

## Week 6

# Enhancing Collision Theory

### 6.1 Threshold Energy and Line-Of-Centers Model

5/2: • Picking up from the previous lecture...

– It follows by plugging in the energy substitutions from last time that

$$u_r f(u_r) du_r = \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} E_r e^{-E_r/k_B T} dE_r$$

– Thus,

$$\begin{aligned} k &= \int_0^\infty du_r f(u_r) k(u_r) \\ &= \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} \int_0^\infty dE_r E_r e^{-E_r/k_B T} \sigma_r(E_r) \end{aligned}$$

– Now assume that only those collisions for which the relative kinetic energy exceeds a threshold energy  $E_0$  result in a collision. Thus, define

$$\sigma_r(E_r) = \begin{cases} 0 & E_r < E_0 \\ \pi d_{AB}^2 & E_r \geq E_0 \end{cases}$$

– Consequently,

$$\begin{aligned} k &= \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} \int_{E_0}^\infty dE_r E_r e^{-E_r/k_B T} \pi d_{AB}^2 \\ &= \left(\frac{8k_B T}{\mu\pi}\right)^{1/2} \pi d_{AB}^2 e^{-E_0/k_B T} \left(1 + \frac{E_0}{k_B T}\right) \\ &= \langle u_r \rangle \sigma_{AB} e^{-E_0/k_B T} \left(1 + \frac{E_0}{k_B T}\right) \end{aligned}$$

– We can use

$$E_a = k_B T^2 \frac{d \ln k}{dT}$$

to relate the above to the activation energy.

- Another simplification we've made is that the reaction cross section is not constant, but actually depends on relative speed.

- Accounting for the collision geometry between the two hard spheres gives rise to the **line-of-centers model**.
- Line-of-centers model:** A model for  $\sigma_r(E_r)$  in which the cross section depends on the component of the relative kinetic energy that lies along the line that joins the centers of the colliding molecules.

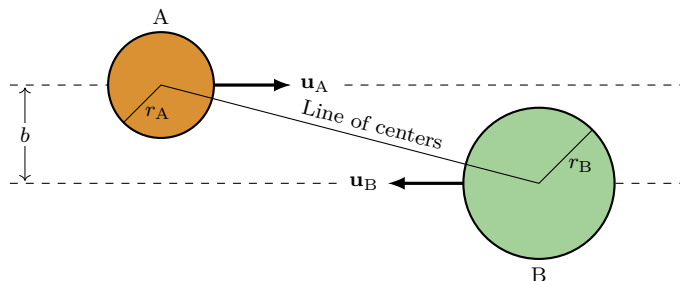


Figure 6.1: Line-of-centers model.

- If we denote the relative kinetic energy along the line of centers by  $E_{loc}$ , then we are assuming that a reaction occurs when  $E_{loc} > 0$ .
- The main thrust of this model is that we are redefining  $E_r$  instead of  $\sigma_r(E_r)$  overall.
- The line-of-centers model asserts that two molecules will collide only if the **impact parameter** is less than the sum of the radii of the colliding molecules.
  - In particular, we (re)define

$$\sigma_r(E_r) = \begin{cases} 0 & E_r < E_0 \\ \pi d_{AB}^2 \left(1 - \frac{E_0}{E_r}\right) & E_r \geq E_0 \end{cases}$$

- It follows from math similar to the above that

$$\begin{aligned} k &= \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\mu \pi}\right)^{1/2} \int_0^\infty dE_r E_r e^{-E_r/k_B T} \sigma_r(E_r) \\ &= \left(\frac{8k_B T}{\mu \pi}\right)^{1/2} \pi d_{AB}^2 e^{-E_0/k_B T} \\ &= \langle u_r \rangle \sigma_{AB} e^{-E_0/k_B T} \end{aligned}$$

- Impact parameter:** The perpendicular distance between the two dashed lines in Figure 6.1. Denoted by  $b$ .
- The cross section exhibits a threshold energy.
  - The dependence of the reaction cross section on the relative kinetic energy of the collision is consistent with the line-of-centers model.
- Relating  $E_0$  to the Arrhenius equation parameters.
  - For the activation energy  $E_a$ , we have

$$\begin{aligned} E_a &= k_B T^2 \frac{d \ln k}{dT} \\ &= k_B T^2 \frac{d}{dT} \left\{ \ln \left[ \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \pi d_{AB}^2 \right] - \frac{E_0}{k_B T} \right\} \end{aligned}$$

$$\begin{aligned}
 &= k_B T^2 \frac{d}{dT} \left\{ \ln T^{1/2} - \frac{E_0}{k_B T} + \text{terms not involving } T \right\} \\
 &= E_0 + \frac{1}{2} k_B T
 \end{aligned}$$

■ Tian wants us to memorize the last line above.

– Considering the line-of-centers collision model and the Arrhenius equation yields

$$A = \langle u_r \rangle \sigma_{AB} e^{1/2}$$

- Tian goes through a practice problem.

## 6.2 Isotropy, Internal Energy, and Center of Mass Assumptions

- 5/4: • Doing away with the assumption that the spheres are isotropic.

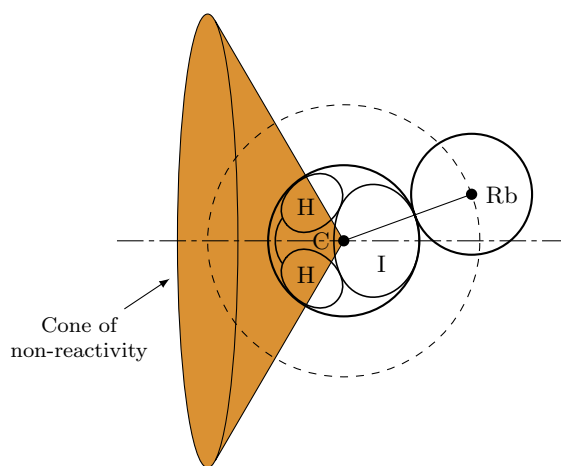
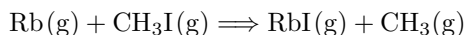


Figure 6.2: Molecules are not isotropic.

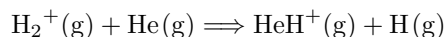
– Consider the reaction



- The rubidium atom must collide with the iodomethane in the vicinity of the iodine atom for a reaction to occur.
- Indeed, many molecules have a **cone of non-reactivity**.

- Additionally, the internal energy of the reactants can affect the cross section of a reaction.

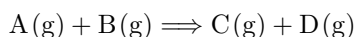
– Consider the reaction



- As the reactant molecule  $\text{H}_2^+$  passes through different vibrational states, its reaction cross section changes.
- We only need to understand that other types of energy can have an effect qualitatively; we do not need to work with the shape of the curves quantitatively.

- A reactive collision can be described in a center-of-mass coordinate system.

– Consider the collision and subsequent scattering process for the bimolecular reaction



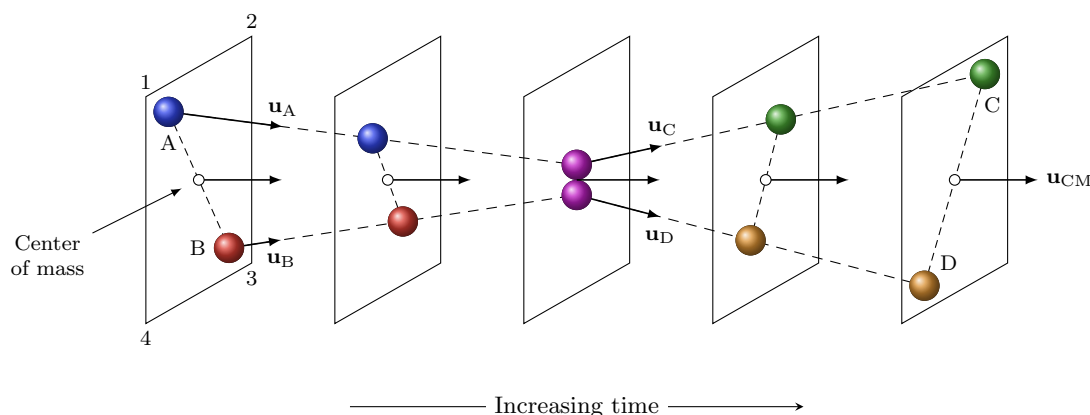


Figure 6.3: Center-of-mass coordinate system.

- Before the collision, A and B are traveling with velocities  $\mathbf{u}_A$  and  $\mathbf{u}_B$ , respectively.
- The collision generates molecules C and D, which then move away from each other with velocities  $\mathbf{u}_C$  and  $\mathbf{u}_D$ , respectively.
- $\mathbf{R}$ , the location of the center of mass, is given by

$$\mathbf{R} = \frac{m_A \mathbf{r}_A + m_B \mathbf{r}_B}{M} \quad M = m_A + m_B$$

- The velocity  $\mathbf{u}_{cm}$  of the center of mass is the time derivative of the position vector. Therefore, it is given by

$$\mathbf{u}_{cm} = \frac{m_A \mathbf{u}_A + m_B \mathbf{u}_B}{M}$$

- We assume that this is an elastic collision (thus, energy is conserved).
- The total kinetic energy is given by

$$KE_{\text{react}} = \frac{1}{2} m_A u_A^2 + \frac{1}{2} m_B u_B^2$$

- Combining the fact that the relative speed of the two molecules<sup>[1]</sup> is given by  $\mathbf{u}_r = \mathbf{u}_A - \mathbf{u}_B$  with the definition of  $\mathbf{u}_{cm}$  yields

$$\mathbf{u}_A = \mathbf{u}_{cm} + \frac{m_B}{M} \mathbf{u}_r \quad \mathbf{u}_B = \mathbf{u}_{cm} - \frac{m_A}{M} \mathbf{u}_r$$

- Note that the change in plus to minus sign between the two above forms hails from our definition of relative speed as A minus B and not the other way around (as we could also very well define it). In other words, it's just a convention thing, and all that matters is that we're consistent.

- It follows that

$$\begin{aligned} KE_{\text{react}} &= \frac{m_A}{2} \left( \mathbf{u}_{cm} + \frac{m_B}{M} \mathbf{u}_r \right)^2 + \frac{m_B}{2} \left( \mathbf{u}_{cm} - \frac{m_A}{M} \mathbf{u}_r \right)^2 \\ &= \frac{1}{2} M u_{cm}^2 + \frac{1}{2} \mu u_r^2 \end{aligned}$$

- Thus, the kinetic energy is composed of two contributions: one due to the motion of the center of mass, and one due to the relative motion of the two colliding molecules.

<sup>1</sup>In particular, the speed of molecule A relative to molecule B, as it is defined.

- We can do a similar analysis for the products to determine that

$$\text{KE}_{\text{prod}} = \frac{1}{2}Mu_{\text{cm}}^2 + \frac{1}{2}\mu'u_r'^2$$

- Note that momentum is conserved, i.e.,

$$m_A\mathbf{u}_A + m_B\mathbf{u}_B = m_C\mathbf{u}_C + m_D\mathbf{u}_D$$

- This implies that  $\mathbf{u}_{\text{cm}}$  does not change from reactants to products.
- The energy associated with the motion of the center of mass is therefore constant, and we will ignore its constant contribution to the total kinetic energy.

$$E_{\text{react,int}} + \frac{1}{2}\mu u_r^2 = E_{\text{prod,int}} + \frac{1}{2}\mu' u_r'^2$$

- $E_{\text{react,int}}$  and  $E_{\text{prod,int}}$  are the total internal energies of the reactants and products, respectively.
- This internal energy takes into account all the degrees of freedom other than translation.

## 6.3 Experimental Techniques and the Simplest Reaction

- 5/6: • Reactive collisions can be studied using crossed molecular beam machines.

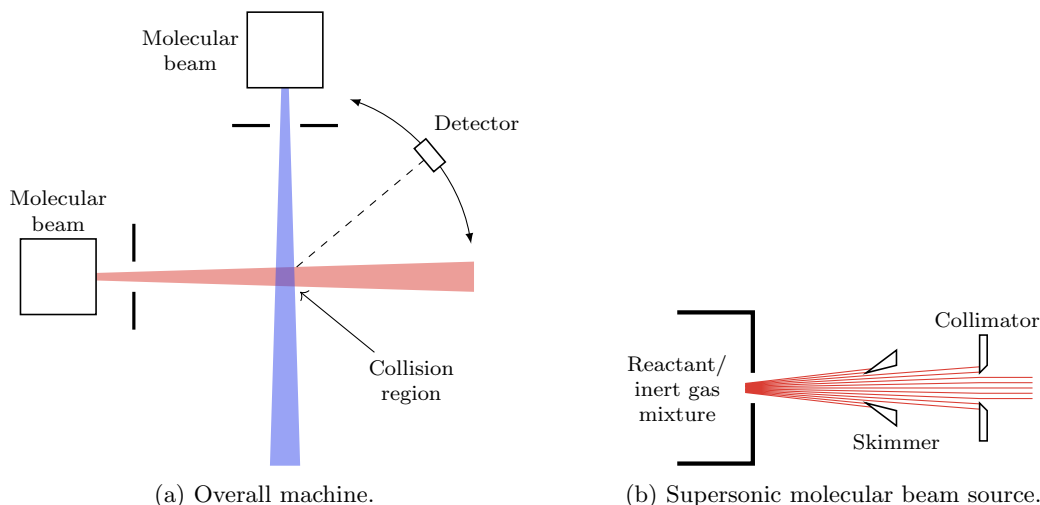


Figure 6.4: Crossed molecular beam machines.

- Figure 6.4a depicts the overall setup in a crossed molecular beam machine. Each reactant is introduced into the vacuum chamber by a molecular beam source. The two molecular beams collide at the collision region.
- Figure 6.4b depicts a supersonic molecular beam source. The reactant is expanded along with an inert gas through a small orifice into the vacuum chamber. A skimmer is used so that a collimated beam of molecules is directed toward the collision region.
- The product molecules are detected using a mass spectrometer.
- A supersonic molecular beam has several important advantages that make it ideal for crossed-beam studies.
  - The supersonic expansion generates a collection of molecules with a high translational energy but a very small spread in molecular speeds.

- In addition, molecules can be prepared with low rotational and vibrational energies.
- If we measure the number of molecules of a particular reaction product that arrive at the detector as a function of time after the collision, we can resolve the velocity distribution of the product molecules.
- If we measure the total number of product molecules as a function of scattering angle, we can determine the angular distribution of the product molecules.

- The reaction

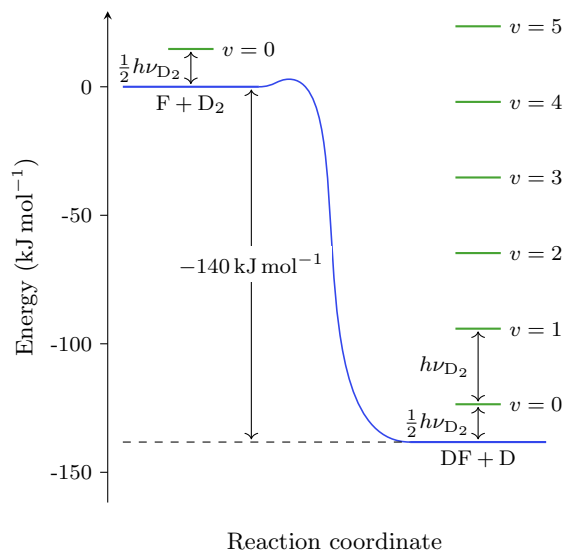
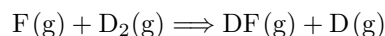


Figure 6.5: Energy diagram for the  $\text{F} + \text{D}_2$  reaction.

- Figure 6.5 depicts the energy of the lowest vibrational state of  $\text{D}_2$  and the energies of the first six vibrational states of  $\text{DF}$ .

■ In drawing these energy states, we have tacitly assumed that the vibrational motion of both  $\text{D}_2$  and  $\text{DF}$  is harmonic.

- The difference between the ground electronic state energies of  $\text{D}_2$  and  $\text{DF}$  is

$$D_e(\text{D}_2) - D_e(\text{DF}) = -140 \text{ kJ mol}^{-1}$$

- The reaction has an activation energy barrier of about  $7 \text{ kJ mol}^{-1}$ .
- Moreover, we have that

$$E_{\text{tot}} = E_{\text{trans}} + E_{\text{int}} = E'_{\text{trans}} + E'_{\text{int}}$$

where  $E_{\text{int}}$  is the internal energy of the reactants,  $E_{\text{trans}}$  is the relative translational energy of the reactants,  $E'_{\text{int}}$  is the internal energy of the products, and  $E'_{\text{trans}}$  is the relative translational energy of the products.

■ Additionally, note that

$$E_{\text{int}} = E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} \qquad E'_{\text{int}} = E'_{\text{rot}} + E'_{\text{vib}} + E'_{\text{elec}}$$

i.e., that  $E_{\text{int}}, E'_{\text{int}}$  are the sum of the rotational, vibrational, and electronic energies of the reactants and products, respectively.

■ Lastly, note that  $E_{\text{elec}} = -D_e(\text{D}_2)$  and  $E'_{\text{elec}} = -D_e(\text{DF})$ .