

**Dr. Y. Jaya Vinse Ruban**

**Department of Chemistry**

**St. Xavier's College (Autonomous)**

**Palayamkottai-627002.**

# Molecular Reaction Dynamics.

**Collision theory of gases**  
**Collision number and frequency factor**  
**Interpretation of Arrhenius relationship**  
**Steric factor**  
**Summary**

▪

# The theoretical explanation of reaction kinetics

- Consider a simple bimolecular reaction  $A + B \rightarrow C$
- From empirical observation the rate is found to obey the Arrhenius law.

$$\text{rate} = k[A][B] \quad \text{where } k = A \exp\left(\frac{-E_a}{RT}\right)$$

- What is the physical interpretation of this rate law?
  - The molecules **A** and **B** must meet
  - The molecules **A** and **B** must be able to interact in a way that leads to reaction
  - The mechanistic route from **A** and **B** to **C** involves some rearrangement of atoms in the molecules **A** and **B**. Bonds are broken and new bonds are formed. There is a **transition state** with higher energy ( $E_a$ ) than the ground state of the individual molecules.
  - The molecules must possess sufficient energy to reach the transition state.
- The development of the theory progressed in the first half of the 20<sup>th</sup> century to cover simple collision theory, thermodynamics, statistical mechanics and molecular dynamics, culminating in transition state theory (Eyring, Evans and Polanyi).

# Collision theory of gases

- In order to derive an expression for the rate constant  $k_r$ , we will consider the frequency of collisions and the distribution of energy for the same simple 2<sup>nd</sup> order bimolecular reaction  $A + B \rightarrow C$

Rate =  $k_r[A][B]$  = rate of collisions x probability of sufficient energy

- Consider the molecules as hard spheres. The **collision number** or **collision density**  $Z_{AB}$  is the total number of collisions of molecules of **A** with molecules of **B** per unit time per unit volume.
- From the **kinetic theory of gases** the **collision number**  $Z_{AB}$  is proportional to
  - the numbers of molecules  $N_A$  and  $N_B$  per unit volume
  - the mean speed of the molecules  $(8kT/\pi \mu_{AB})^{1/2}$
  - the sizes of the molecules expressed as their **collision cross-section**  $\sigma_{AB} = \pi d_{\text{mean}}^2$

$$Z_{AB} = \sigma_{AB} \left\{ \frac{8kT}{\pi \mu_{AB}} \right\}^{1/2} N_A N_B = \sigma_{AB} \left\{ \frac{8kT}{\pi \mu_{AB}} \right\}^{1/2} N_{Av}^2 [A][B] \quad \text{molecules m}^{-3}\text{s}^{-1}$$

- Use  $Z_{AA}$  and  $N_A^2$  for reaction of like molecules; divide by 2 to avoid double-counting

Symbols:  $k$  = Boltzmann constant =  $R/N_{Av}$ ,  $N_{Av}$  = Avogadro number (**n.b. caution re dual use of symbols  $k$ ,  $N$** ),  $\mu_{AB}$  = reduced mass of the molecules =  $m_A m_B / (m_A + m_B)$ .

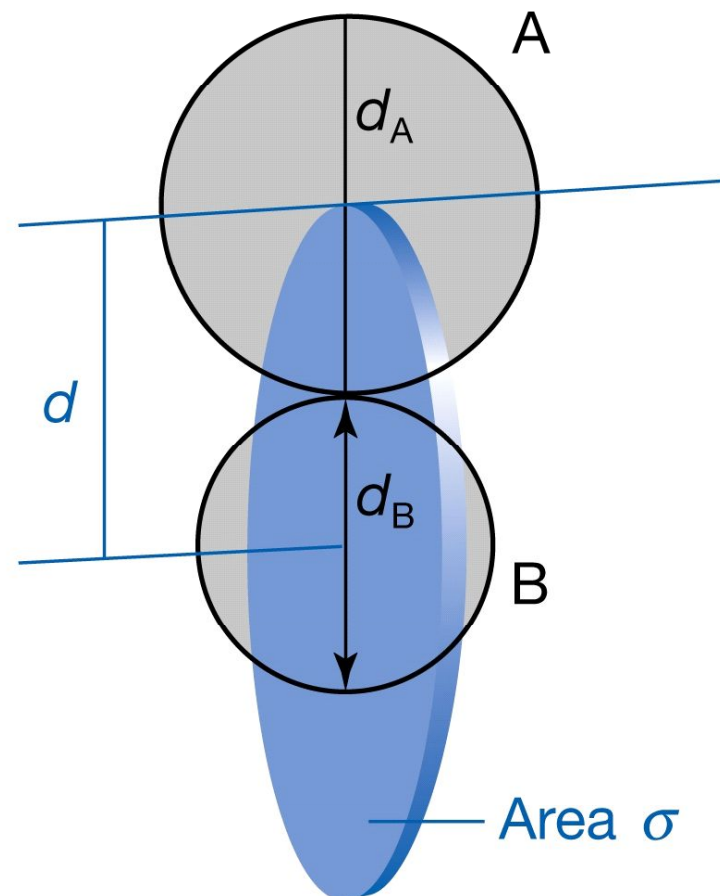
# Collision cross-section

- Molecules can collide anywhere between head-on and glancing. For the minimum glancing collision the centres of the two molecules are separated by the distance of their combined radii  $d = (d_A + d_B)/2$ .

- The collision cross-section is therefore the area of a circle of radius  $d = (d_A + d_B)/2$ .

$$\sigma_{AB} = \pi d^2 = \pi (d_A + d_B)^2/4$$

Diagram from 'Physical Chemistry', 7<sup>th</sup> edn, P.W Atkins & J. de Paula, OUP (2002)  
[www.oup.co.uk/powerpoint/bt/atkins](http://www.oup.co.uk/powerpoint/bt/atkins)



# Hard sphere collision theory (Lewis & Trautz)

- Reaction rate (molecules  $L^{-1}s^{-1}$ ) = collision number x probability of sufficient energy (estimated as the **empirical** Arrhenius relationship).
- For reaction between **A** and **B**

$$\text{Rate (molecules } m^{-3}s^{-1}) = Z_{AB} \exp\left(\frac{-E_a}{RT}\right) = \sigma_{AB} \left\{ \frac{8kT}{\pi\mu} \right\}^{1/2} N_{Av}^2 \exp\left(\frac{-E_a}{RT}\right) [A][B]$$

$$\text{Rate (moles } m^{-3}s^{-1}) = \sigma_{AB} \left\{ \frac{8kT}{\pi\mu} \right\}^{1/2} N_{Av} \exp\left(\frac{-E_a}{RT}\right) [A][B]$$

$$\text{where } z_{AB} = \sigma_{AB} \left\{ \frac{8kT}{\pi\mu} \right\}^{1/2} N_{Av} \quad \text{Hence rate constant } k_r = z_{AB} \exp\left(\frac{-E_a}{RT}\right)$$

**Note**  $k$  = **Boltzmann constant** ( $1.38066 \times 10^{-23} \text{ J K}^{-1}$ ) and so here use  $k_r$  = reaction rate constant

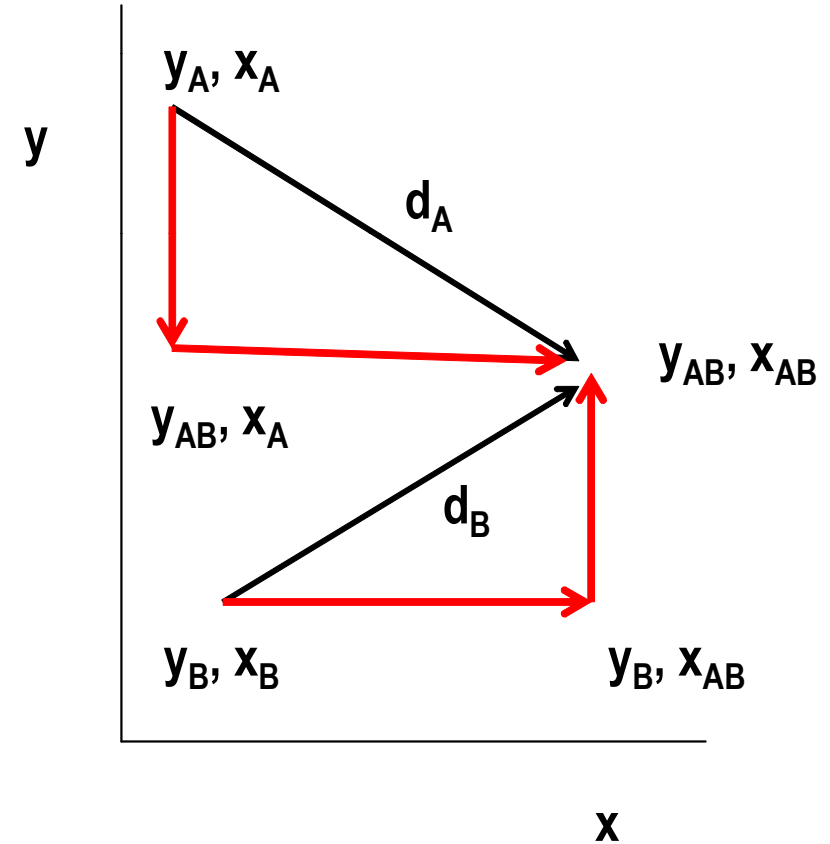
- $Z_{AB}$  was defined as the molecular collision number.  
 $z_{AB}$  is termed the molar collision frequency factor or more simply the **frequency factor** (A)
- Lewis applied this treatment to the reaction  $2HI \rightarrow H_2 + I_2$  at 556K  
Rate constant  $k_r(\text{calc}) = 3.5 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$        $k_r(\text{obs}) = 3.5 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
- The excellent agreement in this case was rather misleading. In general, simple collision theory does not lead to accurate frequency factors. Molecules are not hard spheres!
- Can include a **steric factor**  $P$  for orientation but cannot estimate  $P$  in a satisfactory manner.

# Extended collision theory

- In practice, not all collisions are effective even if the molecules have sufficient energy. Need to justify the Arrhenius term by considering the energy of collisions in more detail.
- The **effective energy** of the collision depends both on the kinetic energies of the molecules and the nature of the collision, i.e., head-on or at an angle.
- Need to determine which collisions will have sufficient energy for reaction and hence estimate **the frequency of such collisions**.
- The nature of the collision of 2 molecules is analogous to the collision of two moving billiards balls.
  - When the collision is central and head-on then the translational kinetic energy of the collision is the sum of the energies of the two balls.
  - When the collision is at an angle or involves glancing contact then the head-on component of the energies is reduced and so less energy is transferred. The **relative velocity** and the **relative kinetic energy** and their alignment with the collision must be considered.

# Relative velocity

- Consider 2 molecules **A** and **B** covering the distances  $d_A$  and  $d_B$  marked out in the plot in the time  $t$  before they collide.
- The magnitude of the velocities is given by distance/ time:  $d_A/t$  and  $d_B/t$
- Molecule **A** has travelled distance  $y_{AB}-y_A$  on the y-axis and distance  $x_{AB}-x_A$  on the x-axis.
- Molecule **A** has velocity components  $y_{AB}-y_A/t = v_{yA}$  in the y-direction and  $x_{AB}-x_A/t = v_{xA}$  in the x-direction.
- Likewise molecule **B** has velocity components  $y_{AB}-y_B/t = v_{yB}$  and  $x_{AB}-x_B/t = v_{xB}$ .
- Hence the relative velocity is  $v_{yA} - v_{yB} = (y_A - y_B)/t$  in the y-direction and  $v_{xA} - v_{xB} = (x_A - x_B)/t$  in the x-direction, the combination making the overall relative velocity  $v_{rel}$ .
- In this case the relative velocity component in the y-direction is greater than the component in the x-direction.





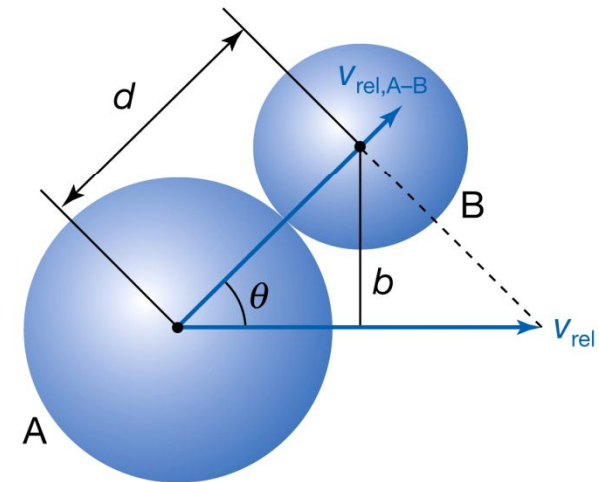
# Extended collision theory continued

- The **relative kinetic energy**  $\epsilon$  of the collision is given by  $\epsilon = \frac{1}{2} \mu v_{\text{rel}}^2$
- If the minimum energy required for reaction is  $\epsilon_A$  (**activation energy per molecule**) and  $\epsilon \geq \epsilon_A$  then the collision may lead to reaction but the **reactive collision cross-section** may be less than  $\sigma_{AB}$ 
  - The function  $\sigma(\epsilon)$  for the reactive collision cross-section varies with the energy of the collision.
  - A collision with energy  $\epsilon < \epsilon_A$  is never effective, i.e.,  $\sigma(\epsilon) = 0$
  - A collision with energy  $\epsilon \gg \epsilon_A$  is effective over the entire range of collision conditions, i.e.,  $\sigma(\epsilon) = \sigma_{AB}$
  - For a collision with energy  $\epsilon > \epsilon_A$ ,  $0 < \sigma(\epsilon) \leq \sigma_{AB}$ .

- The relative velocity component parallel to an axis containing the vector connecting the centres of **A** and **B** (line of centres) is most important.

Head-on collision:  $\mathbf{v}_{\text{rel}}$  is exactly  $\parallel$  to line of centres

Grazing collision:  $\mathbf{v}_{\text{rel}}$  is exactly  $\perp$  to line of centres



- $\sigma(\epsilon)$  can be derived from geometry.

$$\sigma(\epsilon) = \left\{ 1 - \frac{\epsilon_a}{\epsilon} \right\} \sigma_{AB}$$

Diagram: [www.oup.co.uk/powerpoint/bt/atkins](http://www.oup.co.uk/powerpoint/bt/atkins)

# Extended collision theory continued

- Now need to determine the number of molecules that have energy in excess of  $\epsilon_a$ .
- The distribution of molecular energy is derived from the **Maxwell-Boltzmann distribution of molecular speeds** (kinetic theory of gases).
- The fraction of molecules with energy in the range  $\epsilon$  to  $\epsilon + d\epsilon$  is written  $f(\epsilon)d\epsilon$  where  $f(\epsilon)$  is the distribution of energy.

$$f(\epsilon)d\epsilon = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \epsilon^{1/2} \exp\left(\frac{-\epsilon}{kT}\right) d\epsilon$$

- The probability of a qualifying collision by two molecules can be derived from the integral

$$\int_0^{\infty} \sigma(\epsilon) v_{\text{rel}} f(\epsilon) d\epsilon = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \int_0^{\infty} \sigma(\epsilon) \left\{\frac{2\epsilon}{\mu}\right\}^{1/2} \epsilon^{1/2} \exp\left(\frac{-\epsilon}{kT}\right) d\epsilon = \sigma \left\{\frac{8kT}{\pi\mu}\right\}^{1/2} \exp\left(\frac{-\epsilon_a}{kT}\right)$$

- This has the same form as the expression derived from simple collision theory by combination of  $Z_{AB}$  with the empirical Arrhenius expression. Note the weak temperature dependence ( $T^{1/2}$ ) of the frequency factor.
- The molar activation energy  $E_a = N_{Av} \epsilon_a$ . This quantity is still **empirical**.  $E_a/R = \epsilon_a/k$

# Comparison of theory with experiment

- Values of  $\sigma$  estimated from study of non-reactive collisions or molecular structure
- Experimental values of frequency factor **A** measured from Arrhenius plots
- Many experimental values of **A** are  $\ll$  theoretical values, one value below is greater!
- Need to invoke steric factor  $P = A_{\text{expt}}/A_{\text{theory}}$

Reaction	T/K	$E_a$ /kJ mol <sup>-1</sup>	A/(L mol <sup>-1</sup> s <sup>-1</sup> ) <b>Experiment</b>	A/(L mol <sup>-1</sup> s <sup>-1</sup> ) <b>Theory</b>	Steric factor <b>P</b>
$2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$	470	102	$9.4 \times 10^9$	$5.9 \times 10^{10}$	0.16
$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$		111	$2.0 \times 10^9$	$4.0 \times 10^{10}$	0.05
$2\text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$		0	$6.3 \times 10^7$	$2.5 \times 10^{10}$	$2.5 \times 10^{-3}$
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	800	180	$1.24 \times 10^6$	$7.3 \times 10^{11}$	$1.7 \times 10^{-6}$
$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	300	0	$2.4 \times 10^{10}$	$1.1 \times 10^{11}$	0.22
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	600	0	$1 \times 10^{12}$	$2.1 \times 10^{11}$	4.8

Data from 'Reaction kinetics', M.J. Pilling & P.W. Seakins and 'Physical Chemistry', 7<sup>th</sup> edn., P.W. Atkins & J. de Paula

# Summary of collision theory

## Pros

- Simple model, easy to visualise and understand
- Explains the importance of molecular collisions for reaction
- Qualitative prediction of the form of the temperature dependence of the rate constant  $k_r$  (Arrhenius relation)

## Cons

- Predicted values of the frequency factor **A** are often far from experimental results
- Steric factor **P** can allow for conformational effects but
  - the values are empirical and cannot be calculated *a priori*
  - the values do not always correlate with structural complexity

# Oversimplifications of collision theory

- Molecules are not hard uniform spheres
  - They have a variety of shapes as defined by their molecular structures
  - Different atoms are arranged in definite positions within the molecule
  - They are not hard; their shapes can be distorted and some can adopt alternative conformations
- Molecules have vibrational and rotational kinetic energy as well as translational kinetic energy
- Molecules have long range interactions (very big for ions) which help to explain some values of **P**
- Molecules do not react instantly
  - Reactions take place over a finite period
  - The structure of the reaction complex evolves during this time
- Some of these deficiencies will be tackled in **transition state theory**.