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Class ⇒ B.Sc.(Hons) Part-1
Subject ⇒ Chemistry
Chapter ⇒ Chemical Kinetics
Topic ⇒ Rate of reaction, order and Molecularity of a reaction

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* The Branch of chemistry which deals with the rate of reaction is called Chemical Kinetics.

Rate of Reaction

The rate of reaction is defined as the change in Concentration of any of reactant or Products per unit time.

The rate of a reaction tells as to what speed the reaction occurs.

Let us consider a simple reaction

$$A \longrightarrow B$$

The concentration of the reactant A decreases and that of B increases as time passes.

For the given reaction the rate of reaction may be equal to the rate of disappearance of A which is equal to the rate of appearance of B.

Thus,

Rate of reaction = rate of disappearance of A

= rate of appearance of B

or, $$\text{Rate} = -\frac{d[A]}{dt}$$

$$= +\frac{d[B]}{dt}$$

Where [ ] represents the Concentration in moles

per litre where as d represents infinitesimally small change in concentration. Negative sign shows the concentration of the reactant A decreases where as the positive sign indicates the increase in concentration of the product B.

Units of Rate

mole/litre sec OR $mol\ l^{-1} s$
mole/litre min OR $mol\ l^{-1} min^{-1}$
mole/litre hour OR $mol\ l^{-1} h^{-1}$

Order of a Reaction

The sum of the concentration terms on which the rate of a reaction actually depends is called the order of the reaction.

Let us consider the reaction

$$\alpha A + \beta B \longrightarrow \text{Products}$$

According to rate law,

$$\text{Rate} = [A]^{\alpha} [B]^{\beta}$$

$\therefore$ Order of reaction $= \alpha + \beta$

Depending upon whether $\alpha + \beta$ is equal to 0, 1, 2 or 3, the reactions are said to be zero order, 1st order, 2nd order and 3rd order respectively.

α and β are called the orders of the reaction with respect to A and B.

e.g.

Rate law	order of a reaction
(i) rate $= K[N_2O_5]$	1
(ii) rate $= K[H_2][I_2]$	$1+1=2$
(iii) rate $= K[NO_2]^2$	2
(iv) rate $= K[H_2][NO]^2$	$1+2=3$
(v) rate $= K[CHCl_3][Cl_2]^{1/2}$	$1+1/2 = 1\frac{1}{2}$

Molecularity of a Reaction

The number of reacting species (atoms, molecules or ions) which react to bring about a chemical reaction is called Molecularity of a Reaction.

When one, two or three reactant molecules are participating in the reaction are called unimolecular, bimolecular and trimolecular reactions. e.g.

(i) Unimolecular reaction

$$A \longrightarrow \text{Product}$$

e.g. $Br_2 \longrightarrow 2Br$

$\therefore$ Molecularity $= 1$

(ii) Bimolecular reaction

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

e.g. $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

Ethyl acetate Acetic acid Ethanol.

$\therefore$ Molecularity $= 2$

$2HI \longrightarrow H_2 + I_2$

$\therefore$ Molecularity $= 2$

(iii) Trimolecular Reaction

$$A + B + C \longrightarrow \text{Product}$$

e.g. $2NO + O_2 \longrightarrow 2NO_2$

$\therefore$ Molecularity $= 3$

$2NO + Cl_2 \longrightarrow 2NOCl$

$\therefore$ Molecularity $= 3$

Some reactions takes place through a sequence of two or more consecutive steps are complex reactions

e.g. decomposition of N_2O_5

i) $2N_2O_5 \longrightarrow 2NO_2 + 2NO_3$

ii) $NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2$

iii) $NO + NO_3 \longrightarrow 2NO_2$

$2N_2O_5 \longrightarrow 4NO_2 + O_2$ $\therefore$ Molecularity $= 2$

Date:

Differences between order and Molecularity of a Reaction

Order of a Reaction	Molecularity of a Reaction
(i) It is the sum of powers of the concentration terms in the rate law expression	(i) It is no. of reacting species in the chemical reaction.
(ii) It is an experimentally determined value.	(ii) It is a theoretical concept.
(iii) It can have fractional value.	(iii) It is always a whole number.
(iv) It can assume zero value.	(iv) It can not have zero value.
(v) order of a reaction can change with the conditions such as pressure, temperature, concentration.	(v) Molecularity is invariant for a chemical equation.

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