Rate law, Law of mass action and Rate constant.

(1) **Rate law:**The actual relationship between the concentration of reacting species and the reaction rate is determined experimentally and is given by the expression called rate law.

For any hypothetical reaction, $aA + bB \rightarrow cC + dD$

Rate law expression may be, $\boxed{\text{rate } = k[A]^a[B]^b}$

Where a and b are constant numbers or the powers of the concentrations of the reactants A and B respectively on which the rate of reaction depends.

(i) Rate of chemical reaction is directly proportional to the concentration of the reactants.

(ii) The rate law represents the experimentally observed rate of reaction, which depends upon the slowest step of the reaction.

(iii) Rate law cannot be deduced from the relationship for a given equation. It can be found by experiment only.

(iv) It may not depend upon the concentration of species which do not appear in the equation for the overall reaction.

(2) **Law of mass action:**(Guldberg and Wage 1864) this law relates rate of reaction with active mass or molar concentration of reactants. According to this law, "At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reactions."

Active mass = Molar concentration of the substance = $\dfrac{\text{Number of gram moles of the substance}}{\text{Volume in litres}}$

$$= \frac{W/m}{V} = \frac{n}{V}$$

Where $W =$ mass of the substance, m is the molecular mass in grams, 'n' is the number of g moles and V is volume in liter.

Consider the following general reaction, $m_1A_1 + m_2A_2 + m_3A_3 \rightarrow \text{Products}$

Rate of reaction $\propto [A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}$

(3) **Rate constant:** Consider a simple reaction, $A \rightarrow B$. If C_A is the molar concentration of active mass of A at a particular instant, then, $\frac{dx}{dt} \propto C_A$ or $\frac{dx}{dt} = kC_A$; Where k is a **proportionality constant**, called **velocity constant** or **rate constant** or **specific reaction rate constant.**

At a fixed temperature, if $C_A = 1$, then $\boxed{Rate = \frac{dx}{dt} = k}$

"Rate of a reaction at unit concentration of reactants is called rate constant."

(i) **The value of rate constant depends on,** Nature of reactant, Temperature and Catalyst

(It is independent of concentration of the reactants)

(ii) **Unit of rate constant:** Unit of rate constant $= \left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \sec^{-1}$ or $= \left[\frac{\text{mol}}{\text{litre}}\right]^{1-n} \times \sec^{-1}$

Where $n =$ order of reaction

Difference between Rate law and Law of mass action

Rate law	**Law of mass action**
It is an experimentally observed law.	It is a theoretical law.
It depends on the concentration terms on which the rate of reaction actually depends	It is based upon the stoichiometry of the equation
Example for the reaction, $aA + bB \rightarrow \text{Products}$	Example for the reaction, $aA + bB \rightarrow \text{Products}$
Rate $= k[A]^m[B]^n$	Rate $= k[A]^a[B]^b$

Difference between Rate of reaction and Rate constant

Rate of reaction	**Rate constant**
It is the speed with which reactants are converted into products.	It is proportionality constant.
It is measured as the rate of decrease of the concentration of reactants or the rate of increase of concentration of products with time.	It is equal to rate of reaction when the concentration of each of the reactants is unity.
It depends upon the initial concentration of the reactants.	It is independent of the initial concentration of the reactants. It has a constant value at fixed temperature.