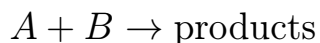


Collision Theory:

The theoretical calculation of reaction rate coefficients is very difficult. We discuss some very simple models here. We consider an elementary process



The rate constant is the result of many collisions of the reactants which enter into a collision with a relative energy $E_{rel} = \mu g^2/2$ where the reduced mass is given by

$$\frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B}$$

The relative velocity is $\mathbf{g} = \mathbf{v}_B - \mathbf{v}_A$. The particles A and B have a distribution of velocities as given by the Maxwell-Boltzmann distribution.

The extent of reaction depends on a quantity called the **CROSS SECTION** for reaction which has units of area. If the particles are considered as rigid spheres, the cross section is simply $\sigma = \pi d_{AB}^2 P(E)$ where $d_{AB} = \frac{1}{2}(d_A + d_B)$ and $P(E)$ is the probability of reaction which is the most difficult to calculate. There is a simple model known as the **LINE-OF-CENTRES** model which states that reaction occurs if the relative energy along the line of centers of the colliding atoms is greater than the activation energy, this model gives

$$P(E) = \begin{cases} \left(1 - \frac{E_a}{E}\right) & E \geq E_a \\ 0 & E \leq E_a \end{cases}$$

To calculate the constant, the cross section has to be averaged over all velocities of A and B, and the result is

$$k(T) = N_A \pi d_{AB} \sqrt{\frac{8RT}{N_A \pi \mu}} e^{-E_a/RT}$$

where N_A is the Avogadro number.

Notice that the pre-exponential factor of this model varies as \sqrt{T} whereas the Arrhenius formula the pre-exponential factor is constant. Experimentally it is very difficult to distinguish between either $Ae^{-E_a/RT}$ and $A'T^p e^{-E_a/RT}$.

Also, the simple collision theory is not rigorous. The problem of calculating rate constants is much more difficult. Often one writes $k(T) = sA'T^p e^{-E_a/RT}$ where s = steric factor and corrects the model so as to agree with experiment.