Chapter 4

Theories of reaction rates

There are two important theories of reaction rates. These are the collision theory developed by Arrhenius and van't Hoff and the modern transition state theory, also called the activated complex theory developed by Eyring, Polanyi and Evans in 1935.

Collision theory of Bimolecular Gaseous Reactions:

Collision theory of bimolecular gaseous reactions aims at the quantitative calculation of the rate of a reaction based on the following two postulates.

1. The products are formed only when the reactant molecules come close and collide with each other.

2. Only those collisions are effective in producing the products which satisfy the criteria of energy of activation and the specific corientation of molecules.

If every collision leads to the formation of product, then the rate of the reaction will entirely be determined by the collision rate, i.e. the frequency with which reactants collide. The calculated rate on this basis sets the upper limit of the reaction rate i.e. the maximum reaction rate that can be observed experimentally. If the molecules are considered to be rigid, hard spheres with no forces of attraction and repulsion, then for the bimolecular elementary reaction.

$$A + A \longrightarrow \text{products}$$

the number of collision per unit volume per unit time is given by

$$Z_{AA} = \frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}N_A^{*2}$$

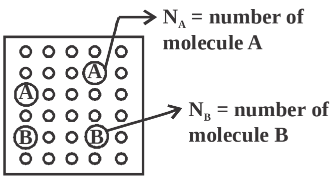
where, σ is the diameter of the molecule A and represents the closeness of approach for the molecular collisions, $\bar{u}$ is the average speed of molecules and N_A^* is the number of molecules per unit volume of the vessel. The average speed is given by

$$\bar{u} = \sqrt{\frac{8kT}{\pi m_A}}$$

where k is Boltzmann constant and m_A is the mass of a single molecule.

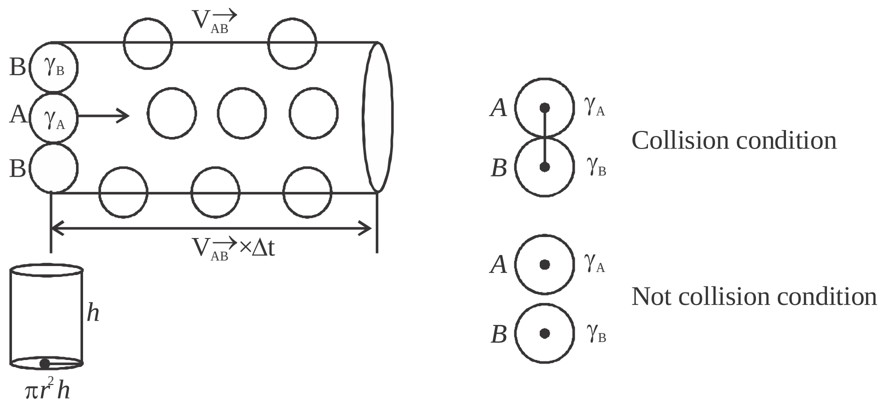
For a general elementary reaction

$$A + B \longrightarrow \text{products}$$



$N_A^* = \frac{N_A}{V}$ = Number of molecule of A per unit volume

$N_B^* = \frac{N_B}{V}$ = Number of molecule of B per unit volume



Volume of cylinder = $\pi(\gamma_A + \gamma_B)^2 (V_{\overrightarrow{AB}} \times \Delta t)$

Number of collision by A molecule with B molecule in Δt time = number of B moleucles inside the cylinder.

$$= N_B^* \times (\text{volume of cylinder})$$

$$= N_B^* \times \pi(\gamma_A + \gamma_B)^2 V_{AB} \times \Delta t$$

Total number of collision by all A molecules in Δt time = $N_A \times N_B^* \pi(\gamma_A + \gamma_B)^2 V_{AB} \times \Delta t$

Total number of collision by *A* molecule per unit time per unit volume

$$\frac{N_A \times N_B^* \pi(\gamma_A + \gamma_B)^2 V_{AB} \times \Delta t}{\Delta t V}$$

$$Z_{AB} = N_A^* N_B^* \pi\, \sigma_{AB}^2 V_{AB} = N_A^* N_B^* \pi\, \sigma_{AB}^2 \sqrt{\frac{8RT}{\pi\mu}}$$

$$Z_{AA} = \frac{1}{2}\left(N_A^* N_A^*\, \pi\sigma_{AA}^2 V_{AA}\right) = \frac{1}{2} N_A^{*2}\, \pi\, \sigma_{AA}^2 \sqrt{\frac{8RT}{\pi M_A}}$$

$$= \frac{1}{2} N_A^{*2} \pi\, \sigma_{AA}^2 V_A \times \sqrt{2} = \frac{1}{\sqrt{2}} N_A^{*2}\, \pi\, \sigma_{AA}^2 V_A$$

the number of collisions per unit volume per unit time between A and B is given by

$$Z_{AB} = \pi\sigma_{AB}^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A^* N_B^* \qquad \text{... (4)}$$

where σ_{AB} is the closeness of approach for the collisions and is equal to the sum of the radii of the molecules A and B or $\sigma_{AB} = \left(\frac{1}{2}\right)(\sigma_A + \sigma_B)$

And μ is the reduced mass $\mu = \frac{m_A m_B}{(m_A + m_B)}$

Energy of activation:

1. This factor, requires that the colliding energetic so that the molecular rearrangement occurs that finally results in the product formation.
2. The energy of activation does not mean the total kinetic energy of the colliding molecules.
   The energy of activation is equivalent to that energy with which the two molecules are pressed together along the specific orientation and that is calculated by Boltzmann's factor according to which this fraction will be, $e^{-E_a/RT}$.
   Thus, the rate of a bimolecular gaseous reaction will be given by

$$\text{Rate} = \left(\text{total number of collisions}\right)\begin{pmatrix}\text{fraction of molecules having} \\ \text{component energy equal to } \varepsilon_0\end{pmatrix}$$

Or,
$$-\frac{dN_A^*}{dt} = r_{\max}\exp\left(-\varepsilon_0/kT\right) = Z_{AB}\exp\left(-\varepsilon_0/kT\right)$$

$$= \left\{\pi\,\sigma_{AB}^2\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A^* N_B^*\right\}\exp\left(-\varepsilon_0/kT\right)$$

The constant k_2 as given by equation (7) will now become

$$k_2 = N_A\,\pi\,\sigma_{AB}^2\left(\frac{8kT}{\pi\mu}\right)^{1/2}\exp\left(-\varepsilon_0/kT\right)$$

Specific orientation of molecules:

According to this factor the rate of reaction also depends upon the orientation of colliding molecule.

For example : For this reaction,

$$H_2 + Br \longrightarrow HBr + H$$

two orientation are posible

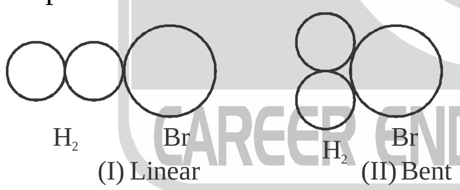
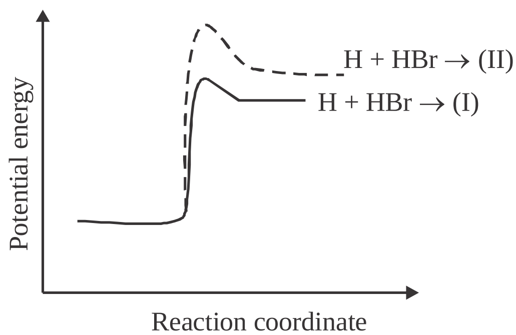


Figure : (I) Three atoms lie on a straight line, and (II) three atoms do not lie on a straight line

The potential energies curves for these two orientation are as shown below–



for this spacific orientation a correction factor is applied in equation (7), and that is called steric factor.

$$k_2 = p\left[\pi\,\sigma_{AB}^2\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A\right]e^{-E_a/kT}$$

where, p is steric factor and $p\left[\pi\,\sigma_{AB}^2\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A\right]$ is known as pre-exponential factor.

The steric factor p is easily less than 1 and consequently predicts a reduced rate

$$\boxed{k_2 = pr_{\max}\, e^{-E_a/kT}} \Rightarrow \boxed{k_2 = p\, Z_{AB}\, e^{-E_0/RT}}$$

SOLVED PROBLEMS

1. Consider an elementary bimolecular gaseous reaction 1 atm at 0ºC having collision diameter of the molecule $3\times10^{-9}\ dm$ and average speed of $5\times10^{3}\ dm\,\sec^{-1}$, then calculate the maximum rate as expected from collision theory and comment of the competative value.

Soln. Maximum rate $= \pi\sigma^2\bar{u}N_A^*N_B^*$

$$N_A^* = N_B^* = \frac{6.023\times10^{23}\ mole^{-1}}{22.4\ litre\ mole^{-1}} = 26.8\times10^{21}\ litre^{-1}$$

Maximum rate = $3.14\times\left(3\times10^{-9}\right)^2\left(5\times10^{3}\right)\times\left(26.8\times10^{21}\right)^2 = 1.11\times10^{32}\ litre^{-1}\sec^{-1}$

Number of molecules are available are very less in comperission to maximum rate it mean reaction will get over the fraction of second.

2. By what factor the rate of reaction will increase if the temperature rises 300 to 310 K.

Soln. We know that, $k \propto \sqrt{T}$; $k_1 \propto \sqrt{T_1}$; $k_2 \propto \sqrt{T_2}$

$$\boxed{\frac{k_2}{k_1} = \sqrt{\frac{T_2}{T_1}}}$$

$$k_2 = k_1\sqrt{\frac{T_2}{T_1}} \Rightarrow k_2 = k_1\sqrt{\frac{310}{300}}$$

$\Rightarrow$ $k_2 = 1.016\, k_1$ (Almost same rate constant)

3. Consider the reaction, $H_2 + C_2H_4 \longrightarrow C_2H_6$

The molecular diameters H_2 and C_2H_4 are 1.8Å and 3.6Å respectively. The pre-exponential factor in the rate constant calculated using collision theory in $m^3(mole^{-1})\ sec^{-1}$ is appear (at 300K)

$$\left[\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A = 1.11\times10^{27}\, m\left(mole^{-1}\right)\sec^{-1}\right] \text{ is}$$

(a) 2.5×10^{8} (b) 2.5×10^{14} (c) 9.4×10^{17} (d) 9.4×10^{23}

Soln. Pre-exponential factor $= p\pi\sigma^2\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A = 1\times3.14\times\left(\frac{\sigma_A+\sigma_B}{2}\right)^2\times1.11\times10^{27}$

$$= 2.5\times10^{8}\ m^3\left(mole^{-1}\right)\sec^{-1}$$

Where, $\sigma_A = 1.3\times10^{-10}\,m$, $\sigma_B = 3.6\times10^{-10}\,m$

Correct option is (a)

4. The bimolecular decomposition of hydrogen iodide is given by the equation $2HI \longrightarrow H_2 + I_2$. Assuming a collision diameter of 3.5 nm and an activation energy of 183.9 kJ mol^{-1} for the reaction, calculate (a) the collision rate, (b) the rate of reaction, and (c) the rate constant for the above reaction at 700K and one atmospheric pressure.

Soln. (a) The number of collisions per unit volume per unit time between two identical molecules is given by

$$Z = \frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}N^{*2}$$

where, $$\bar{u} = \sqrt{\frac{8RT}{\pi M}} = \left[\frac{8(8.314\ JK^{-1}mol^{-1})(700K)}{(3.14)(128\times10^{-3}\ kg\ mol^{-1})}\right] = 340.4\ ms^{-1}$$

$$N^* = \frac{N_A}{V_m} = \frac{(6.023\times10^{23}\ mol^{-1})}{(8.314\ JK^{-1}\ mol^{-1})(700K)/(101.325\times10^3\ Pa)}$$

Hence, $$Z = \frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}N^{*2}$$

$$= \left(\frac{1}{1.414}\right)(3.14)(3.5\times10^{-9}\ m)^2(340.4\ ms^{-1})(1.05\times10^{25}\ m^{-3})^2$$

$$= 1.02\times10^{36}\ m^{-3}s^{-1}$$

The exponential factor is

$$e^{-E_a/RT} = \exp\left[-183.9\times10^3\ J\ mol^{-1}/\{(8.314\ JK^{-1}\ mol^{-1})(700K)\}\right]$$

$$= \exp(-31.6) = 1.89\times10^{-14}$$

Hence, $$-\frac{1}{2}\frac{dN_A}{dt} = \frac{1.93\times10^{22}\ m^{-3}s^{-1}}{6.023\times10^{23}\ mol^{-1}} = 0.032\ mol\ m^{-3}\ s^{-1}$$

$$-\frac{1}{2}\frac{d[A]}{dt} = \frac{1.93\times10^{22}\ m^{-3}}{6.023\times10^{23}\ mol^{-1}} = 17.43\ mol\ m^{-3}$$

Now, $$[A] = \frac{N^*}{N_A} = \frac{1.05\times10^{25}\ m^{-3}}{6.023\times10^{23}\ mol^{-1}} = 17.43\ mol\ m^{-3}$$

Hence, $$k = \frac{-(1/2)\,d[A]/dt}{[A]^2} = \frac{0.032\ mol\ m^{-3}s^{-1}}{(17.43\ mol\ m^{-3})^2} = 1.053\times10^{-4}\ mol^{-1}\ m^3\ s^{-1}$$