CHEMICAL KINETICS

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I) DEFINITIONS:

1) **Chemical kinetics:** It is a branch in physical chemistry which deals with the study of rate of a chemical reaction , the factor affecting their rates and the mechanism by which a chemical reaction occurs.

2)**Rate of reaction:** It is defined as the change in concentration of the reactant or product per unit time.

3) **Average rate:** It is defined as the change in concentration of a reactant or product divided by the time interval over which the change occurs.

4)**Instantaneous rate:** It is defined as the rate of a reaction at a specific instant.

5)**Rate law:** It is defined as an experimentally determined equation that expresses the rate of chemical reaction in terms of molar concentration of the reactants.

6)**Order of a reaction:**It is the sum of the exponents to which the concentration terms in the rate law are raised.

7)**Molecularity of a reaction:** It is defined as the number of reacting species (atoms, ions or molecules)involved in an elementary reaction.

8)**Rate constant or the specific reaction rate**:It is defined as the rate of the reaction when the concentration of the reactant is unity.

9) **Zero order reactions:** The chemical reaction in which the rate of the reaction is independent of the concentration of the reactants and remains constant throughout the course of the reaction are called zero order reactions.

10)**First order reaction:**The reactions in which the rate of reaction depends on the concentration of only one reactant are called first order reactions.

11)**Pseudofirst order reactions or Pseudo unimolecular reactions:** The chemical reactions that have higher order true rate law but are found to behave as first order called pseudomolecular or pseudofirst order reaction.

12)**Half life period:** The time required for a chemical reaction to reduce the original concentration of the reactant to half of its initial value is called half life period.

13)**Integtraed rate law:**The equations which are obtained by integrating the differential rate laws and which give a direct relationship between the concentration of the reactants and time are called integrated rate laws.

II) DISTINGUISH BETWEEN:

1) Distinguish between order and molecularity of a reaction.

Ans:

Sr. No.	**Order of a reaction**	**Sr. No**	**Molecularity of a reaction**
1	It is an experimental determined quantity	**1**	It is a theoretical value i.e. assigned parameter.
2	It may be a fraction or a whole number or even zero.	**2**	It is always a whole number and is never zero.
3	It may change with experimental conditions.	**3**	It does not change with experimental conditions
4	It is the property of both elementary and complex reactions.	**4**	It is the property of only elementary reactions and has no meaning for complex reactions.
5	It is the sum of the exponents to which the concentration terms in the rate law are raised.	**5**	It is defined as the number of molecules or ions taking part in an elementary reaction.

III) DERIVATIONS:

1) Derive an expression for rate constant of a first order reaction.

Ans: Consider the simple first order reaction as shown below:

$$\mathbf{A \longrightarrow products}$$

The differential rate equation for the above reaction is given by

i.e.- $\frac{d[A]}{dt} = k[A]$ ---------------------I

where .- $d[A]/dt$ = Rate of reaction at time t

[A] = Concentration of reactant A

If $[A]_0$ = initial concentration of the reactant at time t =0

and $[A]_t$ = concentration of A after time t=t

then integrating equation I within the limits $[A]=[A]_0$ at t= 0 and $[A]=[A]_t$ **at t=t,** we get

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k\int_0^t dt$$

$$\Big\{\ln[A]\Big\}_{[A]_0}^{[A]_t} = -k\,[t]_0^t$$

$$\ln[A]_0 -- \ln[A]_t = -k(t-0)$$

$$\ln\frac{[A]_t}{[A]_0} = -k.t$$

Therefore $k.t = \ln\frac{[A]_0}{[A]_t}$

i.e. $k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t}$ ----------------II

Converting ln to $\log_{10}$, equation II is written as

i.e. $k = \frac{2.303\log_{10}}{t}\frac{[A]_0}{[A]_t}$ ----------------- III

Equation III is the expression for rate constant of first order reaction.It can be written in two alternative forms as follows:

i) $\ln\frac{[A]_t}{[A]_0} = -k.t$

Taking antilogs on both sides, we get

$$\frac{[A]_t}{[A]_0} = e^{-kt}$$

Therefore $[A]_t = [A]_0 e^{-kt}$

ii) If '**a'** is the initial concentrations of **reactant A** in moles dm^{-3} and **x** is the amount of reactant getting converted to products in time t, then the amount left after **time t** is **(a-x)**

Substituting **$[A]_0$ =a** and **$[A]_t$ =(a-x)** in equation III, we get

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x}$$

2)Show that the half life period of a first order reaction is independent of its initial concentration.

Ans: **Half life period:** The time needed for the reactant concentration to fall to one half of its initial value is called half life period.

Expression: The rate constant of the first reaction is given by

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

where $[A]_0$ = initial concentration of the reactants.
$[A]_t$ = concentration after time t.
k = rate constant of the reaction.

At half life, at **$t = t_{1/2}$** , $[A]_t$ **$= [A]_0/2$**

$$\text{Hence} \quad k = \frac{2.303}{t_{1/2}} \log \frac{[A]_0}{[A]_0/2}$$

$$= \frac{2.303}{t_{1/2}} \log_{10} 2$$

$$= \frac{2.303 \times 0.3010}{t_{1/2}}$$

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

$$\text{Therefore} \quad t_{1/2} = \frac{0.693}{k}$$

The half life period of the reaction is independent of the initial conc. of the reactants.

For a reaction of nth order, **$t_{1/2}$ α $1 / a^{n-1}$**

3) Derive an expression for rate constant for a second order reaction with equal concentrations.

Ans: Consider the following reaction of second order

$$A + B \longrightarrow \text{products}$$

For this reaction

Rate of reaction = k[A][B] --------------------I

i.e $\frac{dx}{dt} = k[A][B]$

Let **a** be the initial concentration in moles dm^{-3} each of reactant A and B.

Let **x** moles dm^{-3} of each of the reactants A and B react in time t.

Therefore after time t,

$$[A] = [B] = (a-x) \text{ moles dm}^{-3} \qquad \text{----------------II}$$

Substituting II in I, we get

$$\frac{dx}{dt} = k(a-x)(a-x) = k(a-x)^2 \qquad \text{-----------------III}$$

$$\frac{dx}{(a-x)^2} = k.dt \qquad \text{------------------IV}$$

Integrating equation IV, we get

$$\int \frac{dx}{(a-x)^2} = k \int dt$$

$$\frac{1}{(a-x)} = k.t + c \qquad \text{where c is the constant of integration ----------V}$$

To find c, we put x= 0 when t= 0 (at the start of the reaction)

$$\frac{1}{a} = c \qquad \text{--------------VI}$$

Substituting equation VI in V, we get

$$\frac{1}{a-x} = k.t + \frac{1}{a}$$

$$\frac{1}{a-x} - \frac{1}{a} = kt$$

$$\frac{a-(a-x)}{a(a-x)} = k.t$$

Therefore $k = \frac{1}{at} . \frac{x}{(a-x)}$

5)Derive an expression for half life of a second order reaction with equal concentration of reactants.

Ans: The time required for a chemical reaction to reduce the original concentration of the reactant to half of its initial value is called half life period.

For a second order reaction with equal concentration, the expression for rate constant is given by

$$\mathbf{k = \frac{1}{at} \frac{x}{a-x}}$$

When t = $\mathbf{t_{1/2}}$, **x =** a/2

Therefore

$$k = \frac{1}{a.t_{1/2}} \cdot \frac{a/2}{a - a/2}$$

$$k = \frac{1}{a.\ t_{1/2}}$$

Therefore

$$t_{1/2} = 1/a.k$$

Thus for a second order reaction, the half life is inversely proportional to its initial concentration.

SHORT ANSWER QUESTIONS:

1) Explain the term 'rate law' with suitable example.

Ans: Rate law: It is defined as an experimentally determined equation that expresses the rate of a chemical reaction in terms of molar concentration of the reactants.

Explanation:

Consider a reaction

$$aA + bB \longrightarrow \text{products}$$

By **law of mass action**

$$\text{Rate} \propto [A]^a [B]^b$$

$$= k [A]^a [B]^b \quad \text{--------------------I}$$

In equation I , the rate of reaction is expressed in terms of product of molar concentration of reactants A and B raised to powers **a** and **b** of concentration of reactants A and B respectively.But these powers may or may not be same as the stoichiometric coefficient of the reactants in the balanced chemical equation

e.g

Consider a reaction

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

By law of mass action,

$$\text{Rate of reaction} = k[N_2O_5]^2$$

But under the experimental conditions, the observed rate is given by

$$\text{Rate of reaction} = k[N_2O_5] \quad \text{---------------------II}$$

Equation II is called rate law equation

For single step reactions, law of mass action and rate law expression are same. However for multistep complex reactions, they differ.

Examples of rate law: **Rate law**

i) $H_2 + I_2 \Longleftrightarrow 2HI$ **Rate** $= k[H_2][I_2]$

ii) $2N_2O \Longleftrightarrow 2N_2 + O_2$ **Rate** $= k[N_2O]$

2) Explain the term order of a reaction.
Ans :

Order of a reaction:

The sum of the exponents to which the concentration terms in the rate law are raised is called overall order of the reaction while the exponent to which the concentration of that reactant in the rate law is raised is called partial order of that reactant.

Consider the reaction

$$aA + bB \longrightarrow products$$

If the rate law expression for the above reaction is

$$Rate = k[A]^a [B]^b$$

then the order of the reaction is

a) **a** with respect to reactant **A**
b) **b** with respect to reactant **B**
and the overall order of the reaction is **(a + b)**.

Eg Consider the following reaction

$$2N_2O_5 \Longleftrightarrow 4NO_{2(g)} + O_{2(g)}$$

The rate law expression for the above reaction is

$$Rate = k[N_2O_5]$$

The power of $[N_2O_5]$ is one. Hence order of the reaction is one though the coefficient of the reaction is 2.

Thus it can be concluded that
i) order is an experimental determined quantity

ii) order for a reaction may be zero, whole number or a fraction.

iii) order of the re reaction has no relation with the coefficient of the reactant molecules in the rate equation.

3) Explain the term 'molecularity' of a reaction.
Ans: It is defined as the number of reacting species (atoms, ions or molecules)involved in each step of a chemical reaction(elementary reaction)

On the basis of molecularity, chemical reactions are of following types:

i)Unimolecular reactions: In this type, only one molecule is involved in the reaction.

$$Eg\ PCl_5 \longrightarrow PCl_3 + Cl_2$$

ii)<u>Bimolecular reaction:</u> It is a reaction which involves two molecules of the reactant.

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

iii)<u>Termolecular reaction:</u> It is a reaction in which three molecules of the reactant are involved in the reaction.

$$2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$$

Molecularity of four is not known because collision of four particles in a single step is not a favorable situation.

i) Molecularity is always a whole number.

ii) It is a theoretical value and is applied to a single step reactions(elementary reactions).

4)Define rate constant or specific reaction rate. Give its unit in SI system.

Ans: The rate constant of the reaction or the specific reaction rate is defined as the rate of the reaction when the concentration of the reactant is unity.

Unit: $(\text{moles dm}^{-3})^{1-n}.\text{sec}^{-1}$.

<u>Derivation:</u> It is derived as follows:

Consider a reaction of n^{th} order.The rate law expression for nth order reaction is given by

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

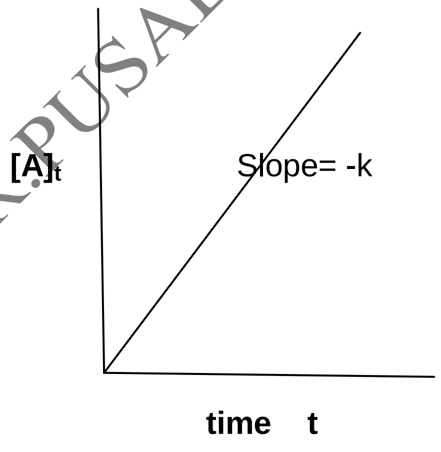
$$\frac{(\text{moles dm}^{-3})}{\text{sec}} = k\,[\text{molesdm}^{-3}]^n$$

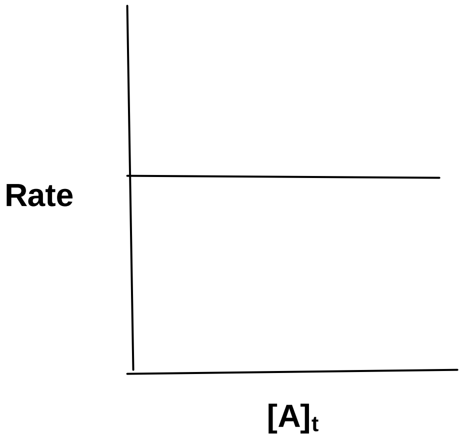
Therefore, $$k = \frac{\text{molesdm}^{-3}}{[\text{molesdm}^{-3}]^n} \cdot \frac{1}{\text{sec.}}$$

$$= (\text{moles dm}^{-3})^{1-n}\,.\text{sec}^{-1}$$

5) Plot a graph of i) conc.vs time. ii) rate of reaction vs concentration for a zero order reaction.

Ans:





6) What are first order reactions? Give suitable examples.

Ans: The reactions in which the rate of reaction depends upon the concentration of only one reactant are called first order reactions.

Explanation: Consider a reaction

$$\mathbf{A \longrightarrow Products}$$

Rate of reaction α [A]

$= k\,[A]^{1}$ ------------- I

where k is the rate constant of the reaction.

In equation I , power of [A] is one therefore it represents first order reaction.

Examples:

i) Decomposition of nitrogen pentoxide

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

Rate = k[N_2O_5] . the power of [N_2O_5] .is one therefore order is one.

ii) Decomposition of ammonium nitrite:

$$NH_4NO_2 \longrightarrow N_{2(g)} + 2H_2O_{(l0}$$

Rate = k[NH_4NO_2] , the power of [NH_4NO_2] is one therefore order is one.

iii) Decomposition of hydrogen peroxide:

$$2H_2O_2(l) \xrightarrow{Pt} 2H_2O(l) + O_2(g)$$

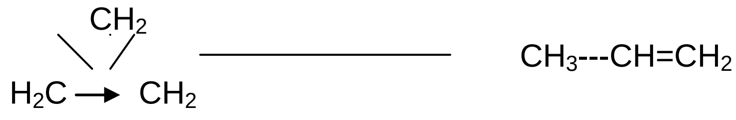
Rate = k[H_2O_2] . the power of [H_2O_2] is one therefore order is one.

iv) Decomposition of phosphorous pentachloride:

$$PCl_5\,(g) \longrightarrow PCl_3\,(g) + Cl_{2(g)}$$

Rate = k[PCl_5] . the power of [PCl_5] is one therefore order is one.

v) Conversion of cyclopropane to propene



Cyclopropane propylene

Rate = k[C_3H_6]

7) Give the characteristics of first order reactions.
Ans:

i) The rate of reaction depends on the concentration of only one reactant.

ii) The expression for the rate constant is given by

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

where $[A]_0$ = initial concentration of the reactant.

$[A]_t$ = amount left after time t.

iii) The half life period of a first order reaction is independent of the initial concentration of the reactants.

iv) A graph of $\log[A]_t$ vs time for a first order reaction is a straight line with slope = $\frac{-k}{2.303}$

v) A plot of rate of first order reaction with concentration of a reactant gives a straight line passing through origin with slope = k.

8)Plot the graphs of the following variables in case of first order reaction and write the expression for slope from each graph.

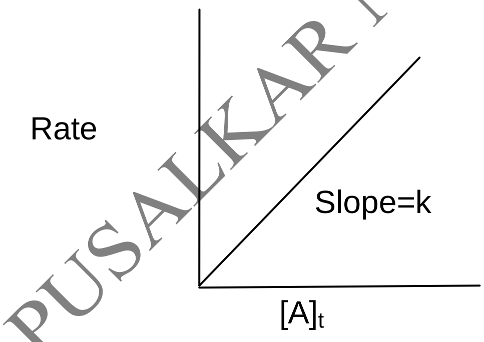
i) rate of reaction vs concentration of reactant

ii) concentration of reactant vs time.

iii) $\log[A]_t$ vs time.

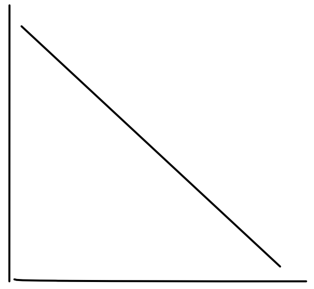
iv) $\log\frac{[A]_0}{[A]_t}$ vs time

Ans: i) **Graph of rate of reaction vs concentration of reactants.**



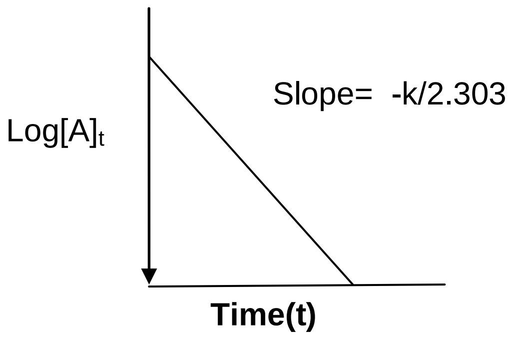
Slope = k

ii)**Graph of concentration of reactants vs time**.

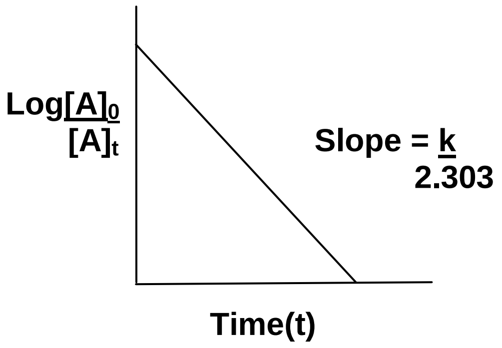


Slope = $\frac{\text{concentration}}{\text{time}}$

iii)**Graph of log$[A]_t$ vs time**.



iv) Graph of $\log\frac{[A]_0}{[A]_t}$ vs time



9)Explain the term 'pseudomolecular or pseudofirst order reaction with a suitable example.

Ans: Consider a reaction

$$A + B \longrightarrow \text{products}$$

The rate law expression for the above reaction is given by

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

If concentration of B is taken in excess , then the rate law expression becomes

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

Thus the observed rate depends on the concentration of A only and is independent of concentration of B. Though two molecules A and B are involved in the reaction, the reaction is first order w.r.t. A and zero order w.r.t. B. Hence overall order of the reaction is one .Such reactions are called pseudomolecular reactions.

Definition of pseudomolecular reaction: The chemical reactions which have higher order true rate law but are found to behave as first order are called pseudomolecular or pseudofirst order reaction.

Examples of psudomolecular reaction or pseudofirst order reaction:

i)**Hydrolysis of methyl acetate:**

$$CH_3COOCH_3 + H_2O \xrightarrow{dil.HCl} CH_3COOH + CH_3OH$$

The molecularity of this reaction is 2 .However , when water is taken in excess, the rate of the reaction is found to change with change in concentration of methyl acetate only. Hence this reaction is a pseudounimolecular reaction.

$$Rate = k[CH_3COOCH_3]$$

The reaction is carried out by mixing a small volume of methyl acetate with excess of dil HCl. A known volume of the reaction mixture is pipetted out at definite time intervals in a conical flask containing few ice pieces and phenolphthalein as indicator and titrated against standard NaOH solution.The amount of acetic acid formed during the hydrolysis is a measure of ester hydrolysed.

Let T_0 be the titre reading at the start of the reaction. i.e on mixing the solutions.

Let T_t be the titre reading at different time intervals.

Therefore , $x= T_t – T_0$ gives the amount of ester hydrolysed at time t

Let T_∞ = titre reading for complete hydrolysis of ester which corresponds to HCl present and total amount of acetic acid produced.

Therefore the total amount of ester hydrolysed is given by

$$a = T_\infty - T_0$$

The expression for rate constant for first order reaction is given by

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

Here $a= T_\infty - T_0$ and $a-x =(T_\infty - T_0) – (T_t – T_0) = T_\infty - T_t$

$$k = \frac{2.303}{t} \log \frac{T_\infty - T_0}{T_\infty - T_t}$$

ii) **Inversion of cane sugar:**

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{dil.HCl} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$Rate = k[C_{12}H_{22}O_{11}] [H_2O]$$

If water is taken in excess, then

$$Rate = k[C_{12}H_{22}O_{11}]$$

The molecularity of the reaction is 2 but the order of the reaction is one. Hence it is a pseudofirst order reaction.

10)Describe the Isolation method of determination of rate law and order of the reaction.

Ans: This method is applicable to chemical reactions with more than two reactants.In this method, the concentration of all the reactants except one(isolated) are taken in large excess so that the rate of the reaction only will depend upon the concentration of the isolated reactant This rate is experimentally determined. The experiment is repeated by isolating one of the reactants each time and determine the rate law with respect to the isolated species.From all the experiments the overall order and rate of the reaction is determined.

Example
Consider the following reaction

$$aA + bB \longrightarrow \text{Products}$$

The rate law equation is

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

If B is taken in excess then A becomes isolated.The initial conc. of B will remain constant through out the experiment i..e. $[B]_0$ = constant.Therefore te rate law becomes

$$\textbf{Rate} = k[A]^x[B]_0^y = k^1[A]^x \text{ where } k^1 = k[B]_0$$

Taking log on both sides we get

$$\log[\text{Rate}] = \log k^1 + x \log[A]$$

By plotting a graph of log(rate) vs log[A], a straight line is obtained with slope = x.is obtained.Thus we get the value of x from this experiment.

In another experiment, If A is taken in excess, then $[A]_0$ = initial concentration of A remains constant during the course of the reaction.The rate law then becomes

$$\text{Rate} = k[A]_0^x[B]^y = k^{11}[B]^y \text{ where } k^{11} = k[A]_0^x$$

Taking log on both sides we get

$$\log[\text{Rate}] = \log k^{11} + y \log[B]$$

By plotting a graph of log(rate) vs log[B], a straight line is obtained with slope = y is obtained.Thus we get the value of y from this experiment.

Thus by knowing the value of x and y, the order of the reaction(x + y) and the rate law can be determined.

11)Describe the half life method of determination of order of the reaction.

Ans: The time taken for a reaction to reduce the initial concentration of the reactant to half of its initial value is called half life of a reaction.

If '**a**' is the initial concentration of the reactant and $t_{1/2}$ is the half life time, then the relation between a and $t_{1/2}$ is given by

$$t_{1/2} \ \alpha \ \frac{1}{\mathbf{a}^{n-1}} \qquad \text{----------------------------I}$$

If a_1 and a_2 are the initial concentration of the reactants at half times $(t_{1/2})_1$ and $(t_{1/2})_2$ respectively, then from equation I we get

$$(t_{1/2})_1 \ \alpha \ \frac{1}{a_1^{\,n-1}} \qquad \text{----------------------------II}$$

and

$$(t_{1/2})_2 \ \alpha \ \frac{1}{a_2^{\,n-1}} \qquad \text{---------------------------------III}$$

Dividing II by III, we get

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{a_2^{\,n-1}}{a_1^{\,n-1}} \qquad \text{-----------------------------IV}$$

Taking log on both sides,we get

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

$$= n\text{-}1 \log a_2/a_1$$

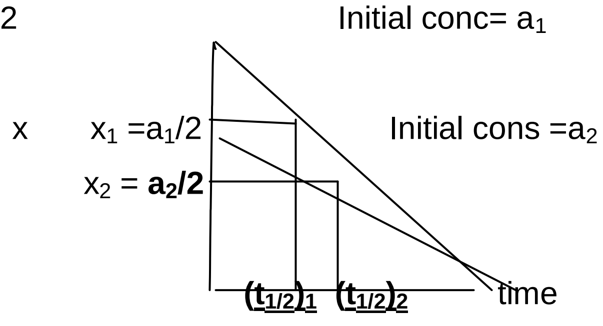
Therefore, $$n-1 = \frac{\log((t_{1/2})_1) - \log((t_{1/2})_2}{\log a_2 - \log a_1}$$

Hence

$$\mathbf{n= 1 + \frac{\log((t_{1/2})_1) - \log((t_{1/2})_2}{\log a_2 - \log a_1}}$$

By plotting a graph of x verses t for different initial concentrations of a_1 and a_2, the half life$(t_{1/2})_1$ and $(t_{1/2})_2$ are determined by dividing the initial concentrations a_1 and a_2 by 2

i.e $x_1 = a_1/2$ and $x_2 = a_2/2$



12) Describe the graphical method of determination of order of the reaction.

Ans: In this method, the concentration of the reactants is determined at different time intervals by a suitable method. A graph of concentration vs time is then plotted. The rate of the reaction at different time interval is obtained by drawing tangents to the curve and subsequently calculating the slopes of the tangents.The order of the reaction is then determined by plotting a graph of rate of the reaction vs conc. as shown below;

i) Rate of reaction vs $(\text{conc.})^1$
ii) Rate of reaction vs $(\text{conc.})^2$

Or in general,

Rate of reaction α $(\text{conc.})^n$

where n = 1, 2, 3 etc.

i)If the rate of the reaction remains constant as observed from the graph of rate of the reaction vs conc., then the reaction is of zero order.

ii)If the plot of rate of reaction against conc. gives a straight line, the reaction is of first order.

In general, if a straight line is obtained by plotting a graph of rate of reaction vs $(\text{conc.})^n$ (where n= 1,2 3 -----) then

Rate = $k[A]^n$ and the order of reaction is 'n'.

Q.13) How is the order of the reaction determined by differential rate method.

Ans : In this method, two different intial concentrations of the reactants are taken and their rates are measured at these concentrations.Then a graph of rate verses concentration is plotted.The rate of the reaction is determined from the slope of the tangents drawn to the curves and then the order of the reaction is determined as follows:

Consider the following reaction

$$A \longrightarrow \text{Products}$$

$$\text{Rate of reaction} = k\,c^n \qquad \text{-------------------I}$$

Where n is the order of the reaction and c is the concentration of the reactant .

If c_1 and c_2 are the initial concentration of the reactants with rates $(dx/dt)_1$ and $(dx/dt)_2$ respectively, then form equation 1 we get

$$\left(\frac{dx}{dt}\right)_1 = k.c_1^n \qquad \text{------------------II}$$

$$\left(\frac{dx}{dt}\right)_2 = k.c_2^{\,n} \qquad \text{------------------------III}$$

Dividing II by III we get,

$$\left(\frac{(dx/dt)_1}{(dx/dt)_2}\right) = \left(\frac{c_1}{c_2}\right)^n \qquad \text{------------------------IV}$$

Applying log on both sides of equation IV we get

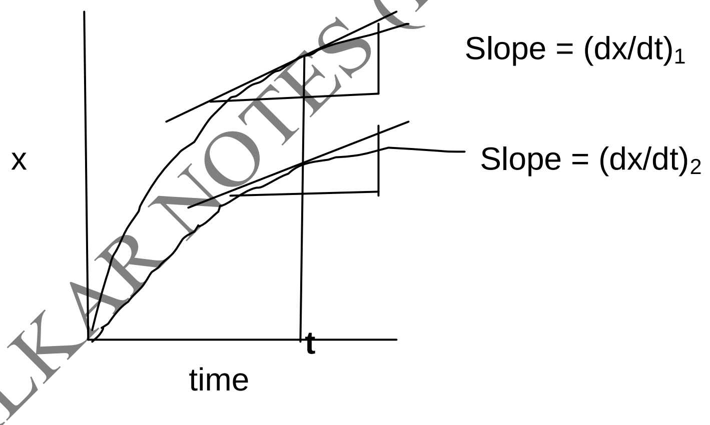
$$\log\left(\frac{(dx/dt)_1}{(dx/dt)_2}\right) = \log\left(\frac{c_1}{c_2}\right)^n$$

$$\log(dx/dt)_1 - \log(dx/dt)_2 = n(\log c_1 - \log c_2)$$

$$n = \frac{\log(dx/dt)_1 - \log(dx/dt)_2}{\log c_1 - \log c_2}$$

$$= \frac{\log(\text{slope})_1 - \log(\text{slope})_2}{\log c_1 - \log c_2}$$

Graph



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