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paper-II

For Deg I Chemistry Hons, Course & Deg I sub course

Chemical Kinetics

Order of a reaction: – The order of a reaction is given by the total number of molecules or atoms whose concentration determine the velocity of the reaction.

It is an experimental quantity ie the value of order can be determined only on the basis of experimental result.

Type of reaction on the basis of order: –

(1) **First order reaction:** – The reaction in which the rate of reaction is determined by the variation of one concentration term only. It rate is expressed by the expression of the type –

$$\frac{dx}{dt} = K_1 \cdot C_A$$

(2) **Second order reaction:** – The reaction in which the rate of reaction is determined by the variation of two concentration terms.

Its rate is given by the expression of the type —

$$\frac{dx}{dt} = K_2 C_A^2$$ (For one type of reactant)

$$\frac{dx}{dt} = K_2 C_A \cdot C_B$$ (For two types of reactants)

(3) Third order reaction :—

A reaction is said to be the third order if three concentration terms determine its rate.

The rate is given by the expression of the type —

From experiment it was found —

$$\frac{dx}{dt} = K_3 \cdot C_A^3$$ (For one type of reactant)

$$\frac{dx}{dt} = K_3 \cdot C_A^2 \cdot C_B$$ (For two types of reactant)

Or

$$\frac{dx}{dt} = K_3 \cdot C_A \cdot C_B^2$$ (20)

$$\frac{dx}{dt} = K_3 \cdot C_A \cdot C_B \cdot C_C$$ (For three types of reactants)

Example of 1st order reaction

Decomposition of $H_2O_2(aq)$ in presence of Pt catalyst

$$H_2O_2(aq) \xrightarrow{Pt\ catalyst} H_2O(l) + \frac{1}{2} O_2(g)$$

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Example of 2nd order reaction

saponification of ethyl acetate by alkali solution.

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

Example of 3rd order reaction

The reduction of $FeCl_3$ (Ferric chloride solution by $SnCl_2$ (aq)

$2\overset{+3}{FeCl_3} + \overset{+2}{SnCl_2} \longrightarrow 2\overset{+2}{FeCl_2} + \overset{+4}{SnCl_4}$

Experimental methods for determining order of a reaction :—

(1) Integration method or Hit and Trial method

In this method known quantities of reactants are mixed in a reaction vessel and the progress of the reaction can be noted by determining the amount of reactant consumed after different intervals of time.

These values are then substituted in the equation of 1st order, second order and 3rd order reaction.

Order of reaction corresponds to that equation which gives the constant value of K.

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In this method, one equation after the other undergoes trial till the correct equation is known. As this method involves the trial of different equations, it is usually called the hit and trial method.

Note:- This method can be used for simple reactions only and not for complex reactions ie a reaction which takes place in several steps.

(2) Graphical method:-

We know that

For 1st order → $\frac{dx}{dt} = K_1(a-x)$

For 2nd order → $\frac{dx}{dt} = K_2(a-x)^2$

For 3rd order → $\frac{dx}{dt} = K_n(a-x)^n$

If a curve is plotted between $\frac{dx}{dt}$ and $(a-x)$ at different time intervals a straight is obtained for the 1st order reaction (fig-2). But if a straight line is obtained by plotting $\frac{dx}{dt}$ against $(a-x)^2$, then the reaction is of 2nd order (fig-3).

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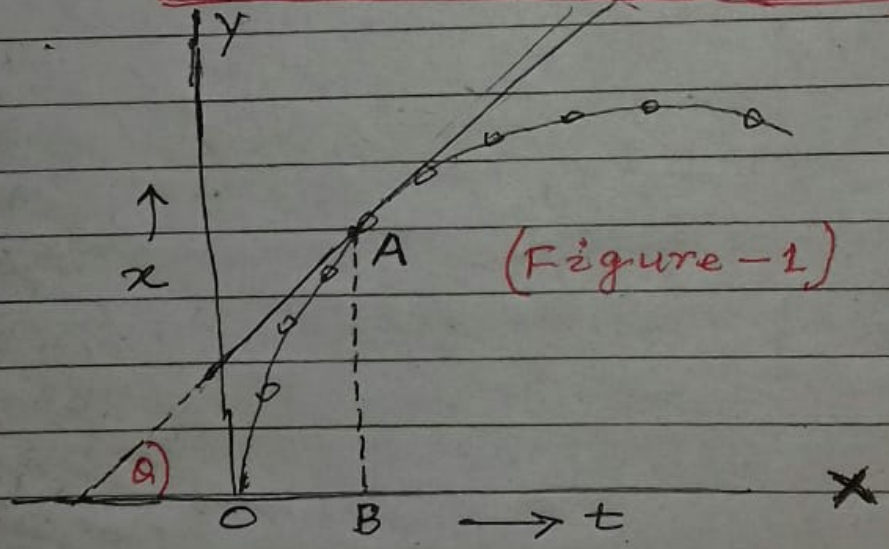
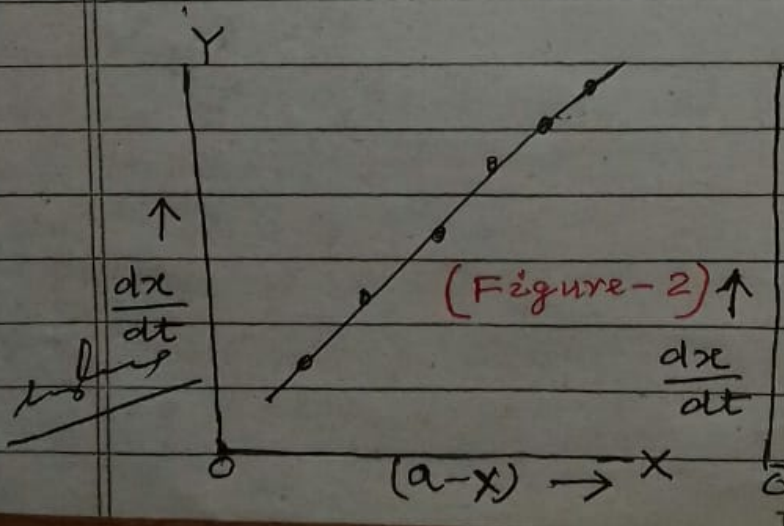
In this method, the value of $\frac{dx}{dt}$ at different time intervals can be obtained by plotting the amount of substance decomposed (x) against time t.

The value of $\tan\theta$ at any time will give the value of $\frac{dx}{dt}$ at that time. (fig-1)

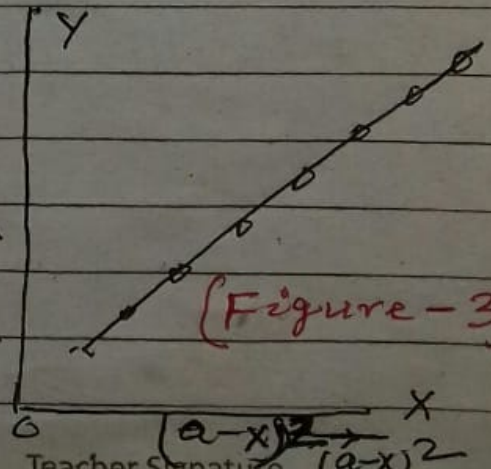
$$\frac{dx}{dt} = \tan\theta = \frac{AB}{BC}$$



(Figure-1)



(Figure-2)



(Figure-3)

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