Collision Theory

Modelling chemical kinetics as governed by collisions between reactant molecules. Rate is dependent on both collision frequency and collision energy

For a bimolecular reaction: $A + B \rightarrow P$,

$$\text{Rate} = Z \exp\left(\frac{-E_a}{RT}\right)[A][B]$$

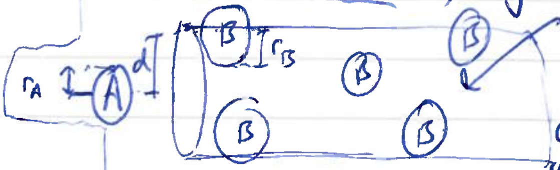
- $[A][B]$ → concentrations of reactants
- Z → Collision frequency factor ①
- $\exp\left(\frac{-E_a}{RT}\right)$ → probability factor ②

$Z \exp\left(\frac{-E_a}{RT}\right) = k$ ← rate constant

① Collision Frequency Factor, Z

$$Z = L \cdot \sqrt{\frac{8RT}{\pi\mu}} \cdot \sigma$$

- L → Avogadro's Number
- σ → Collision cross section, i.e. πd^2, where d is the collision diameter, e.g.



$d = r_A + r_B$

every molecule of B with a center in this cylinder of cross-sectional area πd^2 gets hit.

- $\sqrt{\frac{8RT}{\pi\mu}}$ → Mean relative speed

i.e. the average relative speed at which the molecules move, relative to each other. Derived from the Maxwell-Boltzmann distribution of speeds:

$$\sqrt{\frac{8RT}{\pi\mu}}$$

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- T → Temperature → higher T = faster
- R → gas constant
- π → pi
- μ → reduced mass $\mu = \frac{m_A m_B}{m_A + m_B}$ } "effective" mass of the two-body A+B system.

② Probability Factor, P_F → From Boltzmann Distribution.

$$P_F = \exp\left(\frac{-E_a}{RT}\right) = \frac{N(E > E_a)}{N_{total}}$$

- E_a → Activation Energy
- R → gas constant
- T → temperature
- $N(E > E_a)$ ← number of molecules with kinetic energy greater than E_a
- N_{total} ← total number of molecules.

→ i.e. this is the fraction of collisions in which the molecules have enough energy to react.

Consider Boltzmann Distribution: