CHEMICAL KINETICS

Concepts of chemical kinetics, rate of reaction and factors affecting the rate of reaction

VERY SHORT ANSWER QUESTIONS

1. What is rate of reaction?

Ans: Rate is usually expresses as the ratio of the amount of change in some quantity to the time required to produce that change.

Rate = (Change in some quantity)/(Time taken for the change) = $\Delta X/\Delta t$

The term ΔX means $X_{final} - X_{initial}$ and Δt is the amount of time elapsed

2. What is order of reaction?

Ans: Let us consider a good reaction:

$m_1A + m_2B + m_3C \rightarrow$ product

Let active moles of 'A', 'B' and 'C' be 'α', 'β' and 'γ' respectively. Then, rate of reaction may be given as:

Rate = $k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$

Sum of powers of concentration terms involved in rate law expression is called order of reaction.

$\alpha + \beta + \gamma$ order

3. What are the factors that affect rate of reaction?

Ans: i) Nature of the reactants:

(ii) Concentration of reactants

(iii) Effect of temperature

(iv) Presence of a positive catalyst

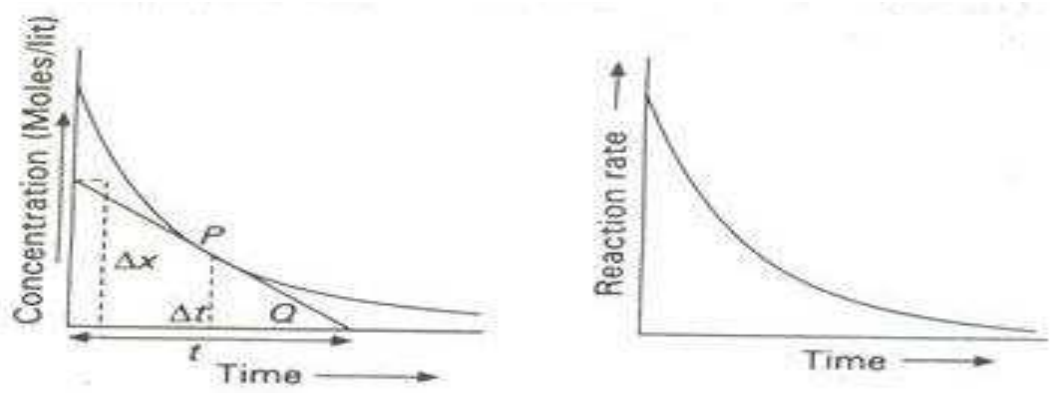
(v) Presence of negative catalyst

SHORT ANSWER QUESTIONS

1. How does rate of reaction change with time?

Ans: Expression of Rate

Since the concentrations of the reactants keep on decreasing with time, the rate of reaction correspondingly decreases with time. Thus, the rate of reaction will depend on the stage considered during progress of the reaction. The rate of reaction is maximum at the initial stage and decreases with time. Theoretically, infinite time would be required for a reaction to complete. But the reaction rate becomes so slow after a certain time that for all practical purposes, the reaction can be considered to be completed. It is evident from fig 8.2 (b) that the rate of reaction is varying from moment to moment.

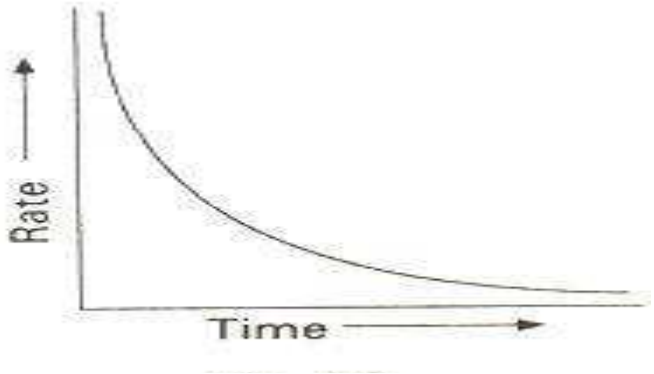


3. How is rate of reaction effected by change of concentration of reactants?

Ans: Concentration of reactants affects the rate of reaction.

Let us consider the reaction:

$A + B \rightarrow C + D$; Rate = k[A][B]



Rate of the above reaction decreases with the passage of time because the concentration of reactants A and B will decrease as time pass on.

4. Explain the effect of temperature on rate of reaction.?

Ans: Effect of temperature

The rate of reaction increases considerably with an increase in temperature. The rates of many reactions are approximately doubled or tripled for every 10^oC rise in temperature. The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperature differing by 10^oC.

μ = Temperature coefficient= $k_{(r+10)}/k_t$

Let temperature coefficient of a reaction be ' μ ' when temperature is raised from T_1 to T_2; then the ratio of rate constants or rate may be calculated as

$$\mathbf{k_{T2}/k_{T1} = (\mu)^{(T_2-T_1)/10} = \mu^{\Delta T/10}}$$

$$\mathbf{\log_{10}(k_{T2}/k_{T1}) = \Delta T/10 \log_{10}\mu}$$

$$\mathbf{k_{T2}/k_{T1} = \text{antilog } [\Delta T/10 \log_{10}\mu]}$$

Its value lies generally between 2 and 3.

LONG ANSWER QUESTIONS

Ans: Factors influencing rate of reaction:

1) Nature of the reactants:

- The rate of reaction depends on the nature of reactants.
- Reactants which require less activation energy react faster than the reactants which require higher activation energy.
- Ionic reactions and neutralisation reactions are very fast in solution as they involve simple exchange of ions.
- Reactions between covalent molecules are generally slow as they involve shuffling of bonds.
  The reactions which involve greater bond rearrangements are slow and the reactions involving lesser bond rearrangements are fast.

Fast reactions	**Slow reactions**
i) $H^+ + OH^- \rightarrow H_2O$	$2H_2O + O_2 \rightarrow 2H_2O$
ii) $2NO + O_2 \rightarrow 2NO_2$	$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$

2) Effect of concentration of reactants:

- According to law of mass action, the rate of a chemical reaction is directly proportional to the product of concentration of reactants.
- In case of gaseous reactions, rate is directly proportional to the product of partial pressures of reactants.
- If concentration is higher, the number of molecules per unit volume is, more and the number of active collisions increases. According to collision theory, rate of reaction increases with increase in the number of collisions.
- The dependence of rate of reaction on the concentration of reactants can be mathematically expressed as $-\frac{dc}{dt} = k.C^n$ (n can take any simple value including zero)

3) Effect of temperature:

- With increase in temperature rate of reaction increases because the number of active collisions or activated molecules increases.

- According to Arrhenius for most of the reactions rate of reaction doubles or triples for every 10° rise in temperature.

  Temperature coefficient ( ) $= \frac{K_{T+10}}{K_T} = 2$ (or) 3

- Arhenious suggested a simple empirical relation between specific rate and temperature.

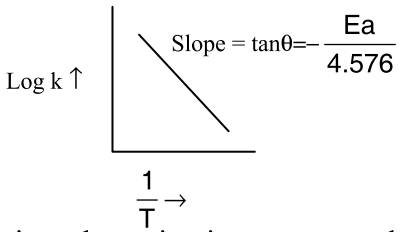
  $K = A.e^{-Ea/RT}$

  $\ell n\, K = \ell n\, A - Ea/RT$

  $2.303\ \ell og\, K = 2.303\ \ell og\, A - Ea/RT$

  $\ell og\, K = \ell og\, A - \frac{Ea}{2.303R} \times \frac{1}{T}$

  Plot of log k Vs $\frac{1}{T}$ gives a linear graph with –ve slope.



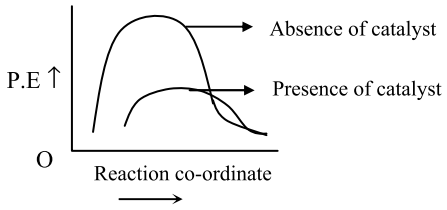
- Slope gives the activation energy and intercept gives frequency factor.

4) Effect of catalyst:

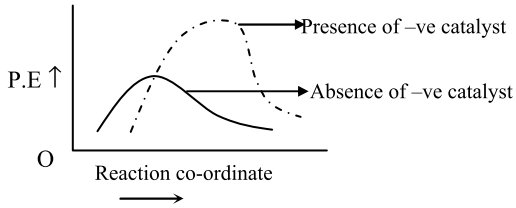
- Catalyst alters the speed of reaction by changing the activation energy.
- Catalyst alters the activation energy by changing the path of the reaction or

mechanism of reaction.

- A positive catalyst increases the rate of reaction by decreasing the activating energy. In case of some reactions, rate is proportional to the concentration of catalyst.
  Ex : Acid catalysed hydrolysis of ester.



- A negative catalyst decreases the rate of reaction by increasing the activation energy.



- Enzymes are biocatalysts for biochemical reactions.

5) <u>Effect of radiation</u>:

- Some chemical reactions take place very fast by absorbing sunlight. Such chemical reactions are called photocatalysed or photo accelerated or photosensitized reactions.

6) <u>Physical state of reactants</u>:

- In heterogeneous system, collisions are not much effective as that of in homogeneous system. There fore reactions are much faster in gaseous and liquid states.
  Rate of reaction:
  Gaseous state > Liquid state >Solid state

7) <u>Physical size of reactants</u>:

- In case of solids, rate increases with decrease in the size of particle. Rate is faster in powdered state than that of undivided state because surface area increases and the possibility of contact between reactant molecules increases.

CHEMICAL KINETICS

Topic-2

Order and molecularity of reactions with examples, zero and first order reaction with examples

VERY SHORT ANSWER QUESTIONS

1. What is order of as reaction?

Ans: The sum of the powers of the concentration terms of reactants in the rate equation is called order of the reaction.
Order of reaction may be zero or fraction or negative or a whole number (n). rder of the reaction can be determined experimentally

2. Name two first order reactions?

Ans: *Examples :*

1. $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2} O_2$
2. $SO_2Cl_{2(g)} \rightarrow SO_{2(g} + Cl_{2(g)}$
3. $H_2O_{2(aq)} \rightarrow H_2O_{(l)} + \frac{1}{2} O_{2(g)}$

3. What is first order reaction?

Ans:

First Order reaction is that reaction whose order is one.

$A \rightarrow$ products

$r = k_1 [A]^1$

equation for rate constant :

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

Units for rate constant: sec^{-1}

4. What is zero order reaction give two examples?

Ans: **Order of reaction zero,**

$A \rightarrow$ products

The concentration of reactant decreases linearly with time. The rate of reaction is uniform. The time required for the completion of reaction is zero.

- Equation for rate constant: $K_o = \frac{x}{t}$.
- Units for rate constant: moles– lit^{-1}– sec^{-1}.
- Half life : $t_{1/2}$ a.

a = initial conc. of the reactants

Examples:

$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$

$2NH_3 \xrightarrow[M_0]{w(or)} N_2 + 3H_2$

$2HI \xrightarrow{Au} H_2 + I_2$

5. What is half life period?

Ans: Half life: It is the time taken for 50% completion of reaction or the time taken for concentration of reactant to become half of its initial value.

- For 1^{st} order reactions, $t_{1/2}$ is independent of initial concentration of reactant.

- The concentration of the reactant left after 'n' half lives,

(a–x) = $\frac{a}{2^n}$.

6. What is molecularity of a reaction?

Ans:

Molecularity of the reaction:

Molecularity of a reaction is the number of reactant molecules taking part in rate determining step. A chemical reaction may take place in one or more steps. Different steps may proceed with different speeds. The slowest step is rate determining step. Molecularity of simple reactions is equal to the stoichiometric coefficients in balanced equation. Molecularity is a theoretical concept. Molecularity is related to mechanism of reaction. Molecularity is always a whole number. Molecularity cannot be zero, –ve, fractional, infinite and imaginary. Generally, moleclarity of a reaction can not be greater than three because more than 3 molecules may not mutually collide with each other.

Examples :

i) $2\ H_2O_2 \rightarrow 2H_2O + O_2$ uni molecular

ii) $2N_2O_5 \rightarrow 2N_2O_4 + O_2$ uni molecular

iii) $PCl_5 \rightarrow PCl_3 + Cl_2$ uni molecular

iv) $2HI \rightarrow H_2 + I_2$ Bimolecular

v) $CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$
Bimolecular

vi) $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
Bimolecular

vii) $2SO_2 + O_2 \rightarrow 2SO_3$ Termolecular

viii) $2CO + O_2 \rightarrow 2CO_2$ Termolecular

ix) $2FeCl_3 + SnCl_2 \rightarrow SnCl_4 + 2FeCl_2$ Termolecular

SHORT ANSWER QUESTIONS

1. **Define order and molecularity of a reaction?**

Ans:

Order of a reaction:

The sum of the powers of the concentration terms of reactants in the rate equation is called order of the reaction.

Order of reaction may be zero or fraction or negative or a whole number (n). rder of the reaction can be determined experimentally

Molecularity of the reaction:

Molecularity of a reaction is the number of reactant molecules taking part in rate determining step. A chemical reaction may take place in one or more steps. Different steps may proceed with different speeds. The slowest step is rate determining step. Molecularity of simple reactions is equal to the stoichiometric coefficients in balanced equation. Molecularity is a theoretical concept. Molecularity is related to mechanism of reaction. Molecularity is always a whole number. Molecularity cannot be zero, –ve, fractional, infinite and imaginary. Generally, moleclarity of a reaction can not be greater than three because more than 3 molecules may not mutually collide with each other.

Examples :

i) $2\ H_2O_2 \rightarrow 2H_2O + O_2$ uni molecular

ii) $2N_2O_5 \rightarrow 2N_2O_4 + O_2$ uni molecular

iii) $PCl_5 \rightarrow PCl_3 + Cl_2$ uni molecular

iv) $2HI \rightarrow H_2 + I_2$ Bimolecular

v) $CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$
Bimolecular

vi) $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
Bimolecular

vii) $2SO_2 + O_2 \rightarrow 2SO_3$ Termolecular

viii) $2CO + O_2 \rightarrow 2CO_2$ Termolecular

2. **How is half life method useful in the determination of order of reaction?**

Half life method

A general expression for the half life, ($t_{1/2}$), is given by

$$\mathbf{t_{(1/2)} \propto 1/a^{n-1}}$$

where 'n' is the order of the reaction.

Starting with different initial concentration a_1 and a_2 for the same reaction, the half lives are $(t_{1/2})_1$ and $(t_{1/2})_2$ respectively are determined. As we know,

$$\mathbf{t_{(1/2)1} \propto 1/a^{n-1}}$$

and $$\mathbf{t_{(1/2)2} \propto 1/a_2^{n-1}}$$

Dividing (i) by (ii),

$$\mathbf{t_{(1/2)1}/t_{(1/2)2} = (a_2/a_1)^{n-1}}$$

3. **Derive relation between the rate constant (K0 and half life period ($t_{½}$) for the first order reaction?**

Ans: A reaction is said to be first order if its rate is determined by the change of one concentration term only.

Consider the reaction

$$A \rightarrow \text{products}$$

Let α be the concentration of A at the start and after time t, the concentration becomes (a-x), i.e, x has been changed into products. The rate of reaction after time 't' is given by the expression

$$dx/dt = k(a-x)$$

$$\text{or } dx/((a-x)) = k\,dt$$

Upon integration of above equation,

$$\int dx/(a-x) = k\int dt$$

$$\text{or} \quad -\log_e (a - x) = kt + c$$

where c is integration constant.

When t = 0 , x = 0,

$$\therefore \quad \mathbf{c = -\log_e a}$$

Putting the value of 'c',

$$-\log_e (a - x) = kt - \log_e a$$

or $\log_e a - \log_e (a - x) = kt$

or $\log_{e\ a/(a-x)} = kt$

or $\mathbf{k = 2.303/t\ \log_{10}\ a/(a-x)}$

The time taken for the completion of same fraction of change is independent of initial concentration. For example, for half change,

$\mathbf{x = 0.5a \quad and \quad t = t_{1/2}}$

$\mathbf{So \quad k = (.303/t_{1/2}\ \log_{10}\ a/0.5a = 2.303/t_{1/2}\ \log_{10}\ 2}$

$\mathbf{= 0.693/t_{1/2}}$

$\mathbf{or \quad t_{1/2} = 0.693/k}$

4. What is Pseudo first order reaction? Explain?

Ans: PSEUDO-ORDER REACTION

Reactions whose actual order is different from that expected using rate law expression are called pseudo-order reactions; e.g.,

(i) $RCl + H_2O \rightarrow ROH + HCl$

Expected rate law:

Rate = $k[RCl]\ [H_2O]$ Expected order = 1+1 =2

Actual rate law:

Rate = k'[RCl]; Actual order = 1

Water is taken in excess; therefore, its concentration may be taken constant. The reaction is, therefore, pseudo first order. Similarly, the acid catalysed hydrolysis of ester, viz.,

$RCOR' + H_2O \leftrightarrow RCOOH + R'OH$

Follow first order kinetics:

Rate = k[RCOOR']

It is also a pseudo-first order reaction.

LONG ANSWER QUESTIONS

1. What is meant by rate law/ Write the rate laws of elementary reactions of fist and second order reactions. Deduce the units for the rate constant (K) oc Zero and first order reactions?

Ans: Rate law and rate constant:

- The equation which relates the rate of the reaction and the concentration of the reactants is known as rate equation or rate law.
- Rate equation is written after the experiment only. It is not related to coefficients of reactants in balanced equation.
- Rate of reaction does not depend on the reactant if it's concentration is large excess.
- "Isolation" methods are usually followed to study rate of the reaction.
- $nA + mB \rightarrow$ products
- rate r $[A]^n [B]^m$; rate = $K[A]^n [B]^m$
- K is called rate constant or specific rate or rate per unit concentration of the reactants.

Order of reaction : zero, $A \rightarrow$ products

The concentration of reactant decreases linearly with time. The rate of reaction is uniform. The time required for the completion of reaction is zero.

Equation for rate constant: $K_o = \frac{x}{t}$.

Units for rate constant: moles– lit^{-1}– sec^{-1}.

Half life: $t_{1/2} \alpha$ a.

a = initial conc. of the reactants

Examples:

$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$

$2NH_3 \xrightarrow[M_0]{w(or)} N_2 + 3H_2$

$2HI \xrightarrow{Au} H_2 + I_2$

Order of reaction: First

$A \rightarrow$ products

$r = k_1 [A]^1$

Equation for rate constant:

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

Units for rate constant: sec^{-1}

The exponential form of the above equation is,

$(a - x) = a.e^{-kt}$

$x = a(1-e^{-kt})$

Half life: It is the time taken for 50% completion of reaction or the time taken for concentration of reactant to become half of it's initial value.

For 1^{st} order reactions, $t_{1/2}$ is independent of initial concentration of reactant.
The concentration of the reactant left after 'n'
half lives, $(a-x) = \frac{a}{2^n}$.
Rate constant, k depends on the
Nature of reactant
Temperature of reaction
Catalyst
Rate constant, k is independent of
Initial concentration of reactant
Time
Half life time: $t_{1/2} \alpha a^0$.
$t_{1/2} = \frac{0.693}{k_1}$

2. Define and explain Molecularity and order of a reaction with suitable examples?

Ans: <u>MOLECULARITY OF REACTION</u>

In general, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation.

OR

The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

e.g., $PCl_5 \rightarrow PCl_3 + Cl_2$ (Unimolecular)

$2HI \rightarrow H_2 + I_2$ (Bimolecular)

$2SO_2 + O_2 \rightarrow 2SO_3$ (Trimolecular)

The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of a reaction.

For example, decomposition of H_2O_2 takes place in the following two steps:

$H_2O_2 \rightarrow H_2O + 1/2O_2$ (overall reaction)

Step 1: $H_2O_2 \rightarrow H_2O + [O]$ (Slow)

Step 2: $[O] + [O] \rightarrow O_2$ (fast)

The slowest step is rate-determining. Thus from step 1, reaction appears to be unimolecular.

Note:

(i) Molecularity is a theoretical concept.

(ii) Molecularity cannot be zero, -ve, fractional, infinite and imaginary.

(iii) Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, e.g. in

$$4HBr + O_2 \rightarrow 2H_2O + 2Br_2$$

$$2MNI_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

In the first reaction molecularity seems to be '5' and in the second reaction molecularity seems to be '23'. Such reactions involve two or more steps; each step has its own molecularity not greater than three, e.g., in first reaction.

$$HBr + O_2 \rightarrow HOOBr$$

$$HOOBr + HBr \rightarrow 2HOBr$$

$$[HOBr + HBr \rightarrow H_2O + Br_2] \times 2$$

$$4HBr + O_2 \rightarrow 2H_2O + Br_2$$

Molecularity of each of the above steps is 2.

ORDER OF REACTION

Let us consider a good reaction:

$m_1A + m_2B + m_3C \rightarrow$ product

Let active moles of 'A', 'B' and 'C' be 'α', 'β' and 'γ' respectively. Then, rate of reaction may be given as:

Rate = $k[A]^{\alpha}\ [B]^{\beta}\ [C]^{\gamma}$

Sum of powers of concentration terms involved in rate law expression is called order of reaction.

$\alpha + \beta + \gamma$ order.

When $\alpha + \beta + \gamma = m_1 + m_2 + m_3$, then

Order of reaction = molecularity of reaction

Order is an experimentally determined quantity. It may be equal to zero, positive, negative, fractional and greater than three. Infinite and imaginary values are not possible.

Examples:

(i) $2H_2O_2 \rightarrow 2H_2O + O_2$

(Observed from law of mass action)

Step 1: $H_2O_2 \rightarrow H_2O + [O]$ [slow]

Step 2: $[O] + [O] \rightarrow O_2$ (fast)

Actual rate $-dx/dt = k[H_2O_2]$

Thus, order of reactions in unity.

3. Describe methods for the determination of order of reaction. ?

Ans: <u>METHODS FOR DETERMINATION OF ORDER OF A REACTION</u>

The important methods used for the following:

1. Method of integration (Hit and trial method)

The most simple method is the one in which the quantities a, x and t are determined and substituted in the kinetic equations of various orders. The equation which gives the most constant value for the specific rate constant (k) for a series of time intervals is the one corresponding to the order of reaction. If all the reactants are at the same molar concentrations, the kinetic equations are:

$k = 2.303/t \log_{10} a/((a-x))$; for first order reactions;

$k = 1/t\ [1/((a-x))-1/a]$; for second order reactions;

$k = 1/t\ [1/(a-x)^2 -1/a^2\ ]$; for third order reactions;

2. Graphical method

A graphical method based on the respective rate laws can also be used.

If the plot of log (a-x) versus 't' is a straight line, the reaction follows second order.

If the plot of $1/(a-x)^2$ versus 't' is a straight line, the reaction follows third order.

In general, for a reaction of nth order, a graph of $1/(a-x)^{n-1}$ versus 't' must be a straight line.

3. Half life method

A general expression for the half life, ($t_{1/2}$), is given by

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

where 'n' is the order of the reaction.

Starting with different initial concentration a_1 and a_2 for the same reaction, the half lives are $(t_{1/2})_1$ and $(t_{1/2})_2$ respectively are determined. As we know,

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

and $t_{(1/2)2} \propto 1/a_2^{n-1}$

Dividing (i) by (ii),

$$t_{(1/2)1}/t_{(1/2)2} = (a_2/a_1)^{n-1}$$

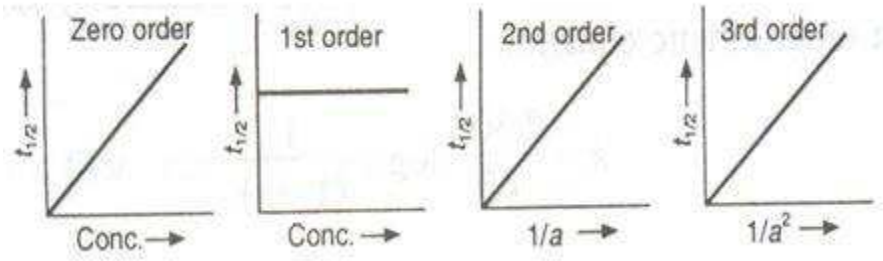
Taking logarithms on both sides,

$\log_{10} (t_{1/2})_1 - \log_{10}(t_{1/2}) = (n^{-1})(\log_{10} a_2 - \log_{10} a_1)$

$$n - 1 = (\log_{10} (t_{(1/2)1} - \log_{10} (t_{1/2})_2)/(\log_{10} a_2 - \log_{10} a_1)$$

or $n = 1 + (\log_{10}(t_{1/2}) - \log_{10}(t_{1/2}))/(\log_{10} a_2 - \text{og}_{10} a_1)$

Plots of half-lives concentration ($t_{1/2} \propto a^{1-a}$):



This relation can be used to determine order of reaction 'n'

4. Van't hoff differential method.

As we know that, the rate of a reaction varies as the nth power of the concentration of the reactant where 'n' is the order of the reaction. Thus, for twp different initial concentrations C_1 and C_2, equations can be written in the form

$$-(dC_1)/dt = kC_1^n \text{ and } -(dC_2)/dt = kC_2^n$$

Taking logarithms,

$$\log_{10}(-(dC_1)/dt) = \log_{10}k + n\log^{10} C_1 \quad \text{.... (i)}$$

$$\text{and } \log10\ (-(dC_2)/dt) = \log_{10}k + n\log^{10} C_2 \quad \text{.....(ii)}$$

Subtracting Eq. (ii) from (i),

$$\log_{10}(-(dC_1)/dt) - \log_{10}((-dC_2)/dt) = n(\log_{10} C_1 - \log_{10} C_2)$$

$$\text{or } n = \log_{10}(-(dC_1)/dt) - \log_{10}((dC_2)/dt)/\log_{10} C_1 - \log_{10} C_2 \quad \text{....(iii)}$$

$-dc_1/dt$ and $-dc_2/dt$ are determined from concentration vs. time graphs and the value of 'n' can be determined.

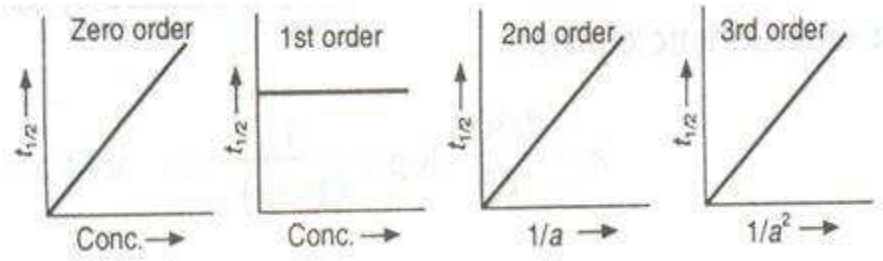
Taking logarithms on both sides,

$$\log_{10} (t_{1/2})_1 - \log_{10}(t_{1/2}) = (n^{-1})(\log_{10} a_2 - \log_{10} a_1)$$

$$n - 1 = (\log_{10} (t(_{1/2})_1 - \log_{10} (t_{1/2})_2)/(\log_{10} a_2 - \log_{10} a_1)$$

$$\text{or } n = 1 + (\log_{10}(t_{1/2}) - \log_{10}(t_{1/2}))/(\log_{10} a_2 - \text{og}_{10} a_1)$$

Plots of half-lives concentration ($t_{1/2} \propto a^{1-a}$):



This relation can be used to determine order of reaction 'n'

4. Derive rate equation for first order reaction and derive expression for half life period?

Ans: <u>First order reactions</u>

A reaction is said to be first order if its rate is determined by the change of one concentration term only.

Consider the reaction

$$A \rightarrow \text{products}$$

Let α be the concentration of A at the start and after time t, the concentration becomes (a-x), i.e, x has been changed into products. The rate of reaction after time 't' is given by the expression

$$dx/dt = k(a-x)$$

$$\text{or } dx/((a-x)) = k\,dt$$

Upon integration of above equation,

$$\int dx/(a-x) = k\int dt$$

or $$-\log_e (a - x) = kt + c$$

where c is integration constant.

When t = 0, x = 0,

$\therefore$ $c = -\log_e a$

Putting the value of 'c',

$$-\log_e (a - x) = kt - \log_e a$$

or $\log_e a - \log_e (a - x) = kt$

or $\log_e a/(a-x) = kt$

or $k = 2.303/t \log_{10} a/(a-x)$

This is known as the kinetic equation for a reaction of the first order. The following two important conclusions are drawn from this equation:

(i) A change in concentration unit will not change the numerical value of k. let the new unit

So $k = 2.303/t \log_{10} na/n(a-x)$

or $k = 2.303/t \log_{10} a/(a-x)$

Thus for first order reaction, any quantity which is proportional to concentration can be used in place of concentration for evaluation of 'k'.

(i) The time taken for the completion of same fraction of change is independent of initial concentration. For example, for half change,

$x = 0.5a$ and $t = t_{1/2}$

So $k = 2.303/t_{1/2} \log_{10} a/0.5a = 2.303/t_{1/2} \log_{10} 2$

$= 0.693/t_{1/2}$

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

Thus, $t_{1/2}$ is independent of initial concentration 'a'.

This time't' in which the initial concentration becomes half is termed as half life period. Half life period of a first order reaction is independent of the initial concentration of the reactant.

Since the velocity constant is independent of concentration and depends inversely on the time, the unit of k will be $time^{-1}$, i.e., sec^{-1} or min^{-1} or $hour^{-1}$. The equation of the first order can also be written in the following form when initial concentration is not known.

5 Derive rate equations for zero order reaction?

Zero order reactions

A reaction is said to be of zero order if its rate is independent of the concentration of the reactants, i.e., the rate is proportional to the zeroth power of the concentration of the reactants.

For the reaction

$A \rightarrow$ products to be of zero order,

$-dx/dt = k[A]^0 = k$

Some photochemical reaction and a few heterogeneous reactions are zero-order reactants. Such reactions are not common.

Example:

1. **Photochemical reaction between hydrogen and chlorine**:

$$H_2(g)\ Cl_2(g) \xrightarrow{hv} 2HCl(g)$$

This photochemical reaction is zero-order reaction. The reaction is studied by placing H_2 and Cl_2 gases over water. the rate of reaction is studied by nothing the rate at which water rises in the vessel due to dissociation of HCl formed. the rate of rise of water is the same as the rate of disappearance of H_2 and Cl_2, i.e., the concentration of the gases phase will not change with time, although the quantities will change.

2. **Decomposition of N_2O on hot platinum surface:**

$N_2O \rightarrow N_2 + 1/2\ O_2$

Rate $[N_2O]^0 = k[N_2O]^0 = k$

$d[N_2O]/dt = k$

3. **Decomposition of NH_3 in presence of molybdenum or tungsten is a zero-order reaction.**

$2NH_3 \rightarrow N_2 + 3H_2$

The surface of the catalyst is almost completely covered by NH_3 molecules. The adsorption of gas on the surface cannot change by increasing the pressure or concentration of NH_3. Thus, the concentration of gas phase remains constant although the product is formed. Therefore, this reaction zero order kinetics.

Other examples of zero order are:

4. **Decomposition of NI on the gold surface**.

5. **Iodations of acetone in presence of H^+ ions**.

$$CH_3COCH + I_2 \rightarrow ICH_2COCH_3 + HI$$

The rate equation of this reaction does not include $[I_2]$ factor, i.e.,

$$-dx/dt = k[CH_3\ COCH_3\ ][H^+]$$

Characteristics of zero order reaction

(a) The concentration of reactant decreases linearly with time.

$$[A]_t = [A]_0 - kt$$

(b) The time required for the reaction to be complete, i.e., time at which [A] is zero.

$$t_{completion} = [A]_0/k = \text{(Initial concentration)/(Rate constant)}$$

(c) The units of k are mol L^{-1} $time^{-1}$.

6. Explain the collision theory of rate of reaction?

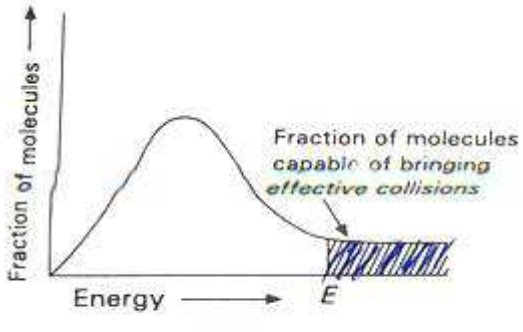
<u>COLLISION THEORY OF REACTION RATE (ARRHENIUS THEORY OF REACTION RATE)</u>

(1) A chemical reaction takes place due to collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z). The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.

(2) Every collision does not bring a chemical change. The collisions that actually produce the products are effective collisions. The effective collisions which bring chemical change are few in comparison to the form a product are ineffective elastic collisions, i.e., molecules just collide and disperse in different directions with different velocities. For a collision to be effective, the following two barriers are to be cleared.

Energy barrier

The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as threshold energy.



In the graph 'E' corresponds to minimum or threshold energy for effective collision in a hypothetical reaction.

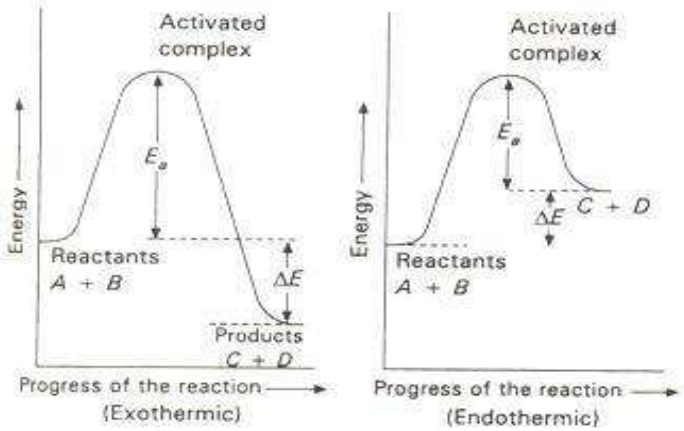
There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy as to cross the energy barrier.

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy.

Activation energy = threshold energy - average kinetic energy of reacting molecules

Threshold energy = initial potential energy of reactant molecules + activation energy.

A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the activated complex. The life span of an activated complex is very small. Thus, the activated complex breaks either into reactants again or new substances, i.e., products. The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products. The energy changes during exothermic and endothermic reactions versus the progress of the reaction are shown in the figure given below.



NUMERICALS

1.The rate constant of a first order reaction is 0.693 sec^{-1}. What is its $t_{½}$?

Sol: Rate constant (K) = $\dfrac{0.693}{\text{Half – life } (t_{½})}$

Given K = 0. 693 sec^{-1}

$$\Rightarrow \quad t_{½} = \frac{0.693}{K} = \frac{0.693}{0.693\ sec^{-1}} = 1\ sec$$

$$\therefore \quad t_{½} = 1\ sec$$

2. The initial concentration of 'A' is 0.3 moles /lit. The concentration after 2.3 minutes is 0.15 moles /lit. What is the value of rate constant?

Sol: Rate constant (K) = $\dfrac{\text{Change in concentration}}{\text{time}}$

Given change in concentration = 0.3 – 0.15 = 0.15 moles /lit

Time = 2.3 min

$$(K) = \frac{\text{Change in concentration}}{\text{Time}} = \frac{0.15}{2.3} = 0.0652 \text{ moles.lit}^{-1}.\text{min}^{-1}$$

CHEMICAL KINETICS

Topic-3

Collision theory and concepts, activation energy and its importance

VERY SHORT ANSWER QUESTIONS

1. What is law of mass action?

This law relates rate of reaction with active mass or molar concentration of reactants.

At a given temperature, the rate of a reaction at a particular instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction."

Active mass = molar concentration of the substance

= (number of gram moles at the substance)/(volume in litres)

= (w/M)/V=n/V

where w = mass of substance and 'M' is the molecular mass in grams. 'n' is the number of g moles and V is volume in litres.

2. 4 g of hydrogen and 128 g of hydrogen iodide are present in a 2 litre flask. What are their active masses?

Solution: Mass of hydrogen = 4 g , Mol. mass of hydrogen = 2

Volume of the flask = 2 litres

Active mass of hydrogen = 4/2*2 = 1 mol L^{-1}

Mass of HI = 128 g

Mol. mass of HI = 128 g

Volume of the flask = 2 litre

Active mass of hydrogen iodide = 128/(128*2) = 0.5 mol L^{-1}

3. **What are very fast reactions?**

Very fast or instantaneous reactions:

These reactions are so fast that they occur as soon as the reactants are bought together. Generally, these reactions involve ionic species and thus known as ionic reactions. These reactions take about 10^{-14} to 10^{-16} seconds for completion. It is almost impossible to determine the rates of these reactions. Some such examples are:

(i) Precipitation of AgCl when solutions of silver nitrate and sodium chloride are mixed.

$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

(ii) Precipitation of $BaSO_4$ when solutions of barium chloride and sulphuric acid and mixed.

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

(iii) Neutralisation of an acid with a base when their aqueous solutions are mixed.

$HCl + NaOH \rightarrow NaCl + H_2O$

Acid Base Salt

4. **What are very slow reactions?**

Very slow reactions:

There are certain reactions which are extremely slow. They make take months together to show any measurable change at room temperature. It is also difficult to study the kinetics of such reactions.

Some examples are:

(i) **Reaction between hydrogen and oxygen at room temperature room temperature**

$2H_2+O_2$ ——> $2H_2O$ (very slow reaction)

(ii) **Reaction of atmospheric H_2S on basic lead acetate**.

White basic lead acetate paint turns black very slowly (due to formation of PbS.)

(iii) Reaction between carbon and oxygen at room temperature

$C + O_2 \quad --\!\!\longrightarrow \quad CO_2$

5. **What are moderate reactions?**

Ans: Moderate reactions:

Between the above two extremes, there are a number of reactions which take place at moderate and measurable rates at room temperature and it is these reactions which are studied in chemical kinetics. Mostly these reactions are molecular in nature. Some common examples of such type are given below:

(i) Decomposition of hydrogen peroxide

$$2H_2O_2 \rightarrow 2HO + O_2$$

(ii) Decomposition of nitrogen pentoxide

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

SHORT ANSWER QUESTIONS

1. What is the importance of Chemical kinetics?

Ans: The chemical reactions can be slowed down or speeded up by changing conditions under which they occur. For example, very slow reaction. $CO + 2H_2 \rightarrow CH_3OH$, can be speeded up by maintaining temperature around 400^oC, pressure about 300 atmosphere and using a catalyst containing ZnO and Cr_2O_3. The decay of food articles can be slowed down by reserving them in refrigerators. There are two principal reasons for studying chemical kinetics.

(i) To predict the rate of a particular reaction under specified conditions:

The conditions can be adjusted to make the reactions to go at a desired rate, either rapidly or slowly or moderately. The field of chemical kinetics is useful in industry as the conditions for maximum yields of industrial products can be ascertained.

(ii) To predict the mechanism of the reaction:

The intelligent guess regarding various elementary processes responsible for the formation of products can be made which should be consistent with experimental data.

2. **What are the main postulates of collision theory?**

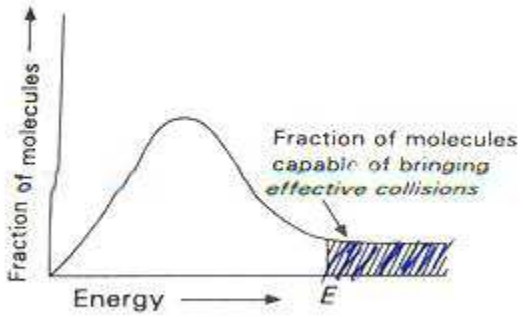
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3. **What are energy barrier, threshold energy and activation energy?**

Ans: Energy barrier

The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as threshold energy.



In the graph 'E' corresponds to minimum or threshold energy for effective collision in a hypothetical reaction.

There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy as to cross the energy barrier.

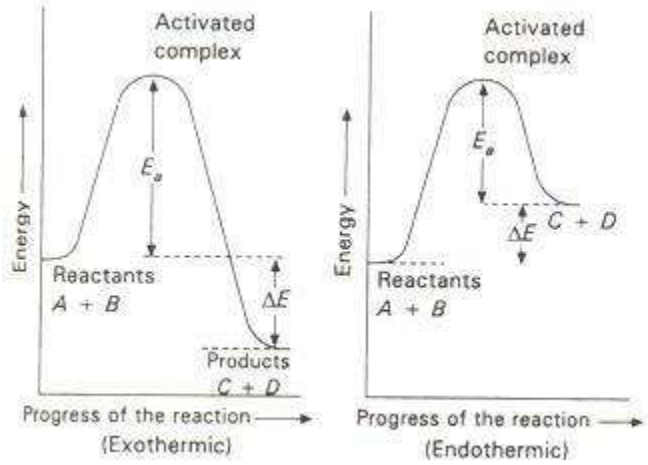
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LONG ANSER QUESTIONS\

1. What are the main postulates of simple collision theory of reaction?

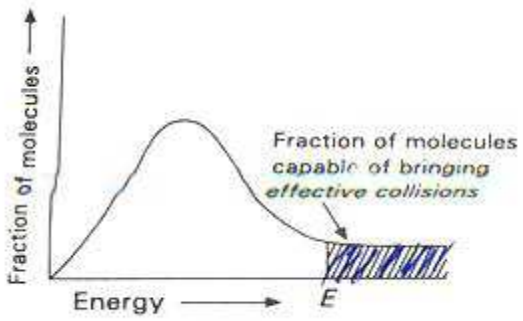
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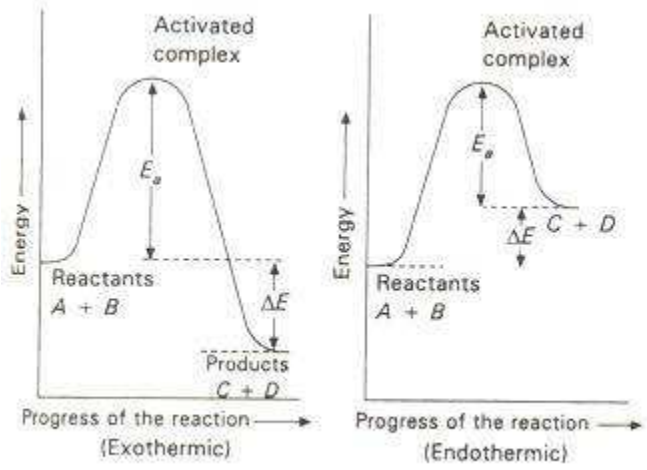
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Thus, every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after collision and then they can go to the right side of the slope and consequently change into products. If the activation energy for a reaction is low, the fraction of effective collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of active molecules increases, i.e., the number of effective collisions will increase and the rate of reaction will increase.

Activation energy E_a - $E_{(activated\ complex)}$ - $E_{(ground\ state)}$

ΔH = activation energy of forward reaction - activation energy of background reactions

Orientation barrier

Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper manner if the reaction is to occur. This has been shown in Fig.8.5.

Rate of reaction is directly proportional to the number of effective collisions.

Rate = dx/dt = collision frequency × factor of effective collisions

= z × f

