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For Deg I Chemistry Hons Paper III &
Deg I sub course

Molecularity of a reaction

It is the sum of the number of molecules of various reactants that take part in a chemical reaction as represented by a balanced chemical equation.

It is theoretical quantity. once the mechanism of reaction is known its molecularity can be calculated.

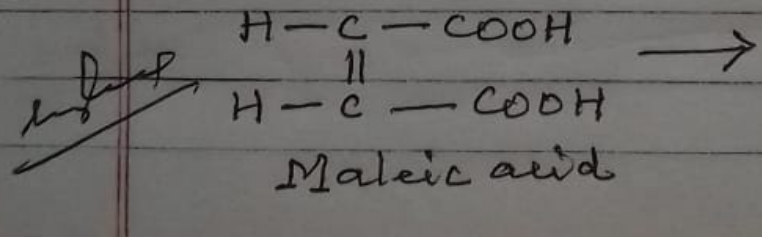
classification of reaction on the basis of molecularity :—

(1) Unimolecular reaction :-

A unimolecular reaction is that in which only one molecule of reactant is involved.

$Br_2 \longrightarrow Br + Br$ (Dissociation of Bromine

conversion of Maleic acid into Fumaric acid



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(2) Bimolecular reaction :-

A bimolecular reaction is one in which two molecules are involved.

e.g Inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

(D+) glucose (l−) Fructose

specific rotation: +52.5° −92°

As two molecules ($C_{12}H_{22}O_{11}$ and H_2O) are taking Part in this reaction, the reaction is bimolecular. The molecularity of the reaction is 2.

Hydrolysis of ester is also bimolecular reaction.

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

(3) Termolecular reaction :-

A Termolecular reaction is one in which three molecules are involved.

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

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

Order & Molecularity of a simple reaction

Previously it was thought that molecularity and order of reaction were identical. It has now been observed that certain examples are known in which these two are not identical.

e.g. Inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

(+) Glucose l(−) Fructose

As we know that the above reaction involves two reactants $C_{12}H_{22}O_{11}$ and H_2O. Thus the molecularity = 2

When the rate of this reaction is determined experimentally it has been found the following rate law ie

$$-\frac{d(C_{12}H_{22}O_{11})}{dt} \propto C_{C_{12}H_{22}O_{11}}$$

As the rate of reaction is determind by the variation of one concentration term $(C_{12}H_{22}O_{11})$ only. The order of reaction = 1

Here Molecularity ≠ order

Order & Molecularity of Complex reaction

Such reactions which complete in two or more steps are called complex reactions.

In complex reaction, each step will have its own molecularity which depend on the number of molecules taking part in that step.

All these steps may Proceed at the same or different rates. But the slowest steps determine the order of over all reaction.

In order to understand the meaning of order and molecularity of a complex reaction,

Let us consider the following complex reaction — Reduction of $HBrO_3$

$$\overset{+5}{HBr}O_3 + 6HI \longrightarrow \overset{-1}{HBr} + 3H_2O + 3I_2$$

(Bromic acid)

Although this reaction involves seven molecules yet it is of the 2nd order reaction. This order of the reaction is justified by the following mechanism —

(1) $HBrO_3 + HI \rightarrow HBrO_2 + HIO$ (slow)

(2) $HBrO_2 + 4HI \rightarrow HBr + 2I_2 + 2H_2O$ (Fast)

(3) $HIO + HI \longrightarrow I_2 + H_2O$ (Fast)

As the first step is slow it means the reaction is of the second order.

The elementary steps involved in the complex reaction has its own molecularity.

For example, the molecularity of step (1), (2) and (3) are 2, 5 and 2 respectively.

The End