UNIT-7 CHEMICAL KINETICS

1. Define rate law

$aA + bB \longrightarrow$ products

rate α $[A]^x [B]^y$

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

Rate is given in terms of molar concentration of reactants raised to the power which may or may not equal to stoichiometric coefficient.

2. Define Rate constant

Rate constant is same as rate of reaction when concentration of all the reactants is unity.

3. What are Zero order reactions?

Rate is independent of the concentration of reactant is called zero order reaction.

A $\longrightarrow$ Product

rate = $k[A]^0$ rate = k

4. What is pseudo first order reaction ?

A second order reaction can be altered to a first order reaction by taking one of the reactants in large excess, such reaction is called pseudo first order reaction.

Example : **Acid hydrolysis of ester**

$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$

5. Define molecularity.

It is the total number of reactant speciesthat are involved in an elementary step.

6. Define order of a reaction.

$aA + bB \longrightarrow$ products

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

overall order = x + y

It is the sum of the powers of concentration terms involved in the experimentally determined rate law.

7. Give examples of first order reaction.

(i) $N_2O_{5(g)} \longrightarrow 2NO_{2(g)} + O_{2(g)}$

(ii) $SO_2Cl_2(l) \longrightarrow SO_2(g) + Cl_2(g)$

(iii) $H_2O_{2(aq)} \longrightarrow H_2O_{(l)} + O_{2(g)}$

(iv) All radioactive decay (v) Isomerisation of cyclopropane to propene

8. Give two examples of zero order reaction.

(i) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

(ii) Decomposition of N_2O on hot platinum surface

$N_2O_{(g)} \xrightarrow{Pt} N_{2(g)} + \frac{1}{2} O_{2(g)}$

(iii) Iodination of acetone in acid medium is zero order with respect to iodine.

9. Give units of rate constant of (a) first order reaction (b) zero order reaction

(a) **First order reaction** : sec^{-1} (b) **Zero order reaction** : mol $L^{-1}s^{-1}$

10. Write Arrhenius equation.

$$K = A.\, e^{-Ea/RT}$$

K = Rate constant

A = Frequency Factor

Ea= Activation energy

R = Gas constant

T = Temperature

11. Define Half life period of a reaction:

The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value.

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

12. What is Rate and Instantaneous rate of reaction?

Rate :

The change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction. Its unit is Mol L^{-1} S^{-1}

$$\text{Rate} = \frac{\text{Change in the concentration of the reactant}}{\text{Change in time}}$$

Instantaneous rate:

The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate.

13. Define Elementary reaction

Each and every single step in a reaction mechanism is called as Elementary reaction.

14. Differentiate order and Molecularity

S.NO	ORDER	MOLECULARITY
1	It is the sum of the powers of concentration terms involved in the experimentally determined rate law.	It is the total number of reactant species that are involved in an elementary step.
2	It can be zero (or) fractional (or) integer	It is always a whole number, cannot be zero or a fractional number
3	It is assigned for a overall reaction	It is assigned for each elementary step of mechanism.

15. Differentiate Rate and Rate constant.

S.NO	RATE OF REACTION	RATE CONSTANT OF REACTION
1	It represents the speed at which the reactants are converted into products at any instant.	It is a proportionality constant
2	It is measured as decrease in the concentration of the reactants or increase in the concentration of products.	It is equal to the rate of reaction, when the concentration of each of the reactants in unity
3	It depends on the initial concentration of reactants.	It does not depend on the initial concentration of reactants.

16. Define Rate determining step with an example

The slowest step in a chemical reaction is called as rate determining step. The rate depends on this step.

Ex. Decomposition of hydrogen peroxide in the presence of I^-

It takes place in two steps

Step-1: $H_2O_2 + I^- \xrightarrow{slow} H_2O + OI^-$ -------- 1

Step-2: $H_2O_2 + OI^- \rightarrow H_2O + O_2 + I^-$ -------- 2

Over all reaction: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

Step 1 is the rate determining step, since both H_2O_2 and I^- are present. It a bimolecular reaction.

17. Explain the effect of a catalyst on reaction rate with an example.

Catalyst is a substance which alters the rate of reaction without itself undergoing any permanent chemical change.

A catalyst lowers the energy of activation and hence greater number of molecules can cross the energy barrier and change over to products, thereby increasing the rate of reaction.

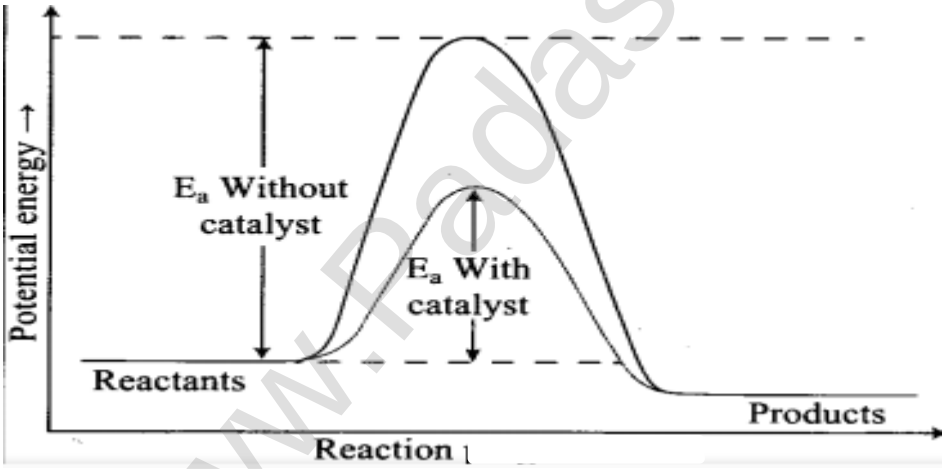
Example: Take 7m1 of O.1N oxalic acid solution, 5m1 of 0.1 N $KMnO_4$ solution and 5m1 of 2N dilute H_2SO_4 in two test tubes labelled as A and B.

The colour of the solution in both the test tubes is pink.

Now add a few crystals of manganese sulphate to the solution in test tube A only. The pink colour of the solution in test A fades up and disappears. But the pink colour of the solution in test tube B remains the same.

This is because manganese sulphate added to the solution of test tube A acts as a catalyst. It increases the rate of oxidation of oxalic acid by $KMnO_4$. Hence the pink colour disappears.

$2KClO_3$ MnO4 $\xrightarrow{\Delta}$ $2KCl + 3O_2$ **(MnO_2 – Catalyst)**



18. Explain briefly the collision theory of bimolecular reactions.

Collision theory is based on the kinetic theory of gases.

$A_{2(g)} + B_{2(g)} \rightarrow 2AB_{(g)}$

The rate would be proportional to the number of collisions per second.

Rate is Number of molecules colliding per litre per second (or)

Rate $\propto$ Collision rate.

The number of collisions is directly proportional to the concentration of both A_2 and B_2.

Collision rate $\propto [A_2]\ [B_2]$ ……(1)

Collision rate = $Z\ [A_2]\ [B_2]$ ……..(2) Where Z is a constant.

For a gas at room temperature (298K) and 1 atm pressure, each molecule undergoes approximately 10^9 collisions per second, i.e., I collision in 10^9 second. Thus, if every collision resulted in reaction, the reaction would be complete in 10^9 second. In actual practice this does not happen.

It implies that all collisions are not effective to lead to the reaction. In order to react, the colliding molecules must possess minimum energy called activation energy.

The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.

Fraction of effective collisions (f) is given by the following expression, $e^{-Ea/RT}$

Fraction of collisions is further reduced due to orientation factor.

The fraction of effective collisions (f) having proper orientation is given by the steric factor P.

Rate = P x f x collision rate

Rate= P x e−EaRT x Z $[A_2]$ $[B_2]$ ……..(1)

As per the rate law, Rate = k $[A_2]$ $[B_2]$ …….(2)

Where k is the rate constant

On comparing equation (1) and (2), the rate constant k is,

$k = p Z e^{-Ea / RT}$

19. Calculate the half life of a first order reaction whose rate constant is 200 s^{-1}

Given:

k= 200 s^{-1}

Solution:

∴ Half – life of a first order reaction is

$t_{1/2}$ = 0.693 / k = 0.693 / 200

= 3.46 x 10^{-3} sec

20. For a reaction: $2NH_{3(g)}$ Pt → $N_{2(g)}$+ $3H_{2(g)}$, Rate = K

1. **Write the order and molecularity of this reaction?**
2. **Write the unit of K.**

1. Order of reaction : Zero order. Molecularity = 2

2. Unit of K = mol L^{-1} sec^{-1}

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