Molecularity of Reaction.

"It is the sum of the number of molecules of reactants involved in the balanced chemical equation".

Or

"It is the minimum number of reacting particles (Molecules, atoms or ions) that collide in a rate determining step to form product or products".

- Molecularity of a complete reaction has no significance and overall kinetics of the reaction depends upon the rate determining step. Slowest step is the rate-determining step. This was proposed by **Van't Hoff.**

Example: $NH_4NO_2 \rightarrow N_2 + 2H_2O$ (Unimolecular)

$NO + O_3 \rightarrow NO_2 + O_2$ (Bimolecular)

$2NO + O_2 \rightarrow 2NO_2$ (Trimolecular)

- Molecularity of a reaction can't be Zero, negative or fractional.
- Molecularity of a reaction is derived from the mechanism of the given reaction.
- Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

$$A_2 + \frac{3}{2}B_2 \rightarrow A_2B_3$$

Mechanism

Step I : $2A \rightarrow A_2$ (Bimolecular)

Step II : $A_2 + \frac{1}{2}B_2 \rightarrow A_2B$ (Trimolecular)

Step III : $A_2B + B_2 \rightarrow A_2B_3$ (Bimolecular)

Example**:** Decomposition of H_2O_2

$2H_2O_2 \rightarrow 2H_2O + O_2$ (Overall reaction Mechanism)

$H_2O_2 \rightarrow H_2O + O$ (Slow)

$H_2O_2 + O \rightarrow H_2O + O_2$ (Fast)

Rate = $K[H_2O_2]$; the reaction is Unimolecular

(1) **Pseudo Unimolecular Reaction:**Reaction whose actual order is different from that expected using rate law expression are called **pseudo-order reaction.** For example,

$RCl + H_2O \rightarrow ROH + HCl$

Expected rate law: $Rate = k[RCl][H_2O]$; Expected order $= 1 + 1 = 2$

Actual rate law: $Rate = k[RCl]$; Actual order =1

Because of water is taken in excess amount; therefore, its concentration may be taken constant. The reaction is therefore, pseudo first order. Similarly the acid catalyzed hydrolysis of ester, viz.,

$RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$ (follow first order kinetic): Rate = k$[RCOOR']$

Those reactions which may have order of reaction as one while Molecularity of reaction 2 or more than two are as follows:

Examples**:** (i) $2N_2O_5 \rightarrow 4NO_2 + O_2$; Order = 1; Molecularity = 2

(ii) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$; $r = k[CH_3COOC_2H_5]$

Order =1 , Molecularity = 2

(iii) Inversion of cane sugar: $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

Sucrose glucose fructose

Order = 1, Molecularity = 2

(iv) $(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$ Order = 1, Molecularity = 2

(v) $2H_2O_2 \xrightarrow{Pt,} 2H_2O + O_2$ Order = 1, Molecularity = 2

Difference between Molecularity and Order of reaction

Molecularity	**Order of Reaction**
It is the number of molecules of reactants terms taking part in elementary step of a reaction.	It is sum of the power of the concentration terms of reactants in the rate law expression.
Molecularity is a theoretical value	Order of a reaction is an experimental value
Molecularity can neither be zero nor fractional.	Order of a reaction can be zero, fractional for integer.
Molecularity has whole number values only i.e., 1, 2, 3, etc.	Order of a reaction may have negative value.
It is assigned for each step of mechanism separately.	It is assigned for overall reaction.
It is independent of pressure and temperature.	It depends upon pressure and temperature.