- **Surface area :** As the surface area of the reactants increases, the reaction rate increases.
- **Effect of temperature on rate of reaction :** Generally, the rate of a reaction increases with increase in temperature. This is because of the increase of average kinetic energy of molecules with increase of temperature.

  The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperatures differing by 10°C.

  Temperature coefficient, $\mu = \frac{k_{t+10}}{k_t}$

  Its value lies generally between 2 and 3.

Key points	
Factors	**Effect on reaction rate**
• Increase in concentration	Increases
• Increase in temperature	Increases
• Presence of catalyst	Increases
• Physical state	Rate is maximum in gaseous state
• Decrease in size of reactant	Increases

ORDER AND MOLECULARITY OF A REACTION

- **Order of a reaction :** Sum of powers of concentration terms involved in the rate law expression is called order of reaction.

  Consider a reaction :

  $$m_1A + m_2B + m_3C \longrightarrow \text{product}$$

  Rate = $k[A]^{m_1}[B]^{m_2}[C]^{m_3}$

  Order of reaction = $m_1 + m_2 + m_3$
- **Molecularity of a reaction :** The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form products is called the molecularity of a reaction.

  $$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$

  $$HBr + O_2 \longrightarrow HOOBr \text{ (R.D. step)}$$

  So molecularity of this reaction is two not five.

	Molecularity	Order
1.	Theoretical concept.	An experimentally determined quantity.
2.	It cannot be zero, fractional, infinite and imaginary.	It can be equal to zero, positive, negative and fractional.
3.	It cannot be greater than three.	Greater than three is also possible.

RATE LAW AND RATE CONSTANT

- **Law of mass action :** The rate of reaction is directly proportional to the product of the active mass (molar concentration) of the reactants raised to powers equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction.

  $$A + B \longrightarrow C + D$$

  Rate $\propto [A][B]$

  Rate = $k[A][B]$ (law of mass action)

  k is constant of proportionality = rate constant

  $[A] = [B] = 1$, rate of reaction = k

  So, rate constant is the rate of the reaction when concentration of each of the reactants is unity. So also known as specific reaction rate.
- **Rate law expression :** Consider a general reaction,

  $$aA + bB + cC \longrightarrow \text{product}$$

  Rate = $k[A]^a[B]^b[C]^c$ (law of mass action)

  Rate = $k[A]^p[B]^q[C]^r$ (rate law expression)

  p, q and r are determined experimentally and may or may not be equal to a, b and c. p, q, r represents the order of reaction with respect to a, b, c.

Characteristics of Rate Constant

- Rate constant is a measure of the rate of reaction. Larger the value of k, faster is the reaction.
- At a fixed temperature, the value of k is constant and is characteristic of the reaction. However, it changes only with temperature.

	Rate of reactions	Reaction rate constant
1.	It is the speed with which reactants are converted into products.	It is the proportionality constant in the rate law and is defined as the rate of reaction when the concentration of the reactants is unity.
2.	It depends upon the initial concentration of the reactants.	It is independent of the initial concentration of the reactants.
3.	Its units are always mol L^{-1} time^{-1}.	Its units depend upon the order of reaction.

- **Units of rate constant :** $\left[\frac{1}{\text{mol/litre}}\right]^{n-1} \times \text{time}^{-1}$

  $= \left(\frac{\text{litre}}{\text{mol}}\right)^{n-1} s^{-1}$

  n = order of reaction.

Illustration 1

The complexation of Fe^{2+} and chelating agent dipyridyl has been studied kinetically in both forward and reverse directions.

$$Fe^{2+} + 3(\text{dipy}) \longrightarrow Fe(\text{dipy})_3^{2+}$$

Rate of forward reaction = $(1.45 \times 10^{13})[Fe^{2+}][\text{dipy}]^3$ and rate of reverse reaction = $(1.22 \times 10^{-4})[Fe(\text{dipy})_3]^{2+}$ Find the rate constant for the complex.

Soln.: At dynamic equilibrium

Rate of formation of complex = Rate of disappearance of complex.

$(1.45 \times 10^{13})[Fe^{2+}][\text{dipy}]^3 = (1.22 \times 10^{-4})[Fe(\text{dipy})_3]^{2+}$

$$\therefore \quad k = \frac{[Fe(\text{dipy})_3]^{2+}}{[Fe^{2+}][\text{dipy}]^3} \frac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = 1.19 \times 10^{17}$$