CHEMICAL KINETICS

Long Answer Questions:

1. Explain the following terms with suitable examples

a) Average rate of a Reaction b) Slow and Fast Reactions c) Order of Reaction

d) Molecularity of a Reaction e) Activation Energy of a Reaction

Ans. **a) Average Rate of Reaction:** Decrease in concentration of reactants (or) increase in concentration of products per unit time is called average rate of reaction.

1) $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

Rate $= \frac{-\Delta[HI]}{2\Delta t} = +\frac{\Delta[H_2]}{\Delta t} = +\frac{\Delta[I_2]}{\Delta t}$

2) $Hg_{(l)} + Cl_{2(g)} \rightarrow HgCl_{2(s)}$

$rate = \frac{-\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = +\frac{\Delta[HgCl_2]}{\Delta t}$

b) Slow and fast reactions: Based on rate of chemical reactions, reactions are classified in to

i. Very fast Reactions: occurs instantaneously

E.g.: All precipitation and neutralization reactions

ii. Very slow Reactions: E.g.: Rusting of Iron

iii. Moderate Reactions: E.g.: Inversion of cane sugar

c) Order of Reaction: The sum of powers of concentration terms of the reactants in the rate law expression is called the order of that chemical reaction. Order of a reaction can be 0, 1, 2, 3 and even a fraction.

In the rate equation rate $= K[A]^x[B]^y$, order of reaction is x + y

Generally the following methods are used to determine the order of a reaction experimentally

1) Integrated equation method or trial and error method

2) Half-Life method

3) Vant's-Hoff differential method

4) Ostwald isolation method

Example:

$H_{2(g)} + I_{2(g)} \Leftrightarrow 2HI_{(g)}$

Rate= $K[H_2][I_2]$, order = 2

d) Molecularity of a Reaction:

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to form products is called molecularity of the reaction.

Molecularity cannot be zero or a non integer and does not exceed three.

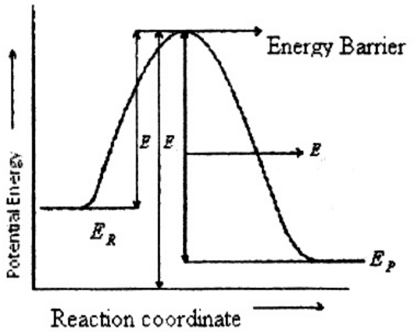
E.g.; unimolecular reaction $NH_4NO_2 \rightarrow N_2 + 2H_2O$

Bimolecular Reaction: $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

Termolecular Reaction: $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

e) Activation Energy of a Reaction:

The difference between threshold energy and energy of normal reacting molecules is called activation energy.



Activation energy (E_a) = Threshold energy (E_T)-Energy of normal molecule

E_p =Energy of products, E_R = Energy of reactants, E_a =activation energy

E_T =threshold energy

$\therefore E_a = E_T - E_R$

*__2. Give a detailed account of the collision theory of reaction rates in bimolecular gaseous reactions?__

Ans. According to this theory

1. Reactant molecules are assumed to be hard spheres and reacting molecules must collide with each other for any reaction to occur.

2. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z)

3. For a bimolecular elementary reaction $A + B \rightarrow products$, Rate of reaction can be expressed as

$Rate = Z_{AB}e^{-Ea/RT}$ Where Z_{AB} collision frequency of reactants A and B

$e^{-Ea/RT}$ = Fraction of molecules with energies equal to or greater than E_a

4. The minimum energy required by the colliding molecules to give products is called threshold energy

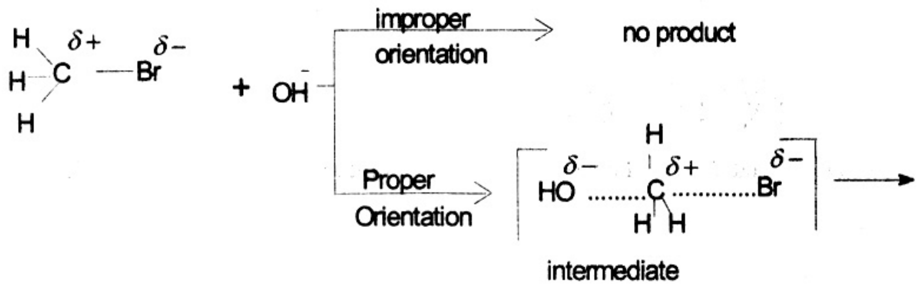
5. The molecules possessing the threshold energy are called activated molecules

6. Collisions occurring between activated molecules are called activated collisions (or) effective collisions

7. To account for effective collisions, another factor 'P' called the probability (or) steric factor is introduced then $rate = PZ_{AB}e^{-Ea/RT}$

$\therefore$ In collision theory, activation energy and proper orientation of the molecules together determine the criteria for effective collisions and hence the rate of a reaction for example, formation of CH_3OH from CH_3Br depends upon orientation of reactant molecules.

The proper orientation of reactant molecules lead to bond formation where as improper orientation makes them simply bounce back and no products are formed



$$HO-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-H + \overline{Br}$$

***3. Define order of a reaction. Give an example to first and second order reaction. How is it obtained experimentally?**

Ans. The sum of powers of the concentration terms of the reactants in the rate law expression is called the order of that chemical reaction. Order of a reaction may be a whole number, negative or fraction.

E.g.: For the reaction $xA + yB \rightarrow products$

Rate $= K[A]^x[B]^y$ $\therefore$ order of reaction = x + y

First order: Reaction in which rate of the reaction is directly proportional to the single concentration term of the reacting substance is called first order reaction.

E.g.: Thermal decomposition of nitrogen pentaoxide

$$2N_2O_5\,(g) \longrightarrow 2N_2O_4\,(g) + O_2\,(g),\ \text{Rate} = k\,[N_2O_5]$$

Decomposition of aqueous hydrogen peroxide

$$2H_2O_2\,(aq) \longrightarrow 2H_2O\,(l) + O_2\,(g),\ \text{Rate} = k\,[H_2O_2]$$

Second order: Reaction in which the rate depends on two concentration terms is called a second order reaction.

E.g.: Decomposition of chlorine monoxide

i.e. $2Cl_2O\,(g) \longrightarrow 2Cl_2(g) + O_2\,(g),\ \text{Rate} = k\,[Cl_2O]^2$

Thermal decomposition of nitrous oxide, $2N_2O\,(g) \longrightarrow 2N_2\,(g) + O_2\,(g),\ \text{Rate} = k\,[N_2O]^2$

Following methods are used to determine the order of reaction experimentally.

1) Integrated equation method or trial and error method
2) Half -life method
3) Van't Hoff differential method
4) Ostwald isolation method

Half-life method

The time required for the initial concentration (a) of the reactants to become half of its value (a/2) during the progress of the reaction is called half life $(t_{1/2})$ of the reaction

The half-life $(t_{1/2})$ is inversely proportional to $a^{(n-1)}$ where 'a' is initial concentration of the reactant and 'n' is the order of the reaction

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

Say a given reaction is started separately with two initial concentrations 'a_1', and 'a_2'. The half - time values $(t_{1/2})_1$ and $(t_{1/2})_2$ are determined experimentally and the order is established from the equation.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Short Answer Questions

*1. **What is 'molecularity' of a reaction? How is different from the 'order' of a reaction? Name one bimolecular and one trimolecular gaseous reaction?**

Ans. The number of reacting species (atoms, molecules or ions) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity.

Order	Molecularity
1. The sum of the powers of the concentration terms of the reactants in a rate equation is called order of reaction	1. The number of atoms or ions or molecules taking part in an elementary reaction is called molecularity.
2. Order of reaction is an experimental quantity	2. It is theoretical quantity and it can be calculated by using reaction Mechanism
3. Order may be whole number/fraction/negative or zero	3. It cannot be zero/non- integer and does not exceed three
4. Order is applicable to elementary as well As complex reactions	4. It is applicable only for elementary reactions

Dissociation of hydrogen iodide in to H_2 and I_2 is a bimolecular reaction.

$$2HI \longrightarrow H_2 + I_2$$

Formation of NO_2 from NO and O_2 is a trimolecular reaction.

$$2NO + O_2 \longrightarrow 2NO_2$$

2. What is half-life $(t_{1/2})$ of a reaction? Derive the equation for the 'half-life' value of zero and first order reactions?

Ans. The half life of a reaction is the time in which the concentration of reactant is reduced to one half of its initial concentration

For a zero order reaction

$$K = \frac{[R_0]-[R]}{t}$$

At $t = t_{1/2}$ $[R] = \frac{[R_0]}{2}$

$$\therefore K = \frac{[R_0]-\frac{[R_0]}{2}}{t_{1/2}} \quad = \frac{[R]_0}{2K}$$

For the first order reaction

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

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

$$K = \frac{2.303}{t_{1/2}}.\log\frac{[R]_0}{[R]_0/2} = \frac{2.303\log 2}{t_{1/2}} = \frac{2.303\times 0.3010}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

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

*__3.__ **Mention the factors that affect the rate of a chemical reaction. Discus the effect of catalyst on the kinetics of a chemical reaction with suitable diagram?**

Ans. Following factors affect the rate of a chemical reaction.

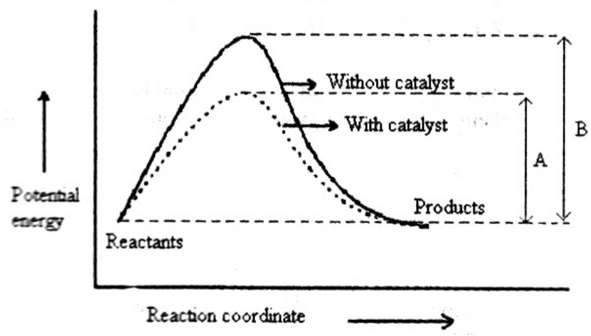
(a) Nature of reactants: Ionic substances react more rapidly than covalent compounds because ions produced after dissociation is immediately available for reaction.

(b) Concentration of reactants: Rate of reaction increases when concentration of reactants is increased.

(c) Temperature: Generally rate of reaction increases on increasing the temperature.

(d) Surface area of the reactants: Rate of reaction increases with increase in surface area of the reactants. That is why powdered form of reactants is preferred than their granular form.

(e) Catalyst: Presence of catalyst also effects the rate of reaction. It decreases the activation energy by forming a reaction intermediate and hence lowers the potential energy barrier. So rate of reaction increases.



Where A = Energy of activation with catalyst
B = Energy of activation without catalyst

4. **What is Arrhenius equation? Derive an equation which describes the effect of rise of temperature (T) on the rate constant (k) of a reaction?**

Ans. Arrhenius rate equation $K = Ae^{-Ea/RT}$

Where 'A' is the Arrhenius factor (or) frequency factor (or) pre-exponential factor

'R' is the gas constant

'E_a' is activation energy

Taking natural logarithm on both sides of equation

$$\ln k = \frac{-E_a}{RT} + \ln A$$

At temperature $T_1, \ln k_1 = \frac{-E_a}{RT_1} + \ln A \rightarrow (1)$

And at temperature $T_2, \ln k_2 = \frac{-E_a}{RT_2} + \ln A \rightarrow (2)$

Equation (2) – (1) $\ln k_2 - \ln k_1 = \frac{-E_a}{RT_2} - \left[\frac{-E_a}{RT_1}\right]$

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \Rightarrow \log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Where K_1 and K_2 are the values of rate constants at temperature T_1 and T_2 respectively

5. Derive the integrated rate equation for a first order reaction?

Ans. For first order reaction, rate of the reaction is proportional to the concentration of the reactant 'R'

For example $R \rightarrow P$

Rate $= \frac{-d[R]}{dt} = K[R]$

$= \frac{d[R]}{[R]} = -Kdt$

Integrating this equation, we get

$\ln[R] = -Kt + I \rightarrow (1)$

Where, I is the constant of integration

When t = 0, $[R] = [R]_0$

From (1) $\ln[R]_0 = -K(0) + I$

$I = \ln[R]_0$

Substitute 'I' in equation (1)

Then $\ln[R] = -Kt + \ln[R_0]$

$K = \frac{1}{t}\frac{\ln[R]_0}{[R]} (\ln = 2.303\log)$

$K = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$ **Or** $K = \frac{2.303}{t}\log\frac{a}{a-x}$

Where a = initial concentration of reactant

X = concentration of reactant consumed

This is integrated from of first order rate equation

Very Short Answer Questions

1. What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be represented quantitatively?

Ans. The rate constant of a reaction increases with increase in temperature and becomes nearly double for every 10^{o} rise in temperature. The effect can be represented quantitatively by Arrhenius equation.

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

2. What is a pseudo first order reaction or pseudo unimolecular reaction?

Ans. A First order reaction with molecularity two is called a pseudo first order reactions or pseudo unimolecular reaction.

Ex; Acid catalysed hydrolysis of ethyl acetate is a pseudo first order reaction, because water is taken large in excess and hence ethyl acetate is said to be isolated.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Rate of the reaction, rate = k $[CH_3COOC_2H_5]$

Its molecularity is 2 but the order of reaction is 1.

3. What is zero order reaction? Give an example?

Ans. The Reaction in which rate of the reaction is independent of the concentration of the reacting substances is called zero order reaction.

E.g. Decomposition of ammonia gas on hot platinum surface

$$2NH_3\,(g) \longrightarrow N_2\,(g) + 3H_2\,(g), \quad \text{Rate} = k\,[NH_3]^{o}$$

4. A reaction has a half life of 10 minutes. Calculate the rate constant for the first order reaction?

Ans. $K = \frac{0.693}{t_{1/2}} = \frac{0.693}{10} = 0.0693\,\text{min}^{-1}$

5. In a first order reactions, the concentration of the reactant is reduced from 0.6 mol/L to 0.2 mol/L in 5min. Calculate the rate constant?

Ans. $K = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{5}\log\frac{0.6}{0.2} = \frac{2.303}{5}\log 3 = \frac{2.303 \times 0.4771}{5} = 0.2197\,\text{min}^{-1}$

6. The half life for a first order reaction is $5 \times 10^{-6}\,\text{sec}$ **what percentage of the initial reactant will react in 2 hours?**

Ans. $K = \frac{2.303}{t}\log\frac{a}{a-x} \Rightarrow \frac{0.693}{5 \times 10^{-6}} = \frac{2.303}{2 \times 60 \times 60}\log\frac{100}{100-x}$

On solving $x = 90.497\%$

7. Show that in the case of first order reaction, the time required for 99.9% completion of the reaction is 10 times that required for 50% completion? (log 2 = 0.3010)

Ans. We know, $K = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$.....$(i)$

$k = \frac{0.693}{t_{1/2}}$, a = 100, x = 99.9

From Equation (i) we get

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\left(\frac{100}{100-99.9}\right)$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log 10^3$$

$$\frac{0.693}{t_{1/2}} = \frac{3 \times 2.303}{t}$$

$$t = 10 \times t_{1/2}$$

8. For a reaction, $A + B \rightarrow product$ **, the rate law is given by** $r = k[A]^{1/2}[B]^2$ **. What is the order of the reaction?**

Ans. Rate law for the reaction is $r = k[A]^{1/2}[B]^2$ $\therefore$Order of the reaction $= \frac{1}{2} + 2 = \frac{5}{2}$

9. A reaction is 50% completed in 2hours and 75% completed in 4hours. What is the order of the reaction?

Ans. First order reaction because $t_{1/2}$ is independent of initial concentration.