

❖ Collision Theory of Reaction Rates and Its Limitations

In 1916, a German chemist Max Trautz proposed a theory based on the collisions of reacting molecules to explain reaction kinetics. Two years later, a British chemist William Lewis published similar results, however, he was completely unaware of Trautz's work. The remarkable work of these two gentlemen was extremely beneficial in explaining the rate of many chemical reactions.

The collision theory states that when the right reactant particles strike each other, only a definite fraction of the collisions induce any significant or noticeable chemical change; these successful changes are called successful collisions and are possible only if reacting molecules have sufficient energy at the moment of impact to break the pre-existing bonds and form all new bonds.

The minimum energy required to make a collision successful is called as the activation energy, and these types of collisions result in the products of the reaction. The rise in reactant concentration or increasing the temperature, both result in more collisions and hence more successful collisions, and therefore, increase the reaction rate. Sometimes, a catalyst is involved in the collision between the reactant molecules that decreases the energy required for the chemical change to take place, and so more collisions would have sufficient energy for the reaction to happen. In this section, we will discuss the collision theory of bimolecular and unimolecular reactions in the gaseous phase.

➤ Collision Theory for Bimolecular Reactions

In order to understand the collision theory for bimolecular reactions, we must understand the cause of a reaction itself first. The primary requirement for a reaction to occur is the collision between the reacting molecules. Therefore, if we assume that every collision results in the formation of the product, the rate of reaction should simply be equal to collision frequency (Z) of the reacting system i.e. the number of collisions occurring in the container per unit volume per unit time. Mathematically, we can say that

$$\text{Rate} = Z \quad (132)$$

However, the actual rate would be much less than what is predicted by the equation (132); which is obviously due to the fact that all the collisions are not effective. Therefore, equation (132) must be modified to represent this factor. If f is the fraction of the molecules which are activated, the rate expression can be written as given below.

$$\text{Rate} = Z \times f \quad (133)$$

Now, according to the Maxwell-Boltzmann distribution of energies, the fraction of the molecules having energy greater than a particular energy E is

$$f = \frac{\Delta N}{N} = e^{-E/RT} \quad (134)$$

Where N is the total number of molecules while ΔN represents the number of molecules having energy greater than E . However, if $E = E_a$, the fraction of activated molecules can be written as

$$f = \frac{\Delta N}{N} = e^{-E_a/RT} \quad (135)$$

Where R is the gas constant and T is the reaction temperature. After putting the value of f from equation (135) into equation (133), we get

$$\text{Rate} = Z e^{-E_a/RT} \quad (136)$$

At this point, two possibilities arise; one, when the colliding molecules are similar and other, is when the colliding molecules are dissimilar. We will discuss these cases one by one.

1. Rate of reaction when the colliding molecules are dissimilar: Consider a bimolecular reaction between different molecules A and B yielding product P as



The number of collisions between A and B occurring in the container per unit volume per unit time can be given by the following relation.

$$Z = n_A n_B \sigma_{AB}^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}} \quad (138)$$

Where n_A and n_B are the number densities (in the units of m^{-3}) of particles A and B , respectively. The term σ_{AB} is simply the average collision diameter i.e. $\sigma_{AB} = (\sigma_A + \sigma_B)/2$. k_B is the Boltzmann's constant ($m^2 kg s^{-2} K^{-1}$). T represents the temperature of the system. The term μ_{AB} represents the reduced mass of the reactants A and B i.e. $\mu_{AB} = m_A m_B / (m_A + m_B)$.

The equation (138) can also be expressed in terms of molar masses by putting $m_A = M_A/N$, $m_B = M_B/N$ and $k = R/N$; where M_A and M_B are molar masses of the reactants, R is the gas constant and N represents to Avogadro number. Therefore, equation (138) takes the form

$$Z = \sigma_{AB}^2 \sqrt{\frac{8\pi \left(\frac{R}{N}\right) T \left(\frac{M_A}{N} + \frac{M_B}{N}\right)}{\frac{M_A}{N} \times \frac{M_B}{N}}} n_A n_B \quad (139)$$

or

$$Z = \sigma_{AB}^2 \sqrt{\frac{8\pi R T (M_A + M_B)}{M_A M_B}} n_A n_B \quad (140)$$

Also, as we know that the reaction rate can be written in terms of molecules of reactants reacting per cm^3 per second as

$$\text{Rate} = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = Ze^{-E_a/RT} \quad (141)$$

or

$$\text{Rate} = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} \times n_A n_B \times e^{-E_a/RT} \quad (142)$$

Now, in order to express the rate in terms of molar concentrations, we need to recall some typical relations like

$$n_A = \frac{N[A]}{10^3} \quad \text{and} \quad n_B = \frac{N[B]}{10^3} \quad (143)$$

also

$$dn_A = \frac{N}{10^3} d[A] \quad \text{and} \quad dn_B = \frac{N}{10^3} d[B] \quad (144)$$

Using the results of equation (143) and (144) in equation (142), we get

$$\text{Rate} = -\frac{N}{10^3} \frac{d[A]}{dt} = -\frac{N}{10^3} \frac{d[B]}{dt} = \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} \frac{N[A]}{10^3} \frac{N[B]}{10^3} e^{-E_a/RT} \quad (145)$$

or

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} [A][B] e^{-E_a/RT} \quad (146)$$

Comparing equation (146) with general rate law expressed in molar concentrations i.e. $\text{Rate} = k[A][B]$, we get

$$k = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} e^{-E_a/RT} \quad (147)$$

Comparing equation (147) with Arrhenius rate constant i.e. $k = Ae^{-E_a/RT}$, we get

$$A = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} \quad (148)$$

2. Rate of reaction when the colliding molecules are similar: Consider a bimolecular reaction between similar molecules A and A yielding product P as



The number of collisions between A and A occurring in the container per unit volume per unit time can be given by the following relation.

$$Z = n_A^2 \sigma^2 \sqrt{\frac{4\pi k_B T}{m_A}} \quad (150)$$

Where n_A is the number density (in the units of m^{-3}) of particle A . The term σ is simply the average collision diameter. k_B is the Boltzmann's constant ($m^2 kg s^{-2} K^{-1}$). T represents the temperature of the system. The term m_A represents the mass of the reactants A .

The equation (150) can also be expressed in terms of molar masses by putting $m_A = M_A/N$ and $k = R/N$; where M_A is the molar mass of the reactant, R is the gas constant and N represents to Avogadro number. Therefore, equation (150) takes the form

$$Z = \sigma^2 \sqrt{\frac{4\pi \left(\frac{R}{N}\right) T}{\frac{M_A}{N}}} n_A^2 \quad (151)$$

or

$$Z = \sigma^2 \sqrt{\frac{4\pi RT}{M_A}} n_A^2 \quad (152)$$

Also, as we know that the reaction rate can be written in terms of molecules of reactants reacting per cm^3 per second as

$$\frac{1}{2} \frac{dn_A}{dt} = Z e^{-E_a/RT} \quad (153)$$

or

$$\text{Rate} = -\frac{dn_A}{dt} = 2 \left(\sigma^2 \sqrt{\frac{4\pi RT}{M_A}} \times n_A^2 \times e^{-E_a/RT} \right) \quad (154)$$

Now, in order to express the rate in terms of molar concentrations, we need to recall some typical relations like

$$n_A = \frac{N[A]}{10^3} \quad (155)$$

also

$$dn_A = \frac{N}{10^3} d[A] \quad (156)$$

Using the results of equation (155) and (156) in equation (154), we get

$$\text{Rate} = -\frac{N}{10^3} \frac{d[A]}{dt} = 2 \left(\sigma^2 \sqrt{\frac{4\pi RT}{M_A}} \times \frac{N^2 [A]^2}{10^6} \times e^{-E_a/RT} \right) \quad (157)$$

or

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{4N}{10^3} \sigma^2 \sqrt{\frac{\pi RT}{M_A}} \times [A]^2 \times e^{-E_a/RT} \quad (158)$$

Comparing equation (158) with general rate law expressed in molar concentrations i.e. $\text{Rate} = k[A]^2$, we get

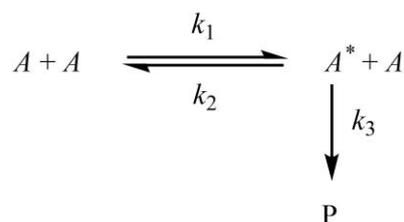
$$k = \frac{4N}{10^3} \sigma^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT} \quad (159)$$

Comparing equation (159) with Arrhenius rate constant i.e. $k = Ae^{-E_a/RT}$, we get

$$A = \frac{4N}{10^3} \sigma^2 \sqrt{\frac{\pi RT}{M_A}} \quad (160)$$

➤ Collision Theory for Unimolecular Reactions

In order to understand the collision theory for unimolecular reactions, we must understand the root cause of these reactions. In a typical unimolecular reaction, a single molecule converts into the product by simply rearranging itself. However, the question that arises here is how these molecules get activated. The mystery was solved by a British physicist, Frederick Alexander Lindemann, who proposed a time-lag between activation and actual reaction. In other words, when ordinary molecules collide with each other, some of them get activated, and the rate depends only upon these molecules but not the ordinary ones i.e.



Where k_1 , k_2 and k_3 are the rate constants for the different processes; while A and A^* are the ordinary and activated molecule. The overall rate of formation of the product can be given as

$$\frac{d[P]}{dt} = k_3[A^*] \quad (161)$$

Now, since the molar concentration of $[A^*]$ is unknown we must apply the steady-state approximation on $[A^*]$.

At steady state

Rate of formation of $[A^*]$ = Rate of disappearance of $[A^*]$

$$k_1[A]^2 = k_2[A^*][A] + k_3[A^*] \quad (162)$$

or

$$k_1[A]^2 = (k_2[A] + k_3)[A^*] \quad (163)$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3} \quad (164)$$

Using the value of $[A^*]$ from equation (164) in equation (161), we get

$$\text{Rate} = \frac{d[P]}{dt} = \frac{k_3 k_1 [A]^2}{k_2 [A] + k_3} \quad (165)$$

Equation (165) gives rise to two possibilities discussed below.

1. If the concentration of reactant A is very high: In this situation, $k_2[A] \gg k_3$, and k_3 can be neglected, therefore, the equation (165) takes the form

$$\text{Rate} = \frac{d[P]}{dt} = \frac{k_3 k_1 [A]^2}{k_2 [A]} \quad (166)$$

or

$$\frac{d[P]}{dt} = \frac{k_3 k_1}{k_2} [A] \quad (167)$$

$$\frac{d[P]}{dt} = k_o [A] \quad (168)$$

Where k_o is the overall rate constant. It is clear from the above result that the unimolecular reactions follow first-order kinetics in such cases.

2. If the concentration of reactant A is very low: In this situation, $k_3 \gg k_2[A]$ and $k_2[A]$ can be neglected, therefore, the equation (165) takes the form

$$\text{Rate} = \frac{d[P]}{dt} = \frac{k_3 k_1 [A]^2}{k_3} \quad (169)$$

$$\frac{d[P]}{dt} = k_1 [A]^2 \quad (170)$$

Where k_1 is the overall rate constant. It is clear from the above result that the unimolecular reactions follow second-order kinetics in such cases.

➤ *Limitations of Collision Theory*

The collision theory of reaction rate is extremely successful in rationalizing the kinetics of many reactions, however, it does suffer from some serious limitations discussed below.

1. This theory finds application only to reactions occurring in the gas phase and solution having simple reactant molecules.
2. The rate constants obtained by employing collision theory are found to be comparable to what has been obtained from the Arrhenius equation only for the simple reactions but not for complex reactions.
3. This theory tells nothing about the exact mechanism behind the chemical reaction i.e. making and breaking of chemical bonds.
4. The collision theory considers only the kinetic energy of reacting molecules and just ignored rotational and vibrational energy which also plays an important role in reaction rate.
5. This theory did not consider the steric factor at all i.e. the proper orientation of the colliding molecules needed to result in the chemical change.

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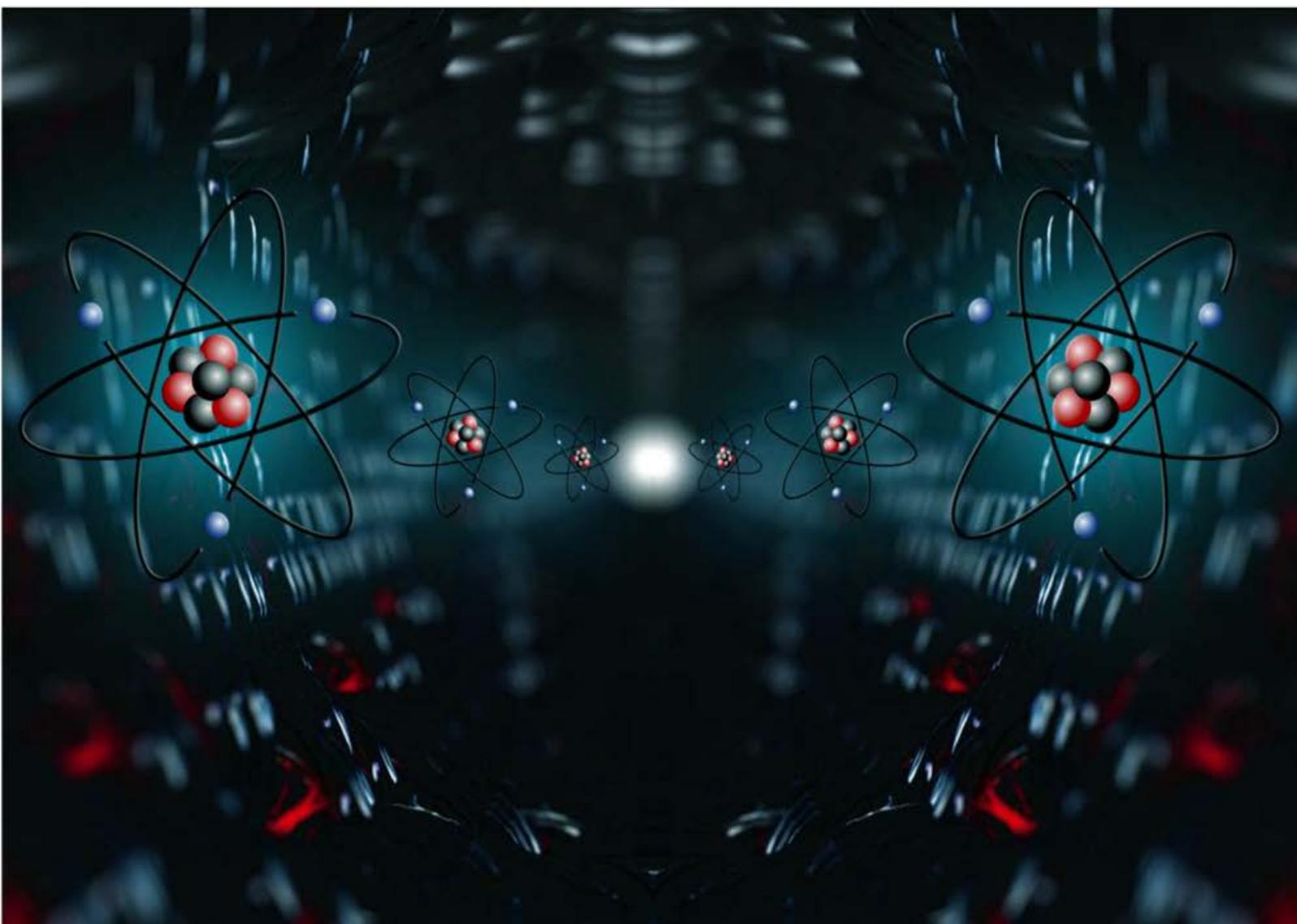
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A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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