

Simple Reaction Rate Constant Theory

John W Daily

Reaction Rate Constant

- Now we will explore the functional form for reaction rate constants.
- Then we will explore the nature of some simple reaction mechanisms.
- Later we will look at some real reaction mechanisms.



Collisional Dynamics

- Collisions are required for reaction to occur.
- Types of changing collisions
 - Mass
 - Momentum
 - Energy
 - Charge
- Collisions are categorized as
 - Elastic - Momentum and translational energy change only (i.e. Billiard balls)
 - Inelastic - Internal energy change, charge exchange (ionization), proton exchange (reaction)

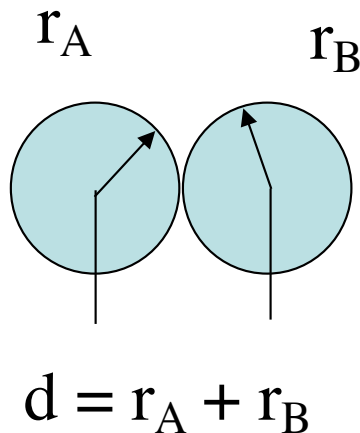
Questions

- For collision to cause a reaction process we must ask these questions:
 - What conditions must be satisfied before a given process can take place?
 - How often are these conditions satisfied per unit volume and time?
- The first question is answered by analyzing the dynamics (classical or quantum) of specific collision trajectories.
- The second is answered by statistics.

$$\left\{ \frac{\partial \text{Quantity}}{\partial t} \right\}_{\text{Coll}} = \int \left\{ \text{Rate at which a certain trajectory occurs} \right\} \left\{ \text{Fraction of collisions that produce result} \right\} d(\text{Trajectories})$$

We can illustrate these ideas in a simple fashion

- Recall the concept of a collision cross section



$$\frac{\text{\# of Collisions of one A with all B}}{\text{Unit time}} = \pi d^2 v_r n_B$$

$$\frac{\text{\# of Collisions of all A with all B}}{\text{Unit time}} = \pi d^2 v_r n_A n_B$$

πd^2 Collision cross section

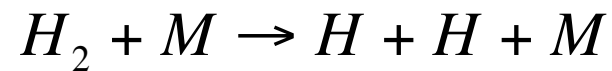
- We can incorporate some collision dynamics into d if we define it to be an *effective* collision diameter, such that the rate of a given process is

$$\frac{dn_A}{dt} = \int \pi d^2 v_r n_A n_B d \left\{ \text{All } v_r, \text{ Orientations} \right\}$$

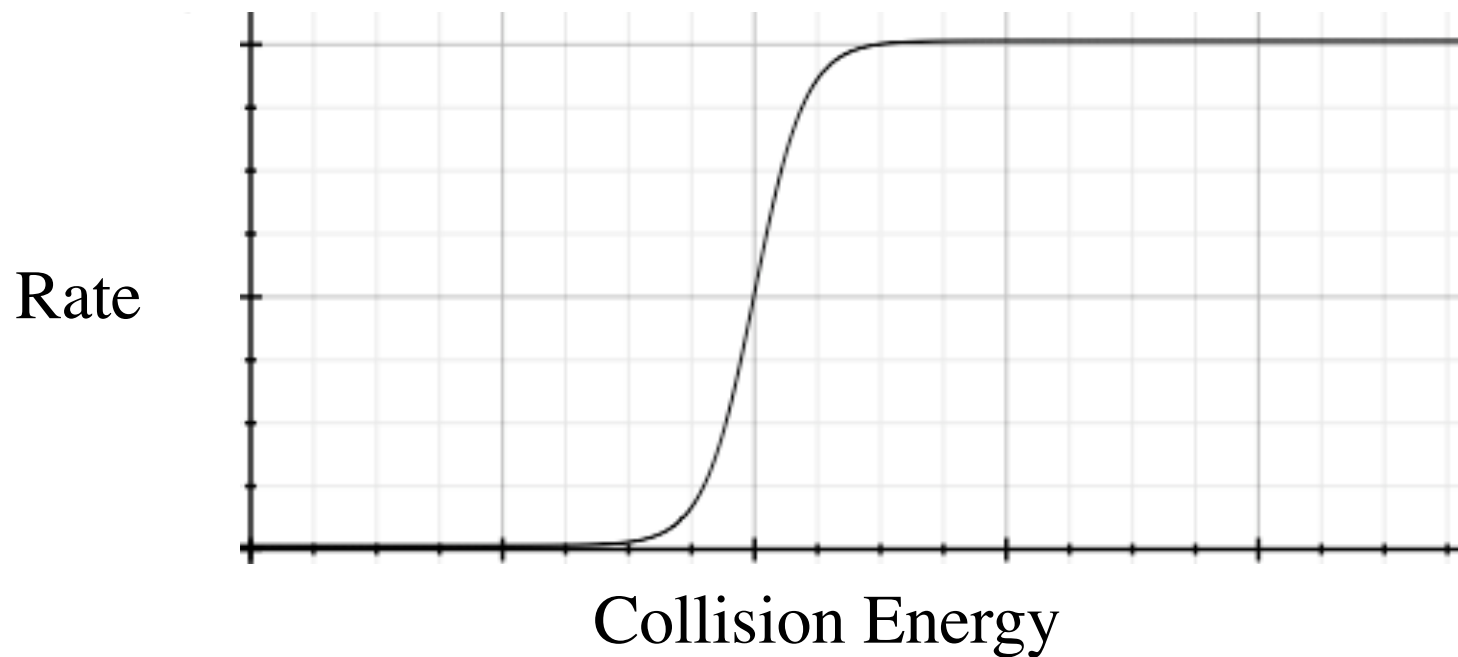
$$k_f = \int \pi d^2 v_r d \left\{ \text{All } v_r, \text{ Orientations} \right\}$$



- For example, suppose we consider



- Then we expect



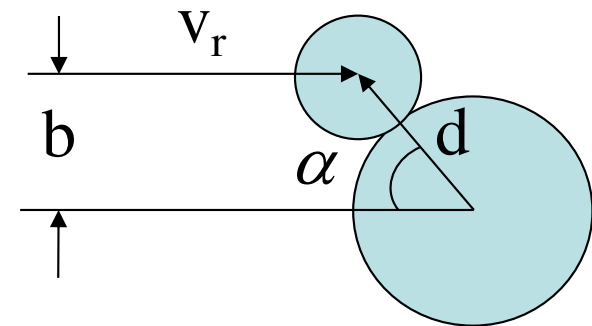
- The maximum amount of energy available in a given collision is

$$\varepsilon_T = \frac{1}{2} \mu v_r^2 \quad \left(\mu = \frac{m_A m_B}{m_A + m_B} \text{ Reduced mass} \right)$$

- This is available, however, only if the molecules collide directly along the line of centers.

$$v_{lc} = v_r \cos \alpha = v \left\{ (d^2 - b^2) / d^2 \right\}^{1/2}$$

$$\varepsilon_{lc} = \varepsilon_T \left(1 - b^2 / d^2 \right)$$



- For a reaction to occur we must have

$$\varepsilon_{lc} \geq \varepsilon_T^0$$

- Where ε_T^0 is a threshold energy about equal to the dissociation energy.
- The equation

$$\varepsilon_{lc} = \varepsilon_T^0 = \varepsilon_T (1 - b^2 / d^2)$$

- defines, for a given v_r , the maximum impact parameter at which reaction can occur.

- Solving

$$b_{\max} = d(1 - \varepsilon_T^0 / \varepsilon_T)^{1/2}$$

- An effective reaction cross section can thus be defined as

$$\sigma = \pi d^2 (1 - \varepsilon_T^0 / \varepsilon_T)$$



- One may show that in center of mass coordinates

$$dZ = n_A n_B \left(\frac{\mu}{kT} \right)^{3/2} \left(\frac{2}{\pi} \right)^{1/2} 2\pi b db v_r^3 e^{-\mu v_r^2 / 2kT} dv_r$$

- is the number of collisions per unit time and volume within b to $b+db$ and v_r to v_r+dv_r
- To get the total rate of collisions we first integrate over the allowed b 's

$$\int_0^{b_{\max}} 2\pi b db = \pi b_{\max}^2$$



- Then we need to integrate over v_r , however, it is easier to transform velocity to kinetic energy

$$\varepsilon_T = \frac{1}{2} \mu v_r^2$$

$$d\varepsilon_T = \mu v_r dv_r$$

- Thus

$$v_r^3 e^{-\mu v_r^2 / 2kT} dv_r = \frac{v_r^2}{\mu} e^{-\varepsilon_T / kT} d\varepsilon_T = \frac{2}{\mu^2} \varepsilon_T e^{-\varepsilon_T} d\varepsilon_T$$



- The rate constant is then

$$k(T) = \left(\frac{1}{\pi\mu} \right)^{1/2} \left(\frac{2}{kT} \right)^{3/2} \int_{\varepsilon_T^0}^{\infty} \pi d^2 (1 - \varepsilon_T^0 / \varepsilon_T) \varepsilon_T e^{-\varepsilon_T / kT} d\varepsilon_T$$

$$k(T) = \pi d^2 \bar{v}_r e^{-\varepsilon_T^0 / kT}$$

where $\bar{v}_r = \left(\frac{8kT}{\pi\mu} \right)^{1/2}$

Arrhenius Form

- This is why we see the rate constant expressed in the Arrhenius form

$$k(T) = AT^n e^{-E_a/kT}$$

- Of course we have not considered the complexities of reaction, only assumed that if the collision provided enough energy, then reaction would occur. Indeed, we have neglected orientation, internal energy state and quantum effects.



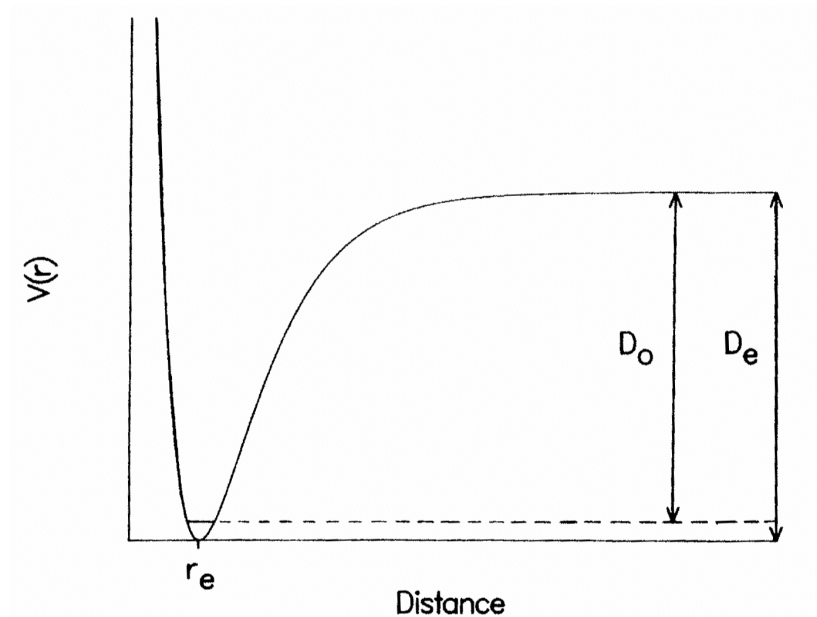
What is required for Reaction to Occur?

- In reality, only if a variety of conditions are met will reaction occur:
 - There must be enough energy available
 - The molecules must be appropriately oriented
 - Reaction must be quantum mechanically allowed
 - Mass, momentum and energy must be conserved.
- We explore these questions by examining the potential energy surface of the combined system of reactants and products.

Potential Determines Force

- Force along an interatomic coordinate

$$F_r = -\frac{dV(r)}{dr}$$



Determining the PES

- Born-Oppenheimer Approximation
 - Electrons move fast, nuclei slowly
 - Electrons are in quasi-steady state
 - Potential field depends only on position of nuclei
- Can calculate using quantum mechanics
 - If from 1st principles
 - Results not highly accurate for complex systems but can provide excellent insight
- Can use empirical expressions
- If form of surface is known or suspected, maybe can determine experimentally
 - Spectroscopy
 - Crossed molecular beam collision experiments



PES for a Series of Reactions

