Classical Trajectory Calculations

\[ H + H-F \rightarrow H-H + F \]

Assignment:
Read Shattuck Chapter 32 sections 2 and 3 (or Atkins, Chapter 27 sections 7 and 8 or McQuarrie and Simon, Chapter 30 sections 7 and 10), before coming to lab on Monday.

Introduction

How do chemical reactions occur? Consider a gas phase reaction. Reactions occur during collisions. For example, in the \( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \) reaction, the chlorine atom must strike the hydrogen molecule. During the collision, the H-H bond is broken and the H-Cl bond is formed. Not every collision leads to a reaction, however. The collisional energy must exceed the activation energy for the reaction. The orientation of the reactants must be correct. Even the timing of the collision must be right for the bond breaking and making steps to occur. The study of these effects is called reaction dynamics. In this lab, you will study the affects of energy and timing on the outcome of chemical reactions. We will find that the conditions for a successful collision, that is a collision that leads to products, are rarely achieved.

What determines if a collision will be successful? We must follow the total energy of the reactants as they form the transition state to determine if a reaction will occur. Before the reactants collide, the molecules will have translational, rotational, and vibrational energy. During the collision, the energies of the reactants are combined into the translational, rotational, and vibrational energy of the transition state. If the available energy in the transition state is partitioned (funneled) into the proper vibrations, bond breaking and making will occur, and the collision will produce products. If the combined energy of the reactants is insufficient or if the energy flows into the wrong internal degrees of freedom, the transition state will fall apart to produce reactants, again.

To make things easier for this lab, we will assume that the molecules don't rotate and that the molecules collide with the best orientation for a successful encounter. The important degrees of freedom will then be just translation and vibration. The reaction is a simple reaction, that between a hydrogen atom and a hydrogen fluoride molecule. During a successful reaction, the molecule and atom exchange partners.

\[ H + H–F \rightarrow H–H + F \]

The collision takes place along the bond axis of the molecule. This orientation is called a collinear collision. Other collision orientations are possible, but they have higher activation energy. The collinear collision therefore is the most important. The coordinate system for the reaction includes the atom-atom distances, \( R_{AB} \) and \( R_{BC} \):

\[
\begin{align*}
\text{H}_A & \quad \text{H}_B–\text{F}_C \\
\mid & \quad \mid \\
R_{AB} & \quad R_{BC}
\end{align*}
\]

The transition state occurs when \( R_{AB} \) is approximately equal to \( R_{BC} \):

\[
\begin{align*}
\text{H}_A & \quad – \quad \text{H}_B — \text{F}_C \\
\mid & \quad \mid \\
R_{AB} & \quad R_{BC}
\end{align*}
\]
Before the reaction, the HF molecule has some vibrational energy, usually zero-point energy, \( \frac{1}{2} h \nu_0 \). Assume the center of mass of HF molecule is stationary. The translational energy in the collision is then determined by the initial kinetic energy of the reactant H atom. The total energy of the reactants must exceed the activation energy for a successful reaction to occur. However, is even more energy better? In other words, does the probability of reaction increase with initial kinetic energy of the H atom? Does the reaction probability increase if the reactant molecule is in an excited vibrational state? Some reactions occur more favorably with the initial energy in translation and some are more favorable if the initial energy is in vibration. The preference for either translational or vibrational energy is called the **energy demand** of the reaction. This exercise is designed to explore these questions.

The reactant molecule is constantly vibrating because of the zero-point energy in vibration. The timing of the collision with respect to the vibrational motion has an effect on the outcome of chemical reaction. For example, if the H atom approaches while the BC molecule is at its minimum internuclear distance the reaction is less likely to occur. If the H atom approaches while the BC molecule is near its maximum internuclear distance, the leaving atom is already moving in the right direction for bond breaking and the reaction is more likely to occur. The effect of collision timing is illustrated in Figure 1.

Theory:

The kinetic energy of a collision is determined by the motion of the two particles relative to each other. For example for the collision of an A atom with a BC molecule, Figure 2, the relative kinetic energy is given by:

\[
E_{\text{rel}} = \frac{1}{2} \mu v_{\text{rel}}^2
\]

where \( E_{\text{rel}} \) is the relative kinetic energy of the collision, \( \mu \) is the reduced mass of the collision partners, and \( v_{\text{rel}} \) is the magnitude of the relative collision velocity, in m s\(^{-1}\). For the collision A + BC the reduced mass is given by:
\[ \mu = \frac{m_A m_{BC}}{m_A + m_{BC}} \frac{1 \text{ kg}}{1000 \text{ g}} \frac{1 \text{ mol}}{N_A} \]

where \( m_A \) is the mass of the A atom and \( m_{BC} \) is the mass of the diatomic molecule, each in grams. \( N_A \) is Avogadro’s number.

\[ \mu = \frac{m_A m_{BC}}{m_A + m_{BC}} \frac{1 \text{ kg}}{1000 \text{ g}} \frac{1 \text{ mol}}{N_A} \]

Figure 2. Relative collision energy is determined by the motion relative to the center of mass. The collision takes place at the center of mass of the A + BC system, which is marked as “… cm”.

Assume that the center of mass of the BC molecule starts at rest. At the beginning of the collision, when the A atom is far from the BC molecule, the relative velocity is given by the initial velocity of the A atom. In the absence of initial vibrational energy in the BC diatomic molecule, the relative kinetic energy, as calculated from Eq. 1, must exceed the barrier height for the reaction. The activation energy for the reaction takes into account the barrier height and the vibrational energy of the reactants and products. One question that we will explore in this exercise is if the \( E_{\text{rel}} \) necessary for a successful collision is decreased if the diatomic molecule is initially in an excited vibrational state. The spectroscopic constants for the reactions that will be studied in this exercise and the corresponding barrier heights and required relative velocities are listed in Table 1. For the H + HF reaction the barrier height for the reaction is 142. kJ mol\(^{-1}\) or 1.471 eV. This barrier corresponds to an initial relative velocity of \( 1.73 \times 10^4 \) m s\(^{-1}\).

Table 1. Molecular Constants for Collisions

<table>
<thead>
<tr>
<th>Property</th>
<th>( \text{H}_2 )</th>
<th>( \text{HF} )</th>
<th>( \text{HBr} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_e (\text{Å}) )</td>
<td>0.742</td>
<td>0.917</td>
<td>1.414</td>
</tr>
<tr>
<td>( D_e (\text{eV}) )</td>
<td>4.749</td>
<td>6.126</td>
<td>3.922</td>
</tr>
<tr>
<td>( \tilde{v}_e (\text{cm}^{-1}) )</td>
<td>4395.2</td>
<td>4138.32</td>
<td>2648.97</td>
</tr>
<tr>
<td>( \frac{1}{2} \hbar \tilde{v}_e (\text{eV}) )</td>
<td>0.265</td>
<td>0.268</td>
<td>0.164</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Barrier height (eV)</th>
<th>Speed needed to surmount (m s(^{-1}))</th>
<th>Position of barrier</th>
<th>( \Delta H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H + HF</td>
<td>1.471</td>
<td>17267</td>
<td>late</td>
<td>endo</td>
</tr>
<tr>
<td>H + HBr</td>
<td>0.484</td>
<td>9726</td>
<td>early</td>
<td>exo</td>
</tr>
</tbody>
</table>

Molecules in the gas phase move with high velocity at room temperature. If the average relative velocity of the collision partners at room temperature exceeds the activation energy, then the
reaction rate at room temperature will be significant. The average relative velocity at temperature T for the colliding partners A + BC can be calculated using kinetic molecular theory:

\[ v_{\text{rel}} = \sqrt{\frac{8 kT}{\pi \mu}} \]

where \( \mu \) is once again the collision reduced mass as given by Eq. 2, and \( k \) is the Boltzmann constant. This relative velocity is the root-mean-square average velocity for the collisions. You may remember from General Chemistry that the root-mean-square average velocity of a molecule is given by \( \sqrt{3kT/m} \). The difference in Eq. 3 is that the velocity is the relative velocity with respect to the center of mass of the collision partners, Figure 2.

The vibrational state of the colliding diatomic molecule is an important consideration in the successes of the collision. Consider H\(_2\) as an example, for the reaction F + H\(_2\). The zero point vibrational energy, \( \frac{1}{2} h\nu_c \), for H\(_2\) is 25.9 kJ/mol or 0.265 eV. The \( \nu = 1 \) level would then be at \( \frac{3}{2} h\nu_c \), which is 77.7 kJ/mol or 0.805 eV. We will vary both the initial velocity and vibrational energy for our simulations. The vibration energy changes in steps of \( h\nu_c \).

The timing of the collision is important; we want the collision to occur at various stages in the vibration. At the beginning of the calculation the B-C bond length is set to the vibrational maximum. To vary the timing of the reaction, the initial distance from the A atom to the BC molecule is varied. A base distance is selected at 4 Å. Then small incremental distances are added to the base value that correspond to fractions of the period of the oscillation of the BC molecules. The distance that the A atom travels during one period of the BC oscillation is \( v_{\text{rel}}/\nu_c \). Using H + HF as an example, the fundamental vibration frequency of HF is:

\[ \nu_c = c \sqrt{\frac{\nu_c}{\nu_e}} = 2.998 \times 10^{10} \text{ cm s}^{-1} (4138.32 \text{ cm}^{-1}) = 1.241 \times 10^{14} \text{ s}^{-1} \]

Assume that the A-atom is traveling at 17300 m \text{s}^{-1}. The distance that atom A travels in one period of the oscillation is then:

\[ R_{360^\circ} = \frac{v_{\text{rel}}}{\nu_c} = \frac{17300 \text{ m s}^{-1}}{1.241 \times 10^{14} \text{ s}^{-1}} = 1.394 \times 10^{-10} \text{ m} = 1.394 \text{ Å} \]

The program displays this information as the vibrational “phase.” For example, the initial distances for the first few phases are:

<table>
<thead>
<tr>
<th>Phase (°)</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>( R_{o,\text{AB}} = 4.0 ) Å</td>
</tr>
<tr>
<td>45°</td>
<td>( R_{o,\text{AB}} = 4.0 + 45^\circ/360^\circ \times (1.394 \text{ Å}) = 4.174 ) Å</td>
</tr>
<tr>
<td>90°</td>
<td>( R_{o,\text{AB}} = 4.0 + 90^\circ/360^\circ \times (1.394 \text{ Å}) = 4.349 ) Å</td>
</tr>
<tr>
<td>135°</td>
<td>( R_{o,\text{AB}} = 4.0 + 135^\circ/360^\circ \times (1.394 \text{ Å}) = 4.523 ) Å</td>
</tr>
</tbody>
</table>

The calculations for this exercise are described in Physical Chemistry Laboratory Experiments by John M. White, experiment 6.5. The program uses the Morse potential for the diatomic potential energy function.

What is the Activation Energy for a Chemical Reaction? One of the goals of these experiments is to get a better feel for the relationship between the barrier height and the activation energy for a chemical reaction. The minimum collision energy for an endothermic reaction is given by the reaction internal energy change at absolute zero. To calculate the minimum collision energy, no barrier for the reaction is assumed to exist, other than the energy necessary to move from the
products to the reactants. The reaction profile for a reaction with the barrier height equal to the thermodynamic internal energy change, at absolute zero K, is shown in Figure 3a. This scenario is the “easiest possible path” along the course of the reaction. The minimum collision energy for this surface assuming $\nu = 0$ for both reactants and products is given by:

$$\text{MCE} = (\text{barrier height}) - (\text{zero point vibrational energy for the reactant BC}) + (\text{zero point vibrational energy for the product AB})$$

Figure 3. (a) The smallest amount of energy to progress from reactants to products is given by the internal energy change at absolute zero. (b). Most reactions have an additional energy requirement that adds to the barrier height and activation energy.

Most reactions have an additional energy requirement that adds to the activation energy, Figure 3b. As a good initial assumption, the minimum collision energy can be approximated assuming the zero point vibrational energy of the transition state is approximately the same as the products. Eq. 6 then gives the approximate minimum collision energy for a reactive trajectory. The minimum collision energy is a good comparison with the total collision energies, $E_{\text{tot}} = E_{\text{rel}} + E_{\text{vib}}$, of reactive trajectories.

The activation energy is the average of the energies of the reactive trajectories, weighted by the Boltzmann probability of the initial vibrational and rotational states. The activation energy includes the vibrational energy difference of the reactant and the transition state. However, the zero point vibrational energy of the transition state is difficult to calculate. The activation energy is most likely greater than the minimum collision energy, and is usually not equal to the barrier height. The question is: how is the activation energy related to the minimum collision energy? This exercise shows that the relationship is not as straightforward as you might suspect.

**Procedure and Questions:**

1. The molecular reaction dynamics applets are on the course home page in the Kinetics section.

2. Choose the H + HF applet. We next need to run a reactive and non-reactive collision so that you can verify the results. (a.) Start with a collision with relative translational energy at 4.0 eV. Set the vibration quantum number to $\nu = 0$. Try all possible phases, $0^\circ$-$315^\circ$, for the collision. No such collisions are successful. (b.) Change the vibrational quantum number to 2 (see Table 1). Try all phases. Each collision in parts (a) and (b) has sufficient total energy to exceed the barrier, by a large margin. What do your results tell you about the probability of a successful collision?
At this point you have only tried two sets of conditions. However, based on these two collision conditions, are collisions with sufficient energy likely to be reactive?

3. Run trajectories with a relative translational energy of 1.584 eV and vibration state $\nu = 0$. Try a few trajectories with the relative translational energy set to 1.583 eV. The smallest collision energy for reactive collisions with $\nu = 0$ is about 1.584 eV. (a). Does the relative translational energy, $E_{\text{rel}}$, exceed the barrier height (Table 1)? (b). Calculate the total collision energy, $E_{\text{tot}} = E_{\text{rel}} + E_{\text{vib}}$, for these collisions. The vibrational energy, $E_{\text{vib}} = \hbar \nu (\nu + \frac{1}{2})$, is listed in the numerical results section. (c). Calculate the minimum collision energy for this surface using Table 1 and Eq. 6. (d). Compare the energies for parts (a), (b), and (c). What does this comparison tell you about the activation energy for the reaction with $\nu = 0$, as compared to the barrier height?

4. Run trajectories with a relative translational energy of 0.864 eV and vibrational state $\nu = 1$. The smallest collision energy for reactive collisions is about 0.864 eV with $\nu = 1$. (a). Must the relative translational energy exceed the barrier height or minimum collision energy for reactive collisions to occur? Is the translational energy demand lessened with excess vibrational energy? (b). Calculate the total energy for these collisions. (c). Compare the total energy for these collisions with the total energy in question 3 and the minimum collision energy. You can use the table at the end of this write-up to help collect your thoughts. Do collisions with $\nu = 1$ require more or less translational energy than the collisions with $\nu = 0$? Does this collision have more or less vibrational energy? Does this surface prefer the initial energy to be in translation or vibration? (d). Does this reaction have an early or late barrier?

5. Run trajectories with a relative translational energy of 0.378 eV and vibrational state $\nu = 3$. Try a few trajectories with the relative translational energy set to 0.377 eV. The smallest collision energy for reactive collisions with $\nu = 3$ is about 0.378 eV. (a). Calculate the total energy for these collisions. (b). Compare the initial vibrational energy to the minimum collision energy that you calculated in 3c. Consider a trajectory with small translational energy, just sufficient to cause the approach of the reactants. Are collisions with predominantly vibrational energy sufficient for reactive collisions? (c). Did the minimum $E_{\text{rel}}$ decrease compared to Question 3? To within 10%, did the minimum $E_{\text{rel}}$ decrease by the amount of added vibrational energy as compared to question 3? Does the activation energy change with initial vibration state? How do you know?

6. Many theories of reaction rates assume that once the activated complex crosses the transition state barrier that products always form. If the activated complex crosses the transition state barrier more than once, then we say that there are multiple crossings. Multiple crossings sometimes lead the activated complex to return to reactants, therefore such theories overestimate the rate of the reaction. Do multiple crossings occur in any of your trajectories in parts 2-5?

7. Now switch to the H + HBr surface. This surface is said to have an early barrier, that is when the $R_{\text{HH}} > R_{\text{HBr}}$. What is the energy demand for an early barrier? (a) Even though quantum mechanically impossible, we can run trajectories with no initial vibrational energy. Run a trajectory with no initial vibrational energy by choosing $\nu = -\frac{1}{2}$. Set the relative translational energy at 0.485 eV, to just exceed the barrier. (b). Run trajectories with zero-point vibrational energy, $\nu = 0$, and relative translational energy at 0.388 eV. Calculate the total collision energy.
(c). Compare with the result from parts a and b. Is there sufficient energy to exceed the barrier height for the $\nu = 0$ trajectory with the relative translational energy less than 0.388 eV? (d). Run a third set of trajectories using a relative translational energy of 0.283 eV and $\nu = 1$. Does this reaction like to have its energy in vibration or translation?

**Summary Tables, Steps 3-7**

\[ H + HF \rightarrow H_2 + F \]

<table>
<thead>
<tr>
<th>Vibration quantum number, $\nu$</th>
<th>initial translation $E_{rel}$ (eV)</th>
<th>initial vibration $E_{vib}$ (eV)</th>
<th>$E_{tot}$ for collision (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (step 3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 (step 4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 (step 5)</td>
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<td></td>
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</tr>
</tbody>
</table>

\[ H + HBr \rightarrow H_2 + Br \]

<table>
<thead>
<tr>
<th>Vibration quantum number, $\nu$</th>
<th>initial translation $E_{rel}$ (eV)</th>
<th>initial vibration $E_{vib}$ (eV)</th>
<th>$E_{tot}$ for collision (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-(\frac{1}{2}) (step 7a)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (step 7b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 (step 7d)</td>
<td></td>
<td></td>
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</tbody>
</table>

Minimum collision energy (Eq. 6) ____________