

Difference between order and molecularity of a reaction

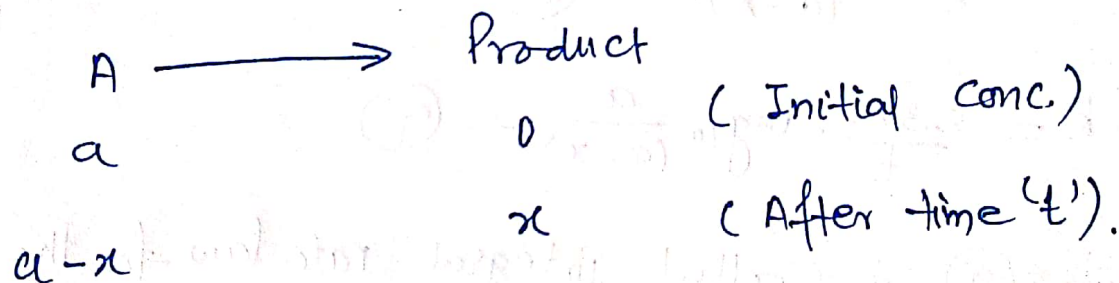
Order of a reaction	Molecularity of a reaction
1. It is equal to the number of molecules whose concentration changes and determine the rate of a reaction.	1. It is equal to the number of reacting molecules taking part in the reaction to form the products.
2. It can have zero value.	2. It can not have a zero value.
3. It may have fractional or negative value.	3. It is always a whole number.
4. It can be determined experimentally.	4. It is a theoretical value.
5. It can be changed with the change in pressure, temperature and concentration.	5. It is invariable for a chemical reaction.
6. Order of a reaction can be equal to the molecularity of reaction and may be less than molecularity.	6. Molecularity can be more than order of reaction.

1st order reaction: ~~Let us~~ The reaction in which the reaction rate is determined by the change of one concentration term of reactant is called 1st order reaction.

Let us consider the following simplest first order reaction:



Suppose initial conc. of A is 'a' and 'x' moles/L of A decomposes in time 't'. Then conc. of A after time 't' is (a-x).



Thus rate of reaction at time 't' is given by

$$\frac{dx}{dt} = k(a-x) \quad \text{--- (1)}$$

OR
$$\frac{dx}{(a-x)} = k \cdot dt \quad \text{--- (2)}$$

Integrating eq. (2), we get

$$\int \frac{dx}{(a-x)} = \int k \cdot dt \quad \text{--- (3)}$$

$$-\ln(a-x) = kt + I \quad \text{--- (4)}$$

when $t=0$, $x=0$, eq. (4) becomes.

$$-\ln a = I \quad \text{--- (5)}$$

Substituting value of I in eq. (4), we get

$$-\ln(a-x) = kt - \ln a \quad \text{--- (6)}$$

$$\text{OR } kt = \ln a - \ln(a-x) \quad \text{--- (7)}$$

$$\text{OR } k = \frac{1}{t} \cdot \ln \frac{a}{(a-x)} \quad \text{--- (8)}$$

$$\text{OR } k = \frac{2.303}{t} \cdot \log_{10} \frac{a}{(a-x)} \quad \text{--- (9)}$$

Equation (9) is called integral rate law for the rate constant of a 1st order reaction.

The unit of velocity constant is time^{-1} because

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{1}{\text{time}} \cdot \frac{\text{Conc.}}{\text{Conc.}} = \frac{1}{\text{time}} = \text{time}^{-1}$$

It is to be noted that time taken to complete a certain fraction of reaction is independent of the initial conc. of the reactant. Suppose $t_{1/2}$ is the time taken to reduce the conc. of reaction A from 'a' to 'a/2'. Then, $x = \frac{a}{2}$, Hence eq. (9) becomes

$$k = \frac{2.303}{t_{1/2}} \cdot \log \frac{a}{a - a/2}$$

$$\text{OR } t_{1/2} = \frac{2.303}{k} \log 2$$

$$\text{OR } t_{1/2} = \frac{2.303 \times 0.3010}{k}$$

$$\text{OR } t_{1/2} = \frac{0.693}{k}$$

Thus half life period of Ist order reaction is independent of the initial conc (a).

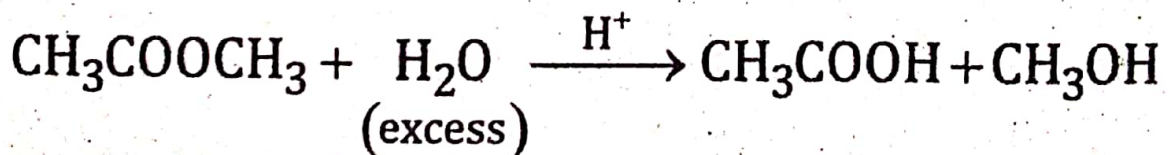
7.10. Pseudo-molecular reactions

A number of reactants are known which have molecularly greater than one but they are of first order reactions. Such reactions are called **Pseudo molecular reactions**.

Pseudo-unimolecular reactions : The reactions which are not unimolecular but under certain conditions, they behave like unimolecular are called **Pseudo-unimolecular reactions**. In such reactions generally water is taken in large excess so that its concentration remains constant during the reaction.

For example :

(a) Hydrolysis of an ester : The reaction is,



When H_2O is present in large excess, its rate of reaction may be written as

$$\begin{aligned} \frac{dx}{dt} &= k [\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}] \\ &= k'[\text{CH}_3\text{COOCH}_3] \end{aligned}$$

Thus, the reaction follows first order kinetics hence it is not a bimolecular reaction but a pseudo-unimolecular reaction.

Each reaction rate coefficient k has a temperature dependency, which is usually given by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}.$$

E_a is the activation energy; R is the gas constant. Since at temperature T the molecules have energies given by a Boltzmann distribution, one can expect the number of collisions with energy greater than E_a to be proportional to $e^{-E_a/RT}$. The coefficient, A , is the pre-exponential factor or frequency factor.

The values for A and E_a are dependent on the reaction. There are also more complex equations possible, which describe temperature dependence of other rate constants that do not follow this pattern.

Temperature is a measure of the average kinetic energy of the reactants. As temperature increases, the kinetic energy of the reactants increases. That is, the particles move faster. With the reactants moving faster this allows more collisions to take place at a greater speed, so the chance of reactants forming into

products increases, which in turn results in the rate of reaction increasing. A rise in ten degrees Celsius results in approximately twice the reaction rate.