EXERCISE

MULTIPLE CHOICE QUESTIONS

1: Choose the correct answer

(1) The rate of a reaction…………..as the reaction proceeds.

(a) Increases   (b) Decrease

(c) Remains the same   (d) May increase or decrease.

(ii) The unit of the rate constant in the same as that of the rate of

reaction in…………..order reaction.

(a) First   (b) Second

(c) Third   (d) Zero.

(iii) For the reaction

2A + B ⟶ C

The rate law of the reaction is,

(a)Rate=k[A]^2[B]   (b) rate=k[A][B]

(c) Rate=k[C]   (d) None

(iv) For the reaction 2A + B ⟶ C + D

The expression for the rate law is, Rate=k[A]^2, the order of reaction in B is

(a) First   (b) Second

(c) Third   (d) None of these

(v) The activation energy for a reaction can be

(a) Increased by increasing temperature

(b) Increased by decreasing temperature

(c) Decreased by increasing concentration of reactants

(d) None of these

(vi) Rate law for the reaction

$R\text{-}X + H_2O \longrightarrow R\text{-}OH + HX$ is, rate=k[R-X]

The rate of reaction will be doubled when

(a) Concentration of H2O is doubled

(b) Concentration of R-X is reduced to half

(c) Concentration of both R-X and H2O is doubled

(d) None of these

(vii) The rate of a catalyzed reaction is independent of the concentration of

(a) Reactants   (b) Products

(c) Catalyst   (d) None of these

(viii) If a reaction proceeds in such a way that order of reaction is independent of the reactants concentration, the overall order of reaction would be

(a) First   (b) Second

(c) Third   (d) Zero

(ix) Reactions with high activation energy are usually

(a) Fast   (b) Slow

(c) Exothermic   (d) Reversible

(x) In a reversible reaction catalyst lowers the activation energy of the

(a) Forward reaction

(b) Reverse reaction

(c) Forward as well as reverse reaction

(d) Forward reaction but increases for the reverse reaction

Answer

i. d	ii. d	iii. a	iv. d	v. d	vi. d	vii. c
viii. d	ix. b	x. c				

2. What is chemical kinetics? How do you differentiate chemical kinetics from chemical equilibrium?

Ans: Chemical Kinetics:

The study of rates of chemical reactions and the factors that affect the rates of chemical reactions is known as kinetics or chemical kinetics.

Chemical equilibrium	Chemical kinetics
i. It is a state at which the reactants and the products do not change their concentration	i. It is branch of chemistry that deals with the study of rates of chemical reaction and the factors that affect the rates of chemical reactions
ii gives us information about the reaction mechanism. .	ii. It is only related with reversible reactions

3. Explain the significance of the rate determining step on the overall rate of multi-step reaction.

Ans: Rate Determining Step:

"The slowest step of a reaction mechanism which determines the overall rate of reaction is called as rate determining step."

Significance:

A reaction may occur in a single step or in many steps. When the reaction proceeds through two or more steps, one of the steps is the slowest

The rate of the slowest step determines the overall rate of reaction. This is because it places a limit on the rate at which the overall reaction can occur. No reaction can proceed faster than the rate-determining step. All the other steps of the reaction mechanism are generally fast.

4. Explain effects of concentration, temperature and surface area on reaction rates.

Ans: 1) Nature of Reactants:

Chemical reactivity:

i. The chemical reactivity of elements is based on their electronic configurations.

ii. Alkali metals have one electron in their outer most s orbital.

iii. They are highly electropositive; react with water violently as compared to alkaline earth metals.

iv. Alkaline earth metals have two electrons in their outermost s-orbital and are less electropositive than alkali metals.

Ionic and covalent reactions:

Reactants having ionic bonds undergo faster reactions than those having covalent bonds.

Reason:

This is because ionic reactions involve the combination of opposite ions, without involving rearrangement of electronic cloud. Whereas, the reaction

between covalent molecules involves electronic redistribution, proceed slowly.

2) Concentration of Reactants:

The rate of a chemical reaction depends upon the collisions among the reacting molecules.

The frequency with which the molecules collide depend upon their concentrations.

iii. This fact is expressed by the law of Mass Action.

iv. It states that the rate of chemical reaction is proportional to the product of molar concentration of the reactants.

vi. Hence, the higher the concentration, the greater the rate of reaction.

Examples:

A mixture of H2 and Cl2 will react twice as fast if the partial pressure of H. or Cl2 is doubled in the presence of excess of the other component. Combustion occurs more rapidly in pure oxygen than in air (21% oxygen).

Limestone ($CaCO_3$) reacts al different rales with different concentrations of HCl. Quantitatively the effect of concentration on reaction rate is expressed by order of the reaction with respect to each reactant.

3) Surface Area:

The basic concept of collision theory is that reactant particles atoms, ions and molecules must collide with each other in order to react.

The rate of a reaction increases with increasing surface area of reactants.

Reason:

This is because increased surface area of reactants increases the possibilities of contacts between their particles. Finely divided solid, therefore react more rapidly than its big pieces.

Examples:

i. Powdered zinc reacts more rapidly with dil HCl than a large piece of zinc.

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$$

The reason is that powdered zinc exposes a greater surface area to collide with HCl molecules.

This increases the number of collisions between the reacting particles, since rate of a chemical reaction depends upon the collision among the reacting molecules. Thus increase in number of collisions increase the reaction rate. Hence powdered zinc reacts faster.

ii. For the same reason aluminium foil reacts with NaOH moderately on warming but powdered aluminium reacts rapidly with cold NaOH.

$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)}$ i. $2Na[Al(OH)_4]_{(aq)} + 3H_{2(g)}$

4) Temperature:

i. Reaction rates generally increase with the increase in temperature

ii. According to the collision theory, the rate of a reaction is proportional to the number of collisions among the reactant molecules.

iii. An increase in temperature increases the average kinetic energy of the molecules This increases average speed of reacting molecules.

iv. An increase in kinetic energy of reactant molecules increases the collision frequency i.e. the number of effective collisions and hence the reaction rate However, only effective collisions bring about the reaction.

Conditions for effective collision:

For a collision to be effective molecules must possess

i. The activation energy

ii. Must be properly oriented

Maxwell Boltzmann curve of kinetic energy:

At ordinary temperature very few molecules possess the energy of activation

All the molecules of a reactant do not possess the same energy at a particular temperature. Most of them possess average energy A fraction of molecules have kinetic energy more than the average energy. The number of molecules having at least kinetic energy equal to Ea at temperature Tis proportional to the shaded area

under the Maxwell Boltzmann curve of kinetic energy.

As the temperature is increased the area of the shaded region increases and more molecules have kinetic energy greater than Ea. An increase in temperature increases the number of reactants molecules that have enough energy for effective collision. It is found that in general the reaction rate increases two to three folds for each 10K increase in temperature.

5. Explain the terms rate of reaction, rate equation, order of reaction, rate constant, rate determining step, activation energy, catalysis and enzymes

Ans: Rates of Reactions:

The rate of reaction is the change in concentration of reactants or products per unit time

OR

"The rate of reaction is defined as the instantaneous change in concentration of a reactant or product at a given time".

Mathematically:

Rate =Change in concentration of a substance/Time taken for change

As the concentration of reactants decreases and concentration of products increases with the passage of time. Therefore, rate of a reaction can also be defined as-
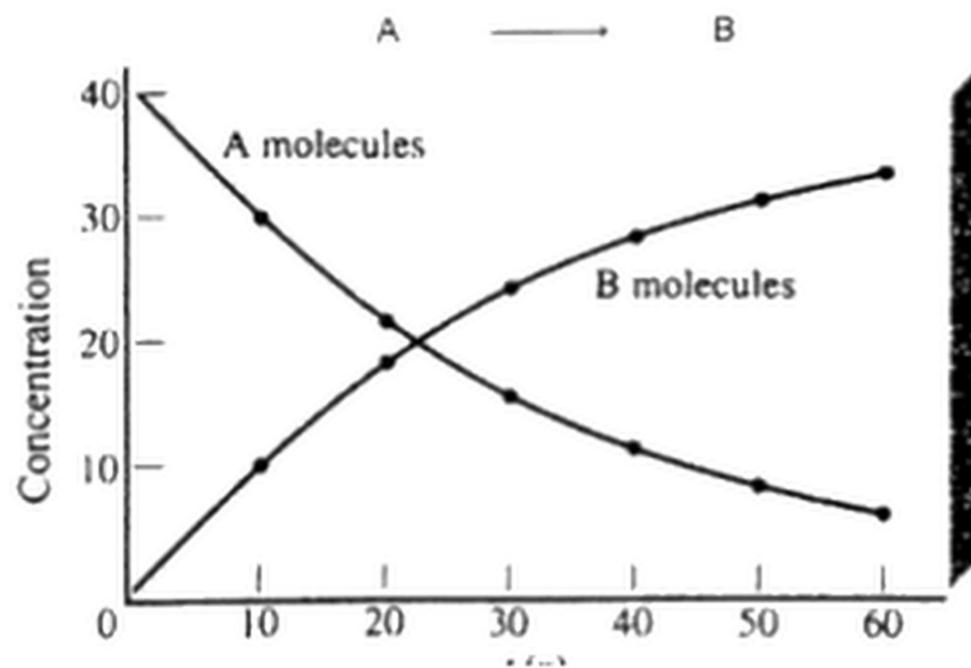
The decrease in concentration of reactants per unit time or the increase in concentration of products per unit time.

Units:

The unit of concentration is mole dm and lime is second, so unit of reaction rate is mole. dm 's-1

Graphical representation:

The change in concentration of reactants and products can be represented graphically for the general reaction

Change in concentration of reactants and products with passage of time

Explanation:

The slope of the graph for both, the reactants and products is steeper in the beginning then al the later stages. This indicates the rapid decrease or increase in concentration of reactant or product respectively.

As the reaction proceeds, the slope becomes less steep showing decrease in rate of reaction. Finally the graph becomes horizontal and the reaction stops the rate of reaction is never uniform.

Concentration of reactants continuously decreases while those products increase with the passage of time. Therefore, the rate of reaction also decreases continuously

Rate Equation:

"An equation that expresses the rate of a reaction in terms of the concentration of reactants is called the rate law or rate equation for the reaction."

Explanation:

For a general reaction

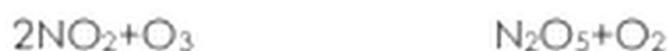A   Product

Rate $\propto$ $[A]^x$

Rate = $k\,[A]^x$

Where k is proportionality constant and is known as rate constant and the expression as rate law or rate equation.

The exponent x in the rate equation is called order of reaction with respect to reactant A.

The exponent can be determined only with the help of experiments

Example:

For the reaction

$2NO_2 + O_3$ $N_2O_5 + O_2$

Experimental studies show that the rate$=k[NO][O_3]$

Therefore rate law or rate equation for the above equation is

rate$=k[NO_2][O_3]$

order of reaction:

order of reaction may be defined as the number of molecules participating in rate determining step.

Explanation:

Consider a general reaction between a moles of A and b moles of B to give mole C and d moles of D.

$aA + bB \longrightarrow cC + dD$

Rate $\propto [A]^x [B]^y$

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

The exponent 'x' is the order of reaction with respect to species A' and exponent is the order of reaction with respect to species 'B'.

Order of the reaction expresses the effect of concentration on the rate of reaction

The sum 'x+y' is called the overall order of the reaction or simply order of the reaction.

"Order of reaction may be defined as the sum of all the exponents to

which the molar concentration terms in the rate equation are raised".

~~x and y may~~ or may not be same as a and b respectively The order of a reaction for a particular species cannot be predicted by looking at the balanced chemical equation it can be determined only by experiment.

For example for the reaction

$$2NO_2 + O_3 \qquad N_2O_5 + O_2$$

Experimental studies show that the Rate=$k[NO_2][O_3]$

Notice that the order with respect to NO, is one whereas the stoichiometric coefficient is two. The order of reaction with respect to O, is also one

Overall order of reaction is two So. the above reaction is second order reaction

Rate constant:

For a general reaction:

A   Product

Rate $\propto [A]^x$

Rate $= k[A]^x$

Where k is proportionality constant and is known as ratio constant and the expression as rate law or rate equation.

When (A) = 1 M

Rate = k

Thus, the rate constant may be defined as the rate of reaction when molar concentration of each of the reactant is unity.

Importance:

Rate constant provides a link between concentration and the rate of reaction Every reaction has its own characteristic rate constant independent of concentration and time. However, value of rate constant changes with temperature

Rate determining step:

"The slowest step of a reaction mechanism which determines the overall rate

of reaction is called as rate determining step.

Explanation:

The path followed by the reactants in forming the products in a chemical reaction is called the mechanism. The rate equation for a reaction is very useful because it provides information about the mechanism of the reaction. A reaction may occur in a single step or in many steps. When the reaction proceeds through two or more steps, one of the steps is the slowest.

Reason:

The rate of the slowest step determines the overall rate of reaction. This is because it places a limit on the rate at which the overall reaction can reaction can proceed faster than the rate-determining step. All the other steps of the reaction mechanism are generally fast

Activation energy:

The minimum amount of energy in addition to average kinetic energy which the particles must possess for effective collision is called activation energy

Catalysis:

A substance which accelerates a chemical reaction but remains chemically unchanged at the end of a reaction is called as catalyst.

Effect of Catalyst on energy of activation
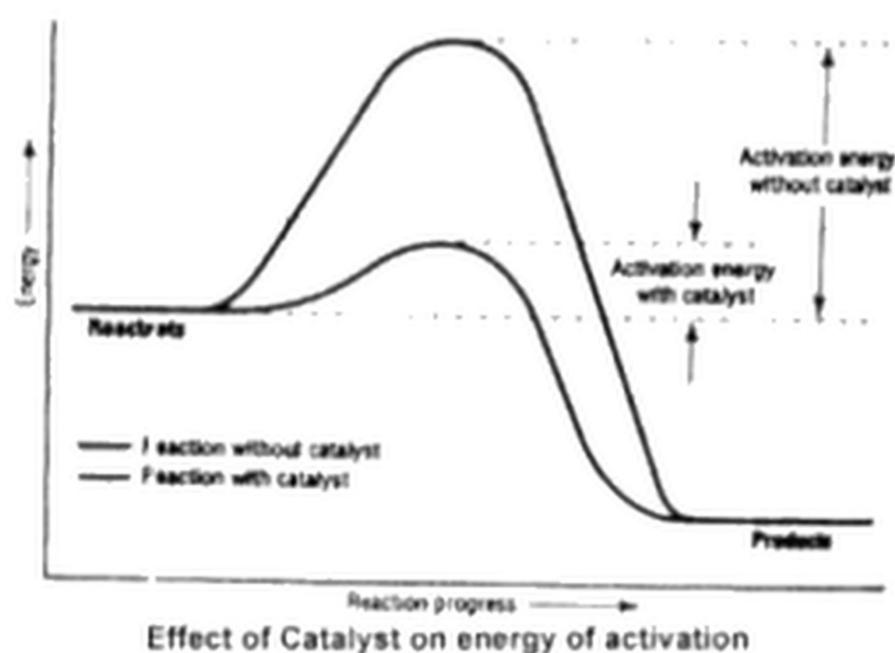
Explanation:

A catalyst provides a new mechanism for the reaction with low energy of activation. Thus catalyst increases the rate of reaction by increasing it energy of activation. A catalyst has no effect on the total thermodynamic or enthalpy of the reaction For this reason a catalyst cannot be used to bring about a chemical reaction, which is not favored thermodynamically.

Enzymes:

These are biochemical catalysts i.e., substances that increase the rate of chemical reactions within living things.

Most of the chemical reactions that occur in living organisms are regulated by molecules called enzymes

Explanation:

Enzymes like catalysts are not consumed during chemical reactions. Virtually all reactions in living cells are catalyzed by enzymes. An enzyme is a specialized protein that catalyzes specific biochemical reaction. Each enzyme catalyzes only one reaction.

6. Relate the ideas of activation energy and the activated complex to the rate of a reaction.

Ans: Activation Energy:

The minimum amount of energy, in addition to the average kinetic energy. which the particles must possess for effective collisions is called activation energy

Explanation:

The reaction will not occur if the energy of reacting particles in less than activation energy.

Thus the rate of a reaction depends upon its energy of activation. The greater the activation energy, the lesser will be the rate of reaction. This is because only a small fraction of molecules possesses enough energy to react. On the other hand, if activation energy is small then a large number of molecules can bring

about effective collisions. Hence, higher will be the rate of reaction.

Consider a reaction between Az and B2 molecules to form a new molecule AB

I these molecules possess energy equal to or more than the activation energy, then

upon collisions their bonds will break and new bonds will be formed

Activated complex or Transition state:

In an effective collision the molecules form an unstable species called

activated complex. Since it is high a energy species, it is short lived and quickly

breaks down to the products. Activated complex is also called a transition state

Reactants   Activated Complex Products
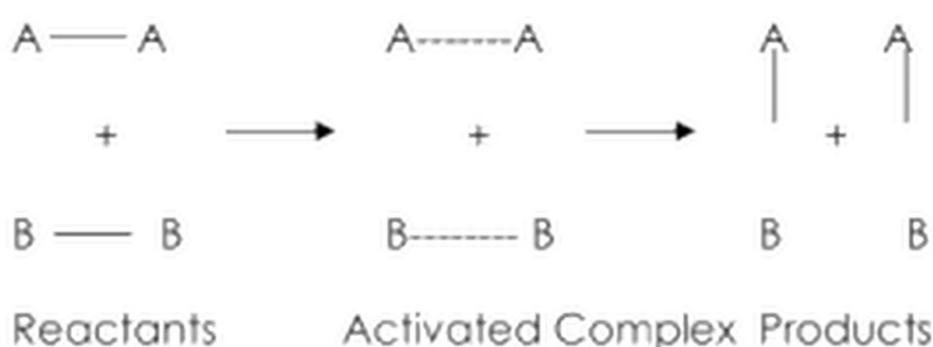
Effective collision of molecules

Explanation of effective collision:

in an effective collision the colliding molecules come close to each other, slow

down just before collision. Their kinetic energy decreases and this results in the

corresponding increase in their potential energy. The activation energy appears as

a hill between reactants and products. Molecules must first climb the energy barrier

before they can roll down the hill to form products Only the colliding molecules with

proper activation energy do so. On the other hand if they lack proper activation

energy, they will be unable to reach the top of the hill and fall back chemically

unchanged.

Potential energy diagram for exothermic reaction:

The potential energy diagram can a so be used to understand the enthalpy

changes in chemical reactions. The heat of reaction is equal to the difference of

energies of reactants and products in an exothermic reaction product are at a

lower energy level than the reactants. In both exothermic and endothermic

reactions activation energy (Ea) is an energy barrier which must be crossed over before the products can be formed. If energy of activation is not available to the reacting particles, the reaction will not start.

Potential energy diagram for endothermic reaction

In endothermic reactions a continuous source of energy is needed to complete the reaction in an endothermic process the products are at higher energy level than the reactants. Fig shows energy profile for exothermic and endothermic reactions.

(a)   Reaction path →   (b)   Reaction path →
(a) Exothermic reaction   (b) Endothermic reaction
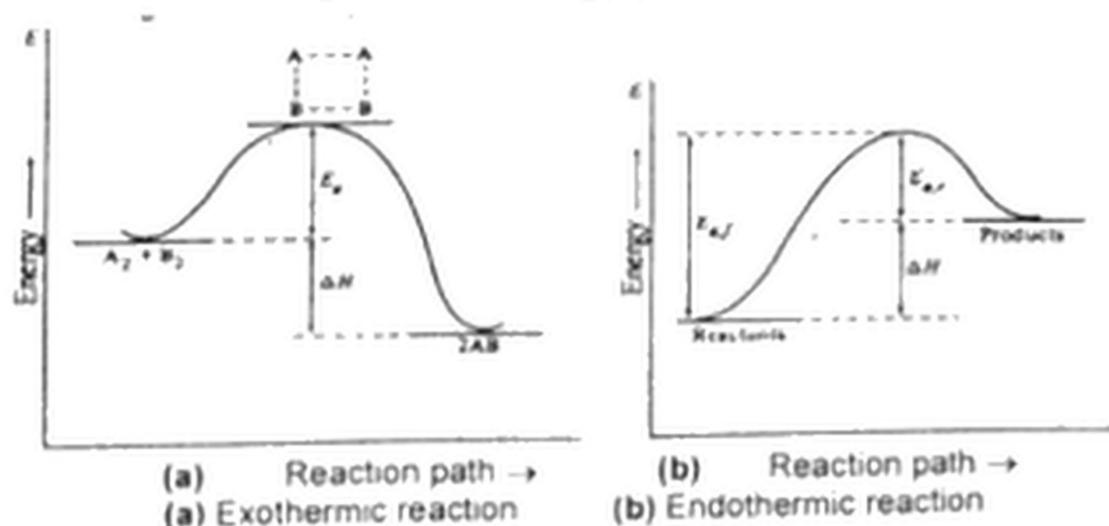
7. Describe that increase in collision energy by increasing the temperature can improve the collision frequency.

Ans: Temperature:

i. Reaction rates generally increase with the increase in temperature.

ii. according to the collision theory, the rate of a reaction is proportional to the number of collisions among the reactant molecules.

iii. An increase in temperature increases the average kinetic energy of the molecules. This increases average speed of reacting molecules

iv. An increase in kinetic energy of reactant molecules increases the collision frequency ie, the number of effective collisions and hence the reaction rate. However, only effective collisions bring about the reaction

Conditions for effective collision;

For a collision to be effective molecules must possess

i. The activation energy

ii. Must be properly oriented.

8. Draw energy diagrams that represent the activation energy and show the effect of a catalyst.

Ans: The diagram shows that the catalyst lowers the activation energy and provides a new mechanism for the reaction. Thus catalyst increases the rate of reaction by decreasing the activation energy.
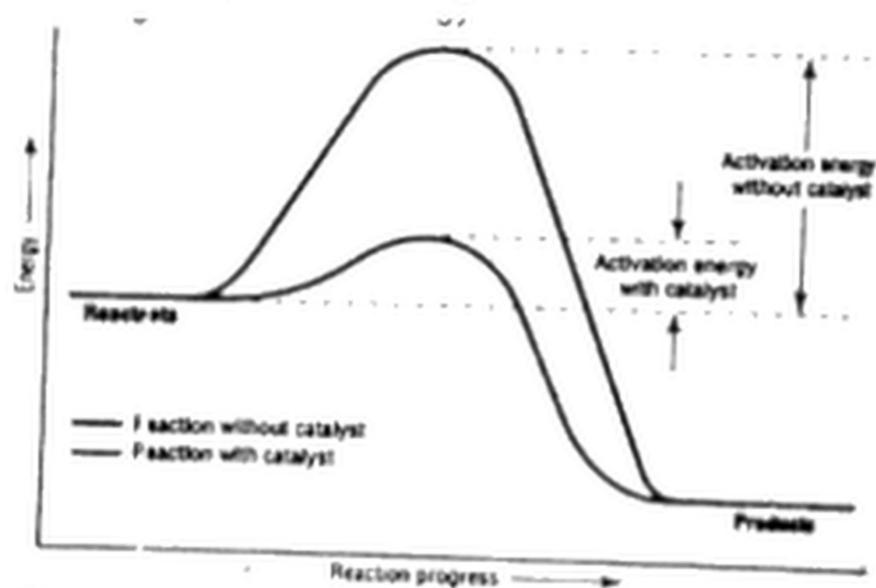
9. Reaction progress

Following curve represent the variation of energy with reaction co-ordinate for a reaction.
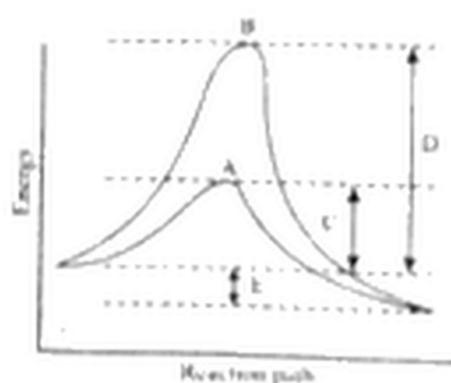
(a) of the curves A and B, one represent the catalyzed and one uncatalyzed reaction, identify A and B

(b) What are the quantities C, D and E.

Ans:

(a) Curve A represents the catalyzed reaction and curve B represents the uncatalyzed reaction.

(b) C represents the activation energy after catalysis.

D represents the activation energy without catalysis.

E represents the enthalpy change of the reaction. It shows that the energy evolved during the reaction as the reaction is exothermic.

10. What is the effect of a catalyst on the following?

(a) The rate of reaction

(b) The energy of activation

(c) The equilibrium position of a reversible reaction

Ans: (a) The rate of reaction:

Rate of reaction increases in presence of catalyst. As catalyst decrease the activation energy therefore they increase the rate of reaction.

(b) The energy of activation:

Catalyst decreases the Energy of activation by providing a new mechanism for the reaction having low energy of activation

(c) The equilibrium position of a reversible reaction:

Catalyst increase the rate of both forward and reverse reaction to the same degree and therefore they have no effect on the equilibrium position of a reversible reaction

11. The reaction of an alkyl halide, R-X with water is as follows

$$R\text{-}X + H_2O \longrightarrow R\text{-}OH + HX$$

If the reaction were a single step process, what would you predict the rate law to be?

Ans: As the reaction occurs in one step so that step is the rate determining step.

According to rate determining step the reaction is first order in both R-X and H_2O

Therefore the rate equation will be

Rate =k [R-X][H_2O]

Order of reaction =1+1=2

So in this case the reaction is second order.

But in these reactions water is generally in large excess. So the rate is independent of its concentration thus the rate equation will become.

Rate =k[R-X]

Order of reaction = 1

So in this case reaction becomes first order.

$\longrightarrow$

12. The reaction of a compound A and B to give C and D was found to be second order in A and second order overall. Write rate expression for the reaction.

Ans: =A+B $\longrightarrow$ C+D

According to the given condition the rate expression for the reaction will be

Rate=k$[A]^2[B]°$

Rate=k$[A]^2$

Overall order of reaction = 2 + 0 = 2.

13. Explain why?

(a) A very small amount of catalyst may prove sufficient to carry out a reaction.

(b) The reaction rate decreases every moment.

(c)The unit of rate constant of a second order reaction is $dm^3 mol^{-1} s^{-1}$

Ans.

(a) A very small amount of catalyst may prove sufficient to carry out a reaction.

Catalysts are always added in small amount because they do not consume during a reaction and remained chemically unchanged at the end of reaction that is why a very small amount of catalyst may be sufficient to carry out a reaction

(b) The reaction rate decreases every moment.

Consider a general reaction and its graphical representation.

A ⟶ B
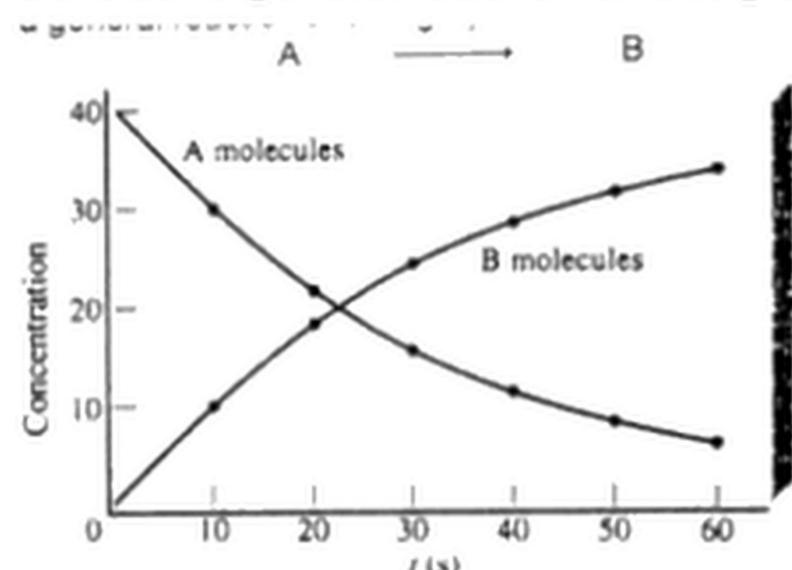
Change in concentration of reactants and products with passage of time

Explanation:

As the reaction proceeds, the stope becomes less steep showing decrease in reaction Finally the graph becomes horizontal and the reaction stops. Thus the rate of reaction is never uniform.

Concentration of reactants continuously decreases while those products increase with the passage of time. Therefore, the rate of reaction also decreases continuously

Conclusion:

Thus the reaction rate decreases every moment and becomes very slow at the end of reaction.

(c) The unit of rate constant of a second order reaction is dm moles.

For a second order reaction, consider a general reaction.

$A + B \longrightarrow C + D$

The rate of react on is directly proportional to the concentration of two

reactants

Rate = K[A] [B]

where 'k' is the rate constant.

$$K = \frac{Rate}{[A][B]}$$

The unit of rate = $mol\, dm^3\, sec^{-1}$

The unit concentration of A and B = mol dm3

Thus units of k will be

$$K = \frac{Rate}{[A][B]} = \frac{mol\, dm^3\, sec^{-1}}{mol\, dm^3 \times mol\, dm^3} = dm^3 mol^{-1} sec^{-1}$$

14. From the equation proposed for the gas phase reaction of NO, with CO, predict the rate law for the reaction. What is the stoichiometric equation for the reaction. Identify reaction Intermediate and write rate law for the reaction.

$NO_2 + NO_2 \longrightarrow NO_3 + NC$

$NO_3 + CO \longrightarrow NO_2 + CO_2$

Ans: Rate Law:

The slowest step of the react on mechanism determines the overall rate of the reaction. According to the slowest step two molecules of NO, are involved in the rate-determining step thus the rate law will be

Rate =k[NO_2]²

Overall order of reaction = 2

Stoichiometric Equation

$NO_2 + NO_2 \longrightarrow NO_2 + NO$

$NO_2 + CO \longrightarrow NO_2 + CO_2$

$$NO_2 + CO \longrightarrow NO + CO_2$$

Reaction Intermediate:

As the specie NO, produce and consume during the course of reaction and does not appear in the overall reaction. So it is the reaction intermediate

15: For the reaction

A + 8 → AB

The following data were obtained for the reaction

Experiment	Initial conc. (mole dm^3)		Initial rate (mole $dm^{-3} s^{-1}$)
	[A]	[B]	
1	0.10	0.01	1.00×10^{-5}
2	0.10	0.02	2.00×10^{-5}
3	0.20	0.01	2.00×10^{-5}
4	0.30	0.02	6.00×10^{-5}

What is the rate equation for the reaction? (Ans: Rate $\propto$ [A][B]

Solution:

i. According to the given data in experiments 1 and 2, initial concentration of IA) is kept constant at O 10 M and we increase the concentration of (B) twice le from 0.01 M to 0.02 M. Thus the initial rate also increases from 1.00×10^{-5} to 2.00×10^{-5} mole $dm^{-3} s^{-1}$

ii. The ratio between these rates will be

$$1.00 \times 10^{-5} : 2.00 \times 10^{-5}$$

$$\frac{1.00 \times 10^{-5}}{1.00 \times 10^{-5}} : \frac{2.00 \times 10^{-5}}{1.00 \times 10^{-5}}$$

$$1 : 2$$

So, when the concentration of B is doubles, the rate of reaction also doubles

It shows that the rate of reaction is proportional to the first power of concentration of [B]

Rate $\propto$ [B]

iii. In Experiments 1 and 3, initial concentration of B is kept constant at 0.01 M and concentration of (A) is doubled i.e. from 0.10 M to 0.20 M. The initial rate increases from 1.00×10^{-5} to 2.00×10^{-5} mole dm^{-3}s^{-1}

iv. The ratio between these rates is

$$1.00 \times 10^{-5} : 2.00 \times 10^{-5}$$

$$\frac{1.00 \times 10^{-5}}{1.00 \times 10^{-5}} : \frac{2.00 \times 10^{-5}}{1.00 \times 10^{-5}}$$

$$1 : 2$$

So, when the concentration of A is doubles the rate of reaction also doubles.

It shows that the rate of reaction is proportional to the first power of concentration of [A]

Rate equation:

So the rate equation for the above reaction is

Rate $\propto$ [A][B]

Rate $= k$[A][B]

The overall order of reaction is 1+1 = 2 (second order reaction)

16. Explain why powdered Zn reacts faster with an acid than a piece of Zn.

Ans: Powdered zinc reacts more rapidly with acid than a piece of zinc. Consider the reaction of zinc with dil. HCl.

$Zn_{(s)} + 2HCl_{(aq)} \qquad ZnCl_{2(aq)} + H_{2(g)}$

Reason:

The reason is that powdered zinc exposes a greater surface area to collide with HCl molecules. This increases the number of collisions between the reacting particles, since rate of a chemical reaction depends upon the collision among the reacting molecules. Thus, increase in number of collisions increase the reaction rate. Hence powdered zinc reacts faster.

17. The rate for the reaction:

$$CO(g) + NO_2 \longrightarrow CO_2(g) + NO(g)$$

at 200^0C is rate $=k[NO_2]^2$ Is the following mechanism consistent with this rate law.

$$2NO_2 \longrightarrow N_2 + 2O_2$$

$$2CO + O_2 \longrightarrow 2CO_2$$

$$N_2 + O_2 \longrightarrow 2NO$$

Ans: The mechanism may be correct if it satisfies the following two conditions. The rate equation shows that in the slowest step two molecules of NO, are involved. The given mechanism is also showing two molecules of NO, in the slow step. So the mechanism satisfies this condition

$$2NO_2 \longrightarrow N_2 + 2O_2$$

$$2CO + O_2 \longrightarrow 2CO_2$$

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO_2 + 2CO \longrightarrow 2NO + 2CO_2$$

The overall equation is not equal to the original equation. Thus, the mechanism does not satisfy this condition.

Conclusion:

The mechanism is incorrect.

18. Predict the rate law for the oxidation of the iodide ton by hypochlorite.

$I^-(aq) + ClO^-(aq) \longrightarrow Cl^-(aq) + IO^-(aq)$

If the reaction proceeds by the following mechanism.

$ClO^- + H_2O \longrightarrow HOCl + OH^-$

$I^- + HOCl \longrightarrow HOI + Cl^-$

$HOI + OH^- \longrightarrow IO^- + H_2O$

Ans: Solution:

The slowest step of the reaction mechanism determines the overall rate of

the reaction. According to the slowest step one Ciolino and one H2O molecule are

participating in the rate determining step, therefore, the rate law is

Rate =k [ClO^{-1}][H$_2$O]

Overall order of reaction = 1+1 = 2 (second order reaction)