Molecularity of a reaction

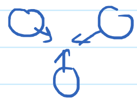
The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

For example:

i) Unimolecular : $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

ii) Bimolecular : $2HI \rightarrow H_2 + I_2$

iii) Trimolecular / Termolecular : $2NO + O_2 \rightarrow 2NO_2$



Elementory reactions

The reactions taking place in one step are called elementary reactions.

Complex reactions

When a sequence of elementary reactions (called mechanism) gives us the product, the reaction is called complex reaction.

Complex reaction occurs in more than one step, each step is an elementary reaction. In a complex reaction, the overall rate of the reaction is controlled by the slowest step of the reaction, it is called rate determining step.

For example:

Decomposition of hydrogen peroxide, catalysed by iodide ion in an alkaline medium, is complex reaction and occurs in two steps:

$$2H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2H_2O + O_2$$

Steps:

i) $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slowest step)

ii) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

First step is slowest step in the given reaction, rate of overall reaction is equal to rate of slowest step

$$r = K[H_2O_2][I^-]$$

- Species which are formed during the course of reaction but are not involved in the overall balanced equation are called intermediates.
- Intermediates never appear in rate law expression.

Example:

$$2O_3 \rightarrow 3O_2 \quad \text{(It is a complex reaction)}$$

Steps:

i) $O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ (fast)

ii) $O + O_3 \xrightarrow{k_3} 2O_2$ (slowest step)

$$r = k_3[O][O_3] \quad - \text{I}$$

$$K_{eq} = \frac{k_1}{k_2} = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \frac{k_1}{k_2}\frac{[O_3]}{[O_2]} \quad - \text{II}$$

Put [O] from II in I

$$r = k_3 \frac{k_1}{k_2}\frac{[O_3]}{[O_2]}[O_3]$$

$$r = k[O_3]^2[O_2]^{-1}$$

Important points:

i) Order of a reaction is an experimental quantity. It can be zero, negative or fraction but molecularity cannot be zero or a non integer.

ii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions.

iii) For complex reaction, rate law depends upon slowest step.