Molecularity and Order of Reaction

The terms **molecularity** and **order of reaction** are fundamental concepts in chemical kinetics that describe different aspects of a chemical reaction. Although these terms are often confused because they may have the same numerical value for some elementary reactions, they are entirely different in meaning and significance. Molecularity is a theoretical concept based on the reaction mechanism, whereas the order of reaction is an experimentally determined quantity obtained from the rate law. A clear understanding of these concepts is essential for interpreting reaction mechanisms and predicting the behaviour of chemical reactions under different conditions.

Molecularity of a Reaction

Molecularity is defined as the number of reacting species, such as atoms, ions, or molecules, that participate simultaneously in a single elementary reaction step to bring about a chemical change. Since it represents the actual number of particles involved in an elementary process, molecularity is always a positive whole number. It can never be zero, fractional, or negative. Molecularity is applicable only to elementary reactions and remains constant for a given elementary reaction.

Depending on the number of reacting particles, molecularity is classified as:

- **Unimolecular (1):** One reacting species participates in the reaction.
- **Bimolecular (2):** Two reacting species collide simultaneously.
- **Termolecular (3):** Three reacting species collide simultaneously. Such reactions are comparatively rare because the probability of three-particle collisions is very low.

Examples of molecularity are:

$$A \rightarrow \text{Products}$$

$$A + B \rightarrow \text{Products}$$

$$A + B + C \rightarrow \text{Products}$$

Order of a Reaction

The **order of reaction** is defined as the sum of the powers of the concentration terms of the reactants appearing in the experimentally determined rate law. Unlike molecularity, the order of a reaction is obtained from experimental observations and indicates how the reaction rate depends on the concentration of reactants. The order of reaction may be zero, fractional, integral, or even negative in certain complex reactions.

For a general reaction,

$$aA + bB \rightarrow \text{Products}$$

if the experimentally determined rate law is

$$\text{Rate} = k[A]^m[B]^n$$

then the overall order of the reaction is

$$\text{Order} = m + n$$

where m and n are the experimentally determined orders with respect to reactants A and B, respectively.

Difference Between Molecularity and Order of Reaction

Molecularity	Order of Reaction
Defined as the number of reacting species involved in a single elementary step.	Defined as the sum of the powers of reactant concentrations in the rate law.
Applicable only to elementary reactions.	Applicable to both elementary and complex reactions.
Determined from the reaction mechanism.	Determined experimentally.
Always a positive whole number.	May be zero, fractional, integral, or negative.
Cannot change for a given elementary reaction.	May change if the reaction mechanism changes.

Molecularity	Order of Reaction
Represents the number of particles participating in a collision.	Represents the dependence of reaction rate on reactant concentration.

For an elementary reaction, the molecularity and the order of reaction are numerically equal. However, for complex reactions involving multiple elementary steps, the order of reaction generally differs from the molecularity because the rate law depends on the rate-determining step rather than the overall balanced chemical equation.