

Q1) State a condition under which a bimolecular reaction is kinetically first order?

A1) Bimolecular reaction becomes kinetically first order when one of the reactants is in excess.

Q2) Write the rate equation for $2A + B \longrightarrow C$ if the order of the reaction is zero?

A2) $\text{Rate} = k [A]^0 [B]^0$ or $\text{Rate} = k$.

Q3) The reaction between H_2 (g) and O_2 (g) is highly feasible yet allowing the gases to stand at room temperature in the same vessel does not lead to the formation of water. Explain?

A3) Activation energy of this reaction is very high. Therefore the reaction does not take place.

or

Q4) Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. Explain?

A4) Activation energy for combustion reactions of fuels is very high at room temperature therefore they do not burn by themselves.

Q5) For a certain reaction large fraction of the molecules has energy more than the threshold energy, yet the rate of the reactions very slow. Why?

A5) Apart from energy considerations, the colliding molecules should have a proper orientation for effective collision. It appears that this condition is not fulfilled in this case. That is why the reaction is very slow.

Q6) Why is the probability of reaction with molecularity higher than three very rare?

A6) The probability of more than three molecules colliding simultaneously is very very small. Hence the probability of reaction with molecularity higher than three is very rare.

Q7) Why does the rate of reaction generally decrease during the course of reaction?

A7) Rate of the reaction depends upon the concentration of reactants. With the progress of the reaction, reactants convert into products. Thus the concentration of the reactant decreases and hence the rate of reaction decreases.

Q8) Thermodynamic feasibility of a reaction alone cannot decide the rate of the reaction. Explain with the help of example?

A9) For a reaction to take place, appropriate activation must be supplied to the reactant. If this not available, the reaction does not take place. For example thermodynamically, conversion of diamond to graphite is possible, but it requires an

activation energy which is not available at room temperature. Hence the reaction does not take place.

Q10) Why in the redox titration of KMnO_4 vs oxalic acid, we heat oxalic acid solution before titration ?

A10) The reaction between KMnO_4 and oxalic acid is slow. On raising the temperature, we provide the required activation energy and the rate of reaction is increases.

Q11) Write the difference between instantaneous rate of a reaction and average rate of reaction?

Instantaneous Rate of Reaction	Average Rate of Reaction
Instantaneous Rate of Reaction at any instant of time is defined as the rate of change in concentration of any one of the reactants or products at that particular instant of time. For a reaction : $\text{A} + 2\text{B} \rightarrow \text{C}$	It is the appearance of product or disappearance of reactants over a long time interval
$\frac{dx}{dt} = \frac{-d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{d[C]}{dt}$	$r_{av} = \frac{-\Delta[A]}{\Delta t} = -\frac{1}{2} \frac{\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$

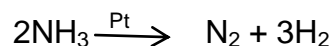
Q12) (a) Why molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

(b) Why can we not determine the order of a reaction by taking into consideration?

A12) (a) A complex reaction proceeds through a number of elementary reactions. Number of molecules involved in each elementary reaction may be different i.e, the molecularity of each step may be different. Therefore, molecularity of overall complex reaction has no sense. On the other hand, order of a complex reaction is determined by the slowest step in its mechanism and is valid even in the case of complex reactions.

(b) Balanced chemical equation often leads to incorrect order or rate law as the rate of reaction may not depend upon all the molecules of a reactant present in the balanced chemical equation.

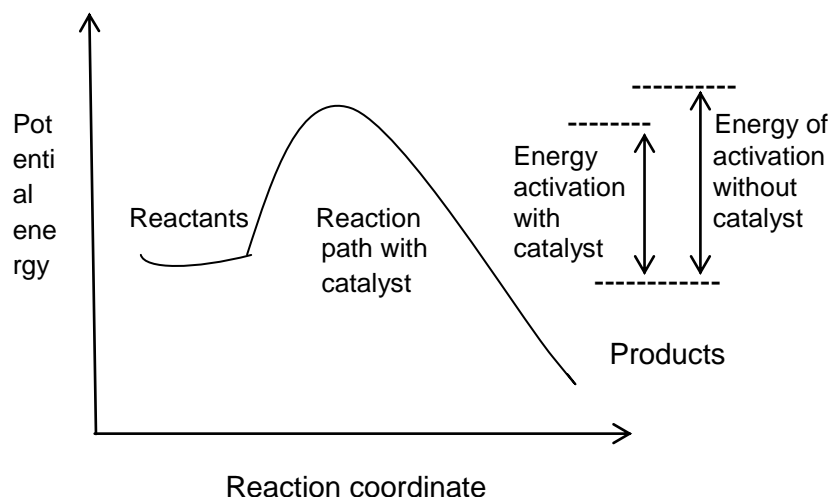
For eg :- Decomposition of NH_3 on Pt surface is actually a zero order reactions which is only determined experimentally & cannot be predicted from the chemical equation.



Q 13) (a) Illustrate graphically the effect of catalyst on activation energy.

(b) Catalyst have no effect on the equilibrium constant. Why?

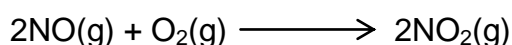
A 13) (a)



The catalyst provides an alternate pathways or reaction mechanism by reducing the activation energy between the reactants and products and hence lowering the potential energy barrier as shown in the figure.

(b) A catalyst does not change the equilibrium constant of a reaction, rather it helps in attaining the equilibrium faster. That is, it catalyses the forward as well as backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

Q14) How can you determine the rate law of the following reaction ?



A14) The rate law can be determined by initial rate method. Keeping the concentration of one of the reactant constant and changing the concentration of the other, the effect on the rate of reaction is determined.

for eg : for the given reaction

(i) Keeping $[\text{O}_2]$ constant, if $[\text{NO}]$ is doubled rate is found to become four times. This shows that. Rate $\propto [\text{NO}]^2$

(ii) Keeping $[\text{NO}]$ constant, if $[\text{O}_2]$ is doubled, rate is also found to become doubled . This shows that Rate $\propto [\text{O}_2]$

(iii) Hence overall rate law will be Rate = $k[\text{NO}]^2[\text{O}_2]$

Q15) How does a change in temperature affect the rate of a reaction? How can this effect on the rate constant of a reaction be represented quantitatively?

A 15) Rate of reaction increases with temperature. Temperature coefficient is the ratio of rate constants of reaction at two different temperatures differing by 10° .

$$\text{Temperature coefficient} = \frac{\text{Rate Constant at } t+10^\circ}{\text{Rate constant at } t^\circ}$$

It is observed that for a chemical reaction with rise in temperature by 10° , the rate constant is nearly doubled.

O3 MARKS

Q16. The half life of decay radioactive ^{14}C is 5730 years. An archeological artifact containing wood had only 80% of ^{14}C activity as found in a living tree. Calculate the age of the artifact?

A16. Radioactive decay is a first order reaction.

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

or

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

For 80% activity, $[A] = 0.8[A]_0$

Substituting in the above equation, we get

$$t = \frac{2.303}{0.693/t_{0.5}} \times \log \frac{[A]_0}{0.8[A]_0}$$

or

$$t = \frac{2.303}{0.693} \times 5730 \times 0.0969 = 1845 \text{ years}$$

Thus, the artifact is 1845 years old.

Q17. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If $1 \mu\text{g}$ of ^{90}Sr was absorbed on the bones of a newly born instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically?

A17) Determine k , using the following relation :

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1}$$

$$k = \frac{2.303}{t} \log \frac{N_0}{N}$$

Substituting the values in the equation of first order, we get

After 10 years, $\frac{0.693}{28.1} = \frac{2.303}{10} \log \frac{1 \mu\text{g}}{N}$

or $\log \frac{1}{N} = \frac{10 \times 0.3010}{28.1} = \frac{3.01}{28.1} = 0.1071$ or $\frac{1}{N} = \text{Antilog } 0.1071 = 1.279$

or $N = \frac{1}{1.279} = 0.7818 \mu\text{g}$

Thus, 0.7818 μg of ^{90}Sr will remain after 10 years

After 60 years, $60 = \frac{2.303}{0.693} \times 28.1 \log \frac{1}{N}$

or $\log \frac{1}{N} = \frac{60 \times 0.3010}{28.1} = \frac{18.06}{28.1} = 0.6427$ or $\frac{1}{N} = \text{Antilog } 0.6427 = 4.392$

or $N = \frac{1}{4.392} = 0.227 \mu\text{g}$.

Thus, 0.227 μg of ^{90}Sr will remain after 60 years.

Q18. For a decomposition reaction, the values of rate constant at two different temperatures are given below :-

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

$k_2 = 2.39 \times 10^{-7} \text{ L}/(\text{mol}\cdot\text{s})$ at 700 K

Calculate the value of E_a for the reaction.

($\log 11.11 = 1.046$) ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

A18.

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

Given, $k_1 = 2.15 \times 10^{-8} \text{ L}/\text{mol s}^{-1}$ at 650K.

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

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

$$\log \frac{2.39 \times 10^{-7} \text{ L}/\text{mol}}{2.15 \times 10^{-8} \text{ L}/\text{mol}} = \frac{E_a}{2.303 \times 8.314 \times 10^{-3} \text{ kJ}/\text{mol}} \left[\frac{1}{650} - \frac{1}{700} \right]$$

$$\begin{aligned}
 \text{Then, } k &= \frac{2.303}{100} \log \frac{p_i}{2p_i - p_t} \\
 &= \frac{2.303}{100} \log \frac{0.4}{(2 \times 0.4 - 0.7)} \\
 &= \frac{2.303}{100} \log \frac{0.4}{0.1} = \frac{2.303}{100} \log 4 \\
 &= \frac{2.303}{100} \times 0.6021 = 0.01387 \\
 &= 1.387 \times 10^{-2} \text{ s}^{-1}
 \end{aligned}$$

Q20) (a) Explain the following terms :

- (i) Rate of reaction
- (ii) Activation energy of reaction

(b) The decomposition of phosphine, PH_3 , proceeds according to the following equation : $4\text{PH}_3(\text{g}) \longrightarrow \text{P}_4(\text{g}) + 6\text{H}_2(\text{g})$

It is found that the reaction follows the following rate equation : $\text{Rate} = k[\text{PH}_3]$.

The half life of PH_3 is 37.9 s at 120°C .

- (i) How much time is required for $3/4^{\text{th}}$ of PH_3 to decompose?
- (ii) What fraction of the original sample of PH_3 remains behind after 1 minute?

A20) (a) (i) **Rate of a reaction** : Rate of a reaction may be defined as change in concentration of reactant or product in unit time.

(ii) **Activation energy of a reaction** : Difference in energy of the reactants and the activated complex in the reaction is called activation energy. Reactants must gain energy to reach the state of activated complex in order to give the products.

(b) $4\text{PH}_3(\text{g}) \longrightarrow \text{P}_4(\text{g}) + 6\text{H}_2(\text{g})$
 Half – life of $\text{PH}_3 = 37.9 \text{ s}$
 $\text{Rate} = k[\text{PH}_3]$

This means that the reaction is of first order. For a first order reaction

$$k = \frac{0.693}{t_{1/2}} \quad \text{or} \quad \frac{0.693}{37.9} = 0.01828496$$

(i) Apply the reaction $k = \frac{2.303}{t} \log \frac{[R]_o}{[R]}$

Here $R = R_o - \frac{3}{4} R_o = \frac{R_o}{4}$

Substituting the values in the equation above, we have

$$0.01828496 = \frac{2.303}{t} \log \frac{[R]_o/4}{[R]_o}$$

or $t = \frac{2.303}{0.01828496} \log 4$

or $t = \frac{2.303}{0.01828496} \times 0.60206$
 $= 75.83 \text{ s}$

(ii) After 1 minute or 60 seconds $k = \frac{2.303}{t} \log \frac{[R]_o}{[R]}$

or $\log \frac{[R]_o}{[R]} = \frac{kt}{2.303}$

Substituting the values, we have $\log \frac{[R]_o}{[R]} = \frac{0.0183 \times 60}{2.303} = 0.4768$

Taking antilogarithms, we have

$$\frac{[R]_o}{[R]} = 2.992$$

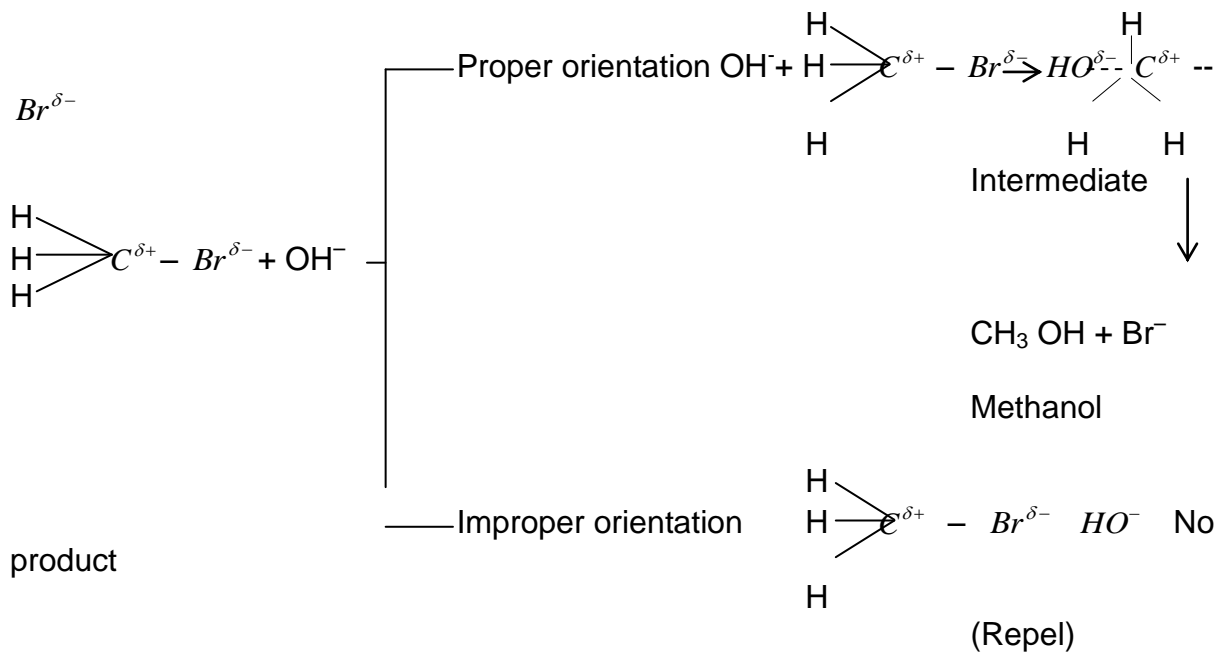
or $\frac{R}{[R]_o} = \frac{1}{2.992} = 0.3342$

Q21) (a) All energetically effective collisions do not result in a chemical change. Explain with the help of an example?

(b) Show that for a first order reaction, the time required for half the change (half –life period) is independent of initial concentration.

A21)(a) All energetically effective collisions do not result in a chemical change because even if colliding molecules have energy greater than the threshold energy, they may not have proper orientation at the time of collision and no breaking of bonds in the reactant molecules and formation of new bonds to form product molecules may occur.

For eg :- The reaction between bromomethane and an alkali may or may not lead to the formation of methanol depending upon whether they have a proper orientation or not at the time of collision.



A22)(b) For a first order reaction, rate constant,

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

$$\text{When, } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

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

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

$$= \frac{2.303 \times 0.3010}{k}$$

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

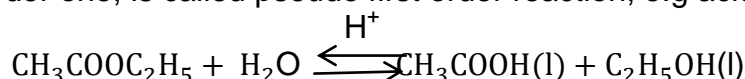
Thus for a first order reaction, half life period is constant & is independent of initial concentration of the reacting species.

Q23)(a) What are pseudo first order reactions? Give one example of each reactions.

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

- (i) How long it will take for 15% of a sample of H_2O_2 to decompose?
- (ii) How long it will take for 85% of the sample to decompose?

A23)(a) **Pseudo first order reaction** The reaction which is bimolecular but has order one, is called pseudo first order reaction, e.g acidic hydrolysis of ester.



- (b) (i) When 15% of a sample of H_2O_2 is decomposed.

$$\text{For a first order reaction, } k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\text{Given, } k = 1.06 \times 10^{-3} \text{min}^{-1}$$

$$[R]_0 = 100\text{M,}$$

$$[R] \text{ (after time, } t) = 100 - 15 = 85\text{M}$$

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

$$t = \frac{2.303}{1.06 \times 10^{-3}} \log 1.176$$

$$= \frac{2.303 \times 0.0704}{1.06 \times 10^{-3}} = 152.9 \text{ min}$$

- (ii) When 85% of a sample of H_2O_2 is decomposed, $[R] = 100 - 85 = 15\text{M}$

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

$$= \frac{2.303}{1.06 \times 10^{-3}} \log 6.667$$

$$= \frac{2.303 \times 0.8240}{1.06 \times 10^{-3}} = 1790.25 \text{ min}$$

Q24) (a) Explain the following terms :

- (i) Order of a reaction.
- (ii) Molecularity of a reaction

(b) The rate of a reaction increases four times when the temperature changes from 300 K to 320 K. Calculate the energy of activation of the

reaction, assuming that it does not change with temperature. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

A24) (a) (i) **Order of a reaction** : The sum of the powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

(ii) **Molecularity of a reaction** : The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction. Thus there are unimolecular, bimolecular, trimolecular reactions when the numbers of molecules taking part are one, two or three.

(b) Apply Arrhenius equation

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

Substituting the values, we have

$$\log \frac{4k_1}{k_1} = \frac{E_a}{2.303 \times 8.314} \left[\frac{320 - 300}{300 \times 320} \right]$$

$$\text{or} \quad \log 4 = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{300 \times 320}$$

$$\text{or} \quad \log 4 = E_a \times 1.088 \times 10^{-5}$$

$$\text{or} \quad 0.6021 = E_a \times 1.088 \times 10^{-5}$$

$$\text{or} \quad E_a = \frac{0.6021}{1.088} \times 10^{-5}$$

$$\text{or} \quad E_a = 5.53 \times 10^4 \text{ J} = 55.3 \text{ kJ/mol.}$$

Q25) (a) A reaction is first order in A and Second order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected when concentrations of both A and B are doubled?

(b) In a reaction between A and B, the initial rate of reaction (r_0) was measured for different initial concentrations of A and B as given below :

$A/\text{mol L}^{-1}$	0.20	0.20	0.40
$B/\text{mol L}^{-1}$	0.30	0.10	0.05
$r_0/\text{mol L}^{-1}$	5.07×10^{-5}	5.07×10^{-5}	7.16×10^{-5}

What is the order of reaction with respect to A & B ?

A 25 (a) (i) $(\text{Rate})_1 \quad \frac{dx}{dt} = K [A] [B]^2$

(ii) If both [A] = [B] are doubled

$$\begin{aligned} (\text{Rate})_2 &= k [2A] [2B]^2 \\ &= 8K [A] [B]^2 \end{aligned}$$

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{8K [A] [B]^2}{k [A] [B]^2} = (\text{Rate})_2 = 8 (\text{Rate})_1$$

i.e The rate increases 8 times

(b) $r_o = k [A]^\alpha [B]^\beta$

$$\begin{aligned} (r_o)_1 &= k \times 5.07 \times 10^{-5} = (0.20)^\alpha (0.30)^\beta && \dots(i) \\ (r_o)_2 &= k \times 5.07 \times 10^{-5} = (0.20)^\alpha (0.10)^\beta && \dots(ii) \\ (r_o)_3 &= k \times 1.43 \times 10^{-4} = (0.40)^\alpha (0.05)^\beta && \dots(iii) \end{aligned}$$

Dividing (i) by (ii)

$$(r_o)_1 / (r_o)_2 = 1 = (0.30/0.10)^\beta = (3)^\beta$$

Therefore $\beta = 0$

Dividing (iii) by (ii)

$$(r_o)_3 / (r_o)_2 = \frac{7.16}{5.07} = (0.40/0.20)^\alpha (0.05/0.10)^\beta$$

or $1.412 = 2^\alpha \left(\frac{1}{2}\right)^\beta = 2^\alpha$ Because $[\beta] = 0$

or $\log 1.412 = \alpha \log 2$

or $\alpha = 0.1523/0.3010 = 0.5$

Thus, order w.r.t A = 0.5 , order w.r.t B = 0

