CLASS 12th

CHEMISTRY

CHEMICAL KINETICS

COLLISION THEORY

COLLISION THEORY (PART I):



Collision Theory

The collision theory asserts that a chemical reaction occurs only when particles collide, meaning they come into contact with each other. However, it is crucial to note that the collision between reactant particles is a necessary condition but not sufficient for a reaction to occur; the collisions must also be effective. Understanding the precise characteristics of an effective collision is vital because it dictates whether particles will react with each other and produce new products.

Molecular Collisions

The higher the number of molecules present, the greater the frequency of collisions. For a reaction to commence, molecules must first collide. To ensure an effective initiation of a reaction, these collisions need to possess adequate energy, specifically kinetic energy, to facilitate bond disruption. With an increase in temperature, molecules exhibit faster movement and engage in more forceful collisions, significantly enhancing the probability of bond cleavages and rearrangements. In the case of reactions involving neutral molecules, they are often unable to occur until they acquire the activation energy required to stretch, bend, or otherwise distort one or more bonds.





Model:

Collision theory

In the image provided, Reactant A is symbolized by the cricket bat, while Reactant B is represented by the cricket ball. The success of the reaction hinges on the batter hitting a boundary. If the batter fails to achieve this, the reaction is deemed unsuccessful.



- **Scenario 1:** The bowler delivers a fastball down the middle of the pitch, and the batsman takes a powerful swing but completely misses the ball.
- **Scenario 2:** The bowler opts for an off-speed delivery, and the batsman cautiously checks his swing. The batsman manages to make slight contact with the ball, causing it to dribble in front of his feet and into foul territory.
- **Scenario 3:** The bowler throws a curveball that seems poised to catch the outside corner of the pitch. The batsman swings forcefully, but the bat grazes the underside of the ball, sending it skewing to the right and flying into the crowd. The umpire declares, "Foul ball, still two strikes!"
- **Scenario 4:** The bowler bowls another pace delivery down the middle of the pitch. The batsman swings and smashes the ball high into the air, clearing the center field wall marked at 410 feet. The umpire signals a six.

CLASS 12th

Collision Theory (part II)

In accordance with collision theory, a reaction occurs due to the collision of molecules. The quantity of collisions per second per unit volume of the reaction mixture is termed collision frequency. At standard temperature and pressure, the collision frequency reaches remarkably high values (approximately 10²⁵ to 10²⁶ in a gaseous reaction). If all these collisions were effective, the reaction would theoretically be completed in a fraction of a second. However, in practical terms, this is not the case. This discrepancy is elucidated based on two factors.

(i) Energy factor

To ensure the effectiveness of a collision, the colliding molecules must possess energy exceeding a specific threshold. The minimum energy required for colliding molecules to achieve an effective collision is referred to as threshold energy. Therefore, at standard temperature and pressure, the majority of molecules may not have energy equal to or greater than this threshold value.

Collisions involving high-energy molecules can overcome repulsion, leading to the formation of an unstable molecule cluster known as the activated complex.



In every chemical reaction, whether exothermic or endothermic, an energy barrier must be surmounted before reactants can undergo transformation into products. Provided that the reactant molecules possess sufficient energy, they can ascend to the peak of the energy barrier following a collision, leading to the conversion into products. When the activation energy for a reaction is low, the proportion of effective collisions is substantial, resulting in a fast reaction. Conversely, with a high activation energy, the fraction of effective collisions is diminished, leading to a slower reaction. Increasing the temperature augments the number of active molecules, thereby elevating the count of effective collisions and consequently accelerating the reaction rate.

Activation energy Ea = E(activated complex) - E(ground state)

 ΔH = activation energy of forward reaction – activation energy of backward reaction.

(ii) Orientation factor

In certain instances, it is observed that despite a higher number of colliding molecules possessing energy exceeding the threshold value, the reaction remains slow. This is attributed to the improper orientation of the colliding molecules at the moment of collision.



Rate of reaction is directly proportional to the number of effective collisions.

Rate $= \frac{dx}{dt} =$ Collision frequency \times fraction of effective molecules

$$= z \times f$$

According to kinetic theory of gases, the fraction of molecules having energy more than a particular value, E at temperature T is given by

$$f = e^{-E_a/RT}$$

Rate = $Ze^{-E_a/RT}$

As rate of reaction is directly related to rate constant K, we can also write $K = Ze^{-E_a/RT}$

Arrhenius Equation

Splitting into two parts

The Van't Hoff equation of thermodynamics elucidates the temperature-dependent alteration in the equilibrium constant of a reaction and is expressed as follows:

$$\frac{\mathrm{dln}_{\mathrm{n}}}{\mathrm{dT}} = \frac{\Delta \mathrm{H}}{\mathrm{RT}^2}$$

If k1 and k_2 be the rate constants of forward reaction and backward reaction, respectively then $Kp = k_1/k_2$.

Further, $\Delta H = Ea_1 - Ea_2$. Putting these in the above equation we get,

$$\frac{\mathrm{dln} \ \mathbf{k}_1}{\mathrm{dT}} - \frac{\mathrm{dln} \ \mathbf{k}_2}{\mathrm{dT}} = \frac{\mathbf{E}_{a_1}}{\mathrm{RT}^2} - \frac{\mathbf{E}_{a_2}}{\mathrm{RT}^2}$$
$$\frac{\mathrm{d}_{\mathrm{lnk}_1}}{\mathrm{dT}} = \frac{\mathbf{E}_{a_1}}{\mathrm{R}^2} + \mathrm{Z}(\mathrm{For} \mathrm{FR})$$
$$\frac{\mathrm{dlnk}_2}{\mathrm{dT}} = \frac{\mathbf{E}_{a_2}}{\mathrm{RT}^2} + \mathrm{Z}(\mathrm{For} \mathrm{BR})$$

were Z is constant

CLASS 12th

CHEMISTRY

Arrhenius sets Z equal to zero and without specifying FR and BR, he gave the following equation called Arrhenius equation.

$$\frac{dlnk}{dT} = \frac{Ea}{RT^2} \qquad ...(i)$$

This equation reveals that the rate of change in the logarithm of the rate constant with temperature is contingent on the activation energy (Ea) of the reaction. A higher Ea results in a smaller rate of change in the logarithm of the rate constant with temperature. In other words, a reaction with a low Ea experiences a gradual increase in rate with temperature, while a reaction with a high Ea undergoes a rapid increase in rate with temperature. Additionally, it is apparent that the rate of increase in the logarithm of the rate constant diminishes as the temperature rises.

Integrating Equation 4 assuming Ea to be constant we get,

or
$$\ln k = -\frac{Ea}{RT} + \ln A \qquad \dots (ii)$$
$$\ln \frac{k}{A} = -\frac{Ea}{RT}$$
or
$$k = Ae^{-Ea/RT} \qquad \dots (iii)$$

Equation (iii) represents the integrated form of the Arrhenius equation. The constant 'A,' known as the pre-exponential factor, is referred to as the frequency factor, as it is somewhat correlated with collision frequency. This constant remains consistent for a specific reaction. As indicated by Equation (iii), when the temperature (T) approaches infinity, the rate constant (k) tends towards 'A.' Consequently, 'A' serves as the rate constant of the reaction at infinite temperature, and the rate constant continually rises with increasing temperature.

In essence, as T approaches infinity, k reaches its maximum value, signifying that 'A' represents the maximum rate constant for a reaction. Additionally, it is crucial to recognize that the exponential term, i.e., e^(-Ea/RT), quantifies the fraction of the total number of molecules in the activated state or the fraction of the total number of effective collisions.

If nEa and n be the number of molecules of reactant in the activated state and the total number of molecules of the reactant present in the reaction vessel respectively, then

$$\frac{n_{E_a}}{n} = e^{-E_a/RT}$$

Equation (ii) may also be put as

$$logk = (-\frac{Ea}{2.303R})\frac{1}{T} + log A ... (iv)$$

Since $\frac{E_a}{2.303R}$ and logA both are constants for a given reaction. So, from equation (iv) it is evident that a plot of log k vs. $\frac{1}{T}$ will be a straight line of the slope equal to $-\frac{E_a}{2.303R}$ and intercept equal to logA as shown below.

$$\frac{-E_{a}}{2.303R} = \tan \theta = -\tan (180 - \theta) = -\frac{0A}{0B}$$
$$Ea = \frac{0A}{0B} \times 2.303R$$
$$\log A = 0A$$

Thus, from this plot Ea. and A both can be determined accurately.

If k1 be the rate constant of a reaction at two different

temperature T1 and T2 respectively then from equation (iv), we may write



CHEMISTRY

$$\log k_{1} = -\frac{E_{a}}{2.303R} \cdot \frac{1}{T_{1}} + \log A$$
$$\log k_{2} = -\frac{E_{a}}{2.303R} \cdot \frac{1}{T_{2}} + \log A$$

Subtracting former from the later, we get

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad \dots (v)$$

Utilizing this equation, it becomes feasible to compute the activation energy (Ea) of a reaction, given that the rate constants of the reaction at two distinct temperatures are known. Alternatively, one can determine the rate constant of a reaction at a specific temperature, provided the rate constant at another temperature and the activation energy (Ea) of the reaction are known.