CHAPTER # 9
CHEMICAL KINETICS

Q1. What information we get from thermodynamics and why it is not enough to understand the stoichiometry and thermodynamics of a reaction?

Ans: Thermodynamics, can tell us whether a reaction occurs spontaneously or not. For example, thermodynamics tells us that the following reaction is highly spontaneous at room temperature and 1 atm pressure.

$$H_2 (g) + \frac{1}{2} O_2 (g) \longrightarrow H_2O (l) \qquad \Delta H = -285.6 \text{ K J mole}^{-1}$$

Explanation:

If we mix these gases under these conditions, we will have to wait a very long time for the reaction to occur. Even a life time would not be long enough to observe any change in the reactants. However, if an electric spark is passed through the mixture, a reaction will occur with explosive violence.

Thus it is **not enough** to understand the stoichiometry and thermodynamics of a reaction.

We must also understand the factors that affect the **rate of the reaction**.

Chemical kinetics:

The branch of Chemistry that concerns reaction rates and factors affecting reaction rates is chemical kinetics.

Q2. Define chemical kinetics and also give its significance.

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**"

Rates of chemical reaction:

Chemical reactions occur at a variety of rates from very rapid to very slow.

Slow reaction:

Some reactions are very slow and may require several weeks to produce enough products.

Example:

Fermentation is a slow reaction,

Fast reaction:

Some reactions complete in few seconds these reactions are called fast reactions.

Example:

Acid-base neutralization reactions are completed in microseconds.

Moderate reactions:

Some reactions proceed at moderate speed and these reactions are called moderate reactions.

Example:

The reactions that contract muscles and transmit impulses along nerves and record photographic images are the examples of moderate reactions.

Significance:

In industry it is important to know the conditions under which the reaction will proceed most economically. Rate information is the most important kind of information used in the deduction of mechanism of a chemical reaction.

Mechanism:

Mechanism means sequence of all chemical steps which leads reactants to products.

Q3. Differentiate between average rate of reaction and instantaneous rate of reaction.

Ans:

Average rate of reaction	Instantaneous rate of reaction
i. "Thus rate of reaction between two specific time intervals is called the **average rate of reaction.**"	**i.** The rate of reaction at a particular instant of time is called **instantaneous rate of reaction**.
ii. The average rate of reaction over any time interval can be determined from the difference in concentrations divided by the difference between the measurement times.	**ii.** It is determined from the slope of tangent to the curve at that time.
iii. It is a constant value.	**iii.** In the beginning of the time intervals, the instantaneous rate is higher than the average rate. At the end of the interval, the instantaneous rate is lower than the average rate.
iv. It is represented by Average rate of reaction = $\frac{x_2 - x_1}{t_2 - t_1} = \frac{\Delta x}{\Delta t}$	**iv.** It is represented by Instantaneous rate of reaction = $\frac{dx}{dt}$

Note:

i. The average rate and the instantaneous rate are equal for only one instant in any time interval.

ii. As the time interval becomes smaller, average rate becomes close to the instantaneous rate.

iii. The average rate will be the same as instantaneous rate when the time interval approaches zero.

Q4. Write and explain the expression for the rate of reaction.

Ans: Rate of reaction:

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

Explanation:

If dx is very small change in concentration of a product in a very small time interval dt, the rate of reaction is expressed as:

Rate of reaction = dx / dt

Consider a general reaction

$$A \longrightarrow B$$

The rate of reaction can be expressed in term of the rate of disappearance of reactant A or the rate of appearance of product B.

$$\frac{dx}{dt} = -\frac{d[A]}{dt}$$

$$\frac{dx}{dt} = +\frac{d[B]}{dt}$$

Where d [A] and d [B] are the changes in the concentrations of A and B respectively.

The **negative sign indicates** a decrease in the concentration of the reactant A. whereas the **positive sign indicates** the increase in the concentration of product B.

Q5. How initial rates can be determined? Explain it with the help of following table which shows the concentration of phenolphthalein in a solution that was initially 0.005 M in phenolphthalein and 0.6 M in OH^- ions. When a solution that contains phenolphthalein in the presence excess base is allowed to stand for a few minutes, the solution which has initially a pink colour, it gradually turns colourless as the phenolphthalein reacts with OH^- ions in solution. Use this data to determine the initial rate.

Experimental data for the reaction between Phenolphthalein and excess Base.

Concentration of Phenolphthalein (M)	Time (s)
0.0050	0.00
0.0045	10.5
0.0040	22.3
0.0035	35.7
0.0030	51.1
0.0025	69.3
0.0020	91.6
0.0015	120.4
0.0010	160.9
0.00050	230.3

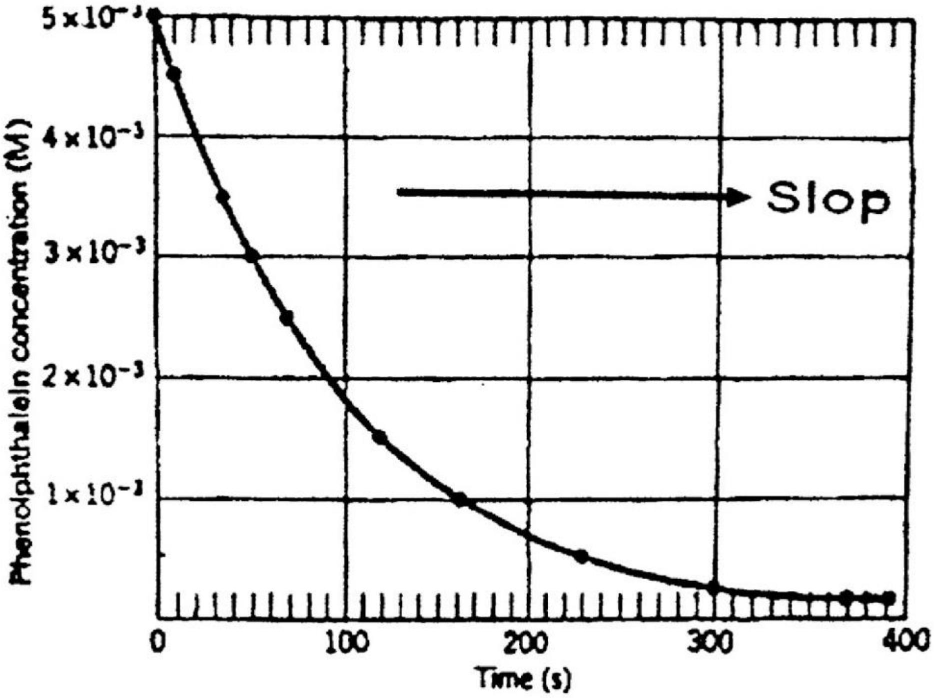
Ans: Determination of Initial Rates:

"Initial rate is the instantaneous rate at the moment the reactants are mixed (i.e. at t = 0)"

Under these conditions product concentrations are negligible. The initial rate is measured by determining the slope of line tangent to the curve at zero time.

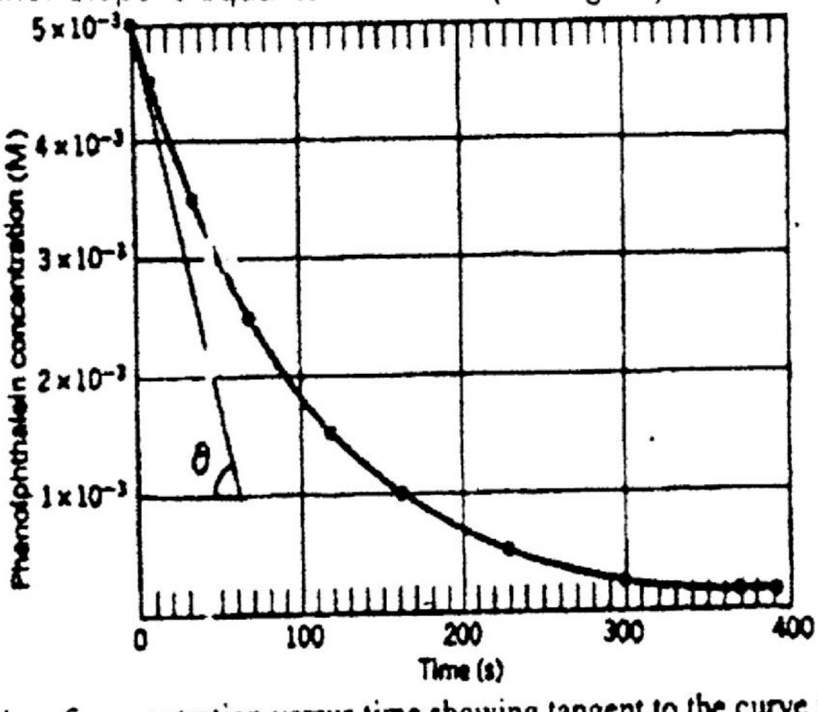
Explanation:

Plot a graph between time on *x*-axis and concentration of phenolphthalein on *y*-axis, following curve will be obtained.



A Plot of concentration versus time for the reaction between phenolphthalein and excess OH^- ions

Draw tangent to the curve through the point at which t = 0 and determine the slope of the line. Slope is equal to initial rate (see figure).



A Plot of concentration versus time showing tangent to the curve when t = 0 for the reaction between phenolphthalein and excess OH^- ions

$$\text{Slope} = \frac{\Delta x}{\Delta t}$$

$$= \frac{4\times10^{-3}}{60}$$

$$6.67\times10^{-5}\ \text{mole dm}^{-3}.\text{s}^{-1}$$

SELF-CHECK EXERCISE 9.1

Ethyl Iodide decomposes at a certain temperature as follows

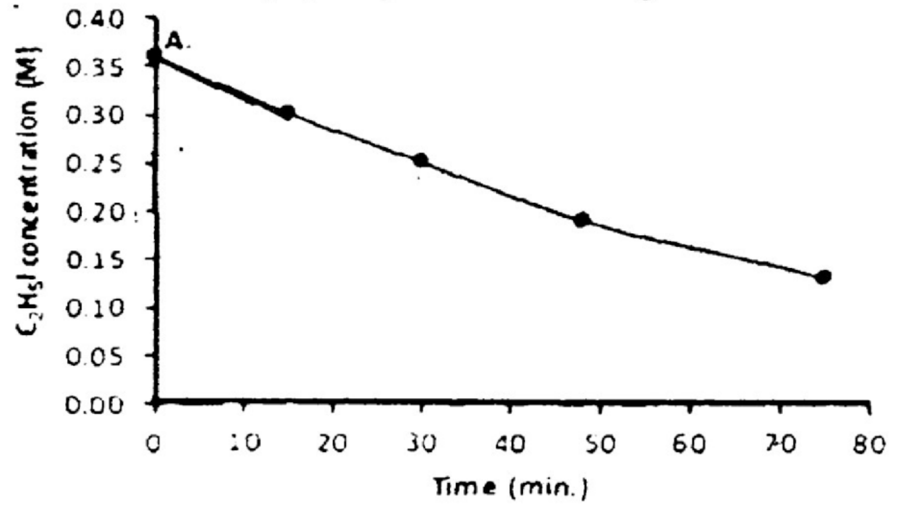
$$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$$

From the following data determine the initial rate of decomposition:

Time(min)	$[C_2H_5I]$ (M)
0	0.36
15	0.30
30	0.25
48	0.19
75	0.13

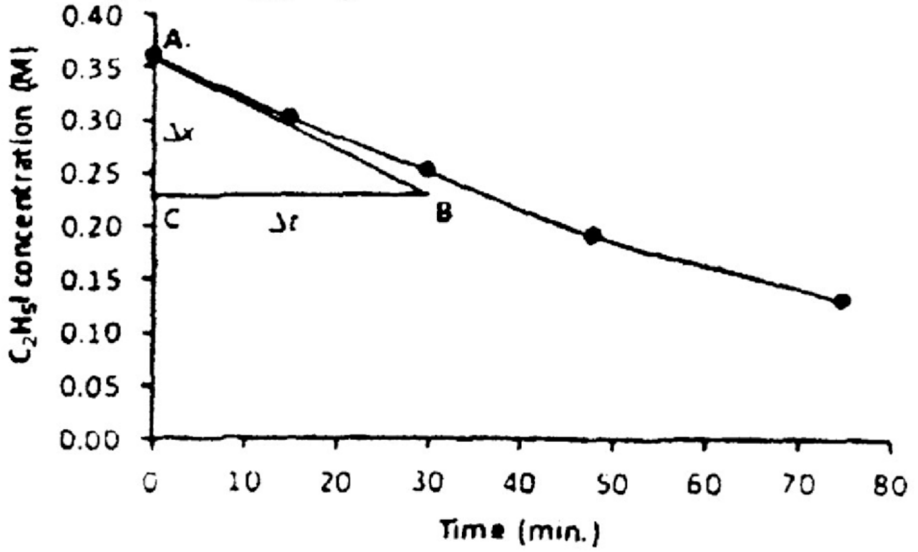
Solution:

(i) Plot a graph between time and concentration of C_2H_5I take time on on x-axis and concentration of C_2H_5I on $y-axis$ following curve will be obtained.



(ii) Draw tangent to the curve through the point at which t = 0 and determine the slope of the line. The slope of line is equal to initial rate.

$$Slope = \frac{\Delta x}{\Delta t} = \frac{0.36 - 0.23}{30 - 0} = 4.33 \times 10^{-3}\ mole\ dm^{-3}.min^{-1}$$



Q6. Explain zero order, first order and second order reactions with the help of examples.

Ans: Zero order reaction:

A reaction that is independent of the concentration of reactant molecules is called zero order reaction.

Examples:

i. An example is the decomposition of ammonia on heated tungsten.

$$2NH_{3(g)} \longrightarrow N_{2(g)} + 3H_{2(g)}$$

$$\text{Rate} = k\,[NH_3]^0$$

The concentration of ammonia decreases at a steady rate until it reaches zero.

ii. The combination of H_2 and Cl_2 in presence of sunlight is also a zero order reaction.

iii. The reactions catalyzed by enzymes also follow zero order kinetics.

First order reactions.

A reaction whose rate of reaction is directly proportional to the first power of concentration of single reactant molecule is called first order reaction.

$$\text{Rate} \propto [A]^1$$

Examples:

i) Thermal decomposition of N_2O_5

$$2N_2O_{5\,(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$$

$$\text{Rate} = k\,[N_2O_5]$$

ii) Decomposition of ammonium nitrite in aqueous solution.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

$$\text{Rate} = k\,[NH_4NO_2]$$

Second order reactions:

A reaction for which sum of exponents of rate equation is two is called second order reaction.

$$\text{Rate} \propto [A]^2 \text{ or Rate} \propto [A]^1\,[B]^1$$

Examples:

i. Decomposition of nitrogen dioxide.

$$2NO_{2(g)} \longrightarrow 2NO_{(g)} + O_{2(g)}$$

$$\text{Rate} = k\,[NO_2]^2$$

ii. $NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2\,(g)}$

$$\text{Rate} = k\,[NO]\,[O_3]$$

$$\text{Order of reaction} = 1 + 1 = 2$$

iii. $2NO_{2\,(g)} + O_{3\,(g)} \longrightarrow N_2O_{5\,(g)} + O_{2(g)}$

$$\text{Rate} = k\,[NO_2]\,[O_3]$$

Q7. Explain third order, fractional order and negative order reactions with the help of examples.

Ans: Third order reactions:

A reaction for which sum of exponents of rate equation is three is is called third order reaction.

$$\text{Rate} \propto [A]^3 \text{ or Rate} \propto [A]^2\,[B]^1 \text{ or Rate} \propto [A]^1[B]^1\,[C]^1$$

Examples:

i. The oxidation of NO by O_2 is an example of a third order reaction.

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

$$\text{Rate} = k\,[NO]^2\,[O_2]$$

ii. $$2FeCl_{3(aq)} + 6KI_{(aq)} \longrightarrow 2FeI_{2(aq)} + 6KCl_{(aq)} + I_{2(s)}$$

$$\text{Rate} = k\,[FeCl_3]\,[KI]^2$$

Fractional order reactions:

A reaction for which sum of exponents of rate equation is in fraction is called fractional order reaction.

Examples:

i) The reaction between H_2 and Br_2 to produce HBr is half order in Br_2 and first order in H_2.

$$H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$$

$$\text{Rate} = k\,[H_2]\,[Br_2]^{1/2}$$

Order of reaction is $1 + 0.5 = 1.5$

ii) $$CHCl_{3(l)} + Cl_{2(g)} \longrightarrow CCl_{4(l)} + HCl_{(g)}$$

$$\text{Rate} = k\,[CHCl_3]\,[Cl_2]^{1/2}$$

Negative order reaction:

A reaction for which sum of exponents of rate equation is negative is called negative order reaction.

Example: $$2O_{3(g)} \longrightarrow 3O_{2(g)}$$

$$\text{Rate} = k\,[O_3]^2\,[O_2]^{-1}$$

When the concentration of oxygen doubles, the rate becomes half.

SELF-CHECK EXERCISE 9.2

The following reaction is first order in H_2 and second order in NO. Write rate law for this reaction. $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$

Half-life of any reaction is defined as the period of time in which half of the concentration of reactants is converted to products.

Solution:

Given: First order in H_2 = Rate $\propto [H_2]$

Second order in NO = Rate $\propto [NO]^2$

Rate law will be: Rate $\propto [H_2]\,[NO]^2$

Rate $= k\,[H_2]\,[NO]^2$

Overall order of reaction = 1 + 2 = 3.

Thus it is a third order reaction.

Important Information

Cosmic rays of high penetrating power constantly bombard earth's atmosphere. These rays consist of electrons, neutrons and atomic nuclei. One of the important reactions between these rays and the atmosphere is the capture of neutrons by the atmospheric nitrogen, (N^{14}) to produce radioactive C^{14} isotope and hydrogen. C^{14} forms carbon dioxide, $^{14}CO_2$ which mixes with the ordinary carbon dioxide in the air. As the C^{14} isotope decays, it emits β-rays. The rate of its decay is measured by the number of electrons emitted per second. This decay obeys first order kinetics. The half-life of this decay is 5.75×10^3 years.

Q8. How can we determine order of reaction and rate law?

Ans: Determination of Reaction Order and Rate Law:

i. The effect of change in concentration of reactants on reaction rates cannot be deduced from a chemical equation.

ii. It can only be determined experimentally by determining the order of chemical reaction.

iii. For this purpose the method of initial rates is an easier way to find the value of the order of reaction.

iv. In this method an experiment is designed in which the concentration of one reactant is changed while everything else is kept constant.

v. The concentration of one of the reactants is changed systematically and the initial rate of reaction on every change is determined.

vi. This method can be understood by the following example:

Example 9.1:

Jet engines release Nitrogen (II) oxide in the upper atmosphere. In the ozone layer of upper atmosphere Nitrogen (II) oxide reacts with ozone to form nitrogen (IV) oxide and oxygen.

$$NO\,(g) + O_3\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)$$

The following data was obtained for this reaction at 25 ^{0} C.

Experiment	Initial [NO]	Initial [O_3]	Initial rate (moles $dm^{-3}\,s^{-1}$)
1	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
2	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
3	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}

Use this data to determine the rate law for the reaction.

Solution:

To determine the order of reaction with respect to a reactant, we examine the relationship between its initial concentration and the rate of reaction while holding the concentration of the other reactant constant.

Experiments 1 and 2:

In experiments 1 and 2 initial concentration of ozone is kept constant at 9.00×10^{-6} M while the concentration of NO is doubled from 1.00×10^{-6} M to 2.00×10^{-6} M; the initial rate increases from 1.98×10^{-4} to 3.96×10^{-4} moles $dm^{-3}s^{-1}$ The ratio between these two rates is

$$1.98\times10^{-4} : 3.96\times10^{-4}$$

$$\frac{1.98\times10^{-4}}{1.98\times10^{-4}} : \frac{3.96\times10^{-4}}{1.98\times10^{-4}}$$

$$1 : 2$$

Thus the initial rate doubles. This means the rate of reaction is directly proportional to the first power of concentration of NO. Rate $\propto$ [NO]

Experiments 1 and 3:

In experiments 1 and 3 initial concentration of NO is kept constant at 1.00×10^{-6} and concentration of ozone is decreased to one third i.e. from 9.00×10^{-6} to 3.00×10^{-6}M. the initial rate decreases from 1.98×10^{-4} to 6.60×10^{-5} moles $dm^{-3}\,s^{-1}$, the ratio between these rates is

$$1.98 \times 10^{-4} \qquad 6.60 \times 10^{-5}$$

$$\frac{1.98 \times 10^{-4}}{1.98 \times 10^{-4}} : \frac{6.60 \times 10^{-5}}{1.98 \times 10^{-4}}$$

$$1 : \frac{1}{3}$$

Conclusion:

Thus, the rate of reaction also decreases one third. This means the rate of reaction is directly proportional to the first power of concentration of O_3.

Rate $\propto [O_3]$

Thus, the rate law for the reaction is Rate $\propto$ [NO] $[O_3]$

Hence this reaction is a **second order reaction**.

Example 9.2:

The following reaction is first order in H_2 and half order in Br_2 write rate law for the reaction

$$H_2 + Br_2 \longrightarrow 2HBr$$

Solution: Given information indicates that

Rate $\propto [H_2]$ ----------------- **(i)**

Rate $\propto [Br_2]^{1/2}$ ----------------- **(ii)**

combining **(i)** and **(ii)** we get the rate law for the reaction

Rate $\propto [H_2]\,[Br_2]^{1/2}$

Rate = k $[H_2]\,[Br_2]^{1/2}$

SELF-CHECK EXERCISE 9.3

1. Phosgene is a toxic gas. It has been used in World War II. This gas is prepared by the reaction of carbon monoxide with chlorine.

$$CO\,(g) + Cl_2\,(g) \longrightarrow COCl_2\,(g)$$

The following data were obtained for kinetic study of this reaction.

Experiments	Initial [CO]	Initial [Cl_2]	Initial rate (moles dm^{-3} s^{-1})
1	1.000	0.100	1.29×10^{-29}
2	0.100	0.100	1.30×10^{-30}
3	0.100	1.000	1.30×10^{-30}

Write rate law for this reaction.

Solution: To determine the order of reaction with respect to a reactant, we examine the relationship between its initial concentration and the rate of reaction while holding the concentration of the other reactant constant.

Experiments 1 and 2:

In Experiments 1 and 2, initial concentration of Cl_2 is kept constant at 0.100 M. The concentration of CO is decreased ten times i.e., from 1.000 M to 0.100 M. The initial rate decreases from 1.29×10^{-29} to 1.30×10^{-30} $mole\ dm^{-3}s^{-1}$.

The ratio between these two rates is

$$1.29 \times 10^{-29} \qquad 1.30 \times 10^{-30}$$

$$\frac{1.29\times10^{-29}}{1.29\times10^{-29}} \qquad \frac{1.30\times10^{-30}}{1.29\times10^{-29}}$$

$$1 \qquad \frac{1}{10}$$

Conclusion:

Thus, the rate of reaction also decreases ten times when concentration of CO is decreased ten times. This means that the rate of reaction is directly proportional to the first power of concentration of CO.

Thus **Rate $\propto$ [CO]**

Experiments 2 and 3:

In Experiments 2 and 3, initial concentration of CO is kept constant at 0.100 M. The concentration of Cl_2 is increased ten times i.e. from 0.100 M to 1.000 M. The initial rate remains constant at $1.30 \times 10^{-30}\ mole\ dm^{-3} s^{-1}$.

Conclusion:

This means that the ratio between them does not change and thus the rate is independent of concentration of CO.

Rate $\propto [Cl_2]^o$

Rate $\propto [CO][Cl_2]^o$

Rate = $k\,[CO]$

Hence it is a first order reaction.

2. The following reaction is second order in NO_2 and is independent of the concentration of CO. Write rate law for the reaction. What is the overall order of the reaction?

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

The given information shows that

Rate $\propto [CO]^o$ .... (1)

Rate $\propto [NO_2]^2$ .... (2)

Combining (1) and (2), we have

Rate $\propto [CO]^o[NO_2]^2$ Or Rate $k[NO_2]^2$

Hence it is a second order reaction.

Q9. Explain in detail the various factors which can affect the rate of reactions.

Ans: Factors Affecting Rate of Reactions:

All the factors, which change the number of effective collisions per second, affect the rate of a chemical reaction. Some of the important factors are as follows.

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:

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

ii. 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:

i. A mixture of H_2 and Cl_2 will react twice as fast if the partial pressure of H_2 or Cl_2 is doubled in the presence of excess of the other component.

ii. Combustion occurs more rapidly in pure oxygen than in air (21% oxygen).

iii. Limestone ($CaCO_3$) reacts at different rates 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.

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

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.

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

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.

Q10. Explain Maxwell Boltzmann curve with the help of diagram.

Ans: Maxwell Boltzmann Curve:

i. At ordinary temperature, very few molecules possess the energy of activation.

ii. All the molecules of a reactant **do not possess the same energy** at a particular temperature.

iii. Most of them possess **average energy.**

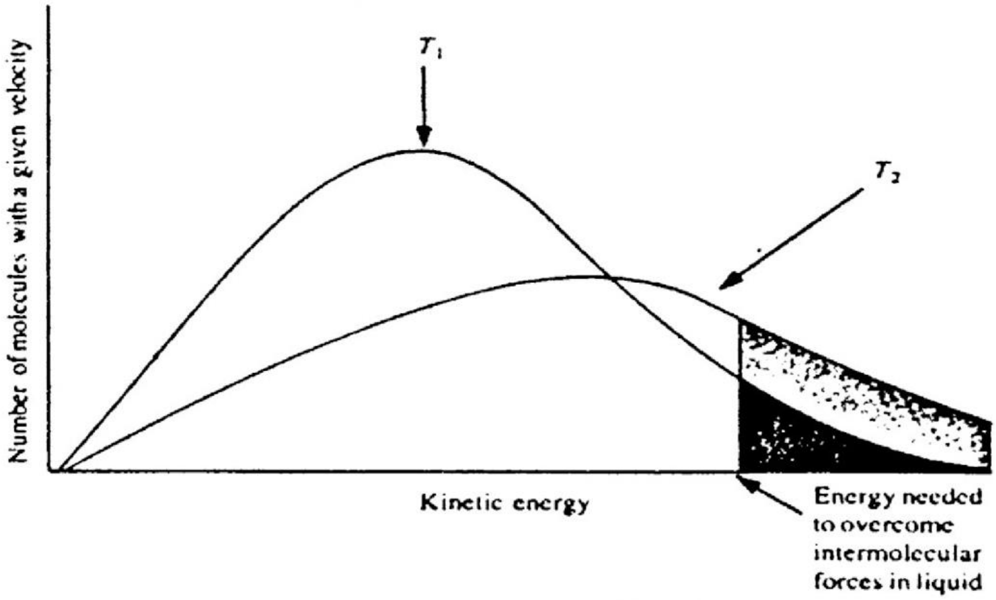
iv. A fraction of molecules have **kinetic energy more than** the average energy.

v. The number of molecules having at least kinetic energy equal to Ea at temperature T is **proportional to the shaded area** under the Maxwell Boltzmann curve of kinetic energy.

vi. As the temperature is increased the area of the **shaded region increases** and more molecules have **kinetic energy greater than Ea.**

vii. An increase in temperature **increases** the number of reactants molecules that have enough energy for **effective collision.**

viii. It is found that in general the reaction rate increases **two to three folds for each 10K increase in temperature.**



Maxwell Boltzmann curve of kinetic energy

Q11. Explain Arrhenius equation and also give its applications.

Ans: Arrhenius (1889) studied the effect of temperature on reaction rates. He found that the effect of temperature on rate of reaction is given by the following equation. This equation is known as **Arrhenius equation**.

Mathematically: $k = Ae^{-Ea/RT}$

k = rate constant,

Ea is energy of activation,

R is the gas constant ($R=8.3143\ JK^{-1}\ mole^{-1}$).

A is constant known as **Arrhenius constant**.

It is related with the frequency of collision and orientation of the reacting molecules. Therefore, rate constant k varies with the temperature It increases with temperature which in turn increases rate of reaction.

Applications:

i. The Arrhenius equation can be used to understand the role of rate constant in the theoretical determination of reaction rates.

ii. This equation can be used to calculate rate constants for a reaction at different temperatures.

iii. The factor by which a rate constant increases with the increase in temperature is also the factor by which rate of reaction increases.

iv. This is because the rate of a reaction is proportional to the rate constant.

Activity

Calculate the factor by which the rate of the following reaction will increase as a result of increase in temperature from 37° C to 47° C. The activation energy for the reaction is 106 KJ^{-1}.

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

Glucose **Fructose**

Solution: Using the Arrhenius equation, derive an equation for the ratio of rate constants k_1 at temperature T_1 and k_2 at temperature T_2. For this purpose write the Arrhenius equation at two temperatures.

$$k_1 = Ae^{\frac{Ea}{RT_1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$k_2 = Ae^{\frac{Ea}{RT2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Divide equation (2) by the equation (1)

$$\frac{k_2}{k_1} = \frac{Ae^{\frac{Ea}{RT_2}}}{Ae^{\frac{Ea}{RT_1}}}$$

$$\frac{k_2}{k_1} = \frac{e^{\frac{Ea}{RT_2}}}{e^{\frac{Ea}{RT_1}}}$$

$$\frac{k_2}{k_1} = e^{\frac{Ea}{RT_2} + \frac{Ea}{RT_1}}$$

$$\frac{k_2}{k_1} = e^{\left(\frac{Ea}{RT_1} - \frac{Ea}{RT_2}\right)}$$

Take natural logarithm of both sides

$$\ln \frac{k_2}{k_1} = \ln e^{\left(\frac{Ea}{RT_1} - \frac{Ea}{RT_2}\right)}$$

$$\ln \frac{k_2}{k_1} = \frac{Ea}{RT_1} - \frac{Ea}{RT_2}$$

Convert natural logarithm into common logarithm

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

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

$$\log \frac{k_2}{k_1} = \frac{Ea}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

This equation relates rate constants and their corresponding temperatures to the activation energy. Substitute Ea, R, T_1 and T_2 in this equation.

$$Ea = 106\ KJ\ mole^{-1}$$

$$= 106 \times 10^3\ J\ mole^{-1}$$

$$R = 8.314\ J\ mole^{-1}K^{-1}$$

$$T_1 = 37^0C + 273 = 310\ K$$

$$T_2 = 47^0C + 273 = 320\ K$$

$$\log \frac{k_2}{k_1} = \frac{106 \times 10^3}{2.303 \times 8.314}\left(\frac{320 - 310}{310 \times 320}\right)$$

$$\log \frac{k_2}{k_1} = \frac{106000}{2.303 \times 8.314}\left(\frac{10}{310 \times 320}\right)$$

$$\log \frac{k_2}{k_1} = 0.5581$$

$$\frac{k_2}{k_1} = \text{AntiLog } 0.5581$$

$$\frac{k_2}{k_1} = 3.6$$

Conclusion:

As the factor by which the ratio of rate constants increases as a result of 10° C increase in temperature is also the ratio of increase in reaction rates. Thus the rate of reaction at 47° C is 3.6 times the rate of 37° C.

Q12. Briefly explain rate determining step with the help of example.

Ans: 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 occur. No reaction can proceed faster than the rate-determining step. All the other steps of the reaction mechanism are generally fast.

Example:

For reaction

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$

$$\text{Rate} = k\,[NO_2]^2$$

The rate equation gives us following information.

i) The reaction is second order with respect to NO_2 and zero with respect to CO. Therefore it is independent of the concentration of CO.

ii) Two molecules of NO_2 are involved in the rate-determining step.

iii) Reaction must proceed in more than one step.

The proposed mechanism for the reaction is as follows.

Step I $\quad NO_{2(g)} + NO_{2(g)} \xrightarrow{\text{Slow}} NO_{3(g)} + NO_{(g)}$

Step II $\quad NO_{3(g)} + CO_{(g)} \xrightarrow{\text{Fast}} NO_{2(g)} + CO_{2(g)}$

Reaction intermediate:

The first step is the rate determining step. Species NO_3 that does not appear in the overall reaction and is consumed during the course of reaction and is called reaction intermediate.

This example also proves that a balanced chemical equation may not give any information about the reaction mechanism.

Example 9.4:

Hypochlorite ion ClO^- in aqueous solution decomposes to chlorate ion ClO^-_3 and chloride ion.

$$3\,ClO^-(aq) \longrightarrow ClO_3^- + 2Cl^-$$

The rate of the reaction is second order in ClO^- ion

Rate = k $[ClO^-]^2$

The following two-step mechanism is consistent with the rate law for the reaction.

Step I: $\quad ClO^-(aq) + ClO^-(aq) \rightarrow ClO_2(aq) + Cl^-(aq)$

Step II: $\quad ClO_2(aq) + ClO^-(aq) \rightarrow ClO^-_3(aq) + Cl^-(aq)$

Overall reaction $\quad 3ClO^-(aq) \rightarrow ClO^-_3(aq) + 2Cl^-(aq)$

Identify the rate-determining step.

Solution:

Rate law for this reaction indicates that two ClO^- ions must participate in the rate-determining step. Therefore Step I is the rate-determining step in this mechanism.

Example 9.5:

Rate = $k[NO_2]\,[O_3]$ for the following reaction indicates that one molecule of NO_2 and one molecule of O_3 participate in the determining step

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

Thus rate law includes the concentration of each of the reactants raised to the power that equals the coefficient for the reactant in the equation for the rate-determining step.

SELF-CHECK EXERCISE 9.4

For the following reaction,

$$2NO_2\ (g) + F_2\ (g) \longrightarrow 2NO_2F\ (g)$$

$$\text{Rate} = k[NO_2]\,[F_2]$$

Which of the following mechanism is consistent with the rate law?

a) $2NO_2 + F_2 \longrightarrow 2NO_2F$

b) $NO_2 + F_2 \longrightarrow NO_2F + F$ **(fast step)**

$NO_2 + F \longrightarrow NO_2F$ **(slow step)**

c) $NO_2 + F_2 \longrightarrow NO_2F + F$ **(slow step)**

$NO_2 + F \longrightarrow NO_2F$ **(fast step)**

d) $F_2 \longrightarrow 2F$ **(slow step)**

$2NO_2 + 2F \longrightarrow 2NO_2F$ **(fast step)**

Solution:

The rate equation shows that in the slowest step (rate determining step), one molecule of NO_2 and one molecule of F_2 will participate thus option c correspond to the rate equation. Hence mechanism (c) is correct for this reaction.

Example 9.6:

NO reacts with H_2 according to the following equation:

$$2NO\ (g) + 2H_2\ (g) \longrightarrow N_2\ (g) + 2H_2O\ (g)$$

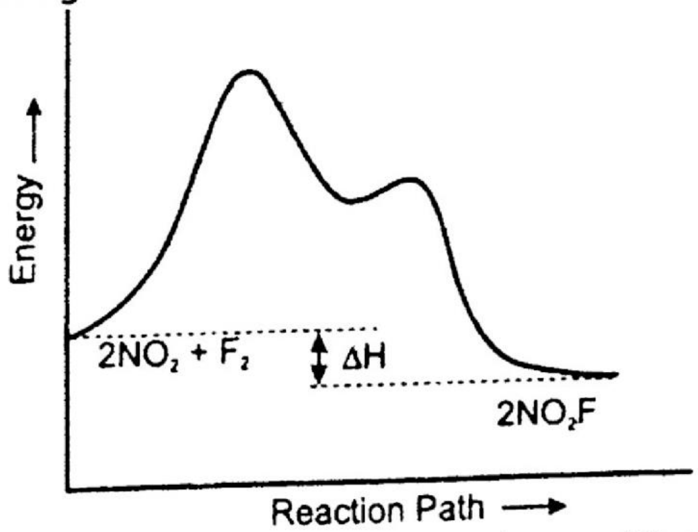
The mechanism for this reaction involves two steps:

$2NO + H_2 \longrightarrow N_2 + H_2O_2$ (slow)

$H_2O_2 + H_2 \longrightarrow 2H_2O$ (fast)

What is the experimental rate law for this reaction?

Potential Energy Diagram and Reaction Mechanism:



Potential energy diagram for the reaction between NO_2 and F_2

Example 9.7:

Potential energy diagram for the reaction between NO_2 and F_2 is given below:

The experimental rate law for this reaction is given below:

Reaction: $2 NO_2 (g) + F_2 (g) \longrightarrow 2NO_2F (g)$ Rate = k $[NO_2]$ $[F_2]$

Propose reaction mechanism.

Solution:

Step 1: Determine the number of elementary steps.

As potential energy diagram shows two peaks, the reaction mechanism must involve two elementary steps.

Step 2: Identify the rate determining step.

As activation energy for step 1 is higher than step 2. Therefore, step 1 will be slow and rate determining step.

Step 3: Use rate law to determine the number of molecules involved in the rate-determining step. Given rate law suggests that one molecule of NO_2 and one molecule of F_2 are involved in this step.

Step 4: Propose two elementary steps for the mechanism.

In the overall reaction two molecules of NO_2 and one molecule of F_2 react to form two molecules of NO_2F. But in the rate determining step only one NO_2 molecule and one F_2 molecule must react to form one NO_2F and a reaction intermediate. In the second elementary step reaction intermediate must react with another molecule of NO_2 to form another molecule of NO_2F. (A species which is formed during a chemical reaction in one step and is consumed in another step is called **reaction intermediate**).

Thus proposed mechanism is,

$$NO_2 + F_2 \longrightarrow NO_2F + F \quad \text{(slow)}$$
$$NO_2 + F \longrightarrow NO_2F \quad \text{(fast)}$$

Step 5: Add the two steps to get the overall reaction which must be same as the reaction under consideration.

$$NO_2 + F_2 \longrightarrow NO_2F + F$$
$$NO_2 + F \longrightarrow NO_2F$$
$$\overline{2NO_2 + F_2 \longrightarrow 2NO_2F}$$

Since sum of elementary steps give the reaction under consideration, the proposed mechanism may be acceptable.

SELF-CHECK EXERCISE 9.5

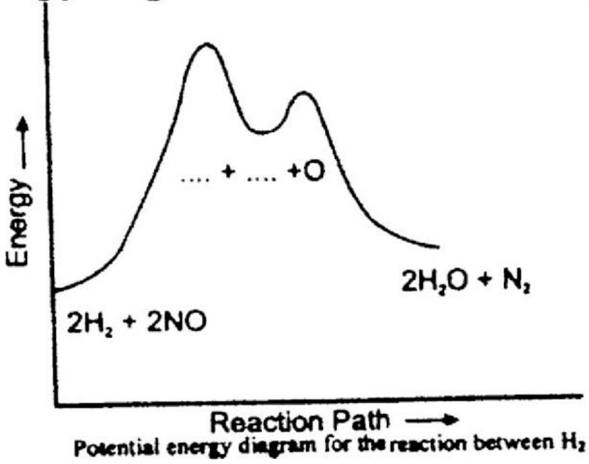
1. **The following data was collected for the reaction between H_2 and NO at 700° C.**

$$2H_2 + 2NO \longrightarrow 2H_2O + N_2$$

Experiment	$[H_2]$	[NO]	Initial rate (moles $dm^{-3}s^{-1}$)
1	0.010	0.025	2.4×10^{-6}
2	0.0050	0.025	1.2×10^{-6}
3	0.010	0.0125	0.6×10^{-6}

Suggest a plausible mechanism that is consistent with the rate law. (Hint: assume the oxygen atom is reaction intermediate).

Potential energy diagram for this reaction is given below.



Potential energy diagram for the reaction between H_2 and NO

Solution:

(a) Determination of Rate Law:

Experiments 1 and 2:

In Experiments 1 and 2, initial concentration of NO is kept constant at 0.025 M. The concentration of H_2 is decreased to one half from 0.010 M to 0.0050 M. The initial rate decreases from 2.4×10^{-6} to 1.2×10^{-6} $mole\ dm^{-3}s^{-1}$

The ratio between these two rates is

$$2.6 \times 10^{-6} \qquad\qquad 1.2 \times 10^{-6}$$

$$\frac{2.4\times10^{-6}}{2.4\times10^{-6}} \qquad\qquad \frac{1.2\times10^{-6}}{2.4\times10^{-6}}$$

$$1 \qquad\qquad \frac{1}{2}$$

Conclusion:

Thus, the rate of reaction decreases to one half when concentration of H_2 is decreased to one half. It shows that the rate of reaction is directly proportional to the first power of concentration of H_2.

Rate $\propto [H_2]$

Experiments 1 and 3:

In Experiments 1 and 3, initial concentration of H_2 is kept constant at 0.010 M and concentration of NO is decreased to one half i.e. from 0.025 M to 0.0125 M. The initial rate decreases from 2.4×10^{-6} to 0.6×10^{-6} $mole\ dm^{-3}s^{-1}$.

The ratio between these rates is

$$2.6 \times 10^{-6} \qquad\qquad 0.6 \times 10^{-6}$$

$$\frac{2.4\times10^{-6}}{2.4\times10^{-6}} \qquad\qquad \frac{0.6\times10^{-6}}{2.4\times10^{-6}}$$

$$1 \qquad\qquad \frac{1}{4}$$

Conclusion:

Thus, the rate of reaction decreases to one fourth when concentration of NO is decreased to one half. It shows that the *rate* of reaction is directly proportional to the second power of concentration of NO.

Rate $\propto [NO]^2$

Rate law:

The rate law for the reaction is

Rate $\propto [NO]^2 [H_2]$
Rate $= k[NO]^2[H_2]$
Overall order of reaction = 2 + 1 = 3.
Hence it is a third order reaction.

(b) Mechanism:

Step 1: ***Determine the number of elementary steps.***

The potential energy diagram shows two peaks, the reaction mechanism must involve two elementary steps.

Step 2: ***Identify the rate determining step.***

As activation energy for step 1 is higher than step 2. Therefore, step 1 will be slow and rate determining step.

Step 3: ***Identify the number of molecules involved In rate-determining step.***

Use rate law to determine the number of molecules involved in the rate-determining step. Rate law suggests that two molecules of NO and one molecule of H_2 are involved in this step.

Step 4: ***Propose elementary steps for the mechanism.***

The overall reaction shows that two molecules of NO and one molecules of H_2 react to form products. However, the rate law equation shows that in the rate determining step two molecules of NO and one molecule of H_2 is involved.
Thus, the mechanism may be written in two steps as given below.
In one elementary step, 2 molecules of NO react with 1 molecule of H_2 to for 2 molecules of H_2O, one molecule of N_2 and one oxygen atom. This is the slow rate determining step. In second step, one molecule of H_2 reacts with one atom of oxygen to give one molecule of water. This is the fast step.
Atomic oxygen is the intermediate in the reaction.

$$2NO + H_2 \longrightarrow 2H_2O + N_2 + [O] \quad (slow)$$
$$H_2 + [O] \longrightarrow H_2O \quad (fast)$$

Step5: ***Add the two steps to get the overall reaction.***

$$2NO + H_2 \longrightarrow 2H_2O + N_2 + [O] \quad (slow)$$
$$H_2 + [O] \longrightarrow H_2O \quad (fast)$$
$$\overline{2NO + 2H_2 \longrightarrow 2H_2O + N_2}$$

Since sum of elementary steps give the reaction under consideration, the proposed mechanism may be acceptable.

2. Following mechanism has been proposed for a reaction.

$$H_2O_{2(aq)} + I^-_{(aq)} \longrightarrow H_2O_{(l)} + OI^-_{(aq)}$$
$$OI^-_{(aq)} + H_2O_{2(aq)} \longrightarrow H_2O_{(l)} + O_2(g) + I^-_{(aq)}$$

Identify catalyst, reaction intermediate and rate determining step.

Solution:

Add the two half reactions

$$H_2O_2(aq) + I^-(aq) \longrightarrow H_2O(l) + OI^-(aq)$$
$$OI^-(aq) + H_2O_2(aq) \longrightarrow H_2O(l) + O_2(g) + I^-(aq)$$
$$\overline{2H_2O_2(aq) \longrightarrow H_2O(l) + O_2(g)}$$

Reaction intermediate:

The OI^- ion is produced and consumed during the course of reaction and is not appeared in the net reaction. Hence OI^- ion is the reaction intermediate.

Rate-determining steps:

Without experimental rate law we can not suggest the rate determining step.

Catalyst:

The I^- ion is used as a reactant in the first step but regenerates in the last step and is not consumed in the reaction. Thus, I^- ion is the catalyst.

3. The rate law for the following reaction

$$2H_2 + 2NO \longrightarrow N_2 + 2H_2O$$

is rate = $k[H_2][NO]^2$. Is the following mechanism is consistent with the rate law? Give reason.

$$H_2 + NO \longrightarrow H_2O + N \quad \text{(slow)}$$
$$N + NO \longrightarrow N_2 + O \quad \text{(fast)}$$
$$O + H_2 \longrightarrow H_2O \quad \text{(fast)}$$

Solution:

The rate equation shows that there must be 2 molecules of NO and one molecule of H_2 in the slowest step(rate-determining step). But there is only one molecule of NO in the slowest step(rate-determining step).Thus the above mechanism is incorrect.

4. The rate law for the reaction,

$$2N_2O \longrightarrow 2N_2 + O_2$$

is rate = $k[N_2O]$. Reaction occurs in two elementary steps. Assume O atom as a reaction intermediate. Write mechanism for the reaction.

Solution:

According to the rate equation slowest and the fast step will be.

$$N_2O \longrightarrow N_2 + |O| \quad (slow)$$
$$N_2O + |O| \longrightarrow N_2 + O_2 \quad (fast)$$

Mechanism:

Add the two steps to get the overall reaction.

$$N_2O \longrightarrow N_2 + |O| \quad (slow)$$
$$N_2O + |O| \longrightarrow N_2 + O_2 \quad (fast)$$
$$\overline{2N_2O \longrightarrow 2N_2 + O_2 \quad (fast)}$$

Q13. Explain collision theory, transition state and activation energy.

Ans: Collision Theory:

Chemical reactions involve the breaking and making of chemical bonds. These changes are accompanied by changes in energies.

Collision theory has been proposed to explain the observed kinetics of reactions.

Conditions for a chemical reaction:

i. For a chemical reaction to occur, the combining atoms or molecules must collide with one another. These collisions may be effective or ineffective depending upon the energy and orientation of the colliding particles.

ii. The effective collision can take place only if the energy of the colliding particles is high enough to overcome the repulsion between electrons around the reacting particles.

iii. Proper orientation means that at the time of collision, the atoms which are required to make new bonds should collide with each other.

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:

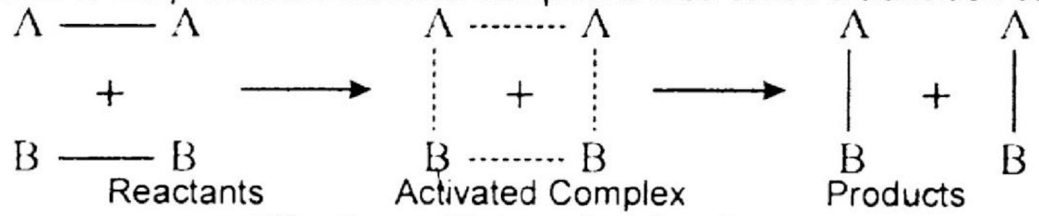
The reaction will not occur if the energy of reacting particles in less than activation energy.

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 possess 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 A_2 and B_2 molecules to form a new molecule AB. If 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.



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:

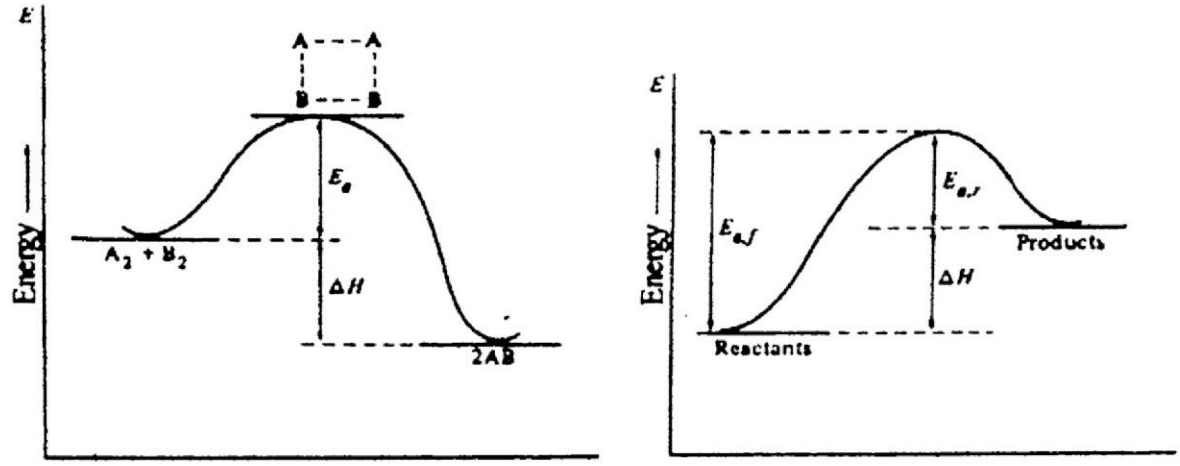
The potential energy diagram can also be used to understand the enthalpy changes in chemical reactions. The heat of reaction is equal to the difference of energies of reactants and products. In an exothermic reaction products are at a lower energy level than the reactants. In both exothermic and endothermic 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.



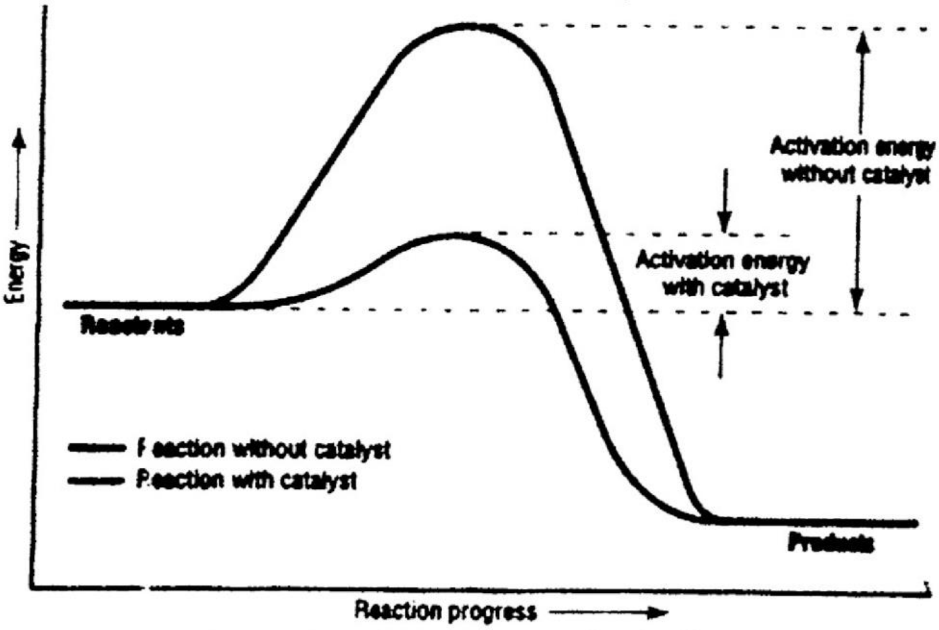
(a) Reaction path → **(b)** Reaction path →

(a) Exothermic reaction **(b)** Endothermic reaction

Q14. Write a note on catalyst how can the increase the rate of reaction?

Ans: 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 decreasing 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 favoured thermodynamically.

Example:

In the stratosphere, conversion of an ozone molecule by an oxygen atom into two O_2 molecules occurs. This reaction has higher energy of activation.

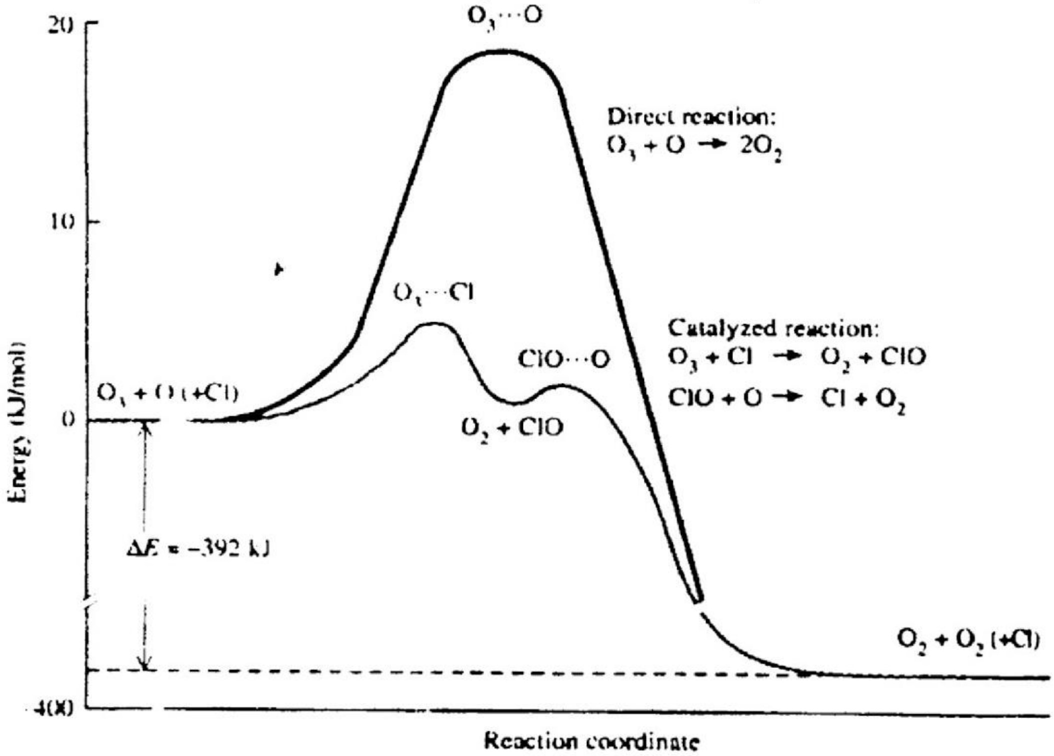
$$O_3 + O \longrightarrow 2O_2 \qquad E_a = 17.1\ KJ\ mole^{-1}$$

Chlorofluorocarbon compounds diffuse up into the stratosphere. These compounds absorb short wave length ultraviolet light from the sum, that breaks carbon-chlorine bonds and produce chlorine atoms. Cl atom catalyze the mechanism requiring less energy of activation.

$$O_3 + Cl \longrightarrow O_2 + ClO \qquad Ea = 2.1\ KJmole^{-1}$$
$$O + ClO \longrightarrow O_2 + Cl \qquad Ea = 0.4\ KJmole^{-1}$$

Net reaction: $O_3 + O \qquad 2O_2 \qquad Ea = 2.5\ KJmole^{-1}$

It shows that the direct reaction between O_3 and O has a substantially higher activation energy than the chlorine catalyzed reaction sequence.



Energy level diagram for the decomposition of ozone in the stratosphere.

Q15. Explain the following terms in detail with the help of examples.

i. Homogeneous catalysis.

ii. Heterogeneous catalysis.

Ans: i. Homogeneous catalysis:

A catalysis in which the catalyst and the reactants are in the same phase is known as homogeneous catalysis., a metal halide or a metal oxide.

Examples of homogeneous catalysis:

i) In the lead chamber process for the manufacture of sulphuric acid, NO gas catalyzes oxidation of SO_2 gas

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons NO_{(g)} \qquad 2SO_{3(g)}$$

ii) Hydrolysis of esters is catalyzed by H_2SO_4

$$CH_3COOC_2H_{5\,(aq)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

iii) An aqueous solution of sucrose is stable for years provided that bacterial growth is inhibited. But when a small amount of an enzyme sucrase is added to the sucrose solution, it is rapidly converted to glucose and fructose.

$$C_{12}H_{22}O_{11}\,(aq) + H_2O\,(l) \xrightarrow{\text{sucrase}} \underset{\text{Glucose}}{C_6H_{12}O_6\,(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6\,(aq)}$$

iv) In the upper atmosphere nitric oxide is responsible for the depletion of ozone. It catalyzes the decomposition of ozone

$$2O_3(g) \xrightarrow{NO\,(g)} 3O_2\,(g)$$

ii. Heterogeneous catalysis:

The catalysis, in which catalyst and the reactants are in different phases, is known as heterogeneous catalysis. Heterogeneous catalysis often contains transition metals as pure metals

Examples of heterogeneous catalysis:

i) In the manufacture of ammonia, finely divided Fe_2O_3 is used as catalyst

$$N_{2(g)} + 3H_{2(g)} \quad Fe_2O_{3(s)} \rightleftharpoons 2NH_3(g)$$

ii) In contact peaces for the manufacture of H_2SO_4, oxidation of SO_2 (g) is catalyzed by V_2O_5(s)

$$2SO_{2(g)} + O_{2(g)} \quad V_2O_5(s) \rightleftharpoons 2SO_{3(g)}$$

iii) Formic acid decomposes into H_2O and CO in presences of Al_2O_3. But it decomposes into H_2 and CO_2 in presence of Cu.

$$HCOOH_{(l)} + Al_2O_3(s) \longrightarrow H_2O_{(l)} + CO_{(g)}$$

$$HCOOH_{(l)} + Cu(s) \longrightarrow H_2(g) + CO_{2(g)}$$

iv) The petroleum, plastic and food industries use catalytic hydrogenation to change the great variety of compounds into more useful substances. The conversion of vegetable oil into margarine is one example. Finally, divided nickel, palladium or platinum is used as catalyst.

$$\text{Vegetable Oil }(l) + H_2\,(g) \quad \text{Ni/Pt/Pd(s)} \longrightarrow \text{Margarine }(s)$$

SELF-CHECK EXERCISE 9.6

Most of new cars are equipped with catalytic converters in exhaust system. These converters contain Pt or Pd or transition metal oxide such as CuO or Cr_2O_3 as catalyst. It oxidizes CO and unburnt a gasoline to CO_2 and H_2O.

It also reduces NO and NO_2 to N_2 and O_2. Identify type of catalysts.

Solution:

In these reactions reactants are in gases state and the catalyst are in solid state Therefore, these reactions are the example of heterogeneous catalysis.

Q16. Explain the term enzymes.

Ans: 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.

Occurrence:

Most of the enzymes are found inside the cells. However, some are found in extra cellular fluids such as saliva, gastric juice etc.

Enzymes may speed up reactions by a factor of $\mathbf{10^{30}}$

Constitution of enzymes:

Some enzymes consist of protein only, but most enzymes contain non-protein components such as carbohydrates, lipids, metals, phosphates etc. The complete enzyme is called **holoenzyme**.

Apoenzyme and co-factor:

The protein part is called apoenzyme and non-protein as co-factor or co-enzyme.

Mechanism of enzyme action:

Enzyme catalysis can be represented by the series of reaction. In the first step, a reactant binds to a specific location on the enzyme called the active site. Hydrogen bonding plays a key role in this binding

$$\underset{\text{Enzyme}}{E} + \underset{\text{Reactant}}{R} \rightleftharpoons \underset{\text{Enzyme-Reactant Complex}}{ER}$$

Binding cause chemical changes in the structure of reactants and forms a product species. The enzyme then releases the product and is ready to repeat the process.

$$\underset{\text{Enzyme-Reactant Complex}}{ER} \rightleftharpoons \underset{\text{Enzyme}}{E} + \underset{\text{Product}}{P}$$

Because an enzyme plays a catalytic role over and over and very rapidly, only a tiny amount of enzyme is required.

Q17. Give daily life application of enzymes.

Ans: Daily Life Application of Enzymes:

i. Since some enzymes can also act outside the cells, therefore, they can be used commercially.

ii. Enzymes are effective in removing stains from fabrics. For this purpose suitable enzymes that can act on substances that are present in the stains are used. These enzymes decompose components of stains to simpler molecules, which are soluble in water and can be removed by washing with water.

Example:

Enzymes like pepsin, trypsin, lipase, and amylase etc are used to remove food stains from fabrics. The food strain may contain carbohydrates, proteins and fats. Amylase acts on starch, pepsin and trypsin acts on protein and lipase on fats.

iii. All these enzymes convert complex water insoluble components of food into simple water-soluble components.

SUMMARY OF KEY TERMS

1. The rate of a chemical reaction is a change in the concentration of reactant or product in the given time. The instantaneous rate of reaction is the infinitesimally small change in concentration that occurs over an infinite infinitesimally small period of time.
2. The rate law is an expression that relates the rate of a reaction to the rate constant and the concentration of reactants raise to an appropriate powers. It can only be determined experimentally.
3. Overall reaction order is sum of the powers to which reactant concentration are raised in the rate law.
4. A reaction mechanism is the sequence of elementary steps that describe the reaction. The rate of reaction is determined by the slowest elementary step called the rate determining step in the reaction mechanism.
5. The rate of a chemical reaction depends upon the activation energy for the reaction. The rate constant and activation energy are related by the Arrhenius equation:

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

6. Reaction rates are influence by the catalyst, which change mechanism of the reaction by decreasing energy of activation.
7. In homogenous catalysis, the catalyst and the reactant are in the same phase whereas in heterogeneous catalysis the catalyst and reactants are in different phases.
8. Enzymes are catalysts in living organism.

EXERCISE

MULTIPLE CHOICE QUESTIONS

1: Choose the correct answer

(i) The rate of a reaction ____________ as the reaction proceeds.

(a) Increases (b) Decreases
(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

$2A + B \xrightarrow{slow} C$, the rate law for the reaction is

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

SUMMARY OF KEY TERMS

1. The rate of a chemical reaction is a change in the concentration of reactant or product in the given time. The instantaneous rate of reaction is the infinitesimally small change in concentration that occurs over an infinite infinitesimally small period of time.
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EXERCISE

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$2A + B \xrightarrow{slow} C$, the rate law for the reaction is

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

(c) rate = k[C] (d) None of these

(iv) For the reaction $2A + B \rightarrow C + D$
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
$R\text{-}X + H_2O \rightarrow R\text{-}OH + HX$ is, rate = $k[R\text{-}X]$. The rate of reaction will be doubled when
(a) Concentration of H_2O is doubled
(b) Concentration of R-X is reduced to half
(c) Concentration of both R-X and H_2O 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

Answers

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 It 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:

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

ii. 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:

i. A mixture of H_2 and Cl_2 will react twice as fast if the partial pressure of H_2 or Cl_2 is doubled in the presence of excess of the other component.

ii. Combustion occurs more rapidly in pure oxygen than in air (21% oxygen).

iii. Limestone ($CaCO_3$) reacts at different rates 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.

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

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.

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

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 T is 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:

$$\text{Rate} = \frac{\text{Change in concentration of a substance}}{\text{Time taken for change}}$$

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.

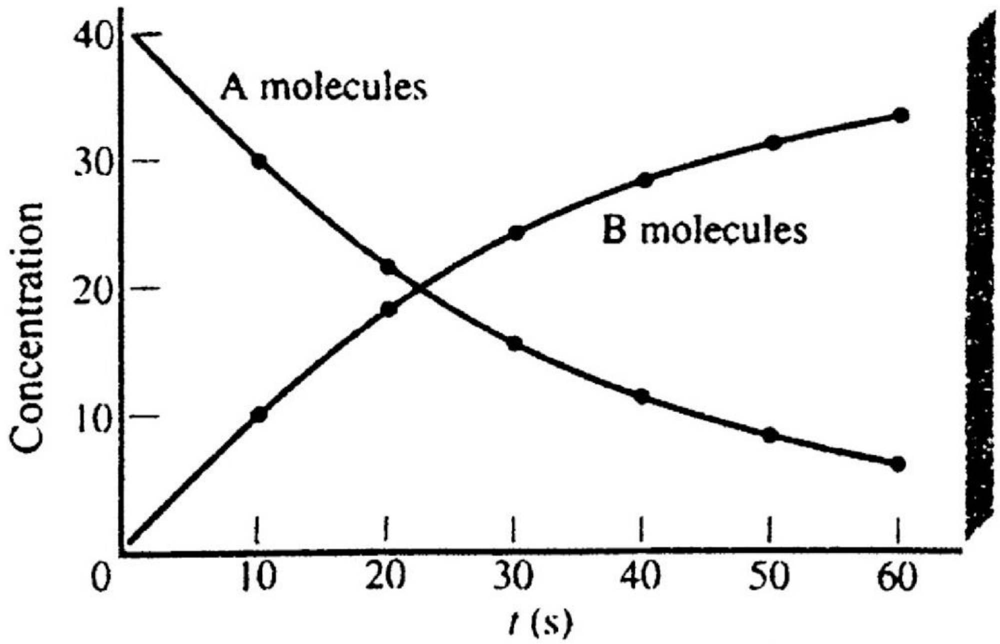
Units:

The unit of concentration is mole dm^{-3} and time is second, so unit of reaction rate is mole. $dm^{-3}\ s^{-1}$

Graphical representation:

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

$$A \longrightarrow B$$



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 at 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. 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.

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:

$$A \longrightarrow \text{Product}$$

$$\text{Rate} \propto [A]^x$$

$$\text{Rate} = k\,[A]^x$$

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 x can be determined only with the help of experiments.

Example:

For the reaction

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

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

Notice that the order with respect to NO_2 is one whereas the stoichiometric coefficient is two.

Therefore, rate law or rate equation for the above reaction is,

$$\text{Rate} = k\,[NO_2]\,[O_3]$$

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 *c* moles C and *d* moles of D.

$$aA + bB \longrightarrow cC + dD$$

The rate equation can be written as

$$\text{Rate} \propto [A]^x\,[B]^y$$

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

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

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

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

Notice that the order with respect to NO_2 is one whereas the stoichiometric coefficient is two.

The order of reaction with respect to O_3 is also one.

Overall order of reaction is two so, the above reaction is second order reaction.

Rate constant:

For a general reaction:

$$A \longrightarrow \text{Product}$$

$$\text{Rate} \propto [A]^x$$

$$\text{Rate} = k\,[A]^x$$

Where k is proportionality constant and is known as **rate 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:

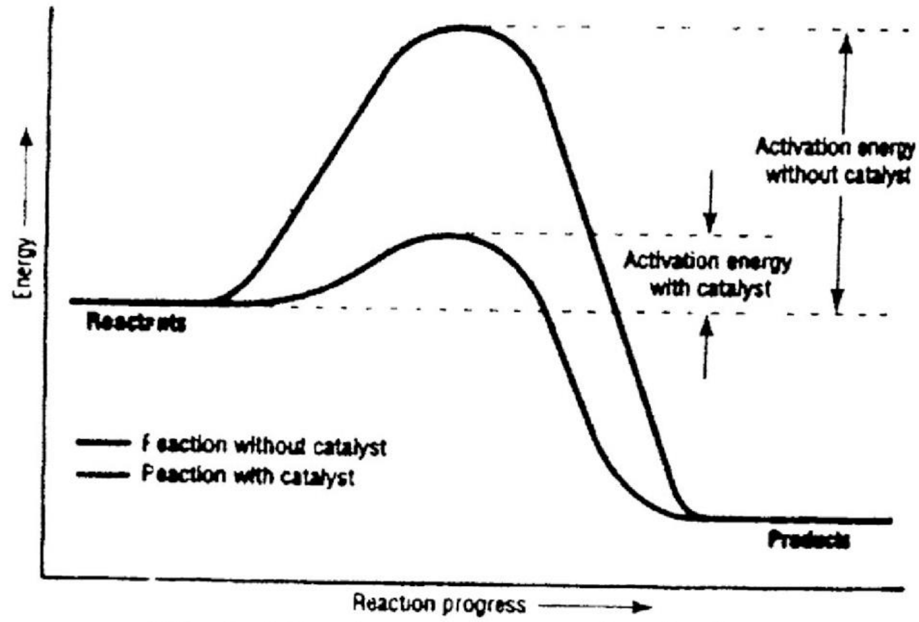
The rate of the slowest step determines the overall rate of reaction. This is because it places a limit on the rate at which the overall reaction can occur. No reaction can proceed faster than the rate-determining step. All the other steps of the reaction mechanism are generally fast.

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 decreasing 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 favoured 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:

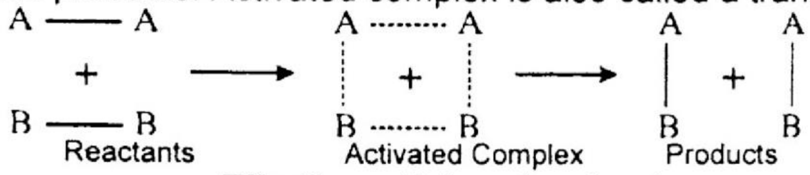
The reaction will not occur if the energy of reacting particles in less than activation energy.

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 possess 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 A_2 and B_2 molecules to form a new molecule AB. If 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.



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.

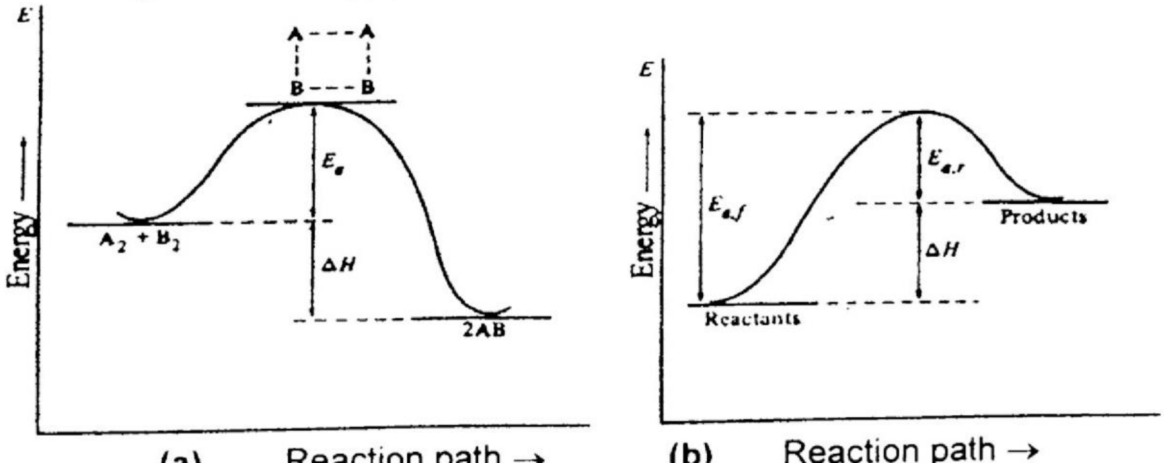
Potential energy diagram for exothermic reaction:

The potential energy diagram can also 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 products 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 i.e. the number of effective collisions and hence the reaction rate. However, only effective collisions bring about the reaction.

Conditions for effective collision:

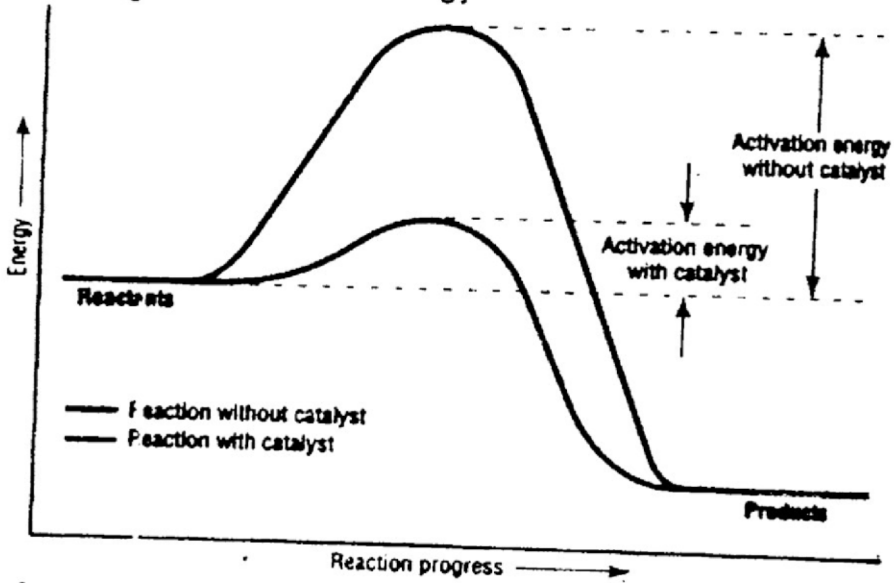
For a collision to be effective molecules must possess

i. The activation energy

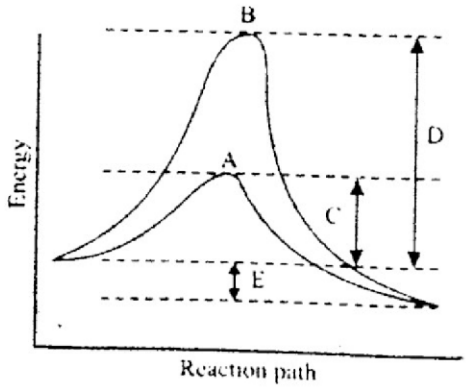
ii. Must be properly oriented.

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. **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

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

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

$$Rate = k[\mathrm{R-X}][\mathrm{H_2O}]$$

$$Order\ of\ reaction = 1 + 1 = 2$$

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.

$$Rate = k[\mathrm{R-X}]$$

$$Order\ of\ reaction = 1$$

So in this case reaction becomes first order.

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

$$Rate = k\,[A]^2[B]^o$$

$$Rate = k\,[A]^2$$

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 $dm^3\ mole^{-1}\ s^{-1}$

Ans:

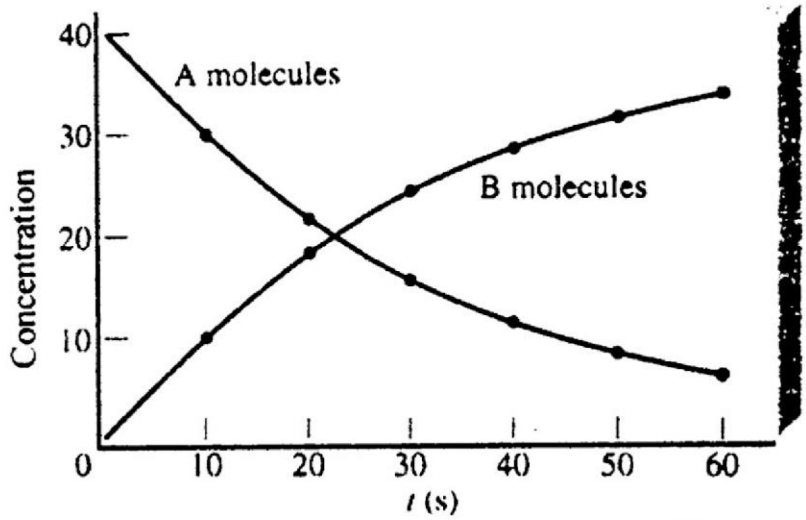
(a) A very small amount of catalyst may prove sufficient to carry out a reaction.

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.

$$A \longrightarrow B$$



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 at 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. 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 $dm^3\ mole^{-1}\ s^{-1}$.

For a second order reaction, consider a general reaction.

$$A + B \longrightarrow C + D$$

The rate of reaction is directly proportional to the concentration of two reactants.

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

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 dm^3

Thus units of k will be

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

14. From the equation proposed for the gas phase reaction of NO_2 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.

$NO_2 + NO_2 \rightarrow NO_3 + NC$ (slow)

$NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

Ans: Rate Law:

The slowest step of the reaction mechanism determines the overall rate of the reaction. According to the slowest step two molecules of NO_2 are involved in the rate-determining step thus the rate law will be.

$$\text{Rate} = k\,[NO_2]^2$$

Overall order of reaction = 2

Stoichiometric Equation:

$$NO_2 + \cancel{NO_2} \rightarrow \cancel{NO_3} + NO \quad \text{(slow)}$$
$$\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2 \quad \text{(fast)}$$

$$NO_2 + CO \rightarrow NO + CO_2 \quad \text{(overall reaction)}$$

Reaction Intermediate:

As the specie NO_3 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 $A + B \rightarrow AB$

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 [A] is kept constant at 0.10 M and we increase the concentration of [B] twice i.e. 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].

$$\text{Rate} \propto [B]$$

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

$$\text{Rate} \propto [A]\,[B]$$

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

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.

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

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

$$2NO_2 \longrightarrow N_2 + 2O_2 \quad \text{(slow)}$$

$$2CO + O_2 \longrightarrow 2CO_2 \quad \text{(fast)}$$

$$N_2 + O_2 \longrightarrow 2NO \quad \text{(fast)}$$

Ans: The mechanism may be correct if it satisfy the following two conditions.