Collision Theory:

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

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

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 probablity of reaction which is the most difficult to calculate. There is a simple model know 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

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

To calculate the constant, the cross section has to be averaged over all velocties 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 $A'T^pe^{-E_a/RT}$.

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