 10 = 90°C i.e. n = 9, so, rate = 2⁹ = 512
26. (a) We can write the rate law as R = k [A]^m [B]ⁿ When [B] is doubled 'R' is also doubled so n = 1 When both [A] and [B] are doubled rate increases by 8 8R = k[2A]^m [2B]ⁿ 2³ = 2^{m+1} ∴ m = 2

Hence rate expression, $R = k [A]^2 [B]$