

Lecture 16

Theories of Reaction Rates

There are two basic theories: Collision theory and activated complex theory.

Simplest is the collision theory – accounts for gas phase reactions

Reactions in solution

1. Diffusion controlled - Diffusion equation can account for rates
2. Activation controlled – Activated complex and thermodynamics are involved

Rates in terms of potential energy surfaces is the more advanced

Both (collision and activated complex) theories say that:

Molecular encounters make them excited making reactions. Excitation can be through collisions (collision theory) or the energy can be taken from surroundings (activated complex, in solutions).

Collision Theory

$A + B \rightarrow \text{Products}$

Rate = $k_2[A][B]$

k_2 to involve 1. Energy 2. Orientation 3. Rate of encounter

$k_2 \propto \text{rate of collisions} \times \text{steric requirement} \times \text{energy requirement}$

Assumptions

- Molecules are hard spheres
- For reactions to occur, molecules must collide
- Reactions occur only if molecules are energetic
- Collisions should transfer certain minimum energy

Number of Collisions

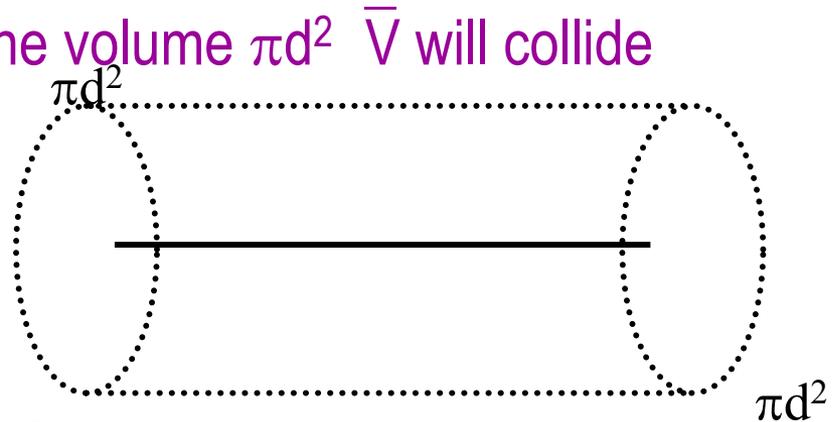
Number of molecules N in volume V

Number of collisions of one molecule per second

is the collision frequency, z

Average velocity of the molecule = \bar{V} m/s, the molecule collides every molecule within the distance, d

Therefore, all the molecules within the volume $\pi d^2 \bar{V}$ will collide with the test molecule per second.

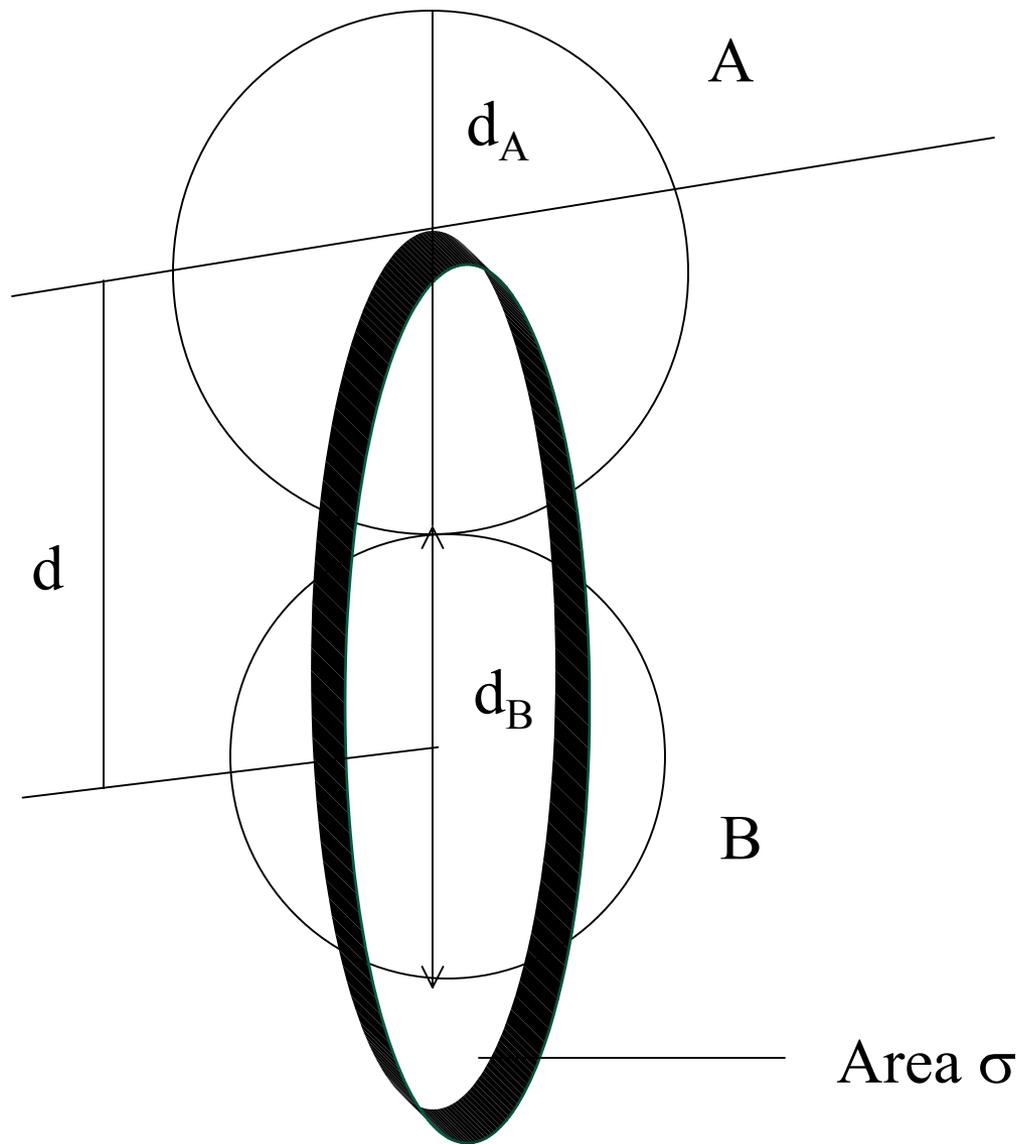


Encounter of A with B

πd^2 - collision cross section

This is the area within which centre of A has to enter around the target molecule B for collisions to occur.

This is the area πd^2 , this is the area covered by the dotted lines.



Volume swept by the molecule/sec

The solid line represents the average velocity of the molecule.

$N/V \rightarrow$ Number of molecules in unit volume

Number of collisions of one molecule, $z = (N/V) (\pi d^2) (\bar{V} \text{ s}^{-1})$

Average speed $\bar{V} = (8kT/\pi m)^{1/2}$

m is replaced by $\mu = (m_1 m_2 / m_1 + m_2)$, reduced mass

identical particles $\mu = m/2$

$$\bar{V} = (8kT/\pi m/2)^{1/2}$$

$$z_{11} = \sqrt{2} N/V \pi d^2 (8kT/\pi m)^{1/2} \text{ s}^{-1}$$

$$z_{11} = \sqrt{2} N/V \pi d^2 (8RT/\pi M)^{1/2} \text{ s}^{-1}$$

$\pi d^2 = \sigma \leftarrow$ Collision cross – section

$$z_{11} = \sqrt{2} N/V \sigma (8kT/\pi m)^{1/2} \text{ s}^{-1}$$

Collision number

Number of bimolecular collisions in 1 m³ per sec,

$$Z_{11} \text{ (s}^{-1}\text{m}^{-3}\text{)} = \frac{1}{2} N/V z_{11}$$

$\frac{1}{2}$ not to count collisions twice

$$= \frac{1}{\sqrt{2}} (N/V)^2 \pi d^2 \bar{V}$$

for different molecules,

$$Z_{12} = (N_A/V) (N_B/V) \pi (r_1 + r_2)^2 (8kT/\pi \mu)^{1/2}$$

Collision Number is very large $\sim 10^{34}$ for N₂ at STP

Rate constant



$$d[P]/dt = k[A][B]$$

if all collisions lead to reactions,

$$d[P]/dt = Z_{AB}/N_{av}$$

Nav → **Avogadro number**

(Since rate is in moles/unit volume and not in molecules/unit volume)

We know,

$$d[P]/dt = k (N_A/V \cdot N_{av}) (N_B/V \cdot N_{av}) \quad \dots 1$$

$$d[P]/dt = Z_{AB}/N_{av} = 1/N_{av} (N_A/V) (N_B/V) \pi d^2 \bar{V} \quad \dots 2$$

Compare 1 and 2

$$k/N = \pi d^2 \bar{V}$$

$$k = N_{av} \pi d^2 \bar{V} \text{ mol}^{-1} \text{ m}^3 \text{ s}^{-1}$$

$$k = N_{av} \sigma (8kT/\pi \mu)^{1/2} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The actual value is very very small !! $\text{H}_2 + \text{I}_2 \rightarrow \text{HI}$

$$\text{Calculated } k = 7.5 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$= 7.5 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$$

$$\text{Observed} \rightarrow 1.15 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1} \text{ !!!}$$

Energy Considerations

We expect the rate constant for a bimolecular reaction to depend on both frequency and energy of the collisions.

The above considerations do not take into account the role of energy:

The reaction of molecular pairs with energy above E_a is given by

$$= \exp.^{-E_a/RT}$$

These are the fruitful collisions leading to products.

$$Z_{AB} \text{ (effective)} = Z_{AB} \times \exp^{-E_a/RT}$$

The rate constant for a bimolecular reactions is

$$k' = N_{AV} \pi d_{AB}^2 (8kT/\pi m_r)^{1/2} \exp^{-E_a/RT}$$

This equation is similar to the Arrhenius law except for \sqrt{T} term in \bar{v}_{AB} of pre-experimental factor.

Kinetic data over a wide range of temperature range show that the pre-experimental factor depends on \sqrt{T} (by about 2%) as predicted.

$$\therefore k = A' \sqrt{T} \exp^{-E_a/RT}$$

$$A' = N_{AV} \pi d_{AB}^2 (8kT/\pi m_r)^{1/2} \text{ mol}^{-1} \text{ m}^3 \text{ sec}^{-1}$$

Steric requirement

Collision energy is not the only criterion.

Relative orientation is important.

Disagreement in A values between theory and experiment

Explained in terms of a steric factor, P

$$k_{11} = P Z_{11} e^{-E_a/RT}$$

$$k_{12} = P Z_{12} e^{-E_a/RT}$$

$$P = (A_{\text{expt}}/A_{\text{theory}})$$

Different equations used

For like molecules

$$\text{Rate} = Z_{AA}/N_{AV} = 1/\sqrt{2} (N_A/V)^2 \pi d^2 \bar{V} (1/N_{AV})$$

$$\text{Rate} = k (N_A/V N_{AV}) (N_A/V N_{AV}) = 1/\sqrt{2} (N_A/V)^2 \sigma \bar{V} (1/N_{AV})$$

$$k/N_{AV} = 1/\sqrt{2} \pi d^2 \bar{V}$$

$$k = 1/\sqrt{2} N_{AV} \pi d^2 \bar{V}$$

$$= 1/\sqrt{2} N_{AV} \pi d^2 (8kT/\pi m)^{1/2}$$

$$= 2 N_{AV} \pi d^2 (\pi kT/m) \text{ mol}^{-1} \text{ m}^3 \text{ s}^{-1}$$

$$k = 2 N_{AV} d^2 (\pi RT/M)^{1/2} e^{-E_a/RT}$$

The steric factor is difficult to evaluate

$$k = P\sigma(8kT/\pi\mu)^{1/2} N_A e^{-E_a/RT}$$

The effective σ can be considered as $P\sigma$ which is taken as the reactive cross section σ^* .

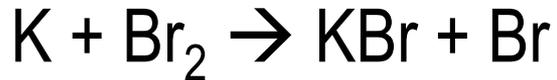
$$k = P\sigma(8kT/\pi\mu)^{1/2} N_A e^{-E_a/RT}$$

$$k = Ae^{-E_a/RT}$$

$$A = P\sigma(8kT/\pi\mu)^{1/2} N_A$$

This kind of evaluation shows that P is very small, of the order of 10^{-6}

One case where P is large is for the reaction,



Here $P = 4.8$ (experimentally)

Suggested to follow Harpoon Mechanism

Harpoon extends the cross-section of reactive encounter

Reaction need not occur as a result of simple mechanical encounter

Calculate P assuming harpoon mechanism

Net change in energy upon transfer of an electron from K to Br_2 to form K^+ and Br_2^- is

$E = I - E_a - e^2/(4 \pi \epsilon_0 R)$, this will go to zero when harpoon will transfer

$$e^2/4\pi\epsilon_0 R = I - E_a$$

$$\text{So, } P = \sigma^*/\sigma = R^2/d^2 = \{e^2/4 \pi \epsilon_0 (I - E_a)\}^2 d^2$$

Value determined is 4.2, in agreement with experiment (4.8).