

CHEMISTRY (XI)**Chapter 11****Reaction Kinetics** **Short Questions****1. Define reaction kinetics.**

Ans: The studies concerned with rates of chemical reactions and the factors that affect the rates of chemical reactions constitute the subject matter of reaction kinetics.

2. Define rate of reaction.

Ans: The rate of a reaction is defined as the change in concentration of a reactant or a product divided by the time taken for the change.

$$\text{Rate of reaction} = \frac{\text{change in concentration of the substance}}{\text{time taken for the change}}$$

It has the units of $\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$

3. Define average rate of reaction and instantaneous rate of reaction.

Ans: The rate at any one instant during the interval is called the instantaneous rate. The rate of reaction between two specific time intervals is called the average rate of reaction.

$$\text{Rate of reaction} = \frac{dx}{dt}$$

4. Define specific rate constant or velocity constant.

Ans: The specific rate constant of a chemical reaction is the rate of reaction when the

concentrations of the reactants are unity.

$$\text{If } [A] = 1 \text{ mol dm}^{-3} \text{ and } [B] = 1 \text{ mol dm}^{-3}$$

$$\text{Rate of reaction} = k \times 1^a \times 1^b = k$$

5. Define order of reaction. Give an example.

Ans: The order of reaction is given by the sum of all the exponents to which the concentrations in the rate equation are raised.

OR

The order of reaction may also be defined as the number of reacting molecules, whose concentrations alter as a result of the chemical change. For example, decomposition of nitrogen pentoxide involves the following equation.



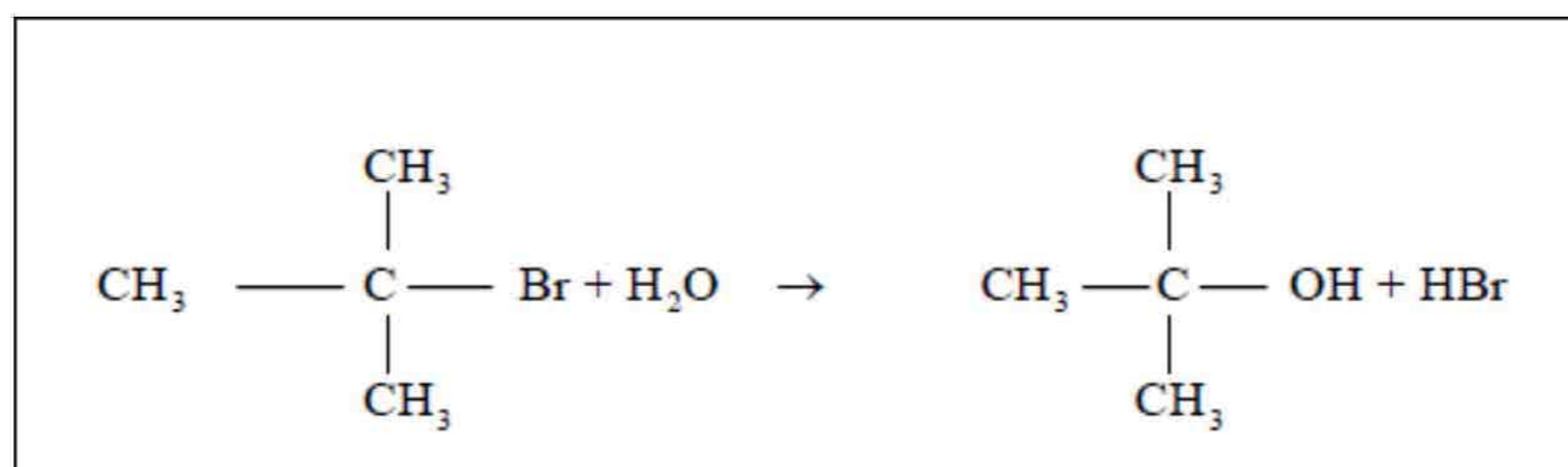
The experimentally determined rate equation for this reaction is as follows:

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

This equation suggests that the reaction is first order with respect to the concentration of N_2O_5 .

6. *Hydrolysis of tertiary butyl bromide is a pseudo first order reaction. Justify.*

Ans: Hydrolysis of tertiary butyl bromide



The rate equation determined experimentally for this reaction is

$$\text{Rate} = k[(\text{CH}_3)_3\text{CBr}]$$

The rate of reaction remains effectively independent of the concentration of water because, being a solvent, it is present in very large excess. Such types of reactions have been named as pseudo first order reactions.



7. Define half-life period. Give an example.

Ans: Half-life period of a reaction is the time required to convert 50% of the reactants into products. For example, the half-life period for the decomposition of N_2O_5 at 45°C is 24 minutes.

8. How radioactive decay is a first order reaction?

Ans: The disintegration of radioactive ${}_{92}\text{U}^{235}$ has a half-life of 7.1×10^8 or 710 million years. If one kilogram sample disintegrates, then 0.5 kg of it is converted to daughter elements in 710 million years. Out of 0.5 kg of ${}_{92}\text{U}^{235}$, 0.25kg disintegrates in the next 710 million years. So, the half-life period for the disintegration of a radioactive substance is independent of the amount of that substance and it is a first order reaction.

9. Half-life period of first order reaction is independent of the initial concentration of reactant. Justify.

Ans: If we decompose $0.10 \text{ mole dm}^{-3}$ of N_2O_5 at 45°C , then after 24 minutes $0.05 \text{ mole dm}^{-3}$ of N_2O_5 will be left behind. Similarly after 48 minutes $0.025(25\%) \text{ mole dm}^{-3}$ of N_2O_5 will remain unreacted and after 72 minutes (3 half times) $0.0125 (12.5\%) \text{ mole dm}^{-3}$ of N_2O_5 , will remain unreacted. The disintegration of radioactive ${}_{92}\text{U}^{235}$ has a half-life of 7.1×10^8 or 710 million years. If one kilogram sample disintegrates, then 0.5 kg of it is converted to daughter elements in 710 million years. Out of 0.5 kg of ${}_{92}\text{U}^{235}$, 0.25kg disintegrates in the next 710 million years. So, the half-life period for the disintegration of a radioactive substance is independent of the amount of that substance and it is a first order reaction.

10. What is the relation between half-life period and order of reaction?

Ans:

$$[t_{1/2}]_1 \propto \frac{1}{a^0}, \text{ since } [t_{1/2}]_1 = \frac{0.693}{k}$$

$$[t_{1/2}]_2 \propto \frac{1}{a^1}, \text{ since } [t_{1/2}]_2 = \frac{1}{k_a}$$

$$[t_{1/2}]_3 \propto \frac{1}{a^2}, \text{ since } [t_{1/2}]_3 = \frac{1.5}{ka^2}$$

In general for the reaction of n^{th} order:

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

11. What is rate determining step?

Ans: The slowest step of a reaction is called the rate determining step. Let us consider the following reaction:

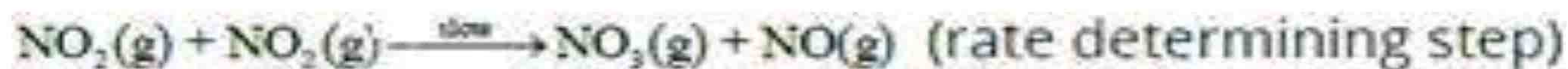


The rate equation of the reaction is found to be:

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

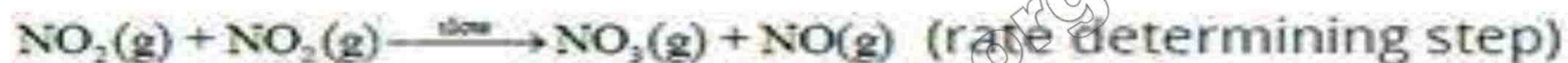
This equation shows that the rate of reaction is independent of the concentration of carbon monoxide. In other words the equation tells us that reaction involves more than one steps and

two molecules of NO_2 are involved in the rate determining step. The proposed mechanism for this reaction is as follows.



12. Define reaction intermediate. Give an example.

Ans: The reaction intermediate has a temporary existence and it is unstable relative to the reactants and the products. For example:



NO_3 is the reaction intermediate.

13. Name the physical methods used to determine rate of reaction.

Ans: Following are the physical methods used to determine rate of reaction:

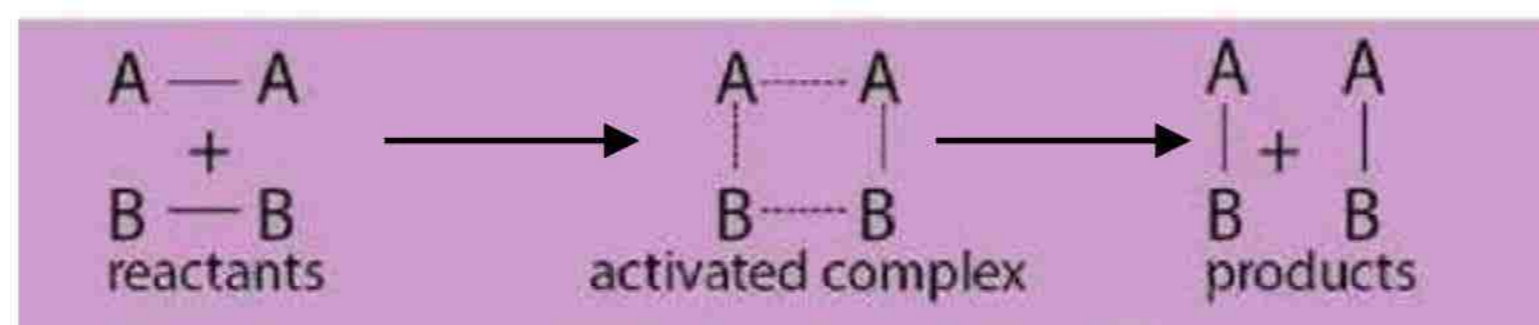
1. Spectrometry
2. Electrical conductivity method
3. Dilatometric method
4. Refractometric method
5. Optical Rotation method

14. Define activation energy.

Ans: The minimum amount of energy, required for an effective collision is called activation energy (E_a).

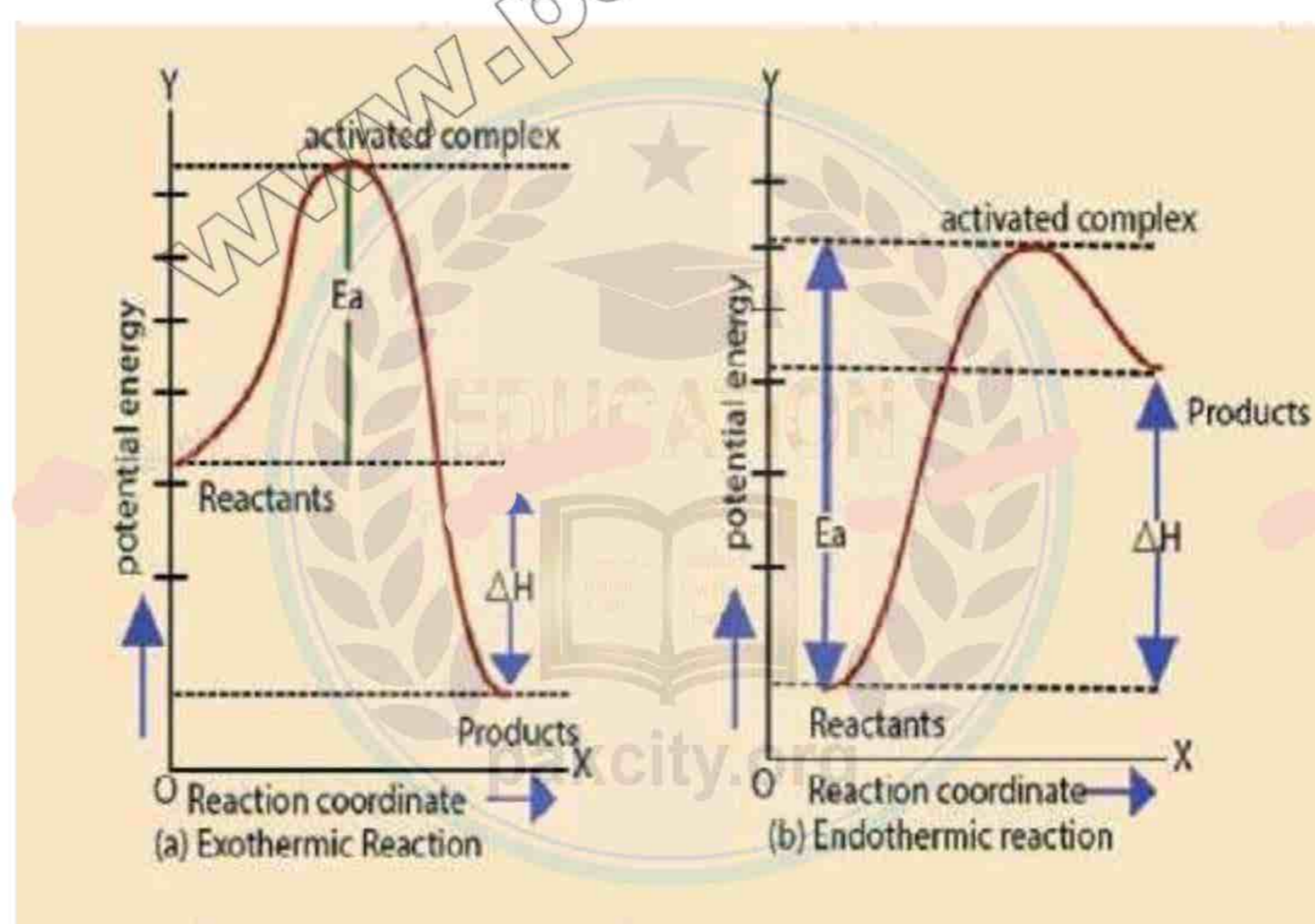
15. Define activated complex. Give an example.

Ans: Activated complex is an unstable combination of all the atoms involved in the reaction for which the energy is maximum. It is a short lived species and decomposes into the products immediately. It has a transient existence that is why it is also called a transition state.



16. Draw potential energy diagram for exothermic and endothermic reaction.

Ans: The potential energy diagram can be used to study the heat evolved or absorbed during the reaction. For exothermic reactions, the products are at a lower energy level than the reactants and the decrease in potential energy appears as increase in kinetic energy of the products. For endothermic reactions, the products are at higher energy level than the reactants and for such reactions a continuous source of energy is needed to complete the reaction.



17. Mention methods to find order of reaction.

Ans: Following are the methods to find order of reaction:

(i) Method of hit and trial

- (ii) Graphical method
- (iii) Differential method
- (iv) Half-life method
- (v) Method of large excess

18. Explain half-life method.

Ans: Half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction.

Therefore, $(t_{1/2})_n \propto \frac{1}{a^{n-1}}$

Let us perform a reaction twice by taking two different initial concentrations 'a₁' and 'a₂' and their half-life periods are found to be t₁ and t₂ respectively.

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

Dividing the two relations:

$$\frac{t_1}{t_2} = \left[\frac{a_2}{a_1} \right]$$

Taking log on both sides:

$$\log \frac{t_1}{t_2} = (n-1) \log \left[\frac{a_2}{a_1} \right]$$

Rearranging

$$n-1 = \frac{\log \left[\frac{t_1}{t_2} \right]}{\log \left[\frac{a_2}{a_1} \right]}$$

$$n = 1 + \frac{\log \left[\frac{t_1}{t_2} \right]}{\log \left[\frac{a_2}{a_1} \right]}$$

So, if we know the two initial concentrations and two half-life values we can calculate the order of reaction (n).

19. What is meant by method of large excess? Explain.

Ans: In this method, one of the reactants is taken in a very small amount as compared to the rest of the reactants. The active masses of the substances in large excess remain constant throughout. That substance taken in small amount controls the rate and the order is noted with respect to that. The reason is that a small change in concentration of a substance taken in very small amount affects the value of rate more appreciably. The hydrolysis of ethyl acetate as mentioned earlier shows that water being in large excess does not determine the order. In this way, the reaction is repeated by taking rest of the substances in small amounts one by one and overall order is calculated.

20. Mention factors affecting rate of reaction.

Ans: Following are the factors affecting rate of reaction:

1. Nature of reactants
2. Concentration of reactants
3. Surface area
4. Light
5. Effect of temperature on rate of reaction
6. Arrhenius equation

21. How activation energy, temperature and rate of reaction are related?

Ans: Arrhenius equation explains the effect of temperature on the rate constant of a reaction. The rate constant 'k' for many simple reactions is found to vary with temperature. According to Arrhenius:

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

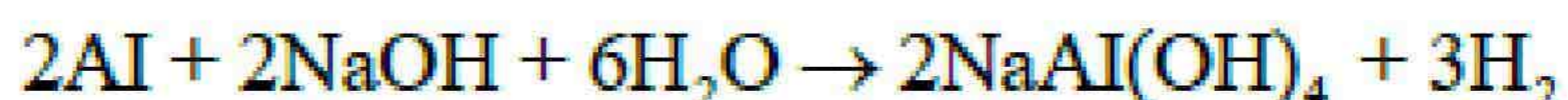
'k' is exponentially related to activation energy (E_a) and temperature (T). R is general gas constant and e is the base of natural logarithm. The equation shows that the increase in temperature, increases the rate constant and the reactions of high activation energy have low 'k' values.

22. What is the effect of nature of reactants on rate of reaction?

Ans: The rate of reaction depends upon the nature of reacting substances. The chemical reactivity of the substances is controlled by the electronic arrangements in their outermost orbitals. The elements of I-A group have one electron in their outermost s-orbital. They react with water more swiftly than those of II-A group elements having two electrons in their outermost s-orbital. Similarly, the neutralization and double decomposition reactions are very fast as compared to those reactions in which bonds are rearranged. Oxidation-reduction reactions involve the transfer of electrons and are slower than ionic reactions.

23. What is the effect of surface area on rate of reaction?

Ans: The increased surface area of reactants increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance. For example, Al foil reacts with NaOH moderately when warmed, but powdered Al reacts rapidly with cold NaOH and H_2 is evolved with frothing.



24. What is the effect of light on rate of reaction?

Ans: Light consists of photons having definite amount of energies depending upon their frequencies. When the reactants are irradiated, this energy becomes available to them and rates

of reactions are enhanced. The reaction of CH_4 and Cl_2 requires light. The reaction between H_2 and Cl_2 at ordinary pressure is negligible in darkness, slow in daylight, but explosive in sunlight. Similarly, light is vital in photosynthesis, and the rate is influenced by light.

25. What is the effect of concentration of reactants on rate of reaction?



Ans: An increase in the concentrations of the reactants will result in the corresponding increase in the reaction rate, while a decrease in the concentrations will have a reverse effect. For example

1. Combustion that occurs slowly in air (21% oxygen) will occur more rapidly in pure oxygen.
2. Limestone reacts with different concentrations of hydrochloric acid at different rates. In the case of a gaseous reactant, its concentration can be increased by increasing its pressure. Therefore, a mixture of H_2 and Cl_2 will react twice as fast if the partial pressure of H_2 or Cl_2 is increased from 0.5 to 1.0 atmosphere in the presence of excess of the other component.

26. How the effect of concentration of reactants on rate of reaction can be expressed mathematically?

Ans:

The effect of change in concentration on the rate of a chemical reaction can be nicely understood from the following gaseous reaction.



$$\text{Rate} \propto [\text{H}_2]$$

The overall rate equation of reaction is

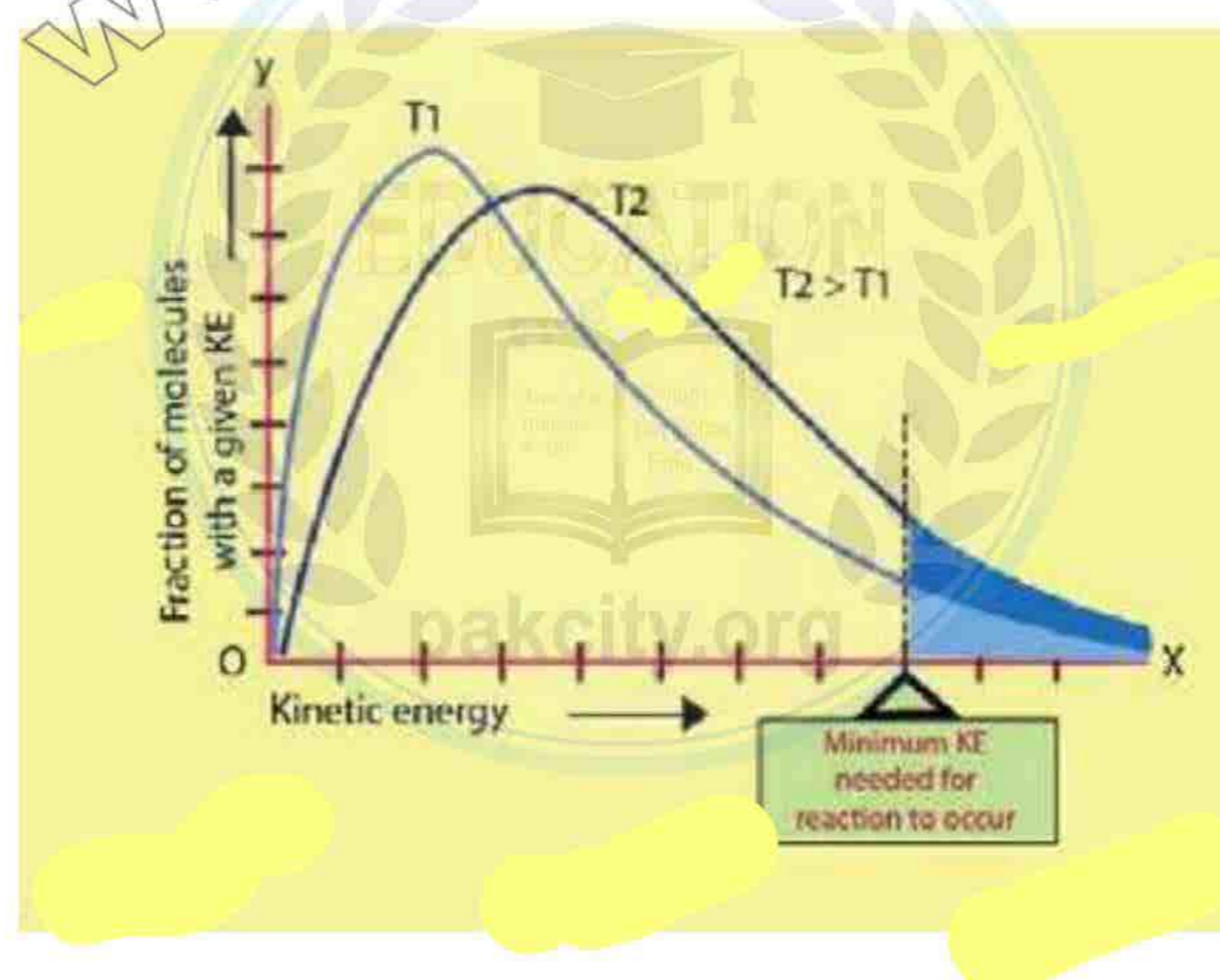
$$\text{Rate} \propto [\text{H}_2][\text{NO}]^2$$

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

Hence, the reaction is a third order one.

27. What is the effect of temperature on rate of reaction?

Ans: For a collision to be effective the molecules must possess the activation energy and they must also be properly oriented. All the molecules of a reactant do not possess the same energy at a particular temperature. A fraction of total molecules will have energy more than the average energy. This fraction of molecules is indicated as shaded area. As the temperature increases, the number of molecules in this fraction also increases. There happens a wider distribution of velocities. The curve at higher temperature T₂ has flattened. It shows that molecules having higher energies have increased and those with less energies have decreased. So, the number of effective collisions increases and hence the rate increases.



28. What happens to the rate of chemical reaction with the passage of time?

Ans: According to law of mass action, rate of reaction is directly proportional to concentration of

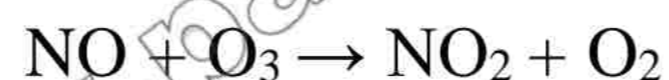
reactants. In all reactions, concentration of reactants decreases with the passage of time. With the decreases in concentration of reactants, rates also show continuous decrease from start till completion of reaction. This justifies that the rate of reaction is an ever changing parameter.

29. Define with example second order reaction?

Ans: Second order reaction: - When the sum of all the exponents to which the concentrations in the rate equation are raised, is equal to two, then the order of reaction is 2 and it is called a second order reaction.

Example

Oxidation of nitric oxide with ozone has shown to be first order with respect to NO and first order with respect to O₃. The sum of the individual orders gives the overall order of reaction as two.



$$\text{Rate} = k [\text{NO}][\text{O}_3]$$

30. How does a catalyst affect a reversible reaction? OR Equilibrium constant is not changed in the presence of a catalyst.

Ans: A catalyst cannot affect the equilibrium constant of a reaction but it helps the equilibrium to be reached earlier. The rates of forward and backward steps are increased equally. Even a small amount of the catalyst proves to be sufficient.

31. Does the physical state of a catalyst changes at the end of reaction?

Ans: A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state. MnO_2 is added as a catalyst for the decomposition of KClO_3 in the form of granules. It is converted to fine powder at the end of reaction. It has been found in many cases that the shining surfaces of the solid catalyst become dull.

32. A very small amount of catalyst may prove sufficient for a reaction. Justify.

Ans: Sometimes we need traces of a metal catalyst to catalyze reactions. For example, 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water.

33. How enthalpy change of a reaction and energy of activation are distinguished?

Ans:

Activation Energy:

The minimum amount of energy in addition to average kinetic energy which is just sufficient to convert the reactants into products is called activation energy.

Enthalpy Change of a Reaction:

The enthalpy change occurs when the certain number of moles of reactants as indicated by the balanced chemical equation react together completely to give the products under standard conditions, i.e. 25°C (298 K) and one atmosphere pressure.

34. Define and give an example of the process of activation of a catalyst.

Ans:

Such substances which promote the activity of a catalyst are called promoters or activators. It is also called "catalyst of a catalyst".

For example, hydrogenation of vegetable oils is accelerated by nickel. The catalyst activity of nickel can be increased by using copper and tellurium.

35. Define catalyst. Give an example.

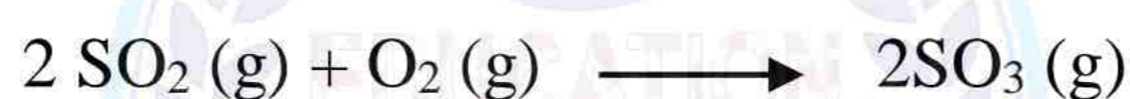
Ans: A catalyst is defined as a substance which alters the rate of a chemical reaction, but remains chemically unchanged at the end of the reaction. A catalyst is often present in a very small proportion. For example, the reaction between H₂ and O₂ to form water is very slow at ordinary temperature, but proceeds more rapidly in the presence of platinum. Platinum acts as a catalyst. Similarly, KClO₃ decomposes much more rapidly in the presence of a small amount of MnO₂. HCl is oxidized to Cl₂ in the presence of CuCl₂.

36. Define catalysis.

Ans: The process which takes place in the presence of a catalyst is called catalysis.

37. Define homogeneous catalysis. Give an example.

Ans: In this process, the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout. The catalyst is distributed uniformly throughout the system. For example, the formation of SO₃ (g) from SO₂ (g) and O₂ (g) in the lead chamber process for the manufacture of sulphuric acid, needs NO (g) as a catalyst. Both the reactants and the catalyst are gases.

**38. Define heterogeneous catalysis. Give an example.**

Ans: In some systems the catalyst and the reactants are in different phases. Mostly, the catalysts are in the solid phase while the reactants are in the gaseous or liquid phase. For example oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO₃.



39. Differentiate between Homogeneous and heterogeneous catalysis. Give two examples.

Ans:

Homogeneous catalysis	Heterogeneous catalysis
In this process, the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout.	In such system, the catalyst and the reactants are in different phases. Mostly, the catalysts are in solid phase, while the reactants are in the gaseous or liquid phase.
<p>Example: The formation of SO₃ (g) from SO₂(g) and O₂ (g) in the lead chamber process needs NO (g) as a catalyst. Both the reactants and the catalyst are gases.</p> $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \xrightleftharpoons{\text{NO}(\text{g})} 2\text{SO}_3(\text{g})$ <p>SO₃ is used for the manufacture of sulphuric acid (H₂SO₄).</p>	<p>Example: Oxidation of ammonia to NO in the presence of solid platinum gauze is an example of heterogeneous catalysis. Reactants are gases while catalyst is solid.</p> $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \xrightleftharpoons{\text{Pt}(\text{s})} 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ <p>NO is used for the preparation of Nitric acid (HNO₃).</p>



40. What is catalytic poisoning? Give two examples.

Ans: Catalytic poisoning happens due to presence of trace amounts of foreign substances which render them ineffective. Such substances are called poisons. For example, in the presence of Co as an impurity with hydrogen the catalytic activity of catalyst is decreased in the Haber's process for the manufacture of NH_3 . The manufacture of H_2SO_4 in the contact process needs platinum as catalyst. The traces of arsenic present as impurities in the reacting gases makes platinum ineffective.

42. Define autocatalyst. Give an example.

Ans:

In some of the reactions, a product formed acts as a catalyst. This phenomenon is called autocatalysis. For example when copper is allowed to react with nitric acid, the reaction is slow in the beginning. It gains the speed gradually and finally becomes very fast. This is due to the formation of nitrous acid during the reaction which accelerates the process.

43. What are enzymes? How they act as catalysts?

Ans:

Enzymes:

Enzymes are defined as catalyst of biological systems (animal and plants). They are either purely made of proteins or contain some non-protein part also for their help. Enzyme increase the rate of reaction within the body of living organisms by decreasing the activation energy of reaction. For example, urease catalyzes the hydrolysis of urea and Lipase catalyzes the hydrolysis of fats.

44. What is meant by negative catalysis?

Ans: When the rate of reaction is retarded by adding a substance, then it is said to be a negative catalyst or inhibitor. For example, tetraethyl lead is added to petrol, because it saves the petrol from pre-ignition.

45. Mention the characteristics of enzyme catalysis. (Mention any two as answer to short question)

Ans: Following are the characteristics of enzymes:

- (i) Enzymes are the most efficient catalysts known and they lower the energy of activation of a reaction.
- (ii) Enzyme catalysis is highly specific, for example, urease catalyses the hydrolysis of urea only and it cannot hydrolyze any other amide even methyl urea.
- (iii) Enzyme catalytic reactions have the maximum rates at an optimum temperature.
- (iv) The pH of the system also controls the rates of the enzyme catalyzed reaction and the rate passes through a maximum at a particular pH, known as an optimum pH. The activity of enzyme catalyst is inhibited by a poison.
- (v) The catalytic activity of enzymes is greatly enhanced by the presence of a co-enzyme or activator.

46. Mention the characteristics of a catalyst (Mention any two as answer to short question)

Ans: Following are the characteristics of a catalyst:

1. A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state. MnO_2 is added as a catalyst for the decomposition

of KClO_3 in the form of granules. It is converted to fine powder at the end of reaction. It has been found in many cases that the shining surfaces of the solid catalyst become dull.

2. Sometimes, we need a trace of a metal catalyst to affect very large amount of reactants. For example, 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water.

Dry HCl and NH_3 don't combine, but in the presence of trace of moisture, they give dense white fumes of NH_4Cl . Thousands of dm^3 of H_2O_2 , can be decomposed in the presence of 1 g of colloidal platinum.

3. A catalyst is more affective, when it is present in a finely divided form. For example, a lump of platinum will have much less catalytic activity than colloidal platinum. In the hydrogenation of vegetable oils finely divided nickel is used.

4. A catalyst cannot affect the equilibrium constant of a reaction but it helps the equilibrium to be established earlier. The rates of forward and backward steps are increased equally.

5. A catalyst cannot start a reaction, which is not thermodynamically feasible. It is now considered that a catalyst can initiate a reaction. The mechanism of a catalyzed reaction is different from that of an uncatalyzed reaction.

47. Enzymes are specific in action. Justify.

Ans:

Enzymes function in the lock and key mechanism. A specific enzyme can combine with a specific substrate having complementary structure. This is called lock-key mechanism of enzyme action.

48. Differentiate between rate and rate constant of reaction?

Ans:

Rate	Rate constant
<p>The rate of a reaction is defined as the change in concentration of a reactant or a product divided by the time taken for the change.</p> <p>Rate of reaction</p> $= \frac{\text{Change in concentration of the substance}}{\text{time taken for the change}}$	<p>The ratio between rate of reaction and concentration of reactants is called rate constant.</p> <p>‘The specific rate constant of a chemical reaction is the rate of reaction when the concentrations of the reactants are unity’.</p>
<p>Calculation of rate:</p> <p>It is calculated as follows</p> $\text{Rate of reaction} = \frac{\text{Change in concentration of reactant or product}}{\text{time taken for the change}}$	<p>Calculation of rate constant(k):</p> <p>It is calculated from rate equation of a reaction.</p>

49. The unit of rate constant of a second order reaction is $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ but, but the unit of rate of reaction is $\text{mol dm}^{-3} \text{s}^{-1}$.

Ans:

$$\text{Rate} = \frac{\Delta[\text{C}]}{\Delta t} = \frac{\text{mole dm}^{-3}}{\text{s}} = \text{mol dm}^{-3} \text{s}^{-1}$$

In case of second order reaction is

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

$$k = \frac{\text{Rate}}{[\text{A}][\text{B}]} = \frac{\text{mol dm}^{-3} \text{mol}^{-1} \text{s}^{-1}}{\text{mol dm}^{-3} \text{mol dm}^{-3}}$$

$$k = \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$$

50. Rate of chemical reaction is an every changing parameter and decreases under the given conditions.

Ans: According to the Law of mass action rate of reaction is directly proportional to concentration of reactants. In all reactions, concentration of reactants decreases with the passage of time. With the decrease in concentration of reactants rates shall also show continuous decrease from start till completion of reaction. This justifies the rate of reaction is an ever changing parameter.

51. The sum of the coefficient of a balanced chemical equation is not necessarily important to give the order of a reaction.

Ans: Rate of reaction is an experimentally determined quantity. It cannot be predicated from balanced chemical equation. The order of reaction is determined from experimentally obtained rate equation. Through balanced chemical equation we can only calculate the molecularity of reaction.

Example:

Consider the decomposition of N_2O_5 .



Apparently it seems to be 2nd order reaction but experimentally determined rate equation is:

$$\text{Rate} = k [\text{N}_2\text{O}_5]$$

It indicates that it is first order reaction.

52. Explain that the half-life method for measurement of the order of a reaction can help us to measure the order of even those reactions which have a fractional order.

Ans: Following equation is used to calculate order (n) of any reaction including fractional order.

$$n-1 = \frac{\log \left[\frac{t_1}{t_2} \right]}{\log \left[\frac{a_2}{a_1} \right]}$$

$$n = 1 + \frac{\log \left[\frac{t_1}{t_2} \right]}{\log \left[\frac{a_2}{a_1} \right]}$$

The values of following parameters must be known, a_1 (concentration of reactant in the first experiment), a_2 (concentration of reactant in the second experiment), t_1 (half-life of reaction in the first experiment) and t_2 (half-life of reaction in the first experiment).

53. A finely divided catalyst may prove more effective. Justify.

Ans: A catalyst is more effective when it is present in a finely divided form. For example a lump of platinum will have much less catalytic activity than colloidal platinum. In the hydrogenation of vegetable oils finely divided nickel is used.

54. 50% of a hypothetical first order reaction completes in one hour. The remaining 50% needs more than one hour to complete.

Ans: First order reaction is independent of concentration of reactant. Suppose initial amount of reactant is 1 mol dm^{-3} and half-life of reaction is 1 hour.

When time according to half-life (1Hour) shall pass the concentration of reactant will be 0.5 mol dm^{-3} . After next hour i.e. after 2 hours the concentration of reactant shall decrease to 0.25 mol dm^{-3} . This will continue till completion of reaction.