Classical Trajectory Calculations

$H + H\text{-}F \rightarrow H\text{-}H + F$

Assignment:

Read 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 $Cl + H_2 \rightarrow HCl + H$ 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.

$$H + H\text{–}F \rightarrow H\text{–}H + F$$

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 a 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}:

$$H_A + H_B\text{–}F_C \rightarrow H_A\text{–}H_B + F_C$$

| | | |
|
R_{AB} R_{BC}

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

H_A — H_B — F_C

| | |

R_{AB} R_{BC}

Before the reaction, the HF molecule will have some vibrational energy, usually its zero-point energy, ½ $h\nu_o$. 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 molecule is at its minimum internuclear distance the reaction is less likely to occur. If the H atom approaches while the 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.

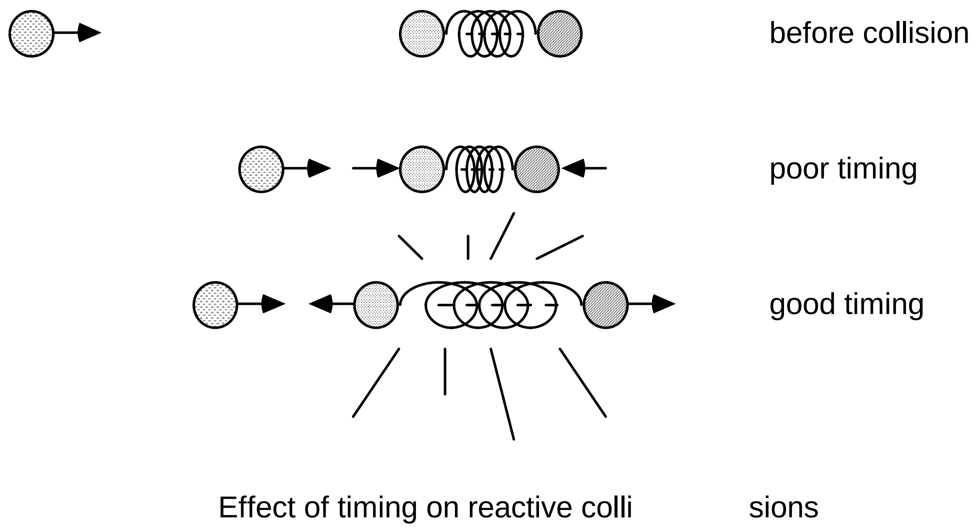

Figure 1. The effect of reaction timing on reactive collisions.

Theory:

The kinetic energy of a collision is determined by the motion of the two particles <u>relative</u> 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:

$$E_{rel} = \frac{1}{2} \mu v_{rel}^2 \qquad 1$$

where E_{rel} is the relative kinetic energy of the collision, μ is the reduced mass of the collision partners, and v_{rel} is the magnitude of the relative collision velocity, in m s^{-1}. For the collision A + BC the reduced mass is given by:

$$\mu = \frac{m_A\, m_{BC}}{m_A + m_{BC}} \frac{1\ \text{kg}}{1000\ \text{g}} \frac{1\ \text{mol}}{N_A} \qquad 2$$

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.

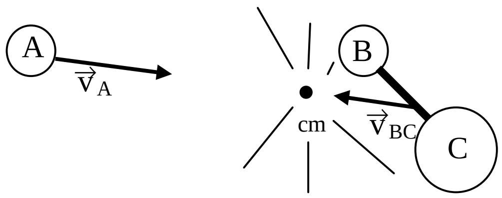

Figure 2. Relative collision energy is determined by the motion relative to the center of mass. The collision takes place at the center of mass of the A + BC system, which is marked as "• cm".

Assume that the center of mass 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 just 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 reacting partners. One question that we will explore in this exercise is if the E_{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 135. kJ mol^{-1} or 1.4 eV. This barrier corresponds to an initial relative velocity of 1.68×10^4 m s^{-1}.

Table 1. Molecular Constants for Collisions

Property	*H_2*	*HF*	*HCl*	*HBr*
r_e (Å)	0.7	0.9	1.2	1.3
D_e (eV)	4.7	6.1	4.6	3.9
$\frac{1}{2} h\nu_e$ (eV)	0.265	0.262	0.185	0.164

Reaction	*Barrier height (eV)*	*Speed needed to surmount (m s^{-1})*	*Position of barrier*	*ΔH*
H + HF	1.4	16842	late	endo
H + HCl	0.21	6340	middle	exo
H + HBr	0.05	3095	early	exo

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:

$$v_{rel} = \sqrt{\frac{8\,kT}{\pi\mu}} \qquad 3$$

where μ 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. <u>Calculate the relative velocity at room temperature for the H + HF collision before coming to lab.</u>

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, ½ $h\nu_e$, for H_2 is 25.9 kJ/mol or 0.265 eV. The $\upsilon = 1$ level would then be at $^3/_2$ $h\nu_e$, 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 $h\nu_e$.

The timing of the collision is important; we want the collision to occur at various stages in the vibration. To vary the timing of the collision we adjust the initial bond length in the molecule, R_{BC}. Again using H_2 as an example, we start with the equilibrium bond length, 0.741Å, and vary this distance in steps up to the amplitude of the vibration, ±A. Remember that for a classical harmonic oscillator with force constant k:

$$E = \tfrac{1}{2}\, k A^2 \qquad 4$$

and that quantum mechanically for the lowest vibrational state:

$$E = \tfrac{1}{2}\, h\nu_e \qquad 5$$

Here ν_o is the fundamental vibration frequency:

$$\nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad 6$$

where k is the force constant for the bond and μ is the reduced mass of the molecule. Solving Equations 4, 5, and 6 for A gives:

$$A = \sqrt{\frac{\hbar}{2\pi\nu_e\mu}} \qquad 7$$

For H_2, $\nu_e = 1.32\text{x}10^{14}\text{s}^{-1}$ and for H_2:

$$\mu = \frac{m_B\, m_C}{m_B + m_C} = \frac{1*1}{1+1}\; N_A^{-1}\; \frac{1\text{kg}}{1000\text{g}} = 8.30\text{x}10^{-28}\text{ kg.}$$

Substituting ν_e and μ into Equation 7 gives A= 0.124 Å. The program displays this information as the vibrational "phase". A phase of "1" corresponds to the minimum bond length, R_{BC} = 0.741 – 0.124 Å. A phase of "3" corresponds to R_{BC} = 0.741 Å and "5" to R_{BC} = 0.741 + 0.124 Å.

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.

Procedure and Questions:

1. Start the Molecular Reaction Dynamics program. Work through the Introduction.

2. Choose the H + HF section. We next need to run a reactive and non-reactive collision so that you can verify the results. Remember to press Enter after you type in any answer. (a.) Start with a collision with Relative translational energy, which is the collision energy, at 4 eV. Set the vibrational state to 0, that is quantum number υ = 0. Try all possible phases, 1-8, for the collision. No such collisions are successful. (b.) Change the vibrational state to 2 (see Table 2). Try all phases. Each collision in parts (a) and (b) has sufficient total energy to exceed the barrier. What do your results tell you about the probability of a successful collision? Are collisions with sufficient energy likely to be reactive?

Table 2: Some reactive combinations.

Reaction	*Collision energy (eV)*	*Vibrational state*	*Vibrational phase*
H + HF	4	2	5
	2	4	5
H + HCl	0.1	0	1
	0.2	0	2
H + HBr	0.1	0	1
	0.15	0	3

3. Run trajectories with a Relative translational energy of 1.2 eV and vibrational state υ = 2. The smallest collision energy for reactive collisions with υ = 2 is about 1.2 eV. (a). Does the collision energy need to exceed the barrier height? (b). Can the energy demand be met by a combination of translational and vibrational energy? (c). Calculate the total energy, translational and vibrational, for these collisions. (d). Calculate the minimum collision energy for this surface assuming υ = 0 for both reactants and products, which is given by the (barrier height) – (zero point vibrational energy for the reactant HF) + (zero point vibrational energy for the product H_2). (e). Compare your answers for parts (c) and (d). What does this comparison tell you about the activation energy for the reaction as compared to the barrier height?

4. Run trajectories with a Relative translational energy of 2.61 eV and vibrational state υ = 1. The smallest collision energy for reactive collisions is about 2.61 eV with υ = 1. (a). Calculate the total energy for these collisions. (b). Compare the total energy for these collisions with the total energy in question 3. Does this collision require more or less translational energy? Does this

collision have more or less vibrational energy? Does this surface prefer the initial energy to be in translation or vibration? (c). Is this an early or late barrier?

5. Run trajectories with a Relative translational energy of 0.88 eV and vibrational state $\upsilon = 3$. The smallest collision energy for reactive collisions with $\upsilon = 3$ is about 0.88 eV. (a). Calculate the total energy for these collisions. (b). Compare the initial vibrational energy to the minimum energy that you calculated in 3d. Is vibrational energy alone sufficient for reactive collisions? (c). Did the minimum collision energy decrease by the amount of added vibrational energy as compared to question 3? Does the activation energy change with initial vibrational 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 several times, then we say that there are multiple crossings. Multiple crossings sometimes lead the activated complex to return to reactants, therefore such theories would overestimate the rate of the reaction. Do multiple crossings occur in any of your trajectories in questions 5?

7. Now switch to the H + HBr surface. This surface is said to have an early barrier, that is when the $R_{HH} > R_{HF}$. (a) Run trajectories with zero-point vibrational energy: $\upsilon = 0$ and Relative translational energy at the smallest allowed value, 0.02 eV. (b). Calculate the total collision energy. (c). Calculate the minimum collision energy for this surface assuming $\upsilon = 0$ for both reactants and products. Compare with the result from part b. Is there sufficient energy to exceed the minimum for this trajectory? (d). Run a second set of trajectories using conditions from Table 2. Does this reaction like to have its energy in vibration or translation?