

REACTIONS AS COLLISIONS

PRÉCIS

In Chapter 7, we started to study collision theory and described how one can use the theory to estimate reaction rates. All of the analysis in Chapter 7 was for a hard-sphere collision. The objective of this chapter is to extend the ideas to more realistic collisions. In particular, we will show how one can use trajectory calculations to calculate rates, outline the forces involved, and provide qualitative information about reactive collisions. The material will draw heavily on simulations. A suitable simulation program is available from <http://www.wiley.com/chemcalkinetics>.

0.1 HISTORICAL INTRODUCTION

The idea that reactions were associated with collisions of molecules dates back to the start of kinetics. The objective of this section will be to provide an historic overview of the ideas so that we have a basis for further discussion.

Recall that in 1884 Van't Hoff had proposed that reactions would obey what is now called *Arrhenius law*:

$$k_1 = k_0 e^{-(E_a/k_B T)} \quad (8.1)$$

where k_1 is the rate constant for a reaction, k_0 is the preexponential for the reaction, E_a is the activation energy for the reaction, k_B is Boltzmann's constant, and T is the temperature. As noted in Chapter 2, this rate form was not initially accepted. However, equation (8.1) eventually was adopted by most investigators.

In Chapter 7, we noted that Arrhenius wrote a series of papers in which he tried to understand why reactions obey equation (8.1). Arrhenius (1889) considered an ideal

reaction:



Arrhenius proposed that if one looked at a chemical system containing A and B, there were two kinds of A molecules in the system: **reactive** A molecules (i.e., A molecules that had the right properties to react), and **unreactive** A molecules (i.e., A molecules that did not have the right properties to react). Arrhenius then assumed that equilibrium was maintained between the reactive and unreactive A molecules to obtain

$$k_1 = (K_0 e^{(\Delta S^\ddagger)/k_B}) e^{-(\Delta H^\ddagger)/k_B T} \quad (8.3)$$

Equation (8.3) is equivalent to equation (8.1) with

$$k_0 = K_0 e^{(\Delta S^\ddagger)/k_B} \quad (8.4)$$

8.2 COLLISION THEORY

In 1899, Arrhenius did not have a model to estimate either K_0 , ΔS^\ddagger or ΔH^\ddagger . However, a few years after Arrhenius' work appeared, Trautz (1916, 1918) and Lewis (1916, 1918) independently proposed what is now called the *collision theory of reactions* in an attempt to get a value for K_0 . We already discussed the findings in Chapter 7. The objective of this section is to review the key equations.

Recall that the objective of collision theory is to use a knowledge of molecular collisions to predict K_0 from equation (8.4). Trautz and Lewis proposed a model to do just that. The model builds on Arrhenius' concept that only hot molecules can react. The model assumes that the rate of reaction is equal to the rate of collisions of the molecules. Consequently, if one can calculate the collision rate, one will then get an expression for K_0 . In the remainder of this section we will present an expression for K_0 following the derivation of Trautz and Lewis.

Trautz and Lewis considered ligand exchange reactions of the form



where a radical A abstracts an atom B from a molecule BC to yield products. Trautz and Lewis noted that the reaction occurs when a hot A molecule collides with a hot BC molecule. Under most circumstances, collisions should be rare events. Consequently, Trautz and Lewis assumed that the rate of reaction was equal to the rate of collisions of hot A molecules with hot BC molecules. Trautz and Lewis then used statistical mechanics to estimate a value for the collision rate, and thereby derived a value for K_0 .

The derivation is given in Chapter 7. The result is

$$r_{A \rightarrow BC} = Z_{A \rightarrow BC} e^{-(\Delta G^\ddagger)/k_B T} \quad (8.6)$$

where $Z_{A \rightarrow BC}$ is the rate of A—BC collisions. Equation (7.22) gives the total rate of collisions between hot A molecules and hot BC molecules.

$$Z_{A \rightarrow BC} = \bar{v}_{A \rightarrow BC} C_A C_{BC} \sigma_{A \rightarrow BC} \quad (8.7)$$

where $\bar{v}_{A \rightarrow BC}$ is the average velocity of A toward BC, C_A and C_{BC} are the concentrations of A and BC, $\sigma_{A \rightarrow BC}$ is the collision cross section, ΔG^\ddagger is the free energy of activation, k_B is Boltzmann's constant, and T is the temperature. Combining equations (8.6) and (8.7) yields

$$r_{A \rightarrow BC} = (\bar{v}_{A \rightarrow BC} \sigma_{A \rightarrow BC}^2 e^{\Delta S^\ddagger/k_B}) (e^{-\Delta H^\ddagger/k_B T}) C_A C_{BC} \quad (8.8)$$

where $\bar{v}_{A \rightarrow BC}$ is the average velocity of A moving toward BC.

Equation (8.8) is a second-order rate law, with an activation barrier of ΔH^\ddagger and a preexponential, k_0 , given by

$$k_0 = \bar{v}_{A \rightarrow BC} \sigma_{A \rightarrow BC}^2 e^{\Delta S^\ddagger/k_B} \quad (8.9)$$

Neither Trautz nor Lewis had a way to calculate ΔS^\ddagger . Consequently, they set ΔS^\ddagger to zero in equation (8.9) to obtain

$$k_0 = \bar{v}_{A \rightarrow BC} \sigma_{A \rightarrow BC}^2 \quad (8.10)$$

Trautz and Lewis also asserted that the molecular velocity in equation (8.10) should be calculated, ignoring that we are considering hot molecules. According to the results in Chapter 6, the average velocity of A moving toward BC is given by

$$\bar{v} = \left(\frac{8k_B T}{\pi \mu_{ABC}} \right)^{1/2} \quad (8.11)$$

where

$$\frac{1}{\mu_{ABC}} = \frac{1}{m_A} + \frac{1}{m_B + m_C} \quad (8.12)$$

and m_A , m_B , and m_C are the masses of A, B, and C, respectively. A derivation of equation (8.11) is given in Section 8.16.4.

Equation (8.10) is the key result for simple collision theory. One should memorize the equation before proceeding.

8.2.1 Predictions of Collision Theory

Next, it is useful to review the predictions of collision theory. We have already discussed the key predictions in Section 7.2. According to collision theory

- Preexponentials for reactions are all about 10^{13} or 10^{14} units of angstroms, molecules, and seconds.
- The preexponentials scale as the molecular diameter. Larger molecules are more reactive than smaller ones.
- It does not matter how the molecules collide, they will always find the right configuration to react.

The first two predictions have excellent agreement with experiment. Preexponentials are usually within a factor of 10 of those predicted by collision theory. Larger molecules are

generally more reactive. The third prediction does not work as well. Molecules often do not find the right configuration to react. All these ideas are discussed in Section 7.2. Any reader who has not read the discussion of collision theory in Section 7.2 should do so before continuing with this chapter.

There are a few examples where the preexponentials differ substantially from those predicted by collision theory. The reaction



has a preexponential of $1.4 \times 10^{10} \text{ \AA}^3/(\text{molecule}\cdot\text{second})$. That is over two orders of magnitude lower than one would expect from [collision theory from equation (8.10)]. In contrast, the reaction



has a preexponential of $5.8 \times 10^{15} \text{ \AA}^3/(\text{molecule}\cdot\text{second})$. That is about two orders of magnitude larger than one would expect from equation (8.10). These are special cases. In most cases, collision theory predicts reasonable preexponential factors. Still, there are a number of examples where Trautz and Lewis' version of collision theory cannot explain the data.

The Trautz–Lewis model failed because it treated the collision between the reactants as a billiard ball collision. Every molecule of A that collided with BC was assumed to react with a fixed probability. In reality, the reaction probability varies with how the collision occurs. For example, consider a simple reaction:



During reaction (8.15), the oxygen reacts with the hydrogen on the middle carbon of pentane. If the incoming oxygen hits the hydrogen on the middle carbon, the reaction can occur. However, if the oxygen hits anywhere else, a $\cdot\text{CH}_2\text{CH}_2\text{CH}_3$ will form. The Trautz–Lewis model ignores the fact that you need special collision geometry to allow the reaction to happen. As a result, their model tends to overestimate rates of reaction in reactions similar to (8.15).

This example shows that in some cases, one needs molecules to collide in the correct way for the desired reaction to occur. The Trautz–Lewis model ignores the need for a special collision geometry to get a desired reaction, so it does not always give a good prediction of the rate.

8.3 AN IMPROVED COLLISION THEORY

In the last section, we noted that the main weakness of the Trautz–Lewis version of collision theory is that it ignores the fact that one needs a special geometry in order for reaction to occur. In the remainder of this chapter, we will discuss some of the work that has been done to improve collision theory. The general approach will be to find a way to determine which collisions actually lead to reaction, and then find a way to use that information to predict a rate. Qualitatively, we will determine which of the collisions lead to reaction by doing a calculation to see how the reactants change during the collision, and using the calculation to determine whether reaction occurs.

In this section we will describe the qualitative effects and the key equations. The quantitative details will be discussed in Sections 8.4 and 8.5.

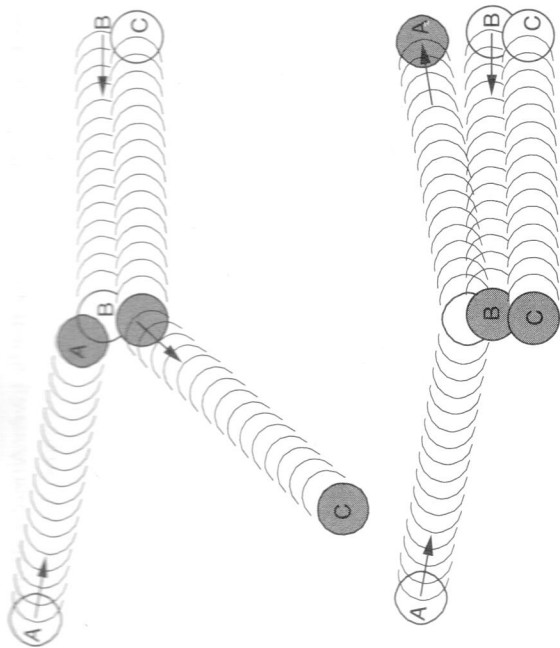


Figure 8.1 A typical collision between A and BC.

First, it is interesting to consider what a collision is like. Figure 8.1 shows two different collisions between A and BC. In the top case, A flew toward BC, A stuck, and C flew away. In this case, reaction happened. In the bottom case, A flew toward BC. A collided with BC but A left again. No reaction occurred.

Now imagine doing a thought experiment where one could watch thousands of molecules and see when collisions happen. If one could watch the collisions, one could calculate a reaction rate. In practice, one cannot watch the collisions of real molecules, but one can simulate the collisions in a computer.

In the next three sections, we will derive equations for the key collision process. First, we will derive an expression for the rate of reaction as a function of the probability that two molecules react when the molecules collide at a given angle and velocity. We will then show how to calculate the reaction probability by watching the dynamics of the particles. We will also need to discuss intermolecular forces. Some of the material is heavy going. We need to introduce several concepts over a short time. However, the reader should work through the materials in order to understand what is said later in the chapter, and in the chapters that follow.

8.3.1 The Reaction Probability

First, it is useful to use statistical mechanics to derive an expression for the rate as a function of the reaction probability. Recall that in statistical mechanics, one uses a statistical ensemble to calculate an average value of a function. Well, a rate is a function, so if one averages the rate over a statistical ensemble of all possible collisions, one can calculate an average rate of reaction. In this section, we will derive an equation for all the key quantities. The result looks formidable. However, in reality, the result is easier than it initially appears.

Let's define P_{reaction} as the probability that a given A molecule reacts with a given BC molecule if the two molecules collide. One can show that the reaction probability varies with

- $v_{A \rightarrow BC}$, the velocity that the A molecule approaches the BC molecule
- E_{BC} , the internal state (i.e., vibrational-rotational energy) of the BC molecule before collision occurs
- The *impact parameter* $b_{A \rightarrow BC}$, which is a measure of how closely A collides with BC
- The *angle of approach*, where ϕ is a measure of the angle of the collision
- The initial position R_{BC} and velocity v_{BC} of B relative to C when collision occurs

Figure 8.2 page 420 shows how $b_{A \rightarrow BC}$ and ϕ are defined. The figure assumes that when atom A collides with the BC molecule, the A atom follows the trajectory shown in Figure 8.2. The impact parameter is defined as the distance between the point that atom A would intersect the plane going through the center of the BC bond and the center of mass of BC if the atom A would fly in a straight line and not be attracted or repelled by BC. The angle of approach is defined as the angle where the A impinges relative to the angle of the B-C bond.

Next we want to briefly discuss why the reaction probability varies with $v_{A \rightarrow BC}$, E_{BC} , $b_{A \rightarrow BC}$, ϕ , R_{BC} , and v_{BC} . The velocity term is obvious. The faster the reactants are moving, the quicker they go over the activation barrier. The E_{BC} term is less obvious. Physically, though, if you put a lot of energy into the BC bond, the BC will stretch, and a bond that is stretching is easy to break. Consequently, the reaction probability generally rises as E_{BC} increases. The impact parameter is a third term. Physically, the reactants need to hit each other to react. Consequently, when $b_{A \rightarrow BC}$ is large, the reaction probability is negligible. While the reaction probability is significant when $b_{A \rightarrow BC}$ is small. The ϕ term is harder to understand. Consider a reaction such as



Notice that the reaction probability will be higher if the incoming deuterium hits the hydrogen than when the deuterium hits the carbon. The ϕ dependence accounts for that.

If you have stationary BC molecules, the first four are all the variables you need. However, if the reactants have internal motion, you need to consider that as well. For example, the CH could be rotating during reaction (8.16). The rotary motion could bring the hydrogen around to cause the hydrogen to collide with the deuterium. That will enhance the rate.

Generally, there are many variables that affect a reaction probability. One should memorize the list on the previous page before proceeding.

8.3.2 An Equation for the Rate as a Function of the Reaction Probability

In statistical mechanics, one calculates everything as an ensemble average. For example, let's assume that we have an expression for the reaction rate as a function of $v_{A \rightarrow BC}$, E_{BC} , ϕ , $b_{A \rightarrow BC}$, R_{BC} , v_{BC} :

$$r_{A \rightarrow BC}(v_{A \rightarrow BC}, E_{BC}, \phi, b_{A \rightarrow BC}, R_{BC}, v_{BC}) \quad (8.17)$$

According to the results in Section 6.4.1, the overall rate, $r_{A \rightarrow BC}$, is calculated by averaging equation (8.17) over $v_{A \rightarrow BC}$, E_{BC} , ϕ , $b_{A \rightarrow BC}$, R_{BC} , v_{BC} . In Chapter 6, we found that the correction expression is

$$r_{A \rightarrow BC} = \sum_{\text{states}} r_{A \rightarrow BC}(v_{A \rightarrow BC}, E_{BC}, \phi, b_{A \rightarrow BC}, R_{BC}, v_{BC}) P_n \quad (8.18)$$

where P_n is the probability that a given state n is occupied.

For the work that follows, it is convenient to replace the probability in equation (8.18) by a distribution function, $D(v_{A \rightarrow BC}, E_{BC}, \phi, b_{A \rightarrow BC}, R_{BC}, v_{BC})$.

I hope that you remember the velocity distribution function $D(v_A)$ from physical chemistry. The velocity distribution function is the probability that the velocity is between v_A and $v_A + \delta(v_A)$. In the same way, $D(v_A \rightarrow BC, E_{BC}, \phi, b_{A \rightarrow BC}, R_{BC}, v_{BC})$ is the probability that $v_{A \rightarrow BC}$ is between $v_{A \rightarrow BC}$ and $v_{A \rightarrow BC} + \delta(v_{A \rightarrow BC})$, E_{BC} is between E_{BC} and $E_{BC} + \delta(E_{BC})$, and so on.

You use $D(v_{A \rightarrow BC}, E_{BC}, \phi, b_{A \rightarrow BC}, R_{BC}, v_{BC})$ in the same way that you use $D(v_A)$. So for example, recall from physical chemistry that if you wanted to calculate the velocity average of some function $F(v_A)$, you would calculate

$$\bar{F} = \int F(v_A) D(v_A) dv_A \quad (8.19)$$

where F is the average value of F . In the same way the average rate becomes

$$r_{A \rightarrow BC} = \iiint \iiint r_{A \rightarrow BC}(v_{A \rightarrow BC}, E_{BC}, \phi, b_{A \rightarrow BC}, R_{BC}, v_{BC}) \times D(v_{A \rightarrow BC}, E_{BC}, \phi, b_{A \rightarrow BC}, R_{BC}, v_{BC}) dv_{A \rightarrow BC} dE_{BC} d\phi db_{A \rightarrow BC} dR_{BC} dv_{BC} \quad (8.20)$$

Equation (8.20) looks pretty formidable, but it is merely saying that one needs to average the rate over six variables. One should memorize this equation before proceeding.

8.3.3 Derivation of an Expression for $r_{A \rightarrow BC}(v_{A \rightarrow BC}, E_{BC}, \phi, b_{A \rightarrow BC}, R_{BC}, v_{BC})$

NEXT, we want to derive an expression for $r_{A \rightarrow BC}(v_{A \rightarrow BC}, E_{BC}, \phi, b_{A \rightarrow BC}, R_{BC}, v_{BC})$. In Section 7.2 we found that for a hard-sphere collision, the reaction rate is given by

$$r_{A \rightarrow BC} = \left(\frac{\text{collision rate}}{Z_{ABC}} \right) \left(\frac{\text{probability of reaction}}{\text{during a collision}} \right) \quad (8.21)$$

where the collision rate is the same as given by equation (8.7). Combining equations (8.7) and (8.21) shows

$$r_{A \rightarrow BC} = C_A C_{BC} \bar{v}_{A \rightarrow BC} C_A C_{BC} \sigma_{A \rightarrow BC} P_{\text{reaction}} \quad (8.22)$$

Equation (8.22) applies only if you have a hard-sphere collision. If you do not have a hard-sphere collision, then the reaction probability is going to vary with the distance between the reactants prior to collision $b_{A \rightarrow BC}$, the angle ϕ , and all the rest of the variables discussed in Section 8.3.2.

Equation (8.22) is not correct for this situation. However, one can derive a correct equation by considering the differential slice of area shown in Figure 8.2, calculating a

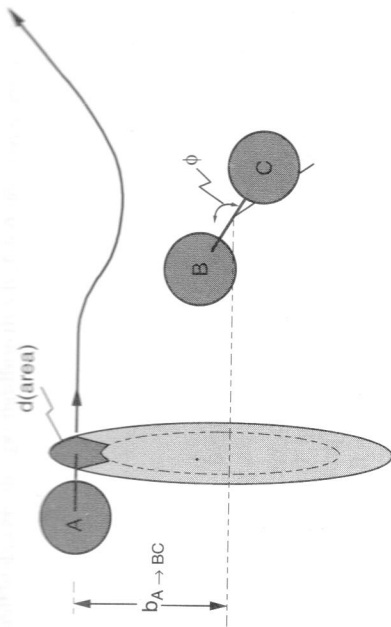


Figure 8.2 A typical trajectory for the collision of an A atom with a BC molecule as calculated by the methods in Section 8.3.2.

differential rate, and then integrating the differential rate $dr_{A \rightarrow BC}$ is given by

$$dr_{A \rightarrow BC} = C_A C_{BC} V_{A \rightarrow BC} P_{\text{reaction}} d(\text{area}) \quad (8.23)$$

where $d(\text{area})$ is the differential area, $(b_{A \rightarrow BC} db_{A \rightarrow BC} d\phi)$.

In reality, the A molecules have a distribution of velocities. Consequently, one has to average over the distribution of velocities. One also has to average over the distribution of internal energies of the B-C molecule since the reaction probability changes if the B-C molecules starts out hot. Combining equations (8.21)–(8.23) and integrating over all the variables yields

$$r_{A \rightarrow BC} = C_A C_{BC} \iiint \iiint P_{\text{reaction}}(v_{A \rightarrow BC}, E_{BC}, b_{A \rightarrow BC}, \phi, \mathbb{R}_{BC}, v_{BC}) v_{A \rightarrow BC} \\ \times D(v_{A \rightarrow BC}, E_{BC}, \mathbb{R}_{BC}, v_{BC}) dv_{A \rightarrow BC} dE_{BC} db_{A \rightarrow BC} d\phi d\mathbb{R}_{BC} dv_{BC} \quad (8.24)$$

In equation (8.24) $D(v_{A \rightarrow BC}, E_{BC}, \mathbb{R}_{BC}, v_{BC})$ is the probability that a given pair of molecules will have a velocity, $v_{A \rightarrow BC}$; an internal energy, E_{BC} ; an internal coordinate, \mathbb{R}_{BC} ; and an internal velocity, v_{BC} ; $b_{A \rightarrow BC}$ is the impact parameter; $P_{\text{reaction}}(v_{A \rightarrow BC}, E_{BC}, b_{A \rightarrow BC}, \mathbb{R}_{BC}, v_{BC})$ is the probability that the molecules will react when collision occurs, and $(b_{A \rightarrow BC} db_{A \rightarrow BC} d\phi)$ is the differential area. Note that the integral in equation (8.24) goes over only positive values of the velocity, since a collision occurs if A moves toward BC, but no collision occurs when A moves away from BC.

Again, we have chosen a sign convention so that if $v_{A \rightarrow BC}$ is a positive when atom A is moving toward BC, while if $v_{A \rightarrow BC}$ is negative, atom A is moving away from BC. We consider only positive velocities in equation (8.24), because if the velocity is negative, the A atom never collides with the BC molecule.

One also needs an expression for k_2 the rate constant for reaction (8.5). The result is

$$k_2 = \iiint \iiint \iiint P_{\text{reaction}}(v_{A \rightarrow BC}, E_{BC}, b_{A \rightarrow BC}, \phi, \mathbb{R}_{BC}, v_{BC}) v_{A \rightarrow BC} \\ \times D(v_{A \rightarrow BC}, E_{BC}, \mathbb{R}_{BC}, v_{BC}) dv_{A \rightarrow BC} dE_{BC} db_{A \rightarrow BC} d\phi d\mathbb{R}_{BC} dv_{BC} \quad (8.25)$$

It is also useful to define the cross section, σ_{BC} by

$$\sigma_{BC}(v_{A \rightarrow BC}, E_{BC}) = \iiint \iiint \iiint P_{\text{reaction}}(v_{A \rightarrow BC}, E_{BC}, b_{A \rightarrow BC}, \phi, \mathbb{R}_{BC}, v_{BC}) \\ \times D_1(\mathbb{R}_{BC}, v_{BC}) b_{A \rightarrow BC} db_{A \rightarrow BC} d\phi d\mathbb{R}_{BC} dv_{BC} \quad (8.26)$$

where $D_1(\mathbb{R}_{BC}, v_{BC})$ is the distribution function for \mathbb{R}_{BC} and v_{BC} . Physically, the cross section is proportional to the rate constant for a set of molecules whose energy and velocity are fixed.

Equations (8.25) and (8.26) are the statistical mechanics expression for the reaction rate. Equation (8.25) looks very complicated, but actually it is not. The equation simply says that you need to average the reaction rate over the velocity distribution of A, the internal energy of BC, the impact parameter, and the angle of approach. Readers should convince themselves that Equation (8.25) computes a reaction rate as an average reaction probability before proceeding.

8.4 MOLECULAR DYNAMICS AS A WAY TO COMPUTE REACTION PROBABILITIES

Equation (8.25) is the key result from the last section. What it says is that one can compute a rate by picking values of the initial velocity, energy, impact parameter, and angle of approach, \mathbb{R}_{BC} , v_{BC} , and then compute the reaction probability. One repeats for a different angle or energy, and computes reaction probability again. The result is a series of plots like those in Figure 8.1. One then plugs into equation (8.25) to compute a rate. An example calculation is given in Example 8.C. This is an easy calculation with a computer. We ask the reader to do the calculation in the homework set, Problems 8.23–8.30.

The objective of this section is to describe how one computes the reaction probability. The general approach is to compute thousands of trajectories as A approaches BC. One then averages to calculate a rate.

Molecular dynamics (MD) is used to compute all of the trajectories. In MD, one takes an A and BC molecule, gives the atoms their initial velocities and positions, and uses a computer to calculate how all of the atoms move in the force field created by all of the other atoms in the system. For example, during the reaction



you start A moving toward BC, as shown in Figure 8.1, and then compute what happens as the reaction proceeds. Generally, the calculations are done by solving Newton's equations of motion for all the atoms in the system.

That is not as difficult as it sounds. Consider a particle, P, that is moving in a force field. Think back to your days in freshman physics. In freshman physics, you probably solved a problem where you computed the trajectory of a cannon ball. The approach was to integrate Newton's equations of motion. If a cannon ball experiences a net force, \vec{F}_P ,

¹ In the literature people sometimes integrate over the angular momentum vector. This is equivalent to the derivation here.

then the position and acceleration of the cannon ball \vec{a}_p are given by

$$\vec{F}_p = m_p \vec{a}_p = m_p \frac{d^2 \mathbf{r}_p}{dt^2} \quad (8.28)$$

where \mathbf{r}_p is the position of the cannon ball, \vec{a}_p is the acceleration, m_p is the cannon ball's mass, and t is time. Note that the force, position, and acceleration in equation (8.28) are vectors.² to a reasonable approximation atoms and molecules usually follow equation (8.28). Consequently, one can use equation (8.28) to determine what happens when atom A collides with molecule B–C.

Equation (8.28) is a simple second-order differential equation. If one knows the initial conditions for the variables in equation (8.28) (i.e., the initial position and initial velocity), one can use the numerical algorithms to the supplementary materials in Chapter 6 to numerically integrate equation (8.28) to calculate the position of particle P as a function of time. A computer program called ReactMD is available from Dr. Masel's Website and from <http://www.wiley.com/chemicalkinetics>. The reader should download that program before proceeding.

We call the position of a particle P as a function of time, the **trajectory** of the particle P. Trajectories are very important to the work in this chapter.

Now the next question is how to use equation (8.28) to calculate what happens during a reaction. Consider a molecule A reacting with a second molecule BC. Let's assume that we know the following: $v_{A \rightarrow BC}$, the velocity with which the A molecule approaches the B–C molecule; E_{BC} , the vibrational–rotational energy of the BC molecule before collision occurs; the initial velocity and position of BC; the “impact parameter,” $b_{A \rightarrow BC}$, and the angle of approach, ϕ . Notice that if we know the forces in equation (8.28), we can calculate the trajectory of the A molecule as it approaches BC. We can also integrate equation (8.28) to obtain the change in the position of B and C. A typical result is given in Figure 8.1. Generally, either the reaction will occur or it will not. If A reacts with BC, the A atom will stay attached to B and the C atom will fly off. In contrast, if no reaction occurs, A will fly away by itself. One can use MD to calculate whether a reaction occurs at any set of initial conditions. Hence, one can get all of the data one needs to numerically integrate equation (8.25).

According to equation (8.25), the reaction rate is equal to the reaction probability (0 or 1 for these collisions) averaged over all of the initial conditions. One can compute the necessary integral by changing the value of the initial positions, and velocities and do the calculation again. If one repeats that process for a wide range of values of all of the parameters, one can plug into equation (8.25) to calculate the reaction rate.

8.4.1 Molecular Dynamics Simulation of Reactive Collisions

The hard part in the computation is the calculation of $P_{\text{reaction}}(v_{A \rightarrow BC}, E_{BC})$. In this section we will describe how one calculates $P_{\text{reaction}}(v_{A \rightarrow BC}, E_{BC})$.

Consider the interaction between three atoms A, B, and C. If A, B, and C are confined to a line, then one can replace $\mathbf{r}_A, \mathbf{r}_B,$ and \mathbf{r}_C —the position vectors for A, B, and C—by scalar quantities, $r_A, r_B,$ and r_C . The classical equations of motion for A, B, and C are

$$m_A \frac{d^2 r_A}{dt^2} = F_A \quad (8.29)$$

² We use \mathbf{r} to designate a position to distinguish \mathbf{r} from a reaction rate.

$$m_B \frac{d^2 r_B}{dt^2} = F_B \quad (8.30)$$

$$m_C \frac{d^2 r_C}{dt^2} = F_C \quad (8.31)$$

where $r_A, r_B,$ and r_C are the positions of atoms A, B and C; $m_A, m_B,$ and m_C are the masses of A, B and C; t is time; and $F_A, F_B,$ and F_C are the net forces on atoms A, B, and C.

If one knows the forces, one can numerically integrate equations (8.29)–(8.31) to calculate $P_{\text{reaction}}(v_{A \rightarrow BC}, E_{BC})$ as a function of the initial velocity and internal energy of the molecules.

8.4.2 How Do We Know the Forces?

In order to get any further on this topic, we will need to introduce considerable new material. First, we need to know all of the forces between the molecules. Then, we need to calculate how each of the molecules move. Sections 8.4.2–8.5 discuss the forces. Section 8.6 discusses how molecules move. Students generally find the materials in this section pretty difficult. However, I advise that you stay with it. It will get easier.

As noted above, in order to do any calculations, one needs to know the forces on all of the particles. For the purposes of discussion, it is useful to define a quantity called the *potential energy surface* for the system, $V_{\text{total}}(r_A, r_B, r_C)$, which is the potential energy of the system as a function of $r_A, r_B,$ and r_C , the position vectors of atoms A, B and C. Recall from freshman physics that if one knows the potential energy of a system of particles, one can calculate the forces on each particle from a very complicated looking equation:

$$\begin{aligned} \vec{F}_A &= -\nabla_A V_{\text{total}} \\ \vec{F}_B &= -\nabla_B V_{\text{total}} \\ \vec{F}_C &= -\nabla_C V_{\text{total}} \end{aligned} \quad (8.32)$$

where $\vec{F}_A, \vec{F}_B, \vec{F}_C$ are the forces on atoms A, B, and C and

$$\begin{aligned} \nabla_A &= \left(\frac{\partial}{\partial x_A}, \frac{\partial}{\partial y_A}, \frac{\partial}{\partial z_A} \right) \\ \nabla_B &= \left(\frac{\partial}{\partial x_B}, \frac{\partial}{\partial y_B}, \frac{\partial}{\partial z_B} \right) \\ \nabla_C &= \left(\frac{\partial}{\partial x_C}, \frac{\partial}{\partial y_C}, \frac{\partial}{\partial z_C} \right) \end{aligned} \quad (8.33)$$

where $X_A, Y_A,$ and Z_A are the x, y, and z coordinates of A; $X_B, Y_B,$ and Z_B are the x, y, and z coordinates of B; and $X_C, Y_C,$ and Z_C are the x, y, and z of C. In actual practice, one never has to worry about equations (8.32) and (8.33). The computer does all the work automatically.

However, the key thing to notice is that if one knows the potential energy surface, V_{total} , for a reaction, one can calculate the trajectories of all of the atoms, which in turn can be used to calculate a reaction probability and hence a reaction rate.

Next, we need to discuss what forces between molecules are like. At this point, I need to discuss a little notation. When people talk about "intermolecular forces", they rarely plot the forces between molecules. Instead, they plot the intermolecular potentials, where as you may recall from above, the potential is related to the force by equation (8.32). The force is the derivative of the potential, or the potential is the integral of the force.

In the literature, it is common to see plots of the potential energy of the system as a function of the intermolecular distance. For example, Figure 8.3 shows a potential energy diagram for the interaction of two neon atoms with one another and the interaction between two fluorine atoms with one another. Notice that in both cases, the potential starts out at zero at long intermolecular distances, reaches a minimum at some intermediate distance, then rises again at short distances. In freshman physics you learned that the force is related to the potential by

$$F_{\text{Ne}} = -\frac{\partial V}{\partial R_{\text{NeNe}}} \quad (8.34)$$

At long distances, $\partial V/\partial R_{\text{NeNe}}$ is positive. According to equation (8.34), the force is negative. So the force pushes R_{NeNe} in the negative direction. R_{NeNe} shrinks, which means that the neons are pulled together. In contrast, at short distances, the $\partial V/\partial R_{\text{NeNe}}$ is negative according to equation (8.34), so the force is positive. The forces push R_{NeNe} in the positive direction. The neons move apart.

Another way to look at this result is to say that the neon-neon potential is attractive at long distances and repulsive at short distances. Physically, what is happening is that the neons attract at long distances because of dispersion (induced dipole-induced dipole) forces. In contrast, they repel at short distances because of a repulsion between the electron clouds and between the atomic cores.

There is a minimum in the potential of intermediate interatomic distances where all the forces balance. The minimum in the potential corresponds to the interatomic distance in neon dimers in the gas phase.

The neon-neon potential looks similar to the potential for the interactions of any two nonpolar molecules. For example, the potential for interaction between two methanes or ethane and a methane looks similar to that in Figure 8.3. There are some slight differences

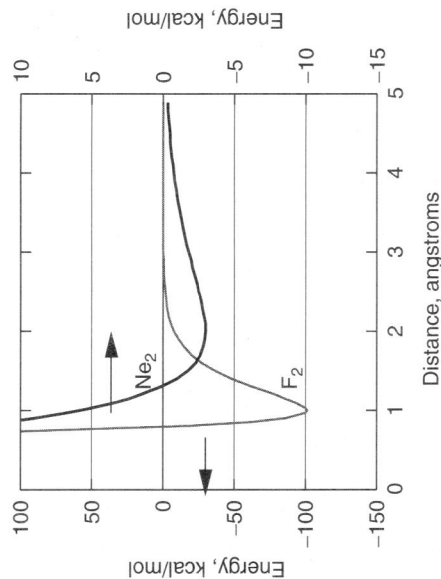


Figure 8.3 A neon-neon potential and a fluorine-fluorine potential.

with polar molecules (e.g., two waters) since the orientation of the dipole affects the new force. Still, one finds that the potential looks qualitatively like the neon-neon potential in Figure 8.3.

Figure 8.3 also shows a fluorine-fluorine potential. The fluorine-fluorine potential looks just like the neon-neon potential. The fluorines attract at long distances, so the potential goes down, but then there is repulsion at short distance as the atomic cores in the fluorine overlap. The well is deeper with two fluorines than with two neons because the fluorines can form a fluorine-fluorine bond. However, the fluorine-fluorine potential looks very similar to the neon-neon potential.

8.4.3 Intermolecular Forces

In order to proceed, we will need to understand why intermolecular potentials look the way they do. Most of you have already learned about intermolecular potentials in your physical chemistry course. Here we will review some of the key ideas to help you understand intermolecular potentials.

Four key forces come into play when atoms or molecules interact with one another:

- Dispersion forces
- Forces due to electron exchange and bonding
- Pauli repulsions
- Nuclear repulsions

8.4.3.1 Dispersion Forces Dispersion forces are weak, long-range physical interactions. Dispersion forces occur whenever there are two molecules in moderate proximity. Consider the two neon atoms shown in Figure 8.4. For the moment, we will treat the neon classically as a nucleus surrounded by electrons. Figure 8.4 shows the instantaneous position of the electrons in our idealized neon. If you start with a single isolated neon, then there will be a distribution of electrons around each neon. The nucleus and the electrons form an instantaneous dipole. The dipole is always fluctuating, and on average neon does not have any net dipole. But there is still an instantaneous dipole.

Now consider bringing the two neons together. Each neon will have an instantaneous dipole. The dipole on one of the neons can attract the dipole on the other neon, provided the two dipoles align. The dipole-dipole interaction lowers the energy of the system. That produces the lowering of the energy seen in Figure 8.3.

An important detail is that you get the lowering of the energy only when the dipoles are aligned. The electrons in the neons are each moving; in order to keep the dipoles aligned,

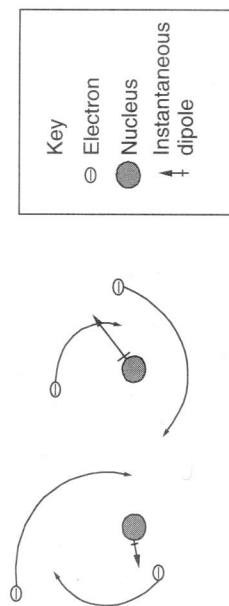


Figure 8.4 The interaction between two neon atoms.

when an electron in one of the neons moves, the electrons on the other neons need to move, too. If the electrons do not move together, the dipoles will go out of alignment. People call this simultaneous motion of the electrons on both neons *correlated motion* or *correlation*. Correlation allows the dipoles to stay aligned, so it produces the lowering of energy shown in Figure 8.3.

8.4.3.2 Pauli Repulsions The neon–neon potential is not attractive at all distances, however. Instead, the potentials are attractive at long distances, but repulsive at short distances as shown in Figure 8.3. It is useful to consider why the repulsions arise in terms of the interactions between the orbitals on each neon. One can understand why the repulsions arise with the aid of Figure 8.5. Figure 8.5 is a plot of the changes in the highest occupied molecular orbitals (HOMOs) of the pair of neons. Positive orbitals are lightly colored in the figure; negative orbitals are darkly colored.

The HOMOs on each neon start out as a p orbital on each neon. Recall that neon has the structure $1s^2 2s^2 2p^6$, so the p orbitals are the highest occupied orbitals of the system. The top part of Figure 8.5 shows what the p orbitals actually look like. In freshman chemistry you might have been told that the p orbitals look like a figure eight. However, when you actually calculate the shapes, you find that the p orbitals look more like two half-spheres with a space between.

Now consider moving the two neons together. The neons can come together with the two positive parts together or apart. Quantum-mechanically, orbitals of the same sign have a bonding attraction while orbitals of the different sign have an antibonding repulsion. The picture in the middle of Figure 8.5 shows the antibonding orbitals, while the picture on the bottom shows the bonding orbitals.

If you had just the bonding and antibonding orbitals, there would be little net repulsion. However, there is an additional effect—when you push the two neons together, the orbitals distort. I like to think of it as pushing two balloons together. The orbitals flatten at the point of intersection because the electrons in the orbitals repel as the result of a quantum effect associated with something called “electron exchange” (see Chapter 11). It

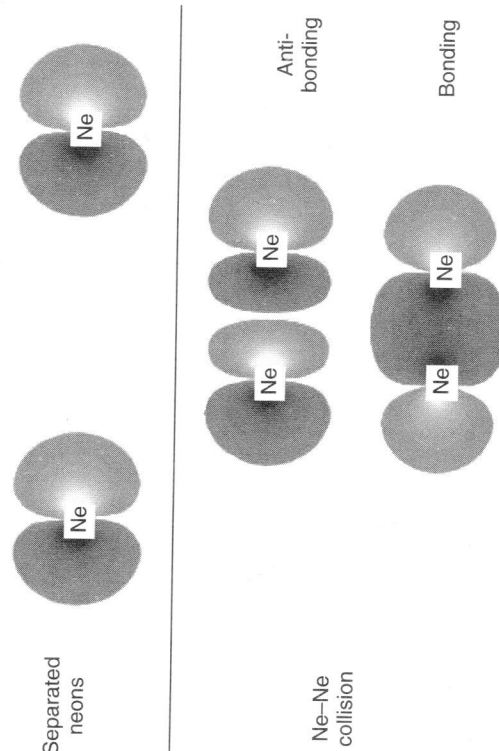


Figure 8.5 The changes in the highest occupied molecular orbital of Ne_2 as the neon atoms move together.

costs energy to distort the orbitals. As a result, when you push two neon atoms too close together, the neons repel. People call this interaction a **Pauli repulsion** because Pauli first showed how it would arise mathematically.

Think about pushing two balloons together. You get a repulsion as the balloon flattens. The same thing happens when you push two orbitals together. The orbitals distort, so they repel.

The net result is a long-range attraction and a short-range repulsion; therefore the neon–neon potential looks like the potential in Figure 8.3. The potential starts out at zero when the neon atoms are far away, reaches a minimum, and rises again. The general shape in Figure 8.3 is typical for the interaction of any molecule with any other; in other words one always sees an attraction potential at long distances and a repulsive potential at short distances.

Next, it is useful to ask how the interactions would change if we replace the two neons with two fluorines. Well, neon and fluorine are somewhat similar. Fluorine is next to neon in the periodic table, and both neon and fluorine are polarizable. However, there is a fundamental difference between the interaction of two neons and two fluorines. A neon atom has one more electron than a fluorine. The two fluorines can form a fluorine–fluorine sigma bond, and there is no antibonding interaction.

Figure 8.6 shows an orbital diagram of the other orbitals in the fluorines. For this case with fluorine, the antibonding orbital is empty, so there is no repulsion.

Of course, one can put only two electrons in a bond. If you try to put three electrons into a bond, you will get a Pauli repulsion. Consequently, there are Pauli repulsions in reactions such as



or



where e^- is an electron.

Now if one pushes the fluorines together, there is another effect, because the nonbonding orbitals in the fluorine begin to overlap. Again, that produces a Pauli repulsion, so the energy rises, and there is no exchange (bonding) interaction to lower the barrier. Detailed calculations show that the fluorine–fluorine potential looks very similar to the neon–neon potential in Figure 8.3. The only key difference is that the fluorine–fluorine potential is sharper and deeper than the neon–neon potential (see Figure 8.3).

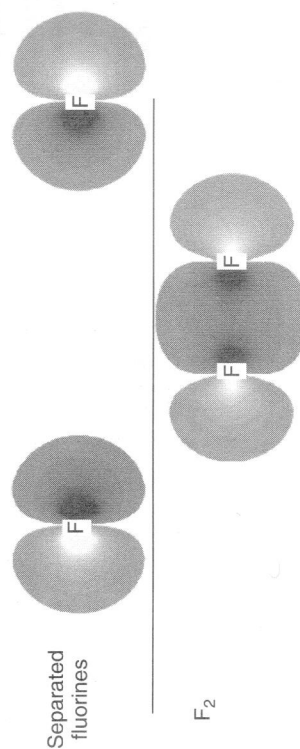


Figure 8.6 The changes in the highest occupied molecular orbital when two fluorines come together.

All atom-atom, atom-molecule, and molecule-molecule potentials look qualitatively like those in Figure 8.3. The potential is attractive at long range, and repulsive at short range, and there is a minimum in between.

8.4.4 Reactive Potentials

The discussion in Section 8.4.3 was for the interaction of two atoms, A and B. Next, we want to consider a generalized reaction:



Recall that reaction (8.37) is called an "exchange" reaction.

When an exchange reaction occurs, there are some extra forces to consider. For example, consider the reaction



Here, the chlorine-fluorine and fluorine-fluorine potentials are both completely attractive. As a result, one might imagine that when a chlorine approaches an F_2 , the chlorine would be attracted to both of the fluorines to form a stable ClF_2 complex. In fact, however, under most conditions, the chlorine atom reacts with the F_2 to form ClF and a fluorine atom.

8.5 POTENTIAL ENERGY SURFACES FOR REACTIONS

In this section, we will describe why you form ClF , and not a stable ClF_2 molecule, and we will describe the active potential. Let's consider reaction (8.38) in more detail.

Figure 8.7 shows an orbital diagram for the interaction of a chlorine atom with a F_2 . The chlorine starts out with a p orbital, while the F_2 starts out with an intact sigma bond. The sigma bond is formed from two p orbitals, so there are nonbonding lobes on either side of the two fluorines corresponding to the nonbonding portions of the p orbitals.

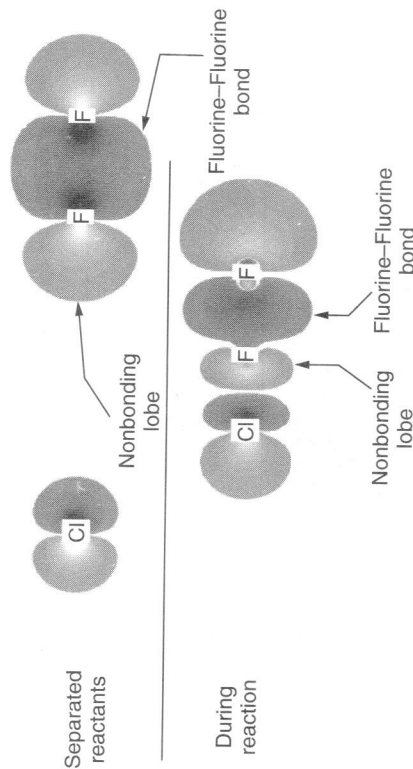


Figure 8.7 The changes in the $3A_{1g}$ orbital when a chlorine approaches a F_2 .

When the chlorine approaches the fluorine, there is a Pauli repulsion between the orbital in the chlorine and the nonbonding lobe in the fluorine. The nonbonding lobe is pushed up against the F-F bond, so the F-F bond distorts. The F-F bond pushes up against the nonbonding orbital in the other fluorine. That pushes the second fluorine away. Eventually, the forces become so strong that the fluorine-fluorine bond breaks.

Most exchange reactions (i.e., reactions of the form $A + BC \rightarrow AB + C$) show similar patterns. One orbital pushes into another. Eventually bonds break leading to products.

8.5.1 Description of Potential Energy Surfaces for Reactions

One can represent this information with a potential energy contour. Note that it is a multidimensional potential energy contour since the potential varies with the positions of the chlorine and both of the fluorines.

Next we will describe what the potential energy diagram is like. For the purposes of discussion, we will consider the reaction



and assume that the reaction occurs when the chlorine approaches the fluorine along the fluorine's bond in Figure 8.8.

There are three atoms in reaction (8.39). If one puts the origin on one of the atoms, then the other two atoms can each move in three directions. Therefore, in principle, one would need to consider a $2 \times 3 = 6$ -dimensional potential energy surface to fully model the reaction. However, in fact, the key dimensions are the ones that involve breaking R_{Cl} , the distance from the incoming chlorine atom and the ${}^{18}F$; and R_{FF} , the length of the F-F bond. For future reference, it is important to note that R_{ClF} and R_{FF} are related to R_{Cl} , R_F^{18} and R_F^{19} , the positions of each of the atoms, by

$$\begin{aligned} R_{ClF} &= |R_{Cl} - R_F^{18}| \\ R_{FF} &= |R_F^{18} - R_F^{19}| \end{aligned} \quad (8.40)$$

Figure 8.9 shows several views of an appropriate potential energy surface for reaction (8.39). The top left figure is a three-dimensional (3D) plot of the potential energy surface. The plot is a plot of the energy of the system as a function of R_{FF} and R_{ClF} . The left side of the figure corresponds to the potential at large R_{ClF} . At this side of the plot, the chlorine atom is far away from the F_2 , so the potential looks just like the F-F potential in Figure 8.3. There is a well and a barrier. Similarly, the right side of the figure corresponds to the large F-F distance. This corresponds to a stable ClF with a potential that is similar to the F-F potential. The back corner of the figure corresponds to all the atoms being

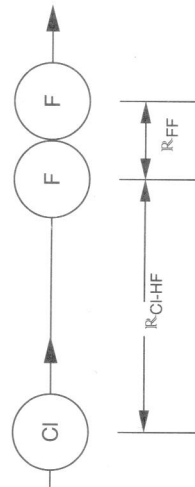


Figure 8.8 The geometry considered in the potential energy surface shown in Figure 8.9.

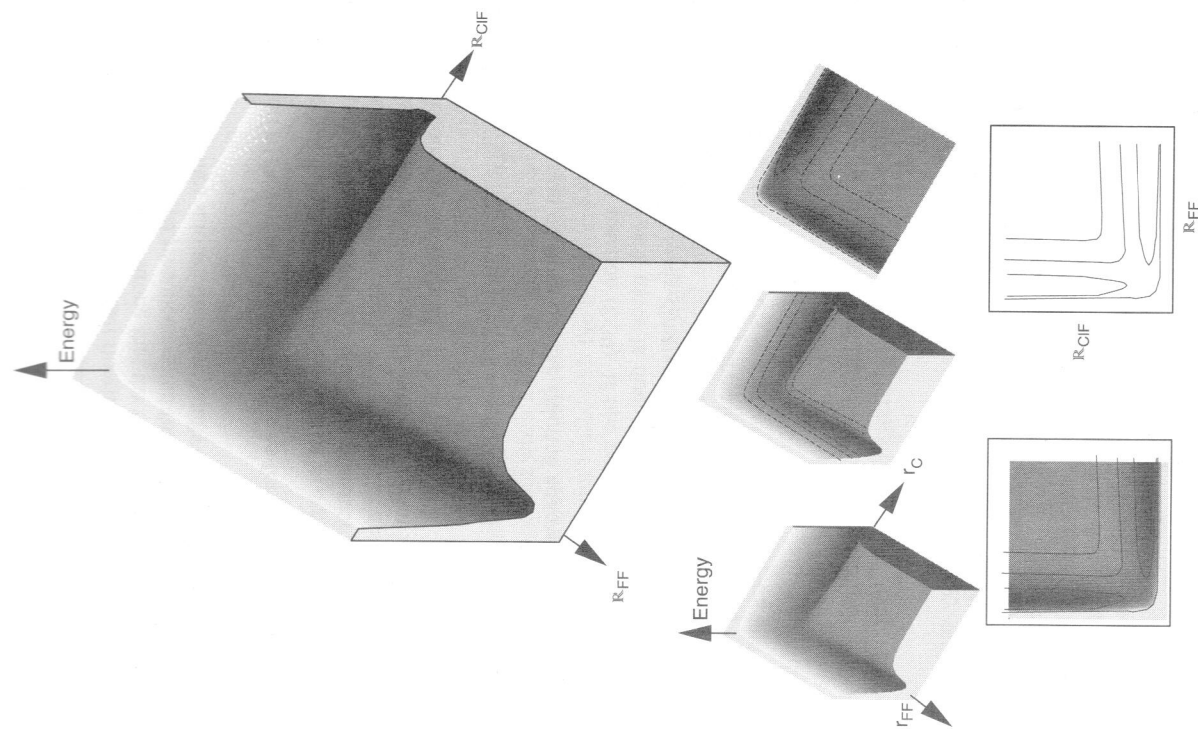


Figure 8.9 A potential energy surface for reaction (8.39).

close together. Notice that this region looks like a little hill in a miniature golf course. There is a saddle point on the top of the hill. In the literature, people call the top of the hill the **col** or the **transition state**.

Unfortunately, when you look in the literature, you find that you do not see potential plots like the one in the top left part of Figure 8.9. Instead, people plot contour plots like

those in the bottom right of Figure 8.9. The contour plot represents the same information as the 3D plot. To get from the 3D plot to the contour plot, you first need to rotate the plot by 180° , and look straight down the plot as shown in the top right of Figure 8.9. Then you add contours as shown in the bottom left. Then you eliminate the shading to the plot on the bottom right of Figure 8.9.

The plot on the bottom right provides the same information as the plot on the upper left. The plot is just harder to see. The lines in the figure are contours of constant energy. The potential is zero in the upper right corner. The potential goes down, moving along the right side of the figure, reaching a minimum at point A. The potential then goes up again, moving to the lower right corner of the figure. Initially, the potential is almost constant, moving left from the lower right corner of the figure. Once one gets halfway across the figure, the potential starts to rise again. The potential eventually reaches a maximum at the lower left corner of the figure. Similarly, the potential starts out at zero at the upper right corner of the figure. The potential goes down moving left from there, reaching a minimum at point B. Then the potential rises again. Physically, the top left portion of the figure, $R_{\text{Cl-F}}$ is large, while $R_{\text{F-F}}$ is small. Therefore, the top left portion of the figure corresponds to the initial state of the system where the chlorine atom is just beginning to approach the fluorine molecule. When chlorine is far away from the fluorine, there will be little interaction between the chlorine and the fluorine. As a result, the potential energy surface will look just like that in a fluorine molecule. The potential will be attractive at long F–F distances and repulsive at short F–F distances. The potential will not depend on $R_{\text{Cl-F}}$. In a similar way, in the bottom right portion of the figure, $R_{\text{Cl-F}}$ is small, while $R_{\text{F-F}}$ is large. Therefore, the bottom right portion of the figure corresponds to the final state of the reaction where the chlorine has reacted with the F_2 to form a stable ClF molecule and an isolated ^{19}F . In that case, there will be little interaction between the ClF molecule and the ^{19}F . As a result, the potential energy surface will look just like that in a ClF molecule. The potential will be attractive at long Cl–F distances and repulsive at short Cl–F distances. The potential will not depend on $R_{\text{F-F}}$.

Now, the lower left portion of the contour plot in Figure 8.9 is complex. The lower left portion of the curve corresponds to the case where the chlorine and the fluorine are close together. Obviously, if the chlorine and the F_2 get too close, the potential will be repulsive. However, at intermediate distances, there will be a metastable Cl–F bond and a metastable F–F bond. As a result, the potential energy of the system will be lower than in the case when the chlorine, ^{18}F , and ^{19}F are all far apart. Still, Figure 8.7 shows that there is a Pauli repulsion between the chlorine and the fluorine. The Pauli repulsion raises the energy of the system. The Pauli repulsion goes away when the ^{19}F moves away. The net effect is that the potential goes up slightly when the chlorine is close enough to the F_2 to react. The Pauli repulsion raises the energy, so it produces a barrier to the reaction.

Most potential energy surfaces for exchange reactions (i.e., reactions of the form $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$) look just like the potential energy surface in Figure 8.9. There is usually a Pauli repulsion, so there is a small barrier to the reaction. The one exception is electron transfer reactions. For example, the reaction



actually occurs via two steps. First an electron is transferred from the sodium to the F_2 :



Then the ions react:



These reactions are very different from reaction (8.39) because the electron transfer eliminates most of the Pauli repulsions. A detailed description of these reactions will be given in Section 8.14. However, for now we will consider only reactions like reaction (8.39), where there is a significant barrier to reaction.

For future reference, we will call the saddle point in the potential in Figure 8.9 the **transition state** for the reaction. Later in this chapter, we will note that an understanding of the properties of the transition states is critical to the understanding of rates of chemical reactions.

Students often have reported some difficulty seeing the saddle point in the potential energy surface, and so I thought that a numerical example would be helpful. Table 8.A.4 (in Section 8.17, page 470) shows some numerical values of a potential energy surface calculated in Example 8.A. In the table, we have defined function $V(r_1, r_2)$ for the reaction $A + BC \rightarrow AB + C$. The potential is a function of r_1 , the B–C distance, and of r_2 , the A–B distance; the potential is also a function of a , r_0 . We then used a spreadsheet to calculate numerical values at V as a function of r_1 and r_2 . Table 8.A.2 shows the formulas in the spreadsheet. Column A gives the values of r_2 , row B gives values of r_1 , and the region from B4 to Q19 shows numerical values of the potential.

Now let's focus on the numerical values in Table 8.A.4. If we start out near the reactants, the potential is low. We started the table at a point where the energy is 3 kcal/mol. When the reactants come together, r_2 is reduced. Notice that the energy goes up with decreasing r_2 .

Next, let us focus on the minimum-energy pathway from reactants to products in Table 8.1 (in Section 8.11). The shaded cells in Table 8.1 show the minimum-energy pathway going from the reactants to the products. Notice that as we move along the minimum-energy pathway from reactants to products, the energy goes up to 8.9 kcal/mol, and then back down to 3 kcal/mol.

The place where the potential is 8.9 kcal/mol is a saddle point in the potential energy surface. It is a local maximum if you approach along the shaded pathway in Table 8.A.4, but it is a local minimum if you go horizontally or vertically in the table. Thus the transition state is a saddle point in the potential energy surface.

We expand these ideas in Examples 7.G and 8.A. The reader should examine those examples before proceeding with this chapter.

8.6 REACTION AS MOTION ON POTENTIAL ENERGY SURFACES

Now that we have the preliminaries out of the way, we can talk about what reactions between molecules are like. The general scheme will be to use molecular dynamics to integrate equation (8.28) to calculate the trajectory of all of the atoms as a reaction proceeds.

In this section we will describe what the trajectories are like and how they lead to reaction. We will only consider reactions with activation barriers in this section. We will consider barrierless reactions (e.g., $\text{Na} + \text{F}_2 \rightarrow \text{NaF} + \text{F}$) in Section 8.14. For discussion purposes, we will consider a general reaction



During reaction (8.44), radical A approaches molecule BC. The A can react to extract atom B from BC or bounce without reacting. There are two key coordinates in the system: R_{AB} , the distance from A to B, and R_{BC} , the distance from B to C.

First, it is useful to note that there are three ways to visualize the reaction:

- As a trajectory in space where all the atoms move
- As a trajectory on the potential energy surface in Figure 8.9 where the bond lengths evolve
- As a plot of the motion of the atoms versus time

It is hard to explain what the motion of atoms is like without doing a simulation. A program called ReactMD is available from Dr. Masef's Website and <http://www.wiley.com/chemkinetics>, which simulates several cases with pictures and animations of the trajectories.

Figure 8.10 shows what the real trajectory is like. In this case, we plotted the positions of the atoms as a function of time. Generally, what happens is that an A atom comes up to the BC. The A atom stops because of the Pauli repulsion. If the A atom happens to

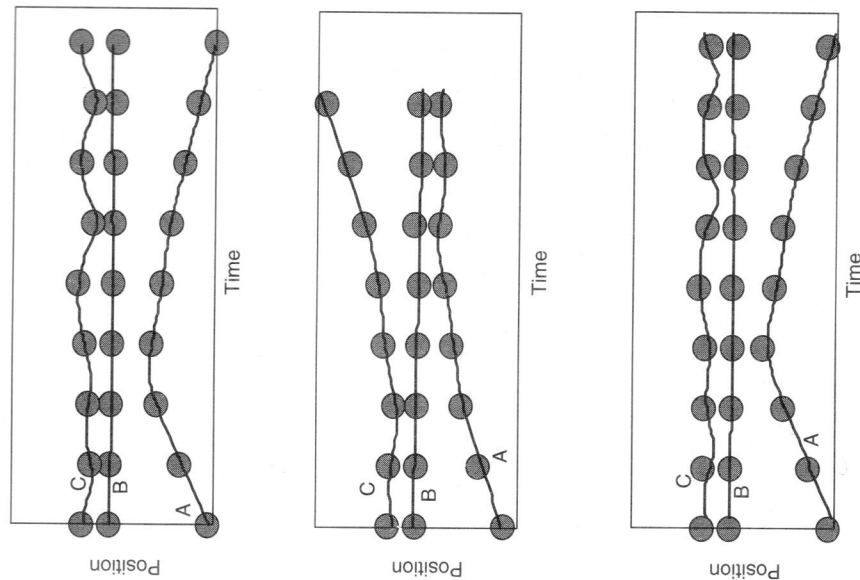


Figure 8.10 A series of trajectories during the reaction $A + BC \rightarrow AB + C$, with $M_A = M_C = 1$, $M_B = 19$, and various initial reactant configurations.

come up just when C is moving away, reaction happens. If not, A bounces off. In the top in the Figure 8.10 case, A is far from BC at the end of process, so no reaction has happened. In contrast, in the middle case, A and B are close together and C has flown away. In this case reaction has occurred.

Do not worry about understanding the details of Figure 8.10 now. We will explain it in further detail later in this chapter.

Marcellin (1912,1914a,b) showed that it is useful to plot the position-time data on a potential energy surface. Recall that when the A approaches the BC, R_{AB} and R_{BC} will change with time. One can plot that change as a trajectory (i.e., line) on the potential energy surface as shown in Figure 8.11. The solid dark line in Figure 8.11 starts at the reactants (i.e., the upper left) and ends at the products (i.e., the lower right). We will call that line a *reactive trajectory* or a *reactive collision*, since if the system follows that trajectory, the system reaches the products so reaction occurs. Similarly, the heavy dashed line starts out at the reactants (i.e., the upper left) and loops back to the upper left (i.e., back to the reactants). We will call such a trajectory a *nonreactive collision*, since if the system follows that line, the system never gets to products so no reaction occurs.

One can calculate a reaction rate from Figure 8.11 by starting with a distribution of molecules, computing a series of trajectories like those in Figure 8.11, and adding up the rate for the cases when the molecules react. Note that in the case shown in Figure 8.9, the potential goes up when the hydrogen comes close enough to the F_2 to react because of the Pauli repulsion between the hydrogen and the F_2 . Therefore, it will take a certain amount of energy to get the hydrogen to react with the fluorine. This is a general result. There is always a Pauli repulsion during any exchange reaction. Consequently, one can conclude that:

It usually costs energy to bring the reactants close enough that they can react. As a result, there is a barrier to most exchange reactions.

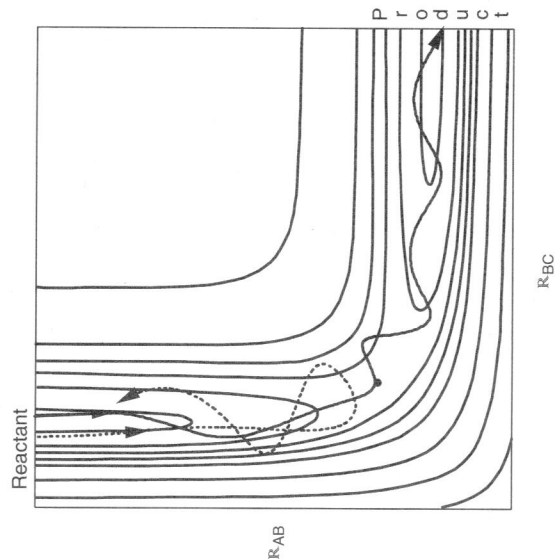


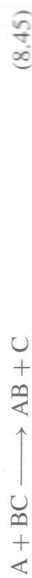
Figure 8.11 A series of typical trajectories for motion over a potential energy contour.

In Chapters 10 and 11, we will show that additional barriers arise because one needs to stretch or break bonds during chemical reactions.

8.7 QUALITATIVE FEATURES OF THE COLLISIONS: EXCHANGE REACTIONS

In the next several sections, we will discuss what reactions are like. We will consider three generic types of reaction: unimolecular reactions, bimolecular recombination reactions, and exchange reactions. The discussion in this section will consider exchange reactions. Other reaction types will be discussed starting at Section 8.10.

Exchange reactions are the most common elementary reactions. An exchange reaction in any reaction of the form



where a radical or atom A, collides with a molecule BC to transfer a ligand B and produce a new radical C. Examples of exchange reactions include



In all cases, one is breaking one bond and forming another. The formation and destruction of bonds is one of the key features of ligand exchange reactions.

In the next several sections, we will describe what ligand exchange reactions are like on a molecular level. For most of the discussion, we will consider a special example: an exchange reaction $H + FH \rightarrow HF + H$. We will assume that the reaction follows the potential energy surface in Figure 8.12. The potential energy surface looks just like the

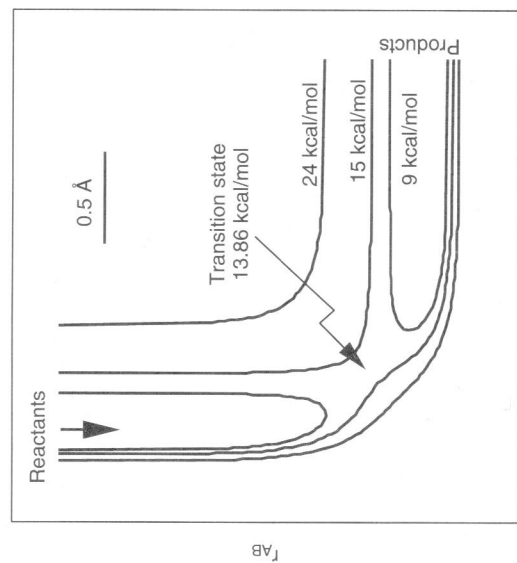


Figure 8.12 An idealized potential energy surface for the reaction $A + BC \rightarrow AB + C$.

ones we discussed earlier in the chapter with broad wells and a barrier in between. We have chosen parameters so that the reaction has a barrier of 13.86 kcal/mol, and the equilibrium bond lengths are 1.04 Å. A and C each have a mass of 1 amu. B has a mass of 19 amu. For discussion purposes, I have set the A-B and B-C bond energies to be 30 kcal/mol, not the 108 kcal/mol seen in HF. I have also artificially tripled the widths of the vibrational wells so that it will be easier to observe the vibrational motion.

Our general approach will be to start atoms moving, and calculate the positions as a function of time, to see whether reaction happens. A detail in the calculations is that one needs to specify the initial conditions to actually do the calculations. Generally one specifies the initial rotational and vibrational states of the BC molecule, the initial velocity of A toward BC, and the initial position of B and C as they vibrate in and out. In the work that follows, we usually fix the total energy and vary the other variables. In these calculations, the total energies is the sum of the rotational and vibrational energies of BC and the translational energy of A toward BC.

Figure 8.13 shows what typical trajectories are like. In this case, we put a total 18 kcal/mol into the incident molecules, and calculated the position of the atoms as a function of time. In both cases we put the same amount of energy in the molecule, but choose different values for the initial B-C position, so we got different results. In the top case (a), the atom A comes in and hits the BC molecule and reacts. Notice that A starts out far away from BC. However, as time evolves, A comes until it is in close proximity to BC. Then there is some complex behavior. Then after some time, C moves away, while A and B stay together. This is a reactive collision because we end up with A bound to B, and C far away.

The next case, (b), is a nonreactive trajectory. In this case, A + BC collides as before. However, A moves away at the end of the collision, so there is no reaction.

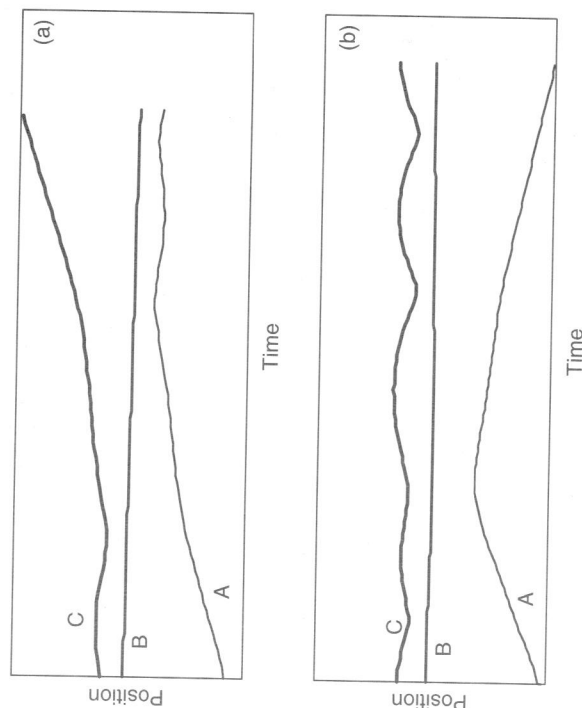


Figure 8.13 Two typical trajectories for the reaction $A + BC \Rightarrow AB + C$, with $M_A = M_C = 1$, $M_B = 19$, $E_{\text{total}} = 18$ kcal/mol ($E_{\text{trans}} = 14$ kcal/mol, $E_{\text{rot}} = 0$ kcal/mol, $E_{\text{vib}} = 4$ kcal/mol). Reaction occurs in the top trajectory but not in the bottom trajectory.

ReactMD generates thousands of trajectories like this. The reader should run some trajectories before proceeding.

Figure 8.14 shows a series of trajectories calculated by putting a total 13.8 kcal/mol into the reactants, and calculating the trajectories of the molecules. Notice that in all cases, no reaction occurs. To keep this in perspective, we choose a case where the incident energy was 13.8 kcal/mol, while the barrier was 13.86 kcal/mol. In all cases, no reaction happens.

One can understand this finding with the aid of Figure 8.15. Figure 8.15 is a replot of the data in Figure 8.14 on a potential energy surface. The trajectories all start out moving toward the transition state. However, there is not enough energy to cross the barrier. Consequently, no reaction happens.

This is a general result. Classically, if the molecule does not have enough energy to cross the barrier, no reaction occurs. Quantum-mechanically, there is a small reaction rate due to a process called tunneling. See Sections 7.3.1, 9.3.1, and 9.5.

At higher energies, one does have some probability of reaction. Figure 8.16 shows a series of trajectories calculated by setting the energy of the incident molecules, and then adjusting all of the other parameters to optimize the probability of reaction. At an energy of 13.6 kcal/mol, the A atom comes in and makes it almost all the way to the transition state. However, the A does not have enough energy to make it over the hill, so the A

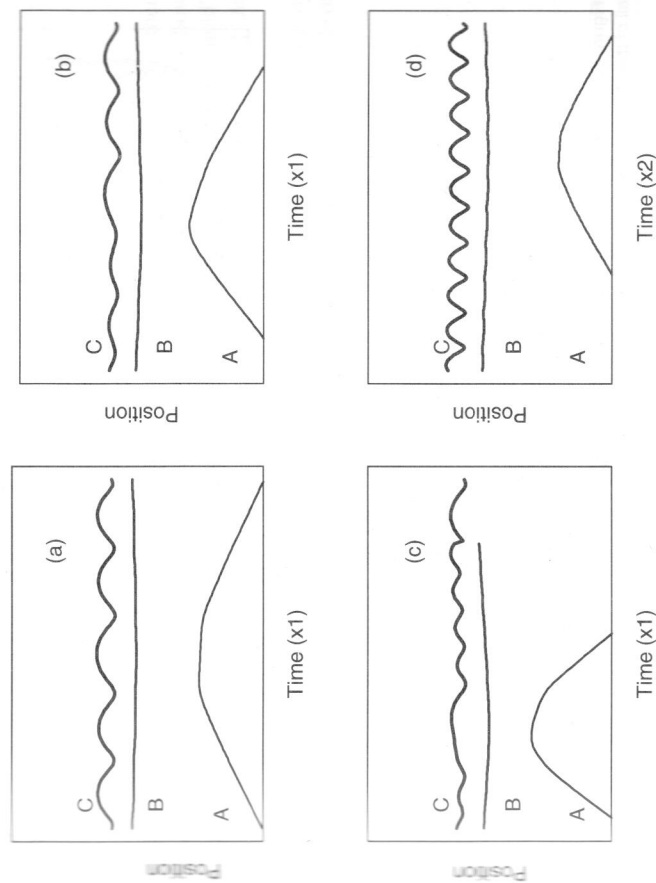


Figure 8.14 A sampling of the trajectories taken by putting a total of 13.8 kcal/mol into the reactants, choosing random initial positions for the atoms, and putting a random amount of rotational energy into the BC bond. We chose the initial velocity of A toward BC so that the total energy was 13.8 kcal/mol, and then we integrated the equations of motion to see whether reaction occurs. In this example, the barrier is 13.86 kcal/mol, so no reaction occurs.

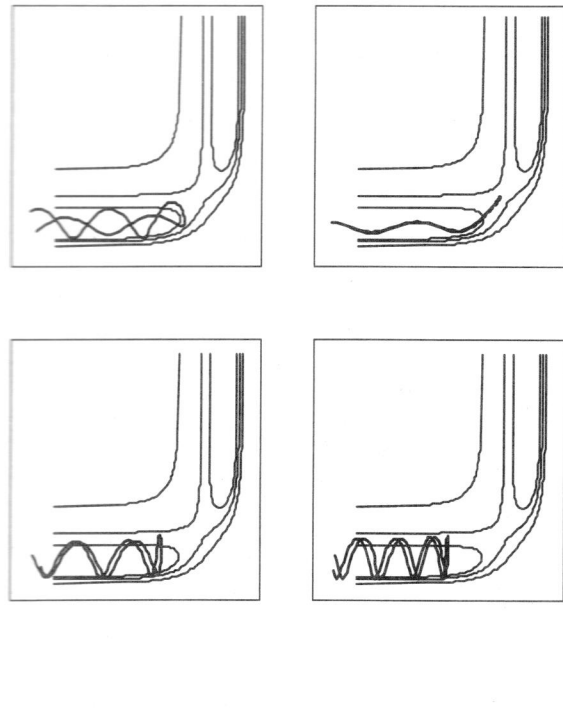


Figure 8.15 A reprint of the data from Figure 8.14 on a potential energy surface.

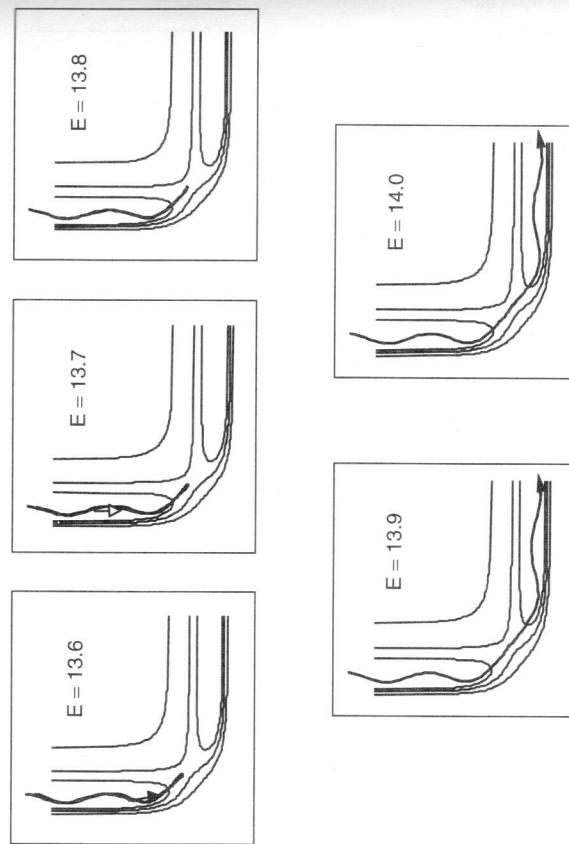


Figure 8.16 A series of trajectories calculated by fixing the total energy of the reactants and then optimizing all of the other parameters. The barrier is 13.88 kcal/mol for this example.

stops before it makes it over the barrier. In the particular case shown, the trajectory seems to double back on itself, so you see only one line in the figure. Actually, there are two lines, one on top of the other. The plots for $E = 13.7$ and 13.8 kcal/mol are similar to those for $E = 13.6$. There is no reaction. However, at $E = 13.9$, reaction occurs, so the

trajectory (i.e., black line) leads from reactants to products. One also observes reaction at $E = 14.0$.

Notice that when the energy is below the saddle point energy, 13.86 kcal/mol, no reaction occurs. However, as soon as the energy goes above 13.86 kcal/mol, the reaction starts. Consequently, there is some probability of reaction whenever the incident molecules have enough energy to traverse the barrier.

This is not obvious from Figure 8.16, but, in fact, when the incoming molecules have barely enough energy to cross the barrier, the reaction probability is relatively small. One needs some excess energy to get reaction to happen at a reasonable rate.

Physically, the trajectory has to go through the pass of the top of the potential energy surface. Figure 8.17 shows a picture of the pass. A molecule with energy E can go through only the part of the pass where the energy is less than E . Figure 8.17 shows two different cases. At a low energy, the molecule can go through only the bottom of the pass, so the rate is low. However, as you raise the energy, the molecule can go through a wide portion of the pass. Consequently, the rate is higher.

Figure 8.18 shows some actual data. The figure shows how the cross section for the reaction $H + H_2 \rightarrow H_2 + H$ varies with the energy of the incoming H atom, where, as noted previously, the cross section is a quantity proportional to the rate constant for the reaction. Notice that the reaction probability is near zero until the molecules have enough energy to cross the barrier. Then the cross section increases rapidly. The cross section decreases again at high energy because the reactants fly past each other before the reaction can occur. Empirically, rates generally reach a maximum at energies 2–3 times the barrier and then decrease again.

Interestingly, there is a small probability of a reaction occurring when the energy is below the top of the barrier. This occurs because of a quantum effect called tunneling, which will be discussed in Chapter 9.

There are lots of other details that affect rates of reactions. When you do an MD calculation, you specify the initial positions and velocities of all of the atoms, and then numerically integrate equation (8.28) (Newton's equations of motion) to calculate how the system changes. It happens that when the energy is what is called "near threshold" (i.e., just above the barrier), small changes in the initial positions and velocities of the atoms can affect whether reaction actually happens.

Generally, reactions are rare events until you are several kcal/mol above the top of the barrier as shown in Figure 8.18. One key parameter is the relative motion of all of

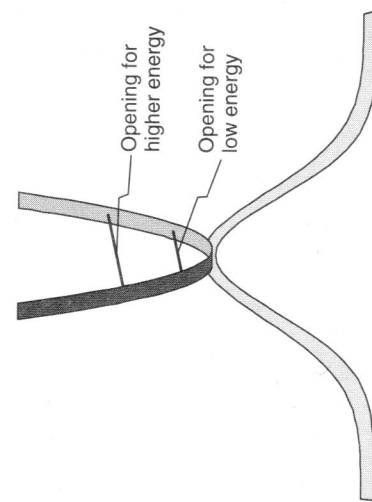


Figure 8.17 A blowup of the top of the barrier.

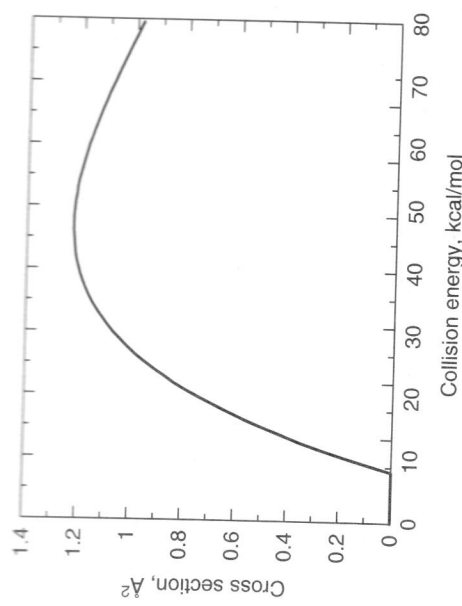


Figure 8.18 The cross section for reaction $H + H_2 \rightarrow H_2 + H$. [Adapted from Tsukiyama et al. (1988) and Levine and Bernstein (1987)].

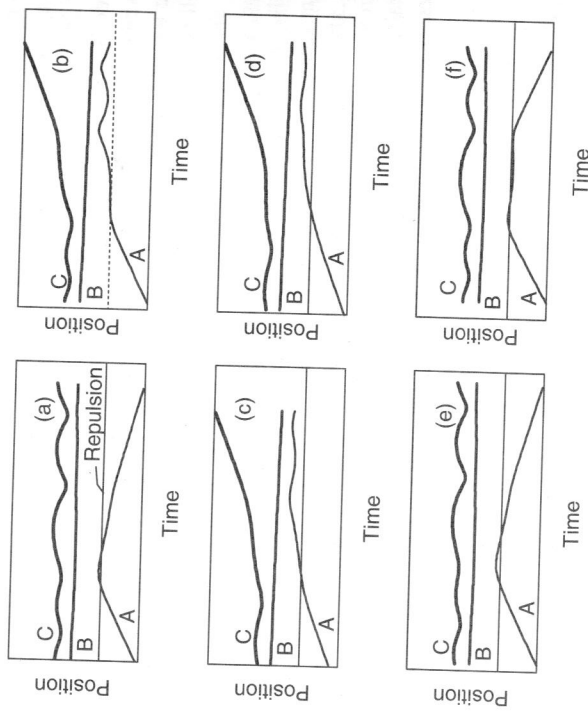


Figure 8.19 A series of cases calculated by fixing free energy at 18 kcal/mol, fixing the vibrational energy at 6 kcal/mol, and varying whether A hits when C is vibrating in toward B or out away from B.

the atoms at the moment of collision. Figure 8.19 shows a series of cases where we let B-C start vibrating, and then delayed the collision, so that A would hit B-C at different times along the B-C vibrational cycle. Sometimes A would hit when the B-C bond was stretched; at other times A would hit when the B-C bond is short. Notice that only about half of the trajectories lead to reaction even though the reactants have 18 kcal/mol, which is more than enough energy to cross the barrier. If you look carefully at the trajectories,

you will notice that the critical variable is the motion of C when A crosses the dashed line in the figures. C vibrates up and back as the reaction proceeds. If A reaches the line in Figure 8.18 when C happens to be moving away, C continues to move away from B-C. In reaction occurs. If C is vibrating in toward B, no reaction occurs. Case (b) is hard to see, but actually C starts to vibrate away just when A hits the dashed line. This example illustrates that you need coordinated motion of all of the atoms in order for reaction to happen. If C is moving away from B anyway, C continues to move away. However, if C is moving in toward B, the incoming A molecule does not have enough momentum to push C away; consequently, no reaction occurs.

People often think about this effect in terms of what happens on a potential energy surface. Figure 8.20 shows a replot of the data in Figure 8.19 on a potential energy surface. Notice that the molecules need to go around a bend in the potential energy surface in order for reaction to happen. Well, the bend is like a bend in a racetrack, and the molecule needs to synchronize its turn in order to get around the track. If the molecule turns at the wrong time, the molecule does not make it around the track even though the molecule has more than enough energy to cross the barrier. Think about what happens at a curve in a racecourse. If the driver turns too fast, the car does not make it around the curve even though it has plenty of power to keep going. In the same way, the molecules need to coordinate their motion as the system reaches the transition state. In particular, the atoms need to be moving to the right as they approach the transition state in Figure 8.20. Motion to the right is equivalent to C moving away from B when A approaches BC.

A related effect is that the molecule needs to be moving in the right direction as it approaches the barrier. The molecules need to be moving up the hill as they approach the barrier in order for reaction to happen. Vibrations parallel to the hill are less effective in carrying molecules over the barrier.

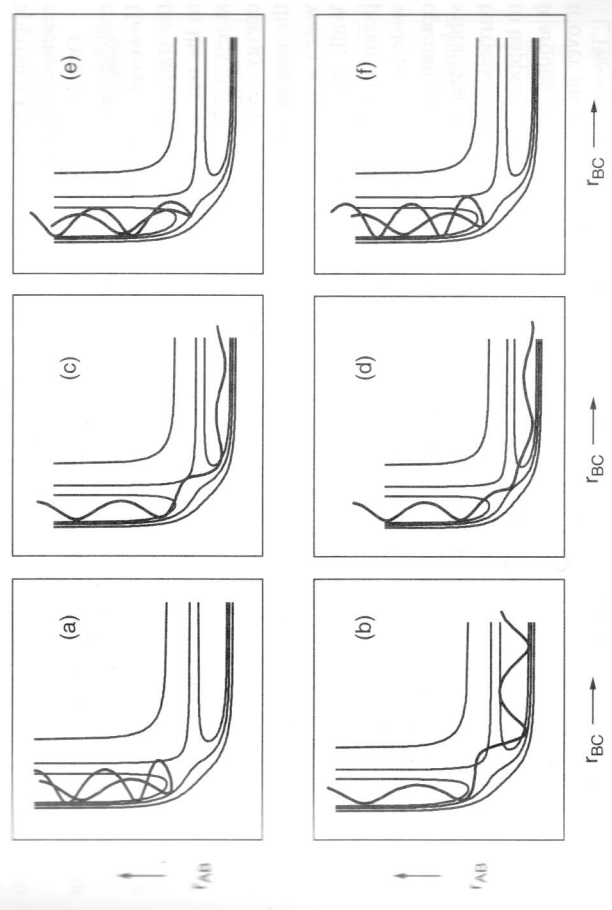


Figure 8.20 A replot of the results in Figure 8.19 on a potential energy surface.

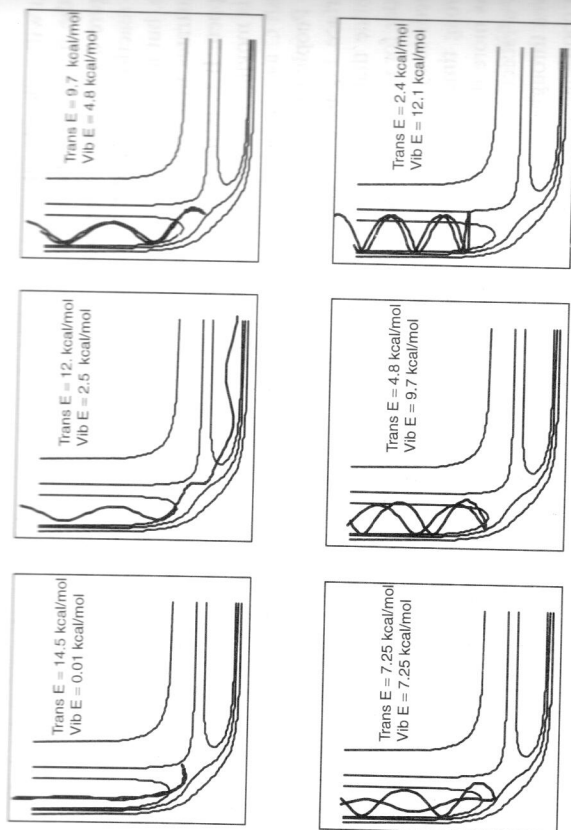


Figure 8.21 A series of cases where the molecules have enough energy to get over the barrier. Notice that some of the molecules do not make it, because the partitioning of the energy between translation and rotation is incorrect.

Figure 8.21 shows some examples where we varied the initial vibrational and translational energies on the molecules and tried to see if the molecules made it over the barrier. In these cases, there is more than enough energy to carry the molecules over the barrier, but sometimes, the molecules are moving in the wrong direction as they approach the barrier. There is no momentum to carry the reactants over the barrier, so no reaction happens.

One might think that the way to optimize the reaction is to put all of the energy in translation to give the molecules as much momentum as possible to go up the barrier. However, the results in Figure 8.21 show that does not really work. The reason is because the trajectory needs to make a left turn on the potential energy before the trajectory gets to the transition state. Consequently, it is necessary to balance the forward motion of the atoms and the turning motion to optimize the reaction probability. Generally, some of the energy needs to be in translation, but other energy needs to be in vibration to optimize the turning of the molecule. Again, there is a close analogy to a racecar. If you ever watch a race, you will notice that the racecars go wide before they go around a curve. Well, the same thing happens with molecules. The trajectory needs to go wide on the potential energy surface to make it around the curve. The trajectory needs to go wide on the wide if they accumulate some vibrational energy before they collide. Consequently, the optimal trajectories always have some vibrational energy. If the molecules have too much vibrational energy, though, the molecules do not have enough momentum to get over the barriers, so one has to carefully balance the vibrational and rotational energy to get reaction to happen. There also is a timing issue. A race driver who turns too early will never make it around the track. In the same way, when molecules vibrate too early, they never make it over the barrier. Perfect timing occurs when C is vibrating out when A comes in.

The trajectories in Figure 8.21 were plotted on a standard potential energy surface. There is some subtlety in looking at the motion on a potential energy surface in that

trajectories can sometimes seem to turn around with no reason. This is an artifact associated with something subtle in the mathematics. Recall that the atoms are really moving on a nine-coordinate potential energy surface, where the nine coordinates are the X, Y, and Z coordinates of atom A; the X, Y, and Z coordinates of atom B; and the X, Y, and Z coordinates of atom C. When you collapse the nine-dimensional space onto a two-dimensional plot, you can get artifacts. In particular, atoms can seem to turn around for no reason.

It happens that if one uses some special coordinates, called *mass-weighted coordinates*, the artifacts vanish. The mass-weighted coordinates are defined by

$$R_1 = R_{AB} + \left[\frac{m_A m_C}{(m_A + m_B)(m_B + m_C)} \right]^{1/2} R_{BC} \quad (8.49)$$

$$R_2 = R_{BC} \left(\frac{m_B (m_A + m_B + m_C)}{(m_A + m_B)(m_B + m_C)} \right)^{1/2} \quad (8.50)$$

Figure 8.22 is a replot of the data in Figure 8.21 on mass-weighted coordinates. Notice that the potential energy surface is slightly skewed. However, the trajectories now look normal. In particular, the trajectories that do not make it stop because they are moving parallel to the hill, rather than up the hill.

Next it is interesting to consider how the shape of the potential energy surface affects the rate of reaction. The effect is substantial. If you have a potential energy that is banked like a racecar, then the incoming molecule can ride around the curve. In such a case, translational energy is easily transferred from the incoming A molecule to the C molecule. However, if you have an L-shaped potential energy, such as that in Figure 8.23, then you need vibrational energy to get around the curve. L-shaped potential energy surfaces are quite common when the reactants A, B, and C are atoms. They are less common when

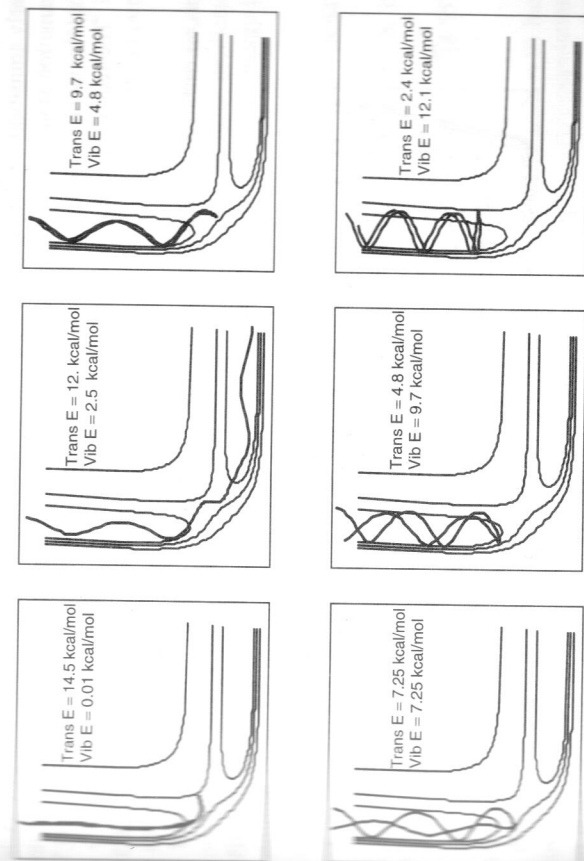


Figure 8.22 A replot of the data in Figure 8.21 in mass-weighted coordinates.

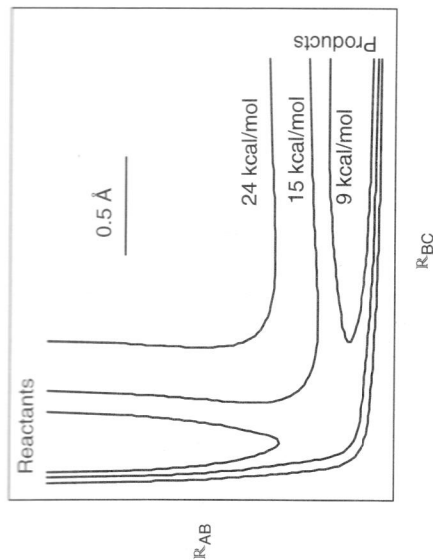


Figure 8.23 An L-shaped potential energy.

A and C are molecular ligands. Still, L-shaped potential energy surfaces do present some particular difficulties during reaction.

8.7.1 Polanyi Rules

Polanyi rules pose some special issues. Polanyi showed that with an L-shaped potential energy surface, the position of the transition state also has a large effect on the energy transfer barrier to reaction. Polanyi noted that one can characterize reactions according to whether they have an early, middle, or late transition state. Figure 8.24 shows an example of the potential energy surface with early, middle, and late transition states. An early transition state is one that arises when the reactants have hardly changed. A late transition state is a transition state where the species look similar to the products, and middle transition states are somewhere in between.



has an early transition state. The reaction



has an early transition state. The reaction

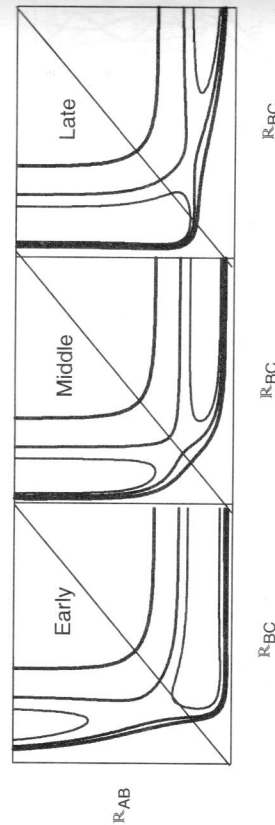


Figure 8.24 Potential energy surfaces with early, middle, and late transition states.

has a middle transition state. The reaction



has a late transition state.

A reaction with an early transition state will reach the transition state before the reactants are significantly deformed. The B–C bond will not be stretched significantly. However, the A–B bond will be much larger than in a stable AB molecule. See Figure 8.24. In contrast, a reaction with a late transition state will reach the saddle point near the end of the reaction. The B–C bond will be almost broken, while the A–B bond will be about the same length as in a stable AB molecule. A reaction with a middle transition state is somewhere in between the two, where the bonds in both the reactants and products are stretched by similar amounts in the transition state.

In this section we will discuss some of the special effects which occur with L-shaped potential energy surfaces. The work will build on findings of Polanyi.

Polanyi showed that $P_{\text{reaction}}(V_{A \rightarrow BC}, E_{BC})$ changes according to whether the reaction has an early, middle, or late transition state. If the reaction has an early transition state, the reaction probability is higher when the translational energy is large than when the B–C vibrational energy is large. In contrast, if the reaction has a late transition state, the reaction probability is higher when the B–C vibrational energy is large than when the translational energy is large. Physically, when there is an early barrier to the reaction, most of the barrier is associated with getting A and BC in close proximity. In that case, the faster A moves toward BC, the more momentum A will carry into the collision. A's momentum allows it to get in close proximity to B–C. That increases the rate of reaction. In contrast, if the reaction has a late transition state, most of the barrier is associated with breaking the B–C bond. In that case, it is better to have energy in the B–C bond before the reaction, rather than having to transfer energy during the collision.

Polanyi showed that reactions generally retain energy during collision; thus, if you have an early transition state so that the A needs to be moving fast during the reaction, then the collisional energy generally stays with A. In that case, the A–B molecules come off hot (i.e., with a high vibrational energy) while C comes off cold (i.e., moving slowly). In contrast, if you have a late transition state, so that A starts out cold while B–C is excited, the A–B will end up cold while B and C will end up with a considerable amount of translational energy.

Polanyi showed that one can measure the vibrational and translational temperatures, by comparing the distribution of vibrational energy levels and velocities to those predicted by Boltzmann's equation. For example, Figure 8.25 shows how the vibrational energy is partitioned in the DF produced during the reaction:



According to Boltzmann's distribution, the P_n , the probability that a given state, n , is occupied should follow

$$P_n = e^{-E_n/k_B T} \quad (8.55)$$

where E_n is the energy of the n th state.

Figure 8.25 shows how P_n actually varies. Notice that the ground state ($n = 0$) has a low probability of being occupied. The $n = 3$ vibrational level has a larger population than does the ground state. This is quite different from the scenario expected from the Boltzmann distribution. The average energy of the HF is 21.3 kcal/mol. Therefore, it

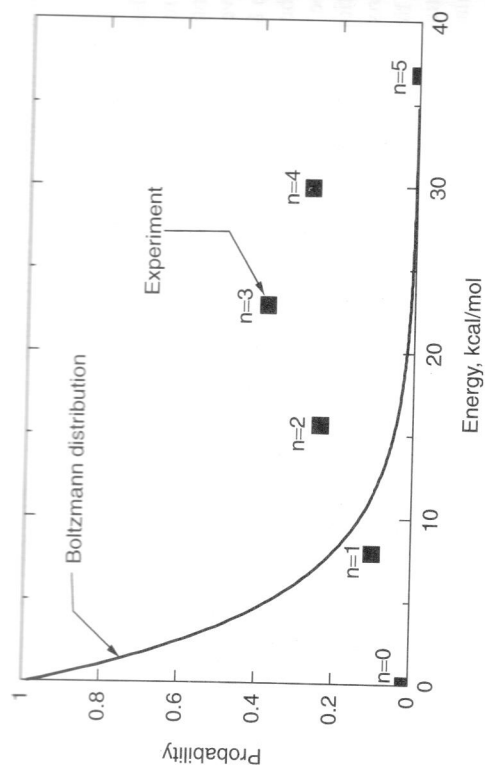


Figure 8.25 The distribution of vibrational energy produced during the reaction $F + H_2 \rightarrow HF + H$. [Results of Polanyi and Woodall (1972)].

seems that the HF is much hotter than the hydrogen atoms, which is as expected for an early transition state.

All of these trends can be explored with the ReactMD program. Any reader who has access to this program is advised to run the program and vary the parameters before proceeding with this chapter.

8.8 SUMMARY OF LINEAR COLLISIONS

At this point, it is useful to summarize what we have learned about linear $A + BC$ collisions.

- First, we found that to a reasonable approximation one can treat the collision of two molecules as a collision between two classical particles following Newton's equations of motion.
- The reactants must have enough total energy to get over the transition state (or col) in the potential energy surface in order for reaction to happen.
- It is not good enough for the molecules to just have enough energy. Rather, the energy needs to be correctly distributed between vibration and translation.
- Coordinated motions of the atoms are needed. In particular, it helps to have C moving away from B when A collides with BC.
- We also find that we need to localize energy and momentum into the B–C bond for reaction to happen.
- The detailed shape of the potential energy surface has a large influence on the rate.

These effects mean that the system has very complex behavior. Note, however, that the latter four effects cause perhaps a factor of only 10 or 100 in rate. There are always some trajectories that make it over the barrier, even though the molecules have barely enough

energy to cross the barrier. If 1% of the trajectories make it, those trajectories will have an important effect on the rate.

8.9 THE NONLINEAR CASE

The discussion in the Sections 8.7 and 8.7.1 considered the dynamics of the reaction $A + BC \rightarrow AB + C$ where A, B, and C are confined to a line. With a linear collision, all of the A atoms that hit the BC molecule will react with a constant probability. However, in reality, A, B, and C are not confined to a line. Instead, the reaction occurs over a three-dimensional space. With a three-dimensional system, the reaction probability varies with how closely the molecules collide. Generally, reaction probabilities are higher when molecules collide head on than when the molecules miss. The object of the next few sections are to discuss these effects.

To start it is useful to note that one can quantify this effect by seeing how the reaction probability varies with the impact parameter $b_{A \rightarrow BC}$. Recall from Section 8.3.1 that the impact parameter is a measure of how close the reactants come to one another. Generally, the reaction probability is high if there is a head-on collision between the reactants. A head-on collision corresponds to an impact parameter of zero. In contrast, the reaction probability is near zero if the reactants miss. A large-impact parameter corresponds to the reactants missing. Generally, the reaction probability varies with the impact parameter. Consequently, the impact parameter has a large effect on the reaction.

Figure 8.26 shows how the reaction probability varies with the impact parameter at intermediate impact parameters. Generally, the reaction probability is highest with an impact parameter of 0. The reaction probability is relatively insensitive to the impact parameter when the impact parameter is small. However, there is a sharp cutoff at a larger impact parameter. As a result, the reaction rate is negligible unless atoms hit with a small impact parameter.

One can understand this behavior qualitatively with the aid of Figure 8.27. When the molecules collide with an impact parameter of zero, all of the momentum of atom A is directed toward BC. In contrast, when the impact parameter is nonzero, one can divide

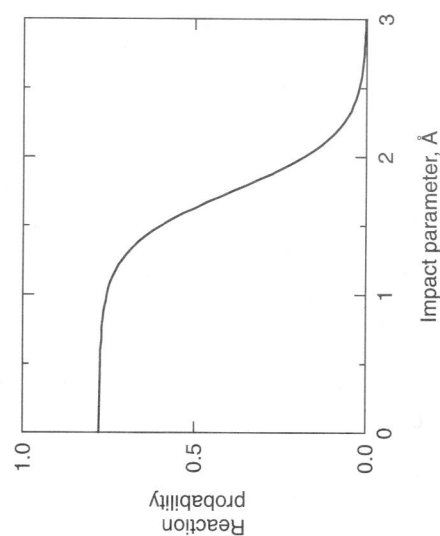


Figure 8.26 The variation in $P_{A \rightarrow BC}$ with changing impact parameter.

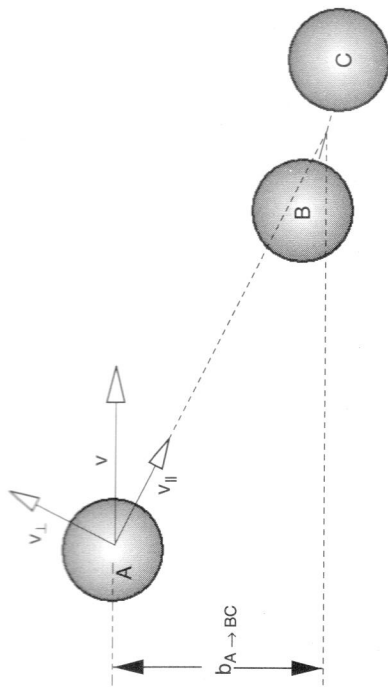


Figure 8.27 The typical trajectory for the collision of an A atom with a BC molecule.

A's momentum into two components as indicated in Figure 8.27. One component, v_{\parallel} , carries A toward BC, while the second component, v_{\perp} , carries A away from BC. v_{\perp} increases as the impact parameter increases. As a result, the probability that atom A will move away from BC increases as the impact parameter increases.

In order to fully model this process for the reaction $A + BC \rightarrow AB + C$, one has to integrate the equations of motion [i.e., equations (8.29) to (8.32)] numerically. In general, that cannot be done analytically. However, one can get the structure of the solution by solving the equations of motion for a simpler reaction, $A + B \rightarrow AB$. A detailed derivation of the key equations will be given in Section 8.16.1 at the end of this chapter. The key result is that when A and B collide with a nonzero impact parameter, the distance from A to B, the \mathcal{R}_{AB} , will act as though A and B are moving in an "effective potential" given by

$$V_{\text{eff}} = \frac{(b_{A \rightarrow BC})^2 E_{\text{KE}}}{\mathcal{R}_{AB}^2} + V_{AB}(\mathcal{R}_{AB}) \quad (8.56)$$

where $V(\mathcal{R}_{AB})$ is the A–B potential, E_{KE} is the kinetic energy of A moving toward B, $b_{A \rightarrow BC}$ is the impact parameter, and \mathcal{R}_{AB} is the distance from A to B. Equation (8.56) arises because whenever v_{\perp} is nonzero, there is a component of angular momentum that carries the reactants apart. One needs extra kinetic energy to overcome that component of angular momentum. The first term on the right of equation (8.56) is the extra kinetic energy you need to overcome the component of the angular momentum that carries the reactants apart. Therefore, we will call this barrier the **angular momentum barrier to reaction**. The extra angular momentum barrier grows as the impact parameter increases. Consequently, the extra angular momentum barrier keeps the molecules from reacting when the impact parameter is large.

Figure 8.28 shows a plot of the effective potential as a function of \mathcal{R}_{AB} to see how that can work out. We choose a case where $V(\mathcal{R}_{AB})$ is what is called a Lennard-Jones potential (i.e., a potential like that in Figure 8.30). When $b = 0$, there is no barrier to prevent A from approaching B. Note, however, that as $b_{A \rightarrow BC}$ increases, a barrier arises. This barrier prevents the reaction from occurring at large-impact parameters.

If one considers a more complex reaction, one finds that the arguments are more subtle. For example, with the reaction $A + BC \rightarrow AB + C$, one can transfer angular momentum from A to C, which slightly reduces the angular momentum barrier to reaction. Still,

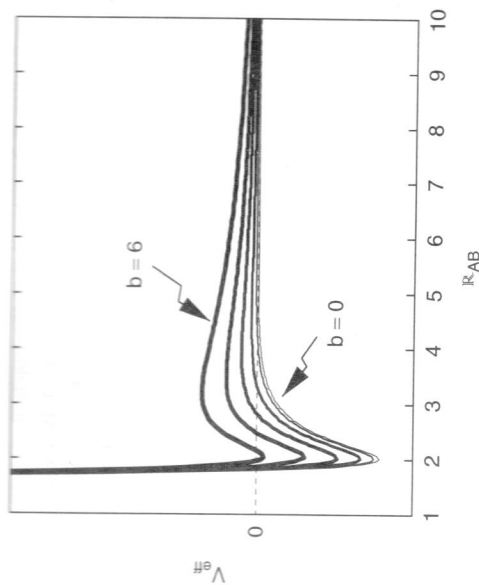


Figure 8.28 A plot of the effective potential as a function of \mathcal{R}_{AB} for a modified Lennard-Jones Potential with $b_{A \rightarrow BC} = 0, 1, 2, 3, 4, 5, 6$.

angular momentum barriers arise in all gas-phase reactions:

The angular momentum barrier prevents reactions from occurring when molecules approach with large-impact parameters. As a result, no reaction occurs unless the reactants get close to each other.

8.9.1 Changes in the Potential Energy Due to Nonlinear Collisions

There is another effect that also changes the potential with nonlinear collisions. Recall that the potential energy surface in Figure 8.9 was calculated for the case where the chlorine atom approached the fluorine directly along the fluorine–fluorine bond. In that case, the potential energy surface is simple. However, if the chlorine approaches along a different angle, the potential energy surface changes.

First note that the incoming chlorine needs to form a bond with the p-orbital. When the chlorine approaches the F_2 at some finite angle away from the fluorine–fluorine bond, the overlap with the p orbital is reduced. That reduces the net attraction between the fluorine and the chlorine. Simultaneously, the overlap with the nonbonding orbitals in the F_2 increases. There is a Pauli repulsion between the nonbonding orbitals and the incoming chlorine. The result is that the barriers increase with a nonlinear collision. There are equations in the literature to quantify the increase, but when this book was being written, the equations did not seem to have good correlation with experiment. Still, the qualitative feature that the barriers to reaction increase with nonlinear collisions will be important to the analysis because the increase in barrier decreases the rate.

8.9.2 Influence on the Overall Rate

Now, it is useful to go back and see how the angular momentum barrier and the variation in the barriers to reaction will change the analysis in Section 8.2 (i.e., collision theory). Note

that the analysis in Section 8.2 assumed that the reaction rate was equal to the collision rate times the probability that molecules that collided actually reacted. The probability is assumed to be constant for all molecules that hit each other. However, the results in the previous section show that the probability is not constant. Thus, some modification of the results in Section 8.2 are needed.

One can account for the variations in the reactive probability by integrating equation (8.24). It is useful to define a reaction cross section, $\sigma_{A \rightarrow BC}^r$, by integrating over the impact parameter, $b_{A \rightarrow BC}$, and ϕ_{ABC} , \mathbf{R}_{ABC} , \mathbf{v}_{ABC} :

$$\sigma_{A \rightarrow BC}(v_{A \rightarrow BC}, E_{BC}) = \iiint \iiint P_{\text{reaction}}(v_{A \rightarrow BC}, E_{BC}, b_{A \rightarrow BC}, \phi, \mathbf{R}_{BC}, v_{BC}) \times D_1(\mathbf{R}_{BC}, v_{BC}) b_{A \rightarrow BC} db_{A \rightarrow BC} d\phi d\mathbf{R}_{BC} dv_{BC} \quad (8.57)$$

where $D_1(\mathbf{R}_{BC}, v_{BC})$ is the distribution function for the internal states of the BC molecule, $b_{A \rightarrow BC}$ is the impact parameter, ϕ_{ABC} is the angle of approach, and \mathbf{R}_{AB} and v_{BC} are the internal positions and velocities of the BC molecule as defined in Section 8.3.1.

For a spherically symmetric case:

$$\sigma_{A \rightarrow BC}^r(v_{A \rightarrow BC}, E_{BC}) = 2\pi \int P_{A \rightarrow BC}(b_{A \rightarrow BC}, v_{A \rightarrow BC}, E_{BC}) b_{A \rightarrow BC} db_{A \rightarrow BC} \quad (8.58)$$

where $P_{A \rightarrow BC}$ is the reaction probability as a function of b averaged over \mathbf{R}_{BC} , v_{BC} , and ϕ . The reaction probability is already in equation (8.58). Therefore, equation (8.25) for the rate constant becomes

$$k_{A \rightarrow BC} = \iiint v_{A \rightarrow BC} \sigma_{A \rightarrow BC}^r(v_{A \rightarrow BC}, E_{BC}) D_2(v_{A \rightarrow BC}, E_{BC}) dv_{A \rightarrow BC} dE_{BC} \quad (8.59)$$

where D_2 is the distribution function for $v_{A \rightarrow BC}$ and E_{BC} .

Equations (8.58) and (8.59) can be used to calculate the rate constant for reaction if $P_{\text{reaction}}(b_{A \rightarrow BC}, v_{A \rightarrow BC}, E_{BC})$ is known. Hence, they are quite useful. An example calculation is given in Example 8.D.

8.10 MORE COMPLEX REACTIONS

All of the simulations we have presented were for cases where A, B, and C are single atoms. However, one can generalize these effects to reactions where the individual species A, B, and C are molecular ligands rather than atoms. Generally, everything we have said so far in this chapter also applies to the case where A, B, and C are molecular ligands. A reaction involves concerted destruction and formation of bonds. Both bond formation and bond destruction processes must occur simultaneously. One can view this process as an energy transfer barrier to reaction. During the reaction $A + BC \rightarrow AB + C$, energy must accumulate in the B-C bond before any reaction occurs. No reaction occurs unless C leaves before A leaves, and A might stay around for only 10^{-14} seconds. As a result, it helps to have the atom B moving away from the rest of the molecule C when the attacking group A moves in toward B.

Another issue is that in order for reaction to occur, the B-C bond that needs to break (i.e., the B-C bond) must somehow acquire enough energy to break before the attacking group A leaves. Therefore, the rate at which energy accumulates in the B-C bond has an

important influence on the reaction rate. Generally, one finds that when the system has barely enough energy to cross the activation barrier, reaction rarely occurs, because the collision energy seldom gets localized in the B-C bond. The reaction rate increases with increasing energy. Note, however, that if A comes in too fast, the A will leave before there is time for reaction to occur. In that case, the reaction rate will go down again.

Another interesting effect is that when you have bigger molecules, the collisions last longer. As a result, the reaction probability increases. It is hard to understand why that happens without detailed analysis. However, when you watch movies of collisions, you find that if you have a reaction of little molecules:



the collision might last only 10^{-12} seconds. However, if two moderate-sized molecules react, such as



the reactants might stick together for 10^{-10} seconds. There are more chances for reaction when the reactants stick together. As a result, the preexponentials for reactions tend to go up as the reactants get bigger.

Physically, collisions last longer with big molecules than with small molecules because of energy partitioning in the molecules. Recall that, in general, molecules have to be moving pretty fast (i.e., molecules need significant translational energy) in order to have enough energy to cross the barrier. When a collision occurs between two small molecules, the molecules continue to move quickly, and as a result, the collision lasts for only an instant. In contrast, with a big molecule, the translational energy can be converted into vibrational energy. It is like bouncing a bowling ball on a mattress. The mattress takes up energy, so the ball does not fly away. In the same way, a small molecule transfers energy to the bigger molecule. The molecules slow down, so the molecules stay in close proximity longer. The molecules can also get entangled with one another. As a result, the reactants stay in closer proximity longer with the big molecules than with small molecules.

8.10.1 State-Selected Chemistry

The other thing you see with a more complex molecule is *state-selected chemistry*. The objective of state-selected chemistry is to use a laser to excite certain vibrational or rotational modes in a molecule in a way that a desired reaction pathway is enhanced. For example, Crim [1996] examined the photodissociation of monodeuterated water (HOD). If you simply photolyze HOD, with a photon, ν , you get two reactions:



Reaction (8.62) is very slightly favored over reaction (8.63) because of a quantum process called "tunneling." However, Crim (1996) found that if they excite the OD bond before photolysis, reaction (8.63) is favored. So far, the enhancements have been a factor of about 200. Unfortunately, you get that only with very expensive lasers, and it works only with small molecules. However, these effects are important in special reactions.

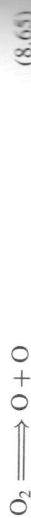
8.11 COMPLEXITIES: UNIMOLECULAR REACTIONS

So far, we have been discussing exchange reactions, where a ligand is exchanged from one species to the next. Those are the simplest reactions. However, there are other reaction types. In the next several sections, we will discuss these other reaction types.

In this section we will discuss unimolecular reactions. Unimolecular reactions are the second most common type of reaction. Unimolecular reactions are reactions of the form



where a stable molecule BC is somehow converted into products. Examples of unimolecular reactions include



In Chapter 4, we noted that unimolecular reactions are never elementary reactions. One can use molecular dynamics to see why that is so. If one starts with a stable molecule, the molecule is by definition stable. It never dissociates.

Consider trying to dissociate F_2 . Figure 8.29 shows a plot of potential energy of F_2 as a function of the F-F distance. The plot is a duplicate of the plot in Figure 8.3. Now consider trying to dissociate an F_2 molecule with an initial state given by the line in the figure. If you start with the F_2 with a state on the line, the fluorines vibrate back and forth. However, the fluorines are trapped in the attractive well. In the state shown, the fluorine-fluorine bond has a total energy of 40 kcal/mol (i.e., the fluorines are held together by 40 kcal/mol. One needs to accumulate the 40 kcal/mol in order for the bond to break. If the F_2 is isolated from its surroundings, energy is considered, so there is no way to accumulate the 40 kcal/mol. As a result, the fluorine cannot fall apart.

Simple unimolecular reactions are never elementary reactions.

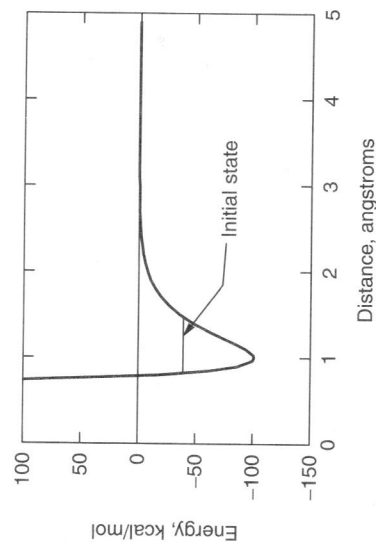


Figure 8.29 A plot of the fluorine-fluorine potential from Figure 8.3.

Of course, one does sometimes observe overall reactions like:



However, that is never an elementary reaction.

Instead, reactions like (8.65), (8.66), and (8.67) occur via bimolecular collision



where X is a collision partner, as discussed below.

Physically, a hot X molecule collides with the O_2 , and transfers energy to the O_2 . The energy accumulates in the O-O bond. Eventually, after several collisions, the O-O bond has enough energy to break. Notice that one needs to accumulate energy in the O-O bond before reaction can happen, which is why a collision partner is needed. One can observe reactions of the form



where ν is a photon, since the photon provides the energy (and momentum) needed to dissociate the molecules.

Another observation is that the rate constant varies according to the nature of the collision partner. For example, Table 8.1 shows how the rate of the reaction $O_2 + X \rightarrow 2O + X$ varies with the collision partner. The rate is zero in the absence of a collision partner. Further, one finds that the rate constant varies by a factor of almost 80 according to whether argon or oxygen is used as the collision partner.

The result of this discussion is that unimolecular reactions are very complicated, and one often needs detailed calculations to make useful predictions.

One of the key things you observe with a unimolecular reaction is that the reaction occurs in two stages. First, the collision partner collides with AB to form a hot AB molecule. Then, the hot molecule decomposes to form product. The hot molecule often lasts for 10^{-9} seconds. By comparison, ligand exchange reactions last only 10^{-13} seconds. Consequently, the preexponentials for unimolecular reactions tend to be much higher than the preexponentials for ligand exchange reactions.

At this point, we will defer our discussion of unimolecular reactions to the next chapter. The thing to remember for now is that unimolecular reactions are never elementary. Instead, one needs a collision partner for reaction to occur.

Table 8.1 Arrhenius parameters for the reaction $O_2 + X \rightarrow 2O + X$

Collision Partner	Preexponential, A^3 /(mol-second) at 4000 K	Activation Energy, kcal/mol
None	0	?
Ar	7.5×10^{14}	118.8
O_2	5.8×10^{16}	118.8

Source: Data from Westley (1980).

8.12 BIMOLECULAR RECOMBINATION REACTIONS

There is one other common type of reaction called a *bimolecular recombination reaction*. Bimolecular recombination reactions are any reaction of the form



where two species bind together to form a stable molecule. Examples of bimolecular reactions include



One would think that reactions (8.72) and (8.74) would be quite rapid. After all, according to Figure 8.3, there is no barrier to bringing two fluorines together. In the same way, there is no barrier to bringing a sodium up to fluorines. Actually, however, the rate of reactions (8.72)–(8.74) and all other bimolecular recombination reactions is zero in the absence of a collision partner.

8.13 ENERGY TRANSFER BARRIER TO REACTIONS

Next, it is useful to discuss why reactions (8.72)–(8.74) do not occur in the absence of a collision partner. The difficulty is associated with an energy transfer barrier to reaction. According to data in the CRC, reaction (8.74) is 181 kcal/mol exothermic. If a sodium would collide with a fluorine, one might think that one could form a sodium fluoride molecule. However, it would be a very hot sodium fluoride molecule since the heat of reaction is 181 kcal/mol exothermic. In fact, heat balance shows that the sodium fluoride would heat up to 34,000 K! Well, at 34,000 K, the sodium fluoride has a high probability of dissociating. The result is that the sodium and fluorine never stay together very long. One can form stable sodium fluoride by cooling off the sodium fluoride before the sodium and the fluorine fly apart. However, one needs to transfer the heat in some way. The only way that heat can be transferred is by convection (i.e., collisions) or radiation (i.e., photons). Consequently, if the reaction does not produce a photon, then one would need a collision partner for reaction to happen.

Reaction (8.74) is a special case, because the reaction is so exothermic. However, next, we want to show that any reaction of the form $A + B \rightarrow AB$, where two reactants combine to form a single product, cannot occur in the absence of a collision partner or photon.

Consider the generalized reaction $A + B \rightarrow AB$. At the start of the reaction, A approaches B with some energy, E_{AB} . For the purpose of discussions, assume that the A–B potential, $V^{(R_{AB})}$, looks like the potential in Figure 8.3. As A approaches B, A is first accelerated since $V^{(R_{AB})}$ is attractive at long distances. However, A begins to slow down again as A and B become very close. One can calculate A's velocity from an energy balance:

$$\left(\begin{array}{c} \text{Total} \\ \text{energy} \end{array} \right) = \left(\begin{array}{c} \text{kinetic} \\ \text{energy} \end{array} \right) + \left(\begin{array}{c} \text{potential} \\ \text{energy} \end{array} \right) \quad (8.75)$$

$$E_{AB} = \frac{1}{2} M_{AB} V_{AB}^2 + V^{(R_{AB})} \quad (8.76)$$

where V_{AB} is the velocity of A toward B, M_{AB} is the effective mass of the AB pair, and $V^{(R_{AB})}$ is the attractive potential between A and B.

It is useful to also calculate the net force on A from equation (8.29). Note that in order for the reaction $A + B \rightarrow AB$ to occur, A must fall into B's attractive well. A's velocity must be small (i.e., like a vibration). Further, the net force on A must be small, or else A will be pushed away from B. It works out, however, that when one actually calculates the velocity from equation (8.76) and the net force from equation (8.29), one finds that one can never get to the situation where both the force and the velocity are small at the same time.

Consider the case where an A atom collides with a B atom. Figure 8.30 shows a plot of A's velocity and the net force on A during a collision. A starts out moving slowly. However, it is accelerated by B's attractive well. The net result is that A's velocity is quite large when A is sitting over the minimum in the A–B potential. As a result, A flies past the potential well. A will eventually stop when the A–B bond is highly compressed. However, the net force on A is tremendous there, so A is pushed away. One can never get to the position where the net force on A is small, and where A is moving slowly enough that A stays bound to B. As a result, A cannot react with B.

The analysis above was for a Morse potential. However, detailed simulations with the program ReactMD show that the reaction $A + B \rightarrow AB$ never occurs. A always scatters (i.e., bounces away) from B independent of the form of A–B potential.

Physically, what is happening is that A is approaching B with some energy, E_{AB} . A has to lose that energy in order to fall into B's attractive well. However, there is no place

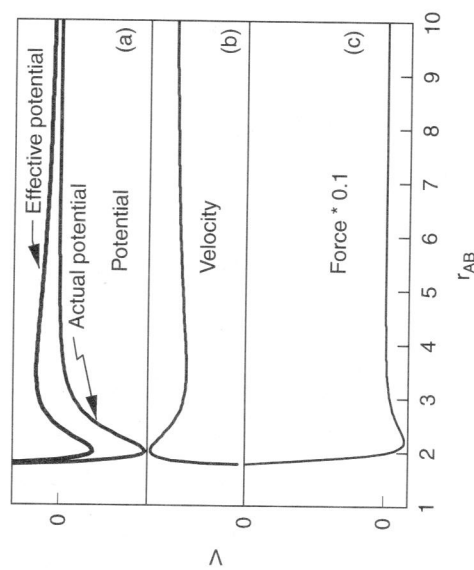


Figure 8.30 (a) A typical potential for the reaction $A + B \rightarrow AB$. (b) The velocity of A toward B. (c) The net force on A.

for the energy to go. As a result, A simply flies out again.

One can generalize this analysis to conclude that elementary reactions of the form



are impossible in the absence of collision partners or photons.

Reactions of the form $A + B \rightarrow AB + \nu$, where ν is a photon, are possible because the photon can carry away energy and momentum. In practice, though, such reactions are rare.

Still, experimentally, one often observes reactions of the form $A + B \Rightarrow AB$. Note, however, that such reactions are never elementary reactions. Instead, one finds that the reaction actually follows a mechanism $A + B + X \rightarrow AB + X$, where X is again a **collision partner**. X can be another molecule in the system, or the walls (i.e., surfaces) of the reaction vessel. The function of the collision partner is to remove energy and momentum from the reactive complex so that A can fall into B's attractive well. Experimentally, the rate of a reaction of the form $A + B \Rightarrow AB$ goes to zero at low pressures because there are no collision partners. However, one can observe reactions of the form $A + B \Rightarrow AB$ at moderate pressures. At moderate pressures, collisions with other molecules in the system occur. Those collisions carry away energy and momentum from the AB complex. As a result, the reaction has a finite rate.

In the problem set, we ask the reader to show that the reaction looks elementary at high pressures. However, the reaction is not really elementary. In particular, the rate constants for the reaction vary with the environment since the collision partner plays an important role in the reaction.

For example, Table 8.2 shows the rate constant for the reaction $NO + O + X \rightarrow NO_2 + X$. Notice that the rate constant is about a factor of 60 lower when the reaction is run in argon than when the reaction is run in water vapor. Clearly, this is a significant effect. Therefore, it is incorrect to view reactions of the form $A + B \Rightarrow AB$ as elementary. Rather, it is better to view the reactions as needing a collision partner.

The same arguments do not apply to ligand exchange reactions. Ligand exchange reactions such as reactions (8.45)–(8.48) all have two species coming into the reaction

Table 8.2 Arrhenius parameters for the reaction $NO + O + X \rightarrow NO_2 + X$

Collision Partner	Preexponential, Activation $\hat{A}^3 / (\text{mol}^2 \cdot \text{second})$	Energy, kcal/mol
None	0	?
Ar	1.7×10^{14}	1.88
O ₂	1.7×10^{15}	1.88
CO ₂	3.84×10^{15}	1.88
H ₂ O	1.1×10^{16}	1.88

Source: Data from Westley (1980).

and two species leaving it. The energy to break bonds can come from the reactants, while the products can carry off any energy created in the process. As a result, the large energy transfer barriers to reaction seen with recombination reactions are not observed with ligand exchange reaction. Instead, one gets collisions, and those collisions lead to reaction.

This leads to the key point in this section:

All elementary chemical reactions must have two or more reactants and two or more products. Reactions of the form $A + B \rightarrow AB$, $AB \rightarrow A + B$, $A \rightarrow C$ are not elementary; collision partners or photons are needed before such reactions can occur.

The reader should memorize this box before proceeding.

8.14 ELECTRON TRANSFER REACTIONS

There is another class of reactions where angular momentum barriers play a key role: reactions that do not have a barrier. We will discuss them in this section.

Consider the reaction



Reaction (8.77) looks very similar to reaction (8.38). The only difference is that we have replaced the chlorine by sodium. At first glance one might think that the potential energy surface for reaction (8.77) would look very similar to that for reaction (8.38). In fact, however, there is very little similarity. Reaction (8.77) actually occurs in two steps. First, the sodium atom approaches the F_2 and exchanges an electron.



Then the sodium ion reacts with the F_2 ion to yield products:



Experimentally, the electron transfer occurs when the reactants are 50 Å apart. Then the reaction proceeds quite quickly. We will describe the features of the electron transfer process in Chapter 11. However, a qualitative picture is given in Figure 8.31.

Figure 8.31 shows the energy of the neutral ($\text{Na} + \text{F}_2$) and ionized state of a NaF_2 complex as a function of the distance between the sodium and the F_2 . When the molecules are far apart, the neutral species are stable. However, as the sodium approaches the F_2 , the charged state has a lower energy. Quantum-mechanically, the electron always goes to the lowest energy state and electrons move at speeds close to the speed of light. Consequently, the electron jumps from the sodium to the F_2 as soon as the charged state has a lower energy than the neutral state. There are some details, based on something called an "avoided" crossing, which will be discussed in Chapter 10. However, the key thing to remember is that if the charged state has a lower energy than the neutral species, the charged species will form. Experimentally, the charged species form when the reactants are 50 Å apart (i.e., before there are significant Pauli repulsions).

Once the charged species form, the reaction happens very rapidly. Recall that Na^+ is a tiny ion. The Na^+ can move all the way up to the F^- without experiencing a significant

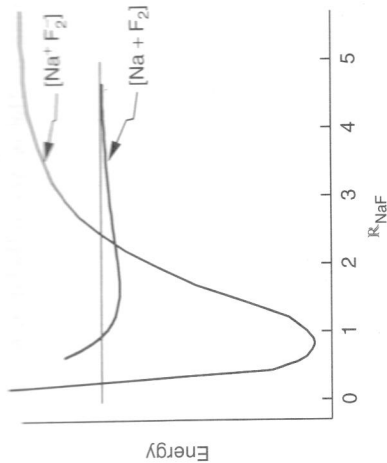


Figure 8.31 The energy of the neutral and charged states of NaF_2 as a function of R_{NaF} , the sodium-fluorine distance.

Pauli repulsion. Further, the Na^+ is drawn in because the positive charge on the sodium is attracted to the negative charge on the F_2^- . As a result, the potential energy surface for the reaction does not show a barrier. Overall, reaction (8.79) is extremely rapid.

Still it is not instantaneous. Recall from Section 8.9 that every reaction has an angular momentum barrier as shown in Figure 8.28. The barrier grows as $b_{\text{A} \rightarrow \text{BC}}$ increases. This barrier prevents reaction (8.79) from occurring when $b_{\text{A} \rightarrow \text{BC}}$ is large. Consequently reaction (8.79) has a finite rate even though there is no barrier for reaction.

In a more general sense, angular momentum barriers to reaction are very important for any reaction with a negligible barrier. After all, the rate should be infinite without the angular momentum barrier to reaction. We will quantify these results in Chapter 9. The thing to remember for now is that reaction rates are finite for barrier reactions because of the angular momentum barrier to reaction.

8.15 SUMMARY

The three primary causes of reaction barriers are

- Hills in the potential energy surface
- Energy transfer barriers
- Angular momentum barriers to reaction

The hills arise because the electron clouds need to be compressed in order for the reactants to get close enough to react. If you do not have enough energy, no reaction can occur.

The energy transfer barriers arise because one needs to put energy into a bond to get a bond to break. If a molecule has enough energy to react, the molecule still might not react because the energy is in the wrong mode.

Similarly, one needs to remove energy to get a new bond to form. If there is no place for the energy to go, you could form only very hot molecules. Hot molecules are unstable. Angular momentum barriers are more subtle, because they are important only with large-impact parameters. Generally, if the impact parameter is large, the reactants will fly apart before they can react.

At this point we need to end our discussion. In this chapter, we have shown that there are three principal causes barriers to reaction. All three of these processes are important to reactions. One should study them in detail.

We have also found that one can explore all of the effects via trajectory calculations. Trajectory calculations are quite important to reactions. The reader should run some trajectories before proceeding further.

8.16 SUPPLEMENTAL MATERIAL

8.16.1 Derivation of the Angular Momentum Barrier to Reaction

As noted previously, there is an angular momentum barrier to reaction. The purpose of the next several pages will be to derive equation (8.56) for the barrier.

The derivation starts by looking at the classical equations of motion of A and B during a collision between A and B.

$$m_A \frac{d^2 \mathbf{R}_A}{dt^2} = \vec{F}_A = -\nabla_A V(\mathbf{R}_A, \mathbf{R}_B) \quad (8.80)$$

$$m_B \frac{d^2 \mathbf{R}_B}{dt^2} = \vec{F}_B = -\nabla_B V(\mathbf{R}_A, \mathbf{R}_B) \quad (8.81)$$

From Newton's second law, the force that A exerts on B must be equal and opposite to the force that B exerts on A:

$$\vec{F}_B = -\vec{F}_A \quad (8.82)$$

It is useful to change coordinates to what is called **center-of-mass coordinates**. Let's define a new vector \vec{X} via

$$\vec{X} = \frac{m_A \mathbf{R}_A + m_B \mathbf{R}_B}{m_A + m_B} \quad (8.83)$$

\vec{X} is the position of the center of mass of A and B. Taking the second derivative of equation (8.83), we obtain

$$\frac{d^2 \vec{X}}{dt^2} = \left(\frac{1}{m_A + m_B} \right) \left(m_A \frac{d^2 \mathbf{R}_A}{dt^2} + m_B \frac{d^2 \mathbf{R}_B}{dt^2} \right) \quad (8.84)$$

Substituting equations (8.80)–(8.82) into equation (8.84) yields

$$\frac{d^2 \vec{X}}{dt^2} = \frac{1}{m_A + m_B} (\vec{F}_A + \vec{F}_B) = 0 \quad (8.85)$$

Therefore, the center of mass of the system moves with a constant velocity throughout the collision. Now, let's develop an expression for R_{AB} , the distance from A to B. The definition of R_{AB} is

$$R_{\text{AB}} = R_B - R_A \quad (8.86)$$

Taking the second derivative of equation (8.86) yields

$$\frac{d^2 R_{\text{AB}}}{dt^2} = \frac{d^2 R_B}{dt^2} - \frac{d^2 R_A}{dt^2} \quad (8.87)$$

Substituting (8.80) and (8.81) into equation (8.87) yields

$$\frac{d^2 \mathbf{r}_{AB}}{dt^2} = \frac{1}{m_B} \mathbf{F}_B - \frac{1}{m_A} \mathbf{F}_A \quad (8.88)$$

but $\mathbf{F}_A = -\mathbf{F}_B$. Therefore

$$\frac{d^2 \mathbf{r}_{AB}}{dt^2} = \left(\frac{1}{m_A} + \frac{1}{m_B} \right) \mathbf{F}_B = \frac{1}{\mu_{AB}} \mathbf{F}_B \quad (8.89)$$

where μ_{AB} is defined by

$$\frac{1}{\mu_{AB}} = \frac{1}{m_B} + \frac{1}{m_A} = \frac{m_A + m_B}{m_A m_B} \quad (8.90)$$

The quantity μ_{AB} is called the **reduced mass** of the system. Rearranging equation (8.89) yields

$$\mu_{AB} \frac{d^2 \mathbf{r}_{AB}}{dt^2} = \mathbf{F}_B \quad (8.91)$$

$$\mathbf{F}_B = -\nabla_B V = - \left(\frac{d}{dX_B}, \frac{d}{dY_B}, \frac{d}{dZ_B} \right) V \quad (8.92)$$

but

$$\mathbf{r}_{AB} = \mathbf{r}_B - \mathbf{r}_A \quad (8.93)$$

$$\mathbf{F}_B = - \left(\frac{d}{dX_{AB}}, \frac{d}{dY_{AB}}, \frac{d}{dZ_{AB}} \right) V \quad (8.94)$$

where X_{AB} , Y_{AB} , and Z_{AB} are the x , y , and z coordinates of \mathbf{r}_{AB} .

It is useful to convert equation (8.91) to spherical coordinates; \mathbf{r}_{AB} , θ_{AB} , and ϕ_{AB} , where \mathbf{r}_{AB} , θ_{AB} and ϕ_{AB} are related to X_{AB} , Y_{AB} , and Z_{AB} , respectively, the X , Y , and Z components of \mathbf{r}_{AB} , by

$$\begin{aligned} X_{AB} &= r_{AB} \cos \theta_{AB} \\ Y_{AB} &= r_{AB} \sin \theta_{AB} \cos \phi_{AB} \\ Z_{AB} &= r_{AB} \sin \theta_{AB} \sin \phi_{AB} \end{aligned} \quad (8.95)$$

For the moment, we will consider only $\phi_{AB} = 0$.

Let's define L_{AB} as the angular momentum of the AB pair by

$$L_{AB} = \mu_{AB} \mathbf{v}_{A \rightarrow B} \mathbf{r}_{AB} = \mu_{AB} \left(\frac{d\mathbf{r}_{AB}}{dt} \right) \mathbf{r}_{AB} \quad (8.96)$$

where $\mathbf{v}_{A \rightarrow B}$ is the instantaneous velocity of A toward B. Next, let's demonstrate that angular momentum is conserved during the collision. When $\phi_{AB} = 0$, it follows that

$$\theta_{AB} = \arctan \left(\frac{X_{AB}}{Y_{AB}} \right) \quad (8.97)$$

$$\begin{aligned} \frac{d\theta_{AB}}{dt} &= \left(\frac{1}{1 + \left(\frac{Y_{AB}^2}{X_{AB}^2} \right)} \right) \frac{d}{dt} \left(\frac{Y_{AB}}{X_{AB}} \right) \\ &= \left(\frac{1}{1 + Y_{AB}^2/X_{AB}^2} \right) \left(\frac{1}{X_{AB}} \frac{\partial Y_{AB}}{\partial t} - \frac{Y_{AB}}{X_{AB}^2} \frac{\partial X_{AB}}{\partial t} \right) \end{aligned} \quad (8.98)$$

Multiplying the top and bottom of equation (8.98) by X_{AB}^2 yields

$$\frac{d\theta_{AB}}{dt} = \frac{X_{AB} \frac{dY_{AB}}{dt} - Y_{AB} \frac{dX_{AB}}{dt}}{X_{AB}^2 + Y_{AB}^2} = \frac{X_{AB} dY_{AB}}{r_{AB}^2} - \frac{Y_{AB} dX_{AB}}{r_{AB}^2} \quad (8.99)$$

Now consider:

$$\frac{dL_{AB}}{dt} = \frac{d}{dt} \left(\frac{\mu_{AB} r_{AB}^2 \partial \theta_{AB}}{\partial t} \right) \quad (8.100)$$

Substituting equation (8.99) into equation (8.100) yields

$$\frac{dL_{AB}}{dt} = \frac{d}{dt} \left(\mu_{AB} \left(X_{AB} \frac{dY_{AB}}{dt} - Y_{AB} \frac{dX_{AB}}{dt} \right) \right) \quad (8.101)$$

Performing the algebra, we obtain

$$\frac{dL_{AB}}{dt} = \mu_{AB} \frac{dX_{AB}}{dt} \frac{dY_{AB}}{dt} + \mu_{AB} X_{AB} \frac{d^2 Y_{AB}}{dt^2} - \mu_{AB} \frac{dX_{AB}}{dt} \frac{dY_{AB}}{dt} - \mu_{AB} Y_{AB} \frac{d^2 X_{AB}}{dt^2} \quad (8.102)$$

where the first and third terms cancel. Therefore

$$\frac{dL_{AB}}{dt} = \mu_{AB} X_{AB} \frac{d^2 Y_{AB}}{dt^2} - \mu_{AB} Y_{AB} \frac{d^2 X_{AB}}{dt^2} \quad (8.103)$$

One can use equations (8.92) and (8.94) to show

$$\mu_{AB} \frac{d^2 X_{AB}}{dt^2} = \cos \theta_{AB} \frac{\partial V(\mathbf{r}_{AB})}{\partial r_{AB}} = - \frac{X_{AB}}{r_{AB}} \frac{\partial V(\mathbf{r}_{AB})}{\partial r_{AB}} \quad (8.104)$$

$$\mu_{AB} \frac{d^2 Y_{AB}}{dt^2} = \sin \theta_{AB} \frac{\partial V(\mathbf{r}_{AB})}{\partial r_{AB}} = - \frac{Y_{AB}}{r_{AB}} \frac{\partial V(\mathbf{r}_{AB})}{\partial r_{AB}} \quad (8.105)$$

Substituting equations (8.104) and (8.105) into equation (8.103) yields

$$\frac{dL_{AB}}{dt} = X_{AB} \left(- \frac{Y_{AB}}{r_{AB}} \frac{\partial V(\mathbf{r}_{AB})}{\partial r_{AB}} \right) - Y_{AB} \left(- \frac{X_{AB}}{r_{AB}} \frac{\partial V(\mathbf{r}_{AB})}{\partial r_{AB}} \right) \quad (8.106)$$

Note that all of the terms on the right of equation (8.106) cancel. Therefore

$$\frac{dL_{AB}}{dt} = 0 \quad (8.107)$$

Equation (8.106) is a key result because it shows that angular momentum is a conserved quantity. Next, we will show that the energy of the system, E_{AB} , is a conserved quantity where the energy is given by

$$E_{AB} = \frac{1}{2}\mu_{AB}v_{A \rightarrow B}^2 + V(\mathbf{R}_{AB}) \quad (8.108)$$

where $v_{A \rightarrow B}$ is the instantaneous velocity of A toward B and $V(\mathbf{R}_{AB})$ is the A-B potential. Note

$$(v_{A \rightarrow BC})^2 = \left(\frac{dX_{AB}}{dt}\right)^2 + \left(\frac{dY_{AB}}{dt}\right)^2 \quad (8.109)$$

Combining equations (8.108) and (8.109) yields

$$E_{AB} = \frac{1}{2}\mu_{AB} \left[\left(\frac{dX_{AB}}{dt}\right)^2 + \left(\frac{dY_{AB}}{dt}\right)^2 \right] + V(\mathbf{R}_{AB}) \quad (8.110)$$

Now consider the quantity $\frac{dE_{AB}}{dt}$. Differentiating (8.110), we obtain

$$\frac{dE_{AB}}{dt} = 2\mu_{AB} \left[\frac{dX_{AB}}{dt} \left(\frac{d^2X_{AB}}{dt^2}\right) + \frac{dY_{AB}}{dt} \left(\frac{d^2Y_{AB}}{dt^2}\right) \right] + \frac{dv(\mathbf{R}_{AB})}{d\mathbf{R}_{AB}} \frac{d\mathbf{R}_{AB}}{dt} \quad (8.111)$$

Note

$$R_{AB} = \sqrt{X_{AB}^2 + Y_{AB}^2} \quad (8.112)$$

Therefore

$$\frac{dR_{AB}}{dt} = \frac{1}{\sqrt{X_{AB}^2 + Y_{AB}^2}} \left(X_{AB} \frac{dX_{AB}}{dt} + Y_{AB} \frac{dY_{AB}}{dt} \right) \quad (8.113)$$

Substituting equation (8.112) into the first term in (8.113) and rearranging yields

$$\frac{dR_{AB}}{dt} = \left[\frac{X_{AB}}{R_{AB}} \left(\frac{dX_{AB}}{dt}\right) + \frac{Y_{AB}}{R_{AB}} \left(\frac{dY_{AB}}{dt}\right) \right] \quad (8.114)$$

Substituting (8.114) into (8.111) yields

$$\begin{aligned} \frac{dE_{AB}}{dt} = & \mu_{AB} \left[\left(\frac{dX_{AB}}{dt}\right) \left(\frac{d^2X_{AB}}{dt^2}\right) + \left(\frac{dY_{AB}}{dt}\right) \left(\frac{d^2Y_{AB}}{dt^2}\right) \right] \\ & + \frac{dV(\mathbf{R}_{AB})}{d\mathbf{R}_{AB}} \left[\frac{X_{AB}}{R_{AB}} \left(\frac{dX_{AB}}{dt}\right) + \frac{Y_{AB}}{R_{AB}} \left(\frac{dY_{AB}}{dt}\right) \right] \end{aligned} \quad (8.115)$$

Rearranging equation (8.115) yields

$$\begin{aligned} \frac{dE_{AB}}{dt} = & \left(\frac{dX_{AB}}{dt}\right) \left[\mu_{AB} \left(\frac{d^2X_{AB}}{dt^2}\right) + \frac{X_{AB}}{R_{AB}} \frac{dV(\mathbf{R}_{AB})}{d\mathbf{R}_{AB}} \right] \\ & + \left(\frac{dY_{AB}}{dt}\right) \left[\mu_{AB} \left(\frac{d^2Y_{AB}}{dt^2}\right) + \frac{Y_{AB}}{R_{AB}} \frac{dV(\mathbf{R}_{AB})}{d\mathbf{R}_{AB}} \right] \end{aligned} \quad (8.116)$$

But according to equations (8.104) and (8.105)

$$\mu_{AB} \frac{dX_{AB}}{dt} + \frac{X_{AB}}{R_{AB}} \frac{dV(\mathbf{R}_{AB})}{d\mathbf{R}_{AB}} = 0 \quad (8.117)$$

$$\mu_{AB} \frac{dY_{AB}}{dt} + \frac{Y_{AB}}{R_{AB}} \frac{dV(\mathbf{R}_{AB})}{d\mathbf{R}_{AB}} = 0 \quad (8.118)$$

Therefore

$$\frac{dE_{AB}}{dt} = 0 \quad (8.119)$$

E_{AB} is a conserved quantity!

Next, we want to use conservation of energy to derive an equation for the angular momentum barrier for reaction. Equation (8.108) can be rewritten as

$$E_{AB} = \frac{1}{2}\mu_{AB}(v_{\parallel}^2 + v_{\perp}^2) + V(\mathbf{R}_{AB}) \quad (8.120)$$

where v_{\parallel} and v_{\perp} are the two components of the molecule's velocity as defined in Figure 8.27. Next, it is useful to derive an expression for v_{\perp} during the A-B collision. v_{\perp} provides angular momentum to the A-B pair, so let's start by calculating the angular momentum of the system. Consider the situation long before a collision occurs. Atom A is moving toward atom B with a velocity, v_0 . Combining equations (8.95) and (8.98) shows

$$L_{AB}^0 = \mu_{AB}R_{AB}^2 \left(\frac{d\theta}{dt}\right) = X_{AB} \left(\frac{dY_{AB}}{dt}\right) - Y_{AB} \left(\frac{dX_{AB}}{dt}\right) \quad (8.121)$$

where L_{AB}^0 is the initial value of L_{AB} . Initially

$$Y_{AB} = b, \quad \frac{dY_{AB}}{dt} = 0, \quad \frac{dX_{AB}}{dt} = v_0 \quad (8.122)$$

where v_0 is the velocity of A toward B at the beginning of the reaction [i.e., when R_{AB} is large so that $V(\mathbf{R}_{AB}) = 0$]. Substituting equation (8.122) into equation (8.121) shows

$$L_{AB}^0 = -b\mu_{AB}v_0 \quad (8.123)$$

Note that angular momentum is a conserved quantity. Therefore, L_{AB} is the value of the angular momentum at any point during the A-B collision must equal the initial value:

$$L_{AB} = L_{AB}^0 - b\mu_{AB}v_0 \quad (8.124)$$

For future reference, it is useful to note that when R_{AB} is large so that $V(\mathbf{R}_{AB})$ is zero, equation (8.120) becomes

$$E_{AB} = \frac{1}{2}\mu_{AB}v_0^2 \quad (8.125)$$

Next, it is useful to derive an expression for v_{\perp} in terms of the angular momentum for the collision.

$$v_{\perp} = R_{AB} \frac{d\theta}{dt} \quad (8.126)$$

Substituting equation (8.96) into equation (8.126) yields

$$v_{\perp} = \frac{L_{AB}}{R_{AB}\mu} \tag{8.127}$$

Substituting equations (8.124) and (8.127) into equation (8.120) shows

$$E = \frac{1}{2}\mu_{AB} \left(\frac{dR_{AB}}{dt} \right)^2 + \frac{L_{AB}^2}{2\mu_{AB}R_{AB}^2} + V(R_{AB}) \tag{8.128}$$

Substituting equations (8.123) and (8.125) into equation (8.128) yields

$$E = \frac{1}{2}\mu_{AB} \left(\frac{dR_{AB}}{dt} \right)^2 + \left[\frac{E_{AB}b^2}{R_{AB}^2} + V(R_{AB}) \right] \tag{8.129}$$

It is useful to define an effective potential, V_{eff} , by

$$V_{\text{eff}}(R_{AB}) = \frac{E_{AB}b^2}{R_{AB}^2} + V(R_{AB}) \tag{8.130}$$

Substituting (8.130) into equation (8.129) and rearranging yields

$$\frac{dR_{AB}}{dt} = \pm \sqrt{\frac{2}{\mu_{AB}}(E - V_{\text{eff}}(R_{AB}))} \tag{8.131}$$

Equations 8.130 and 8.131 are the key results cited earlier in the text.

8.16.2 Mass-Weighted Coordinates and the Affine Transformation

In the main body of this chapter, we found that we could represent the behavior of the system as a trajectory on a potential energy surface. If the reactants are confined to a plane, the general equations of motion for the reaction $A + BC \Rightarrow AB + C$ are

$$\frac{d^2R_A}{dt^2} = \frac{1}{m_A}F_A \tag{8.132}$$

$$\frac{d^2R_B}{dt^2} = \frac{1}{m_B}F_B \tag{8.133}$$

$$\frac{d^2R_C}{dt^2} = \frac{1}{m}F_C \tag{8.134}$$

where

$$F_A = -\frac{\partial V(R_{AB}, R_{BC})}{\partial R_A} = +\frac{\partial V(R_{AB}, R_{BC})}{\partial R_{AB}} \tag{8.135}$$

$$F_B = -\frac{\partial V(R_{AB}, R_{BC})}{\partial R_B} = +\frac{\partial V(R_{AB}, R_{BC})}{\partial R_{BC}} - \frac{\partial V(R_{AB}, R_{BC})}{\partial R_{AB}} \tag{8.136}$$

$$F_C = -\frac{\partial V(R_{AB}, R_{BC})}{\partial R_C} = -\frac{\partial V(R_{AB}, R_{BC})}{\partial R_{BC}} \tag{8.137}$$

where we have noted that

$$R_{AB} = R_B - R_A \tag{8.138}$$

$$R_{BC} = R_C - R_B \tag{8.139}$$

If you want to follow the trajectory, you need to see how R_{AB} and R_{BC} evolve in time. Combining equations (8.132)–(8.134) yields

$$\frac{d^2R_{AB}}{dt^2} = \frac{d^2R_B}{dt^2} - \frac{d^2R_A}{dt^2} = \frac{1}{m_B}F_B - \frac{1}{m_A}F_A \tag{8.140}$$

$$\frac{d^2R_{BC}}{dt^2} = \frac{d^2R_C}{dt^2} - \frac{d^2R_B}{dt^2} = \frac{1}{m_C}F_C - \frac{1}{m_B}F_B \tag{8.141}$$

Substituting equations (8.135)–(8.137) into equations (8.140) and (8.141) yields

$$\frac{d^2R_{AB}}{dt^2} = -\left(\frac{1}{m_A} + \frac{1}{m_B} \right) \frac{\partial V(R_{AB}, R_{BC})}{\partial R_{AB}} + \frac{1}{m_B} \frac{\partial V(R_{AB}, R_{BC})}{\partial R_{BC}} \tag{8.142}$$

$$\frac{d^2R_{BC}}{dt^2} = -\left(\frac{1}{m_B} + \frac{1}{m_C} \right) \frac{\partial V(R_{AB}, R_{BC})}{\partial R_{BC}} + \frac{1}{m_B} \frac{\partial V(R_{AB}, R_{BC})}{\partial R_{AB}} \tag{8.143}$$

By comparison, if R_{AB} and R_{BC} followed Newton's equation of motion, you would expect the R_{AB} to follow

$$\frac{d^2R_{AB}}{dt^2} = -\frac{\mu_1}{\mu_1} \frac{\partial V(R_{AB}, R_{BC})}{\partial R_{AB}} \tag{8.144}$$

where μ_1 is a constant.

Therefore, there is an extra term in equations (8.142) and (8.143) that one would not expect from Newton's equation of motion. In actual practice, that is not much of a problem, since people normally integrate equations (8.142) and (8.143) numerically. However, in the literature, people sometimes change the coordinates so that the system follows Newton's equation. So-called **mass-weighted coordinates** are used to eliminate the extra terms in equations (8.142) and (8.143). The mass-weighted coordinates, R_1 and R_2 , are defined by

$$R_1 = R_{AB} + \left[\frac{m_A m_C}{(m_A + m_B)(m_B + m_C)} \right]^{1/2} R_{BC} \tag{8.145}$$

$$R_2 = R_{BC} \left(\frac{m_B(m_A + m_B + m_C)}{(m_A + m_B)(m_B + m_C)} \right)^{1/2} \tag{8.146}$$

Equations (8.145) and (8.146) are called the *affine transformation*. After considerable algebra, one can show that R_1 and R_2 obey

$$\mu_1 \frac{d^2R_1}{dt^2} = -\frac{\partial V(R_{AB}, R_{BC})}{\partial R_1} \tag{8.147}$$

$$\mu_1 \frac{d^2R_2}{dt^2} = -\frac{\partial V(R_{AB}, R_{BC})}{\partial R_2} \tag{8.148}$$

One then plugs into equation (8.58) to calculate a reactive cross section. The process is repeated for thousands of values of $v_{A \rightarrow BC}$ and E_{BC} . One then takes an average using equation (8.59) to calculate a rate. Such calculations are easy to do provided one knows an accurate potential energy surface for the reaction. Generally, the results of the calculations agree quite well with experiment provided the potential energy surface is accurate and tunneling is negligible. As a result, such calculations are reasonably common, although not as common as you might imagine since the computations are quite time-consuming.

8.16.4 The Velocity Distribution in Center at Mass Coordinates

Next, we want to use the results in Section 8.16.1 to derive an expression for the $\bar{v}_{A \rightarrow BC}$, the average velocity of A toward BC.

According to the analysis in Section 6.4.1 and Example 6.B, the average velocity of any molecule is

$$\bar{v}_{A \rightarrow BC} = \frac{\iiint v_{A \rightarrow BC} \exp(-E/k_B T) d\vec{v}_{A \rightarrow BC}}{\iiint \exp(-E/k_B T) d\vec{v}_{A \rightarrow BC}} \quad (8.151)$$

According to equation (8.107), during a collision of A with BC, the total energy is given by

$$E = \frac{1}{2} \mu_{AB} (v_{A \rightarrow BC})^2 + V(R_{ABC}) \quad (8.152)$$

We will consider only the case where R_{ABC} is so large that $V(R_{ABC})$ is negligible. Equation (8.152) then becomes

$$E = \frac{1}{2} \mu_{ABC} (v_{A \rightarrow BC})^2 \quad (8.153)$$

Substituting equation (8.153) into equation (8.154) yields

$$v_{A \rightarrow BC} = \frac{\iiint v_{A \rightarrow BC} \exp(-\frac{1}{2} \mu_{ABC} (v_{A \rightarrow BC})^2) d\vec{v}_{A \rightarrow BC}}{\iiint \exp(-\frac{1}{2} \mu_{ABC} (v_{A \rightarrow BC})^2) d\vec{v}_{A \rightarrow BC}} \quad (8.154)$$

Equation (8.154) is identical to equation (6.106) except that the mass is μ_{AB} . We do the integral in Example 6.B. The results are

$$v_{A \rightarrow BC} = \left(\frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2} \quad (8.155)$$

8.17 SOLVED EXAMPLES

Example 8.A Properties of Potential Energy Surfaces Assume that the potential energy surface for the reaction $D + H_2 \rightarrow HD + H$ is given by

$$\begin{aligned} W(r_1, r_2) = & W(e^{-2a(r_1-r_0)} - 2e^{-a(r_1-r_0)} \\ & + W(e^{-2a(r_2-r_0)} - 2e^{-a(r_2-r_0)}) + \\ & + V_P(e^{-a(r_1+r_2-2r_0)}) + W \end{aligned} \quad (8.A.1)$$

with

$$\frac{1}{\mu_1} = \frac{1}{m_A} + \frac{1}{m_B + m_C} \quad (8.149)$$

Figure 8.32 shows a diagram of the potential energy surface for the reaction $F + H_2 \rightarrow HF + H$ plotted in mass-weighted coordinates. One finds that the coordinate is inclined by an angle θ where

$$\sin \theta = \left[\frac{m_A m_C}{(m_A + m_B)(m_B + m_C)} \right]^{1/2} \quad (8.150)$$

The reaction $F + H_2 \rightarrow HF + H$ has an unusually large tilt because the fluorine is so much heavier than the hydrogens.

The advantage of mass-weighted coordinates is that if you think about the motion of the system as rolling a marble over the potential energy surface, then the marble will follow the correct trajectory in a mass-weighted coordinate for an impact parameter of zero. One still has an effective potential when the impact parameter is nonzero.

8.16.3 MD/MC Calculations of Reaction Rate Constants

One can, in principle, combine Monte Carlo (MC) and molecular dynamics (MD) calculations to estimate rate constants for each type of reaction discussed in the last two sections. The general procedure is to start with an ensemble of reactant molecules, and assume that the internal states of the reactant molecules are in equilibrium before reaction occurs. One then uses a Monte Carlo routine similar to that discussed in Chapter 6 to choose initial conditions for the molecules, while a molecular dynamics routine is used to calculate the reactive cross section. For example, if one were examining the reaction $A + BC \rightarrow AB + C$, one would use the Monte Carlo routine to pick initial values of $v_{A \rightarrow BC}$ and E_{BC} , where $v_{A \rightarrow BC}$ and E_{BC} are as defined at the beginning of Section 8.6. The calculations are easier if one modifies the Monte Carlo routine to pick only those values of $v_{A \rightarrow BC}$ and E_{BC} that meet the constraint that the total energy of the molecules be sufficient to traverse the activation barrier for reaction. One then picks several values of the impact parameter b and integrates equations (8.29)–(8.31) to calculate $P_{A \rightarrow BC}(b)$.

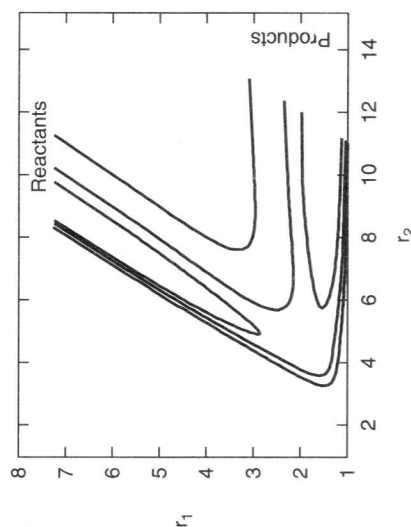


Figure 8.32 A potential energy surface for $F + H_2 \rightarrow HF + H$ in mass-weighted coordinates. After Bender, 1972.

where $V(r_1, r_2)$ is the potential energy surface, r_1 is the H-H distance, r_2 is the H-D distance, $W = 109.4 \text{ kcal/mol}$, $a = 1.95 \text{ \AA}^{-1}$, $t_0 = 0.74 \text{ \AA}$, and $V_P = 258 \text{ kcal/mol}$.

- (a) Use a spreadsheet to calculate values for the potential energy surface for r_1 and r_2 varying between 0.5 and 2 \AA .
- (b) Trace the minimum-energy pathway from reactants to products.

Solution I solved this in Excel. A piece of my spreadsheet is shown in Tables 8.A.1 and 8.A.2. The original spreadsheet is available at <http://www.wiley.com/chemcalc/kinetics>.

First I defined my own functions in Excel using the macro module. The macro module allows you to define your own functions in Excel. You use it by first inserting a module worksheet in Excel, using the Insert-Macro-Module on the Excel menu. You then type in a program in a language called *Visual BASIC*.

Table 8.A.1 shows my module. The first line defined the function V as public (available to the rest of the system) and of type variant (general). I could have also declared it as single (single-precision real number) or double (double-precision real number) as described in Chapter 2. I then defined the function and included an end statement.

I then used the function in my spreadsheet. Table 8.A.2 shows the spreadsheet. I listed r_1 values in cells A4, A5, A6, . . . and r_2 values in cells B3, C3, D3, I named cell B1 = w , cell B2 = vp , cell D1 = a , and cell D2 = r_0 .

I then calculated a matrix of $V(r_1, r_2)$ values, so cell B4 contains $V(r_1, r_2)$ with $r_1 = b\$3$ and $r_2 = \$a4$, cell B5 contains $V(r_1, r_2)$ with $r_1 = B\$3$ and $r_2 = \$A5$, and cell C4 contains $V(r_1, r_2)$ with $r_1 = C\$3$ and $r_2 = \$A4$.

Table 8.A.1 The module used to declare the function V in Excel

Public Function v(r1, r2, r0, a, w, vp) As Variant
$v = w * (\text{Exp}(-2 * a * (r1 - r0)) - 2 * \text{Exp}(-a * (r1 - r0)))$
$v = v + w * (\text{Exp}(-2 * a * (r2 - r0)) - 2 * \text{Exp}(-a * (r2 - r0)))$
$v = v + vp * \text{Exp}(-a * (r1 + r2 - 2 * r0))$
$v = v + w$
End Function

Table 8.A.2 A part of the spreadsheet showing the formulas used to calculate the potential

	A	B	C	D
1	$w =$	109.4	$a =$	1.954
2	$vp =$	258	$r_0 =$	0.74
3	$r_2 \backslash r_1$	0.5	0.6	0.7
4	0.5	$=v(B\$3, \$A4, r_0, a, w, vp)$	$=v(C\$3, \$A4, r_0, a, w, vp)$	$=v(D\$3, \$A4, r_0, a, w, vp)$
5	0.6	$=v(B\$3, \$A5, r_0, a, w, vp)$	$=v(C\$3, \$A5, r_0, a, w, vp)$	$=v(D\$3, \$A5, r_0, a, w, vp)$
6	0.7	$=v(B\$3, \$A6, r_0, a, w, vp)$	$=v(C\$3, \$A6, r_0, a, w, vp)$	$=v(D\$3, \$A6, r_0, a, w, vp)$
7	0.8	$=v(B\$3, \$A7, r_0, a, w, vp)$	$=v(C\$3, \$A7, r_0, a, w, vp)$	$=v(D\$3, \$A7, r_0, a, w, vp)$

Table 8.A.3 Alternate spreadsheet to calculate the potential

	A	B	C	D	E
1	$w =$	109.4	$a =$	1.954	
2	$vp =$	258	$r_0 =$	0.74	
3	$r_2 \backslash r_1$	0.5	0.6	0.7	0.8
4	0.5	$=w * (\text{Exp}(-2 * a * (B\$3 - r_0)) - 2 * \text{Exp}(-a * (B\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A4 - r_0)) - 2 * \text{Exp}(-a * (\$A4 - r_0))) + vp * \text{Exp}(-a * (B\$3 + \$A4 - 2 * r_0)) + w$	$=w * (\text{Exp}(-2 * a * (C\$3 - r_0)) - 2 * \text{Exp}(-a * (C\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A4 - r_0)) - 2 * \text{Exp}(-a * (\$A4 - r_0))) + vp * \text{Exp}(-a * (C\$3 + \$A4 - 2 * r_0)) + w$	$=w * (\text{Exp}(-2 * a * (D\$3 - r_0)) - 2 * \text{Exp}(-a * (D\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A5 - r_0)) - 2 * \text{Exp}(-a * (\$A5 - r_0))) + vp * \text{Exp}(-a * (D\$3 + \$A5 - 2 * r_0)) + w$	$=w * (\text{Exp}(-2 * a * (E\$3 - r_0)) - 2 * \text{Exp}(-a * (E\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A4 - r_0)) - 2 * \text{Exp}(-a * (\$A4 - r_0))) + vp * \text{Exp}(-a * (E\$3 + \$A4 - 2 * r_0)) + w$
6	0.6	$=w * (\text{Exp}(-2 * a * (B\$3 - r_0)) - 2 * \text{Exp}(-a * (B\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A5 - r_0)) - 2 * \text{Exp}(-a * (\$A5 - r_0))) + vp * \text{Exp}(-a * (B\$3 + \$A5 - 2 * r_0)) + w$	$=w * (\text{Exp}(-2 * a * (C\$3 - r_0)) - 2 * \text{Exp}(-a * (C\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A5 - r_0)) - 2 * \text{Exp}(-a * (\$A5 - r_0))) + vp * \text{Exp}(-a * (C\$3 + \$A5 - 2 * r_0)) + w$	$=w * (\text{Exp}(-2 * a * (D\$3 - r_0)) - 2 * \text{Exp}(-a * (D\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A6 - r_0)) - 2 * \text{Exp}(-a * (\$A6 - r_0))) + vp * \text{Exp}(-a * (D\$3 + \$A6 - 2 * r_0)) + w$	$=w * (\text{Exp}(-2 * a * (E\$3 - r_0)) - 2 * \text{Exp}(-a * (E\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A6 - r_0)) - 2 * \text{Exp}(-a * (\$A6 - r_0))) + vp * \text{Exp}(-a * (E\$3 + \$A6 - 2 * r_0)) + w$
7	0.8	$=w * (\text{Exp}(-2 * a * (B\$3 - r_0)) - 2 * \text{Exp}(-a * (B\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A7 - r_0)) - 2 * \text{Exp}(-a * (\$A7 - r_0))) + vp * \text{Exp}(-a * (B\$3 + \$A7 - 2 * r_0)) + w$	$=w * (\text{Exp}(-2 * a * (C\$3 - r_0)) - 2 * \text{Exp}(-a * (C\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A7 - r_0)) - 2 * \text{Exp}(-a * (\$A7 - r_0))) + vp * \text{Exp}(-a * (C\$3 + \$A7 - 2 * r_0)) + w$	$=w * (\text{Exp}(-2 * a * (D\$3 - r_0)) - 2 * \text{Exp}(-a * (D\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A7 - r_0)) - 2 * \text{Exp}(-a * (\$A7 - r_0))) + vp * \text{Exp}(-a * (D\$3 + \$A7 - 2 * r_0)) + w$	$=w * (\text{Exp}(-2 * a * (E\$3 - r_0)) - 2 * \text{Exp}(-a * (E\$3 - r_0))) + w * (\text{Exp}(-2 * a * (\$A7 - r_0)) - 2 * \text{Exp}(-a * (\$A7 - r_0))) + vp * \text{Exp}(-a * (E\$3 + \$A7 - 2 * r_0)) + w$

The word *macro module* does not work with all spreadsheets, so I have also included a spreadsheet with all of the formulas inserted directly. It is Table 8.A.3.

The numerical values in the spreadsheet are presented in Table 8.A.4. The reactants start out with r_2 large, so row 19 is close to the reactants. If we read across row 19, we find that the minimum comes in column E, so cell E19 is close to the reactants.

Similarly, the products have r_1 large, so column Q is close to the products. If we read down column Q, we find that the minimum comes in row 7, so cell Q7 is close to the products.

Next, we need to trace a path from reactants to products. We can take any path we want. However, the lowest energy path goes up then down.

The transition state lies between cells I10 and H11. Notice that the transition state is sort of in a local minimum, because most of the surrounding cells have a higher energy. However, the energy decreases along the shaded I10-H11 diagonal, so the transition state is really a saddle point.

We ask the reader to continue these results in the homework set.

Example 8.B Numerical Integration of Newton's Equations of Motion The objective of this example is to use the algorithms from Example 4.B (numerical integration) to numerically integrate Newton's equations of motion.

Integrate the equations of motion for the hypothetical reaction $A + B \Rightarrow AB$.

Solution Consider two atoms, A and B, that satisfy

$$m_A \frac{d^2 R_A}{dt} = F_{AB} \tag{8.B.1}$$

$$m_B \frac{d^2 R_B}{dt} = -F_{AB} \tag{8.B.2}$$

where R_A and R_B are the positions of A and B, m_A and m_B are the masses of A and B, and F_{AB} is the force on A due to the presence of B. The negative sign in equation (8.B.2) arises because of Newton's second law (where any force is met by an equal and opposite force).

R_A , R_B , and F_{AB} in equations (8.B.1) and (8.B.2) are vectors. However, it is useful to convert them to scalar quantities. Let's define X_A , Y_A , and Z_A , and X_B , Y_B , and Z_B to be the X, Y, and Z coordinates of A and B; v_{XA} , v_{YA} , v_{ZA} , v_{XB} , v_{YB} , and v_{ZB} to be the X, Y, and Z components of the velocity of A and B; and F_X , F_Y , and F_Z to be the X, Y, and Z components of F_{AB} . Then equations (8.B.1) and (8.B.2) become

$$\frac{dX_A}{dt} = v_{XA} \tag{8.B.3}$$

$$\frac{dY_A}{dt} = v_{YA} \tag{8.B.4}$$

$$\frac{dZ_A}{dt} = v_{ZA} \tag{8.B.5}$$

$$m_A \frac{dv_{XA}}{dt} = F_X \tag{8.B.6}$$

$$m_A \frac{dv_{YA}}{dt} = F_Y \tag{8.B.7}$$

$$m_A \frac{dv_{ZA}}{dt} = F_Z \tag{8.B.8}$$

$$\frac{dX_B}{dt} = v_{XB} \tag{8.B.9}$$

$$\frac{dY_B}{dt} = v_{YB} \tag{8.B.10}$$

$$\frac{dZ_B}{dt} = v_{ZB} \tag{8.B.11}$$

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	w=	109a=															
2	v _p =	258r=	0.74														
3	r ₂ \r ₁	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
4	0.5	628.0	482.7	376.4	297.9	239.3	195.2	161.8	136.1	116.2	100.8	88.6	79.0	71.4	65.3	60.4	56.5
5	0.6	482.7	358.2	268.9	204.4	157.4	122.9	97.2	78.0	63.4	52.3	43.7	37.1	31.8	27.7	24.5	21.9
6	0.7	376.4	268.9	193.7	140.8	103.3	76.5	57.3	43.3	33.1	25.6	20.0	15.7	12.5	10.0	8.1	6.6
7	0.8	297.9	204.4	140.8	97.4	67.7	47.4	33.4	23.8	17.2	12.6	9.4	7.1	5.5	4.4	3.6	3.0
8	0.9	239.3	157.4	103.3	67.7	44.4	29.4	19.8	13.8	10.1	7.9	6.1	5.8	5.8	5.9	6.1	6.6
9	1.0	195.2	122.9	76.5	47.4	29.4	18.7	12.7	9.6	8.9	8.3	8.6	9.3	10.2	11.1	11.9	12.7
10	1.1	161.8	97.2	57.3	33.4	19.8	12.7	9.6	8.9	9.7	12.6	15.4	18.3	21.1	23.6	27.8	29.6
11	1.2	136.1	78.0	43.3	23.8	13.8	9.6	8.9	9.7	12.6	16.3	20.2	24.0	27.5	30.7	37.9	45.6
12	1.3	116.2	63.4	33.1	17.2	10.1	8.3	8.9	10.3	12.6	15.4	18.3	21.1	23.6	27.5	30.7	37.9
13	1.4	100.8	52.3	25.6	12.6	7.9	8.1	8.1	11.1	15.4	20.2	25.1	29.6	33.7	37.4	43.5	48.8
14	1.5	88.6	43.7	20.0	9.4	6.7	8.6	8.6	12.9	18.3	24.0	29.6	34.7	39.4	43.5	48.8	52.6
15	1.6	79.0	37.1	15.7	7.1	6.1	9.3	9.3	14.7	21.1	27.5	33.7	39.4	44.4	48.8	52.7	55.9
16	1.7	71.4	31.8	12.5	5.5	5.8	10.2	10.2	16.5	23.6	30.7	37.4	43.5	48.8	53.5	57.6	61.0
17	1.8	65.3	27.7	10.0	4.4	5.8	11.1	11.1	18.2	25.9	33.5	40.6	47.0	52.7	57.6	61.8	65.4
18	1.9	60.4	24.5	8.1	3.6	5.9	11.9	11.9	19.6	27.8	35.9	43.3	50.0	55.9	61.0	65.4	69.2
19	2	56.5	21.9	6.6	3.0	6.1	12.7	12.7	20.9	29.6	37.9	45.6	52.6	58.7	64.0	68.5	72.3

Table 8.A.4 Numerical values in the spreadsheet above

The following computer program does an integration. Shaded lines in the programs are continuation lines.

Therefore, one can calculate the motion of the two atoms by picking initial velocities and positions and numerically integrating equations (8.B.3)–(8.B.14).

We still need to get an expression for the sources. Let's define R_{AB} as the distance from A to B:

$$R_{AB} = \sqrt{(X_A - X_B)^2 + (Y_A - Y_B)^2 + (Z_B - Z_A)^2} \quad (8.B.15)$$

According to equation (8.32):

$$F_X = -\frac{dV_{AB}}{dX_A}$$

where V_{AB} is the A–B potential.

Combining equations (8.B.14) and (8.B.15) yields

$$F_X = \frac{dV_{AB}}{dX_A} = -\frac{dR_{AB}}{dX_A} \frac{dV_{AB}}{dR_{AB}} = \frac{(X_B - X_A) dV_{AB}}{R_{AB} dR_{AB}} \quad (8.B.16)$$

Similarly

$$F_Y = \frac{(Y_B - Y_A) dV_{AB}}{R_{AB} dR_{AB}} \quad (8.B.17)$$

$$F_Z = \frac{(Z_B - Z_A) dV_{AB}}{R_{AB} dR_{AB}} \quad (8.B.18)$$

This gives us a system of equations that can be integrated numerically.

In order to do the numerical integration, one needs to convert the equations slightly.

Let's define

$$W(1) = X_A, W(2) = Y_A, W(3) = Z_A, W(4) = X_B, W(5) = Y_B \quad (8.B.19)$$

$$W(6) = Z_B, W(7) = v_{XA}, W(8) = v_{YZ}, W(9) = v_{ZA}$$

$$W(10) = v_{XB}, W(11) = v_{XB}, W(12) = v_{ZB}$$

The equations of motion become

$$\frac{dW(i)}{dt} = W(i+6) \quad \text{for } i = 1-6 \quad (8.B.20)$$

$$\frac{dW(i)}{dt} = \frac{W(i-3) - W(i-6) dV_{AB}}{R_{AB} m_A dR_{AB}} \quad \text{for } i = 7-9 \quad (8.B.21)$$

$$\frac{dW(i)}{dt} = \frac{W(i-9) - W(i-6) dV_{AB}}{R_{AB} m_A dR_{AB}} \quad \text{for } i = 10-12 \quad (8.B.22)$$

In order to do a numerical integration, you need to also know the Jacobian:

$$dF dW(i, j) = \frac{d}{dW(j)} \left(\frac{dW(i)}{dt} \right) \quad (8.B.23)$$

```

PROGRAM integratemd
C Solve diffegu for MD problem
INTEGER KMAXX, NMAX, NVAR$
PARAMETER (KMAXX=200, NMAX=50, NVARS=12)
INTEGER kmax, kount, nbad, nok, I
REAL dxsav, eps, hstart, time1, time2, w(NVAR$)
COMMON /path/kmax, kount, dxsav, xp(KMAXX), yp(NMAX, KMAXX)
REAL ma, mb
REAL r0, well, range, JAB, rab, QAB
common /potent/r0, well, range, JAB, rAB, QAB

COMMON /masses/ma, mb
EXTERNAL stiff, derivs, rkqs
ma=1.
mb=35.
kmax=0
hstart=1.e-3
eps=1.e-6
r0=2.
well=5.
range=1
time2=0.
C
w(1)=-10
w(2)=0.
w(3)=0.
w(4)=0.
w(5)=0
w(6)=0.
w(7)=1.0
w(8)=0.
w(9)=0.
w(10)=0.
w(11)=0.
w(12)=0.
C next open data file and write out initial
conditions
open(unit=4, file= 'traject.txt',
action= 'write', status= 'replace')
write(4, 100) vab, time2, (w(i), i=1, 12)
write(6, 100) vab, time2, w(1), w(7)
C next start solving the equation

```

```

do while ((time2.lt. (20.))
1 .and. (w(1).gt.(-10.1))
2 .and. (w(1).lt.(10.1)))
time1=time2
time2=time1+0.1
C
C odeint integrates the rate equation from
ctime1 to time2
C
call odeint(w,NVARS,time1,time2,
eps,hstart,0,nok,nbad,derivs,
rkqs)
100 format(1x,f5.2,12( ,2x,f7.3))
write(4,100)time2, (w(i),i=1,12)
write(6,100)time2,w(1),w(7)
10 end do
write(*, (/1x,a,t30,i3) )
Successful steps: ,nok
write(*, (1x,a,t30,i3) ) Bad steps: ,nbad
999 write(*,*) NORMAL COMPLETION
STOP
END

```

```

SUBROUTINE derivs(time,w,f)
C
C subroutine to calculate the
C derivatives
C
REAL time,w(12),f(12)
REAL ma,mb
integer I
REAL r0, well, range,JAB, rab,QAB
common /potent/r0, well, range, JAB,
rAB,QAB
COMMON /masses/ma,mb
C Assume a morse potential, i.e.
C VAB= well*(exp(-2.*(rAB-r0)/range)
C 1 -2*exp(-(rAB-r0)/range))
rAB=sqrt((w(1)-w(4))**2+
(w(2)-w(5))**2+
(w(3)-w(6))**2)
QAB= 2*well/range*(exp(-(rAB-
r0)/range)
-exp(-2*(rAB-r0)/range))/rab
do 10 i=1,6
f(i)=w(i+6)
10 enddo
do 20 i=7,9
f(i)= QAB*(w(i-3)-w(i-6))/ma

```

```

90 enddo
do 30 i=10,12
f(i)= QAB*(w(i-9)-w(i-6))/mb
90 continue
return
END
SUBROUTINE jacobn(time,w,dfdt,dfdw,n,nmax)
INTEGER n,nmax,I
REAL time,w(*),dfdt(*),dfdw(nmax,nmax)
REAL r0, well, range,JAB, rab,QAB
common /potent/r0, well, range, JAB,
rAB,QAB
do 15 i=1,n
dfdt(i)=0.
do 11 j=1,n
dfdw(i,j)=0.0
11 enddo
15 enddo
rAB=( w(1)-w(4))**2 + (w(2)-w(5))**2 +
(w(3)-w(6))**2)
rAB=sqrt(rab)
QAB= 2.*well/range*(exp(-(rAB-r0)/range)
-exp(-2*(rAB-r0)/range))/rAB
JAB= 2.*well/range/range*(
-exp(-(rAB-r0)/range)
+2.*exp(-2*(rAB-r0)/range)
/rAB/rAB-QAB/Rab)
20 do i=1,6
dfdw(i,i+6)=1.
20 enddo
do 30 i=7,9
do 29 j=1,3
dfdw(i,j)= JAB*(w(i-3)-w(i-6))/ma
*(w(j)-w(j+3))
dfdw(i,j+3)= JAB*(w(i-3)-w(i-6))/ma
*(w(j+3)-w(j))
29 enddo
dfdw(i,i-3)=dfdw(i,i-3)+QAB/ma
dfdw(i,i-6)=dfdw(i,i-6) -QAB/ma
30 enddo
do 40 i=10,12
do 39 j=1,3
dfdw(i,j)= JAB*(w(i-9)-w(i-6))/ma
*(w(j)-w(j+3))
dfdw(i,j+3)= JAB*(w(i-9)-w(i-6))/ma
*(w(j+3)-w(j))
39 enddo
dfdw(i,i-9)=dfdw(i,i-9)+QAB/mb
dfdw(i,i-6)=dfdw(i,i-6) -QAB/mb
40 enddo
return
END

```


Example 8.C Numerical Integration of Equation (8.135). The advantage of the computer program is that it is easily generalized to three dimensions. However, a simpler result can be obtained by integrating equations (8.134) and (8.135). The following program uses the IMSL Runge-Kutta routine to do that. There is some subtlety in the program since equation (8.135) has two roots, and you can get stuck when the velocity equals zero. However, the following equation takes care of those subtleties.

```

PROGRAM radialinte
C Solve diffegu for MD problem
  USE numerical_libraries
  INTEGER NVAR5
  PARAMETER (NVAR5=1)
  INTEGER i,ido
  REAL time1,time2,w(NVAR5)
  Real parm(50)
  REAL ma,mb,mu
  Logical flag
  REAL r0, well, range,E,b
  common /potent/r0, well, range, E, flag, b
  COMMON /masses/ma,mb,mu
  EXTERNAL derivs
  ma=1.
  mb=35.
  mu=1./(1/ma+1/mb)
  parm(1)=1.e-3
  eps=1.e-6
  r0=2.
  well=5.
  range=1
  IDO=1
  flag=.false.
  b=0.
C The k's re the rate constants
  time2=0.
  w(1)=10
  E=0.5*mu*(1.**2)
c next open data file and write out initial conditions
open(unit=4,file='traject.txt',action='write',
  ,status='replace')
  write(4,100)time2, w(1)
  write(6,100)time2,w(1)
c next start solving the equation
do while ((time2.lt. (20.))
  1 .and. (w(1).gt.(-10.1))
  2 .and. (w(1).lt.(10.1)))
  time1=time2
  time2=time1+0.1
C
c IVPK integrates the rate equation
C
  CALL IVPK (IDO, NVAR5, derivs,
  time1,time2,EPS,PARAM,w)

```

```

100 format(1x,f5.2,12(
write(4,100)time2, w(1)
write(6,100)time2,w(1)
10 end do
999 write(*,*) NORMAL COMPLETION
STOP
END
subroutine derivs (N,t,w,wprime)
integer N
logical flag
real t,w(*),wprime(*),Veff,VAB,rAB
REAL ma,mb,mu
REAL r0, well, range,E,b,Eeff
common /potent/r0,well,range,E,flag,b
COMMON /masses/ma,mb,mu
rAB=w(1)
VAB= well*(
  exp(-2.*(rAB-r0)/range)
-2*exp(-(rAB-r0)/range))
Veff=VAB+E*b*b/rAB/rAB
Eeff= E-Veff
if(Eeff.gt.0)then
wprime(1)= -sqrt(2*mu*Eeff)
if(flag)wprime(1) =-wprime(1)
else
wprime(1)= 10.
endif
if(abs(wprime(1)).lt.0.01) flag=.true.
return
end

```

Example 8.D Calculating the Rate Constant Using Equation (8.60) Figure 8.17 shows some data for the cross section for the reaction $H + H_2 \rightarrow H_2 + H$ as a function of E_T , the translational energy of H approaching H_2 . The energy is measured in center-of-mass coordinates as described in Section 8.9.

Assume that the cross section follows:

$$\sigma_{A \rightarrow BC}^r = \begin{cases} 0 & \text{For } E_T \leq 0.35 \text{ eV} \\ 12 \text{ \AA}^2 \left(\frac{1 - e^{0.35 \text{ eV} - E_T}}{5.08 \text{ eV}} \right) \times e^{-E_T/2 \text{ eV}} & \text{For } E_T \geq 0.35 \text{ eV} \end{cases} \quad (8.D.1)$$

where E_T is the translational energy. Calculate the rate constant for the reaction at 300 K.

Solution

According to equation (8.60), if there is no E_{BC} dependence, then

$$k_{A \rightarrow BC} = \int_0^{\infty} v_{A \rightarrow BC} \sigma_{A \rightarrow BC}^r D(v_{A \rightarrow BC}) dv_{A \rightarrow BC} \quad (8.D.2)$$

According to results in Example 6.D:

$$D(v_{A \rightarrow BC}) = \frac{(v_{A \rightarrow BC})^2 \exp\left(-\frac{\mu_{ABC}}{2k_B T} (v_{A \rightarrow BC})^2\right)}{\int_0^\infty (v_{A \rightarrow BC})^2 \exp\left(-\frac{\mu_{ABC}}{2} (v_{A \rightarrow BC})^2\right)} \quad (8.D.3)$$

where μ_{ABC} is the reduced mass of ABC, k_B is Boltzmann's constant, and T is the temperature. Looking up the integral in the CRC yields

$$D(v_{A \rightarrow BC}) = \frac{4}{\sqrt{\pi}} \left(\frac{\mu_{ABC}}{2k_B T}\right)^{3/2} (v_{A \rightarrow BC})^2 \exp\left(-\frac{\mu_{ABC}}{2k_B T} (v_{A \rightarrow BC})^2\right) \quad (8.D.4)$$

Combining equations (8.D.2) and (8.D.4) and substituting $E_T = \frac{1}{2}\mu_{ABC}(v_{A \rightarrow BC})^2$ yields

$$k_{A \rightarrow BC} = \sqrt{\frac{8k_B T}{\pi\mu_{AB}}} \int_0^\infty \left(\frac{E_T}{k_B T}\right) \sigma_{A \rightarrow BC}^T e^{-E_T/k_B T} d\left(\frac{E_T}{k_B T}\right) \quad (8.D.5)$$

Note

$$\sqrt{\frac{8k_B T}{\pi\mu_{AB}}} = \bar{v}_{A \rightarrow BC} \quad (8.D.6)$$

Therefore

$$k_{A \rightarrow BC} = \bar{v}_{A \rightarrow BC} \int_0^\infty \left(\frac{E_T}{k_B T}\right) \sigma_{A \rightarrow BC}^T e^{-E_T/k_B T} d\left(\frac{E_T}{k_B T}\right) \quad (8.D.7)$$

For future reference, it is useful to define an average cross section, $I_{A \rightarrow BC}$, by

$$I_{A \rightarrow BC} = \int_0^\infty \left(\frac{E_T}{k_B T}\right) \sigma_{A \rightarrow BC}^T e^{-E_T/k_B T} d\left(\frac{E_T}{k_B T}\right) \quad (8.D.8)$$

Equation (8.D.7) then becomes

$$k_{A \rightarrow BC} = \bar{v}_{A \rightarrow BC} I_{A \rightarrow BC} \quad (8.D.9)$$

Let's define a new variable, W , by

$$W = \frac{E_T - 0.35 \text{ eV}}{k_B T} \quad (8.D.10)$$

Substituting equation (8.D.5) into equation (8.D.4) yields

$$k_{A \rightarrow BC} = \bar{v}_{A \rightarrow BC} e^{-0.35 \text{ eV}/k_B T} \times \int_{-0.35 \text{ eV}/k_B T}^\infty \left(\frac{Wk_B T + 0.35 \text{ eV}}{k_B T}\right) \sigma_{A \rightarrow BC}^T e^{(-W)} dW \quad (8.D.11)$$

For future reference, it is useful to note

$$k_B T = 0.6 \text{ kcal/mol} = 0.026 \text{ eV/molecule} \quad (8.D.12)$$

$$\frac{1}{\mu_{ABC}} = \frac{1}{2 \text{ amu/mol}} + \frac{1}{1 \text{ amu/mol}} = \frac{1.5}{1 \text{ amu}} \quad (8.D.13)$$

According to equation (7.29)

$$\begin{aligned} \bar{v}_{A \rightarrow BC} &= (2.52 \times 10^{13} \text{ \AA/second}) \left(\frac{T}{300 \text{ K}}\right)^{1/2} \left(\frac{1 \text{ amu}}{\mu}\right)^{1/2} \\ &= (2.52 \times 10^{13} \text{ \AA/second}) \left(\frac{300 \text{ K}}{300 \text{ K}}\right)^{1/2} \left(\frac{1 \text{ amu}}{1 \text{ amu}/1.5}\right)^{1/2} \\ &= 3.08 \times 10^{13} \text{ \AA/second} \end{aligned} \quad (8.D.14)$$

Substituting equation (8.D.9) into (8.D.7) and adding the appropriate conversion factors yields

$$k_{A \rightarrow BC} = (2.94 \times 10^{13} \text{ \AA/second}) e^{-0.35 \text{ eV}/k_B T} \times \int_{-0.35 \text{ eV}/k_B T}^\infty \left(\frac{W + 0.35 \text{ eV}}{k_B T}\right) \sigma_{A \rightarrow BC}^T \exp(-W) dW \quad (8.D.15)$$

Note: $\sigma = 0$ for $E_T < 0.35 \text{ eV}$. Therefore

$$k_{A \rightarrow BC} = \frac{2.94 \times 10^{13} \text{ \AA}}{\text{molecule-second}} e^{-0.35 \text{ eV}/k_B T} \times \int_0^\infty (W + 0.35 \text{ eV}/k_B T) \sigma_{A \rightarrow BC}^T e^{(-W)} dW \quad (8.D.16)$$

Let's define $I_{A \rightarrow BC}$ and $F(W)$ by

$$I_{A \rightarrow BC} = \int_0^\infty \left(\frac{W + 0.35 \text{ eV}}{k_B T}\right) \sigma_{A \rightarrow BC}^T e^{(-W)} dW \quad (8.D.17)$$

$$F(W) = \left(\frac{W + 0.35 \text{ eV}}{k_B T}\right) \sigma_{A \rightarrow BC}^T \quad (8.D.18)$$

Combining equations (8.D.15) and (8.D.16) yields

$$I_{A \rightarrow BC} = \int_0^\infty F(W) e^{(-W)} dW \quad (8.D.19)$$

One can conveniently integrate equation (8.D.17) using the Laguerre integration formula:

$$\int_0^\infty F(W)e^{-W} dW = \sum_i B_i F(W_i) \quad (8.D.20)$$

where the B_i and W_i values are as given in the following spreadsheet for the calculations:

	A	B	C	D	E	F
02	kbT=	=D2*0.00198 /23.05	T=	300		
03					I=	=SUM (F5:F10)
04	W	Et	S	F(w)	B _i	term in sum
05	0.22285	=A5*kbT +0.35	=12*(1-EXP((0.35- \$B5)/5.08))* EXP(-\$B5/2)	=B5*\$C5 /kbt	0.458964	=D5*E5
06	1.118893	=A6*kbT +0.35	=12*(1-EXP((0.35- \$B6)/5.08))* EXP(-\$B6/2)	=B6*\$C6 /kbt	0.417	=D6*E6
07	2.99273	=A7*kbT +0.35	=12*(1-EXP((0.35- \$B7)/5.08))* EXP(-\$B7/2)	=B7*\$C7 /kbt	0.113373	=D7*E7
08	5.77514	=A8*kbT +0.35	=12*(1-EXP((0.35- \$B8)/5.08))* EXP(-\$B8/2)	=B8*\$C8 /kbt	0.0103991	=D8*E8
09	9.83747	=A9*kbT +0.35	=12*(1-EXP((0.35- \$B9)/5.08))* EXP(-\$B9/2)	=B9*\$C9 /kbt	0.000261017	=D9*E9
10	15.98287	=A10*kbT +0.35	=12*(1-EXP((0.35- \$B10)/5.08))* EXP(-\$B10/2)	=B10*\$C10 /kbt	8.98547e-7	=D10*E10

Here are the results:

	A	B	C	D	E	F
02	kbT=	0.02577	T=	300		
03					I=	0.747826
04	W	Et	S	F(w)	B _i	term in sum
05	0.22285	0.355743	0.011349	0.156665	0.458964	0.071904
06	1.118893	0.378834	0.056199	0.826153	0.417	0.34506
07	2.99273	0.427123	0.146036	2.420454	0.113373	0.274414
08	5.77514	0.498826	0.26998	5.225937	0.010399	0.054345
09	9.83747	0.603512	0.43199	10.11683	2.61E-04	0.002641
10	15.98287	0.76188	0.6385	18.87694	8.99E-07	1.7E-5

Therefore

$$I_{A \rightarrow BC} = 0.748 \text{ \AA}^2 \quad (8.D.21)$$

$$k_{A \rightarrow BC} = 3.08 \times 10^{13} \frac{\text{\AA}}{\text{second}} \times (0.748 \text{ \AA}^2) e^{-0.35 \text{ eV}/k_B T} \quad (8.D.22)$$

$$k_{A \rightarrow BC} = 2.3 \times 10^{13} \frac{\text{\AA}^3}{\text{molecule-second}} e^{-0.35 \text{ eV}/k_B T} \quad (8.D.23)$$

Notice that the activation barrier is about 0.35 eV (i.e., the minimum energy to get reaction) even though the reaction probability is small below 0.5 eV. It is not exactly 0.35 eV, though. In the problem set, we ask the reader to calculate the rate constant at other temperatures. Both $\bar{v}_{A \rightarrow BC}$ and $I_{A \rightarrow BC}$ are temperature-dependent. If you make an Arrhenius plot of the data, you find that the activation barrier is but close to but not exactly 0.35 eV, even though the reaction probability is negligible at $E = 0.35$ eV.

Example 8.E Calculating the Cross Section A program called ReactMD is available from Dr. Masel's website. Assume that you used the program to calculate the reaction probability as a function of impact parameter, and the data in Table 8.E.1 were obtained. Calculate the cross section for the reaction.

Solution The cross section is given by

$$\sigma = 2\pi \int_0^\infty P(b)b db \quad (8.E.1)$$

We can integrate using the trapezoid rule. Here is a spreadsheet to do the calculations:

	A	B	C
03	b	P(b)	b P(b)
04	0	0.84	=A4*B4
05	0.2	0.83	=A5*B5
06	0.4	0.85	=A6*B6
07	0.6	0.78	=A7*B7
08	0.8	0.8	=A8*B8
09	1	0.75	=A9*B9
10	1.2	0.8	=A10*B10
11	1.4	0.83	=A11*B11
12	1.6	0.72	=A12*B12
13	1.8	0.21	=A13*B13
14	2	0.1	=A14*B14
15	2.2	0	=A15*B15
16			
17		integral=	=0.5*(C4+C15)+SUM(C5 : C14)
18		σ=	=2*PI()*C17

Table 8.E.1 Results from the calculation of reaction probability as a function of impact parameters

$b_{A \rightarrow BC}$, Å	$P(b)$	$b_{A \rightarrow BC}$, Å	$P(b)$
0	0.84	1.2	0.80
0.2	0.83	1.4	0.83
0.4	0.85	1.6	0.72
0.6	0.78	1.8	0.21
0.8	0.80	2.0	0.10
1.0	0.75	2.2	0

Here are the results:

	A	B	C
03	b	$P(b)$	
04	0	0.84	0
05	0.2	0.83	0.166
06	0.4	0.85	0.34
07	0.6	0.78	0.468
08	0.8	0.8	0.64
07	1	0.75	0.75
10	1.2	0.8	0.96
11	1.4	0.83	1.162
12	1.6	0.72	1.152
13	1.8	0.21	0.378
14	2	0.1	0.2
15	2.2	0	0
16			
17		integral=	6.216
18		$\sigma =$	39.05628

Example 8.F Calculation of the Cross Section for a Hard-Sphere Collision.

Assume that you have two molecules colliding as shown in Figure 8.F.1, and assume that the reaction occurs whenever

$$\frac{1}{2} \mu_{AB} (v_{\perp})^2 < E^{\ddagger} \tag{8.F.1}$$

Derive an expression for the cross section.

Solution From Figure 8.F.1, we obtain

$$v_{\perp} = v_{AB} \sin \theta \tag{8.F.2}$$

where v_{AB} is the velocity of the molecule.

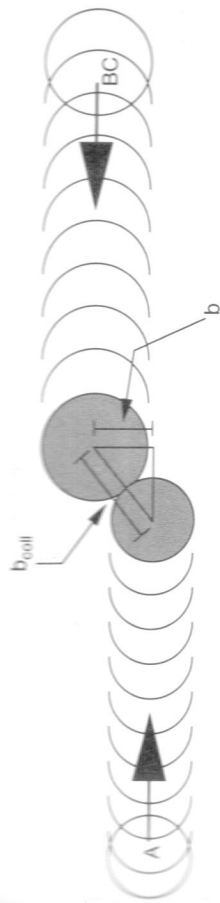


Figure 8.F.1 A hard-sphere collision.

From geometry, we have

$$\sin \theta = \sqrt{1 - \left(\frac{b}{b_{\text{coll}}}\right)^2} \tag{8.F.3}$$

Therefore

$$\frac{1}{2} \mu_{AB} (v_{\perp})^2 = \frac{1}{2} \mu_{AB} (v_{AB})^2 \left[1 - \left(\frac{b}{b_{\text{coll}}}\right)^2\right] = E_T \left[1 - \left(\frac{b}{b_{\text{coll}}}\right)^2\right] \tag{8.F.4}$$

where E_T is the translational energy.

Therefore, reaction occurs whenever

$$E_T \left[1 - \left(\frac{b}{b_{\text{coll}}}\right)^2\right] > E^{\ddagger} \tag{8.F.5}$$

Let us define b_{coll} by

$$E_T \left[1 - \left(\frac{b}{b_{\text{coll}}}\right)^2\right] = E^{\ddagger} \tag{8.F.6}$$

or

$$(b_{\text{coll}})^2 = (b_{\text{coll}})^2 \left(\frac{E_T - E^{\ddagger}}{E_T}\right) \tag{8.F.7}$$

By definition

$$P_{A \rightarrow BC} = \begin{cases} 1 & \text{if } b \leq b_{\text{crit}} \\ 0 & \text{if } b > b_{\text{crit}} \end{cases} \tag{8.F.8}$$

where $P_{A \rightarrow BC}$ is the reaction probability.

From equation (8.59)

$$\sigma_x^{\ddagger} = \pi \int_0^{b_{\text{coll}}} b P_{A \rightarrow BC}(b) db \tag{8.F.9}$$

Combining equations (8.F.8) and (8.F.9) and integrating yields

$$\sigma_x^{\ddagger} = \pi (b_{\text{crit}})^2 \tag{8.F.10}$$

Combining equations (8.F.7) and (8.F.9) yields

$$\sigma_x^i = \begin{cases} \pi(b_{\text{coll}})^2 \left(\frac{E_T - E^\ddagger}{E_T} \right) & \text{for } E_T > E^\ddagger \\ 0 & \text{elsewhere} \end{cases} \quad (8.F.11)$$

Equation (8.F.10) is called the *hard-sphere cross section*.

In the homework set, we ask the reader to show that if one plugs equation (8.F.11) into equation (8.D.7), one obtains

$$k_{A \rightarrow BC} = \pi(b_{\text{coll}})^2 e^{-E^\ddagger/k_B T} \quad (8.F.12)$$

8.18 SUGGESTIONS FOR FURTHER READING

A general discussion of the influence of dynamics on reactions can be found in:

- A. J. Alexander and R. N. Zare, Anatomy of elementary chemical reactions, *J. Chem. Educ.* **76**, 1105 (1998).
 R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford University Press, Oxford, UK, 1987.
 R. Schinke, *Photodissociation Dynamics*, Cambridge University Press, Cambridge, UK, 1993.
 W. H. Miller, Quantum and semiclassical theory of chemical reaction rates, *Faraday Discuss.* **110**, 1 (1998).
 G. C. Schatz, Quantum effects in gas phase bimolecular reactions, In W. Hase, ed., *Advances in Classical Trajectory Methods*, JAI Press, Stamford, 1998, p. 205.
 D. M. Hirst, Potential energy surfaces and Reaction dynamics, Taylor & Francis, London (1985).

8.19 PROBLEMS

8.1 Define the following terms:

- (a) Collision theory
 (b) Molecular dynamics
 (c) Newton's equations of motion
 (d) Impact parameter
 (e) Angle of approach
 (f) Distribution function
 (g) Trajectory
 (h) Cross section
 (i) Bimolecular exchange reaction
 (j) Recombination reaction
 (k) Barrierless reaction
 (l) L-shaped potential surface
 (m) Polanyi rules
 (n) Collision partner
 (o) Reaction collision
 (p) Unreactive collision
 (q) Reduced mass
 (r) Reaction probability
 (s) Classical equations of motion
 (t) Effective potential
 (u) Potential energy surface
 (v) Dispersion force
 (w) Electron exchange and bonding
 (x) Pauli repulsion
 (y) Transition state
 (z) Mass-weighted coordinates
 (aa) Early transition state
 (bb) Middle transition state
 (cc) Late transition state

8.3 Equation (8.25) has a giant integral.

- (a) Why do we need to integrate over all of these variables?
 (b) What does the distribution function do in the equation?

8.3 Explain in your own words why the potential looks the way it does in Figure 8.3. Why is there a well? Why does the potential rise again at short distances?

8.4 Explain in your own words why Figure 8.9 looks the way it does.

- (a) Why is there a well in the F-F and Cl-F potentials?
 (b) Why is there a repulsion at short F-F and Cl-F distances?
 (c) Why is there a barrier to reaction?
 (d) Identify the reactants, products, and transition state on the figure.
 (e) How does the contour plot correspond to the two-dimensional original?

8.5 The objective of this problem is to review some of the results in this chapter.

- (a) Why did we say that the top trajectory in Figure 8.13 lead to reaction while the bottom trajectory did not?
 (b) Which trajectories lead to reaction in Figure 8.15?
 (c) Why were there no reactions in Figure 8.15?
 (d) Which trajectories lead to reaction in Figure 8.16?
 (e) Why did some of the trajectories in Figure 8.16 lead to reaction while others did not?
 (f) Which trajectories lead to reaction in Figure 8.19?
 (g) What is different about the trajectories that lead to reaction in Figure 8.19 and those that do not?
- (h) Repeat (f) and (g) for Figure 8.20.
 (i) Repeat (f) and (g) for Figure 8.21.

8.6 Explain in your own words why Figure 8.18 looks the way it does.

- (a) Why is there negligible reaction when $E_T < 9$ kcal/mol? (Note: $E^\ddagger = 9.3$ kcal/mol.)
 (b) Why does the cross section rise from 10 to 40 kcal/mol?
 (c) Why does the cross section drop again at high energies?
 (d) If you work at a temperature of 500 K, what is the probability that a state at 9 kcal/mol, 12 kcal/mol, 25 kcal/mol, 50 kcal/mol, 200 kcal/mol will be occupied?

8.7 Explain in your own words why the trends summarized in Section 8.8 are observed.

8.8 Explain in your own words why the reaction probability decreases as the impact parameter increases.

8.9 Explain in your own words why unimolecular reactions are impossible in the absence of a collision partner.

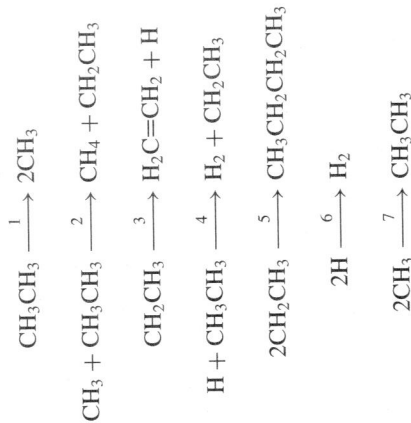
8.10 Explain in your own words

- (a) How the angular momentum barrier to reaction arises? When is it important? How does it affect reaction?

- (b) How the energy transfer barrier to reaction arises? When is it important? How does it affect reactions?
- 8.11 Explain how the energy and angular momentum barriers to reaction could affect the following reactions:



- 8.12 The reaction $\text{CH}_3\text{CH}_3 \Rightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2$ proceeds by the following approximate mechanism:



On the basis of the results in this chapter:

- (a) Which of the reactions need collision partners? If a reaction needs a collision partner, explain what the collision partner will do. If the reaction does not need a collision partner, explain why not.
- (b) How do energy transfer barriers to reaction affect each of the reactions above?
- (c) How do momentum transfer barriers to reaction affect each of the reactions above?

- 8.13 In Section 8.2.1 we noted that the reaction



has an unusually low preexponential [$1.4 \times 10^{10} \text{ \AA}^3/(\text{molecule}\cdot\text{second})$], while the reaction



has a normal preexponential [$7 \times 10^{12} \text{ \AA}^3/(\text{molecule}\cdot\text{second})$].

- (a) Make a diagram of the reactants. Based on the geometry alone, how much larger will the cross section for reaction (P8.13.2) be than for equation (P8.13.1)?

- (b) Now put in the van der Waals radii. How much will the CH_3 groups constrain reaction (P8.13.1)? (*Hint*: Look at the fraction of the solid angle that is blocked).
- (c) Are these effects large enough to explain the supposed factor of 500 difference in rate?
- (d) Do you have any other ideas what could cause the preexponential or equation (P8.13.1)? (*Hint*: Qualitatively, how will rotational motion of the $\text{CH}_3\text{CH}_2\text{CH}_3$ affect the rate of both reactions?)

- 8.14 In Section 8.2 we noted that the reaction



has an unusually large preexponential [$5.8 \times 10^{15} \text{ \AA}^3/(\text{molecule}\cdot\text{second})$].

- (a) Use the preexponential to estimate the average cross section for the reaction, namely, $\sigma_{A \rightarrow BC}$ in equation (8.10).
- (b) How can the cross section be that big? Would the attractive forces between two oxygen atoms be large enough to give this large of a cross section?
- (c) What if a complex formed? Could that account for the results?
- (d) What if the key reaction were:



where O_2^* is an excited O_2 molecule? How large would the O_2 need to be to account for the preexponential? That is, how large of an oxygen–oxygen bond would be needed to account for the preexponential?

- (e) Now consider the reaction
- $$2\text{O} \longrightarrow \text{O}_2 \quad (\text{8.14.2})$$

Assume that the potential follows

$$V_{AB}(R_{AB}) = 119 \text{ kcal/mol} \left[e^{\frac{1.21 \text{ \AA} - R_{AB}}{2.58 \text{ \AA}}} - 1 \right]^2 - 1$$

In Figure 8.28, we found that when b is large there is a barrier to reaction. Calculate the barrier height as a function of b . [*Hint*: Use equation (8.56) to calculate V_{eff} as a function of R_{AB} . Use the solver function on Excel to calculate the barrier in the effective potential.]

- (f) What value of b gives a barrier of $E = 2 \text{ kcal/mol}$ (i.e., $2k_B T$ at 500 K)?
- (g) Assume that all molecules react when b is such that the barrier is less than E and no reaction occurs. Estimate the cross section for reaction (P8.14.2).
- (h) How does the cross section in (g) compare to the value estimated in a)?

- 8.15 How does the computer program in Example 8.B work?

- (a) Show that the program is correctly plotting a trajectory.
- (b) Where are the intermolecular forces calculated?

- (c) Where is the actual integration done?
- (d) Why are there 12 variables with only two atoms?
- (e) What would you need to do to the program to enable it to handle the reaction $A + BC \rightarrow AB + C$?
- (f) What extra equations would you need in (c)?
- (g) What extra forces would you need? Be sure to consider the effects of orbital compression like that in Figure 8.7.

8.16 Describe in your own words the key features in the bottom picture in Figure 8.7. Where are orbitals being compressed? How do the forces arise on the rightmost fluorine atom? How is the fluorine-fluorine bond distorted?

8.17 Refer to Table P8.17. How does the preexponential calculated in Example 8.C compare to that estimated by:

- (a) Collision theory (Chapter 7)
- (b) Transition state theory (assume a linear transition state)

8.18 In Example 8.D, we derived an expression for the rate of the reaction $H + H_2 \rightarrow H_2 + H$. As part of the derivation, we calculated a messy integral. The integral is temperature-dependent.

- (a) Calculate the preexponential and the rate of reaction at 200, 300, 500, 700 and 1000 K. The spreadsheet is available in the instructions materials.
- (b) Make an Arrhenius plot of the reaction rate. How close is the activation barrier to the 0.35 eV expected from equation (8.D.23)?
- (c) How close is the preexponential inferred from your Arrhenius plot to the preexponentials you estimated in (a)?
- (d) Use transition state theory to see how the preexponential should vary with temperature.
- (e) How well does the actual temperature dependence compare to that expected from transition state theory? (*Hint*: Make a log-log plot of the preexponential vs. T. How does your slope compare to what is expected?)

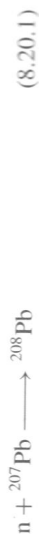
8.19 Assume that the cross section for a reaction follows

$$\sigma_x = \begin{cases} 0 & \text{for } E < E^\ddagger \\ \sigma_0 \left(1 - \frac{E^\ddagger}{E}\right) & \text{for } E \geq E^\ddagger \end{cases}$$

Table P8.17 Data for Problem 8.17

r	H	H ₂	Linear TST
Mass	1 amu	2 amu	3 amu
R _{H-H}	—	0.7417 Å	0.87 Å
Vibrations	—	4395 cm ⁻¹	2012 cm ⁻¹
	—	—	965 cm ⁻¹
E [‡]	—	—	965 cm ⁻¹
	—	—	8.5 kcal/mol

- (a) Assume $\sigma_0 = 1.5 \text{ \AA}^2$ and $E^\ddagger = 13.86 \text{ kcal/mol}$. Numerically integrate equation (8.D.7) to calculate the preexponential rate constant for the reaction to calculate the rate constant at 300 K.
 - (b) Integrate the expression analytically.
 - (c) How does your result compare to collision theory (Section 8.2)?
- We discussed chemical reactions in this chapter, but the concepts are useful for nuclear reactions as well. Consider the reaction



where n is a neutron.

- (a) Assume that you have a nuclear reactor that is producing neutrons with the following energy distribution:

$$D(E) = \left(\frac{E}{E_0}\right)^{1/2} \frac{e^{-E/E_0}}{E_0} \quad (8.20.2)$$

with $E_0 = 1.5 \text{ keV}$. Figure P8.20 shows data for the cross section for the reaction. Estimate the rate constant.

- (b) How thick of a piece of lead will be needed to stop 99.99% of the neutrons? Lead is 22% ²⁰⁷Pb. Assume the other isotopes of lead do not react with neutrons.
- (c) Calculate the conversion of neutrons with an energy of 20 keV. Are they all trapped?
- (d) In actual practice, the neutrons undergo something called “inelastic collisions”, where they give up energy to the lattice. How will the inelastic collisions affect your answer in (c)?

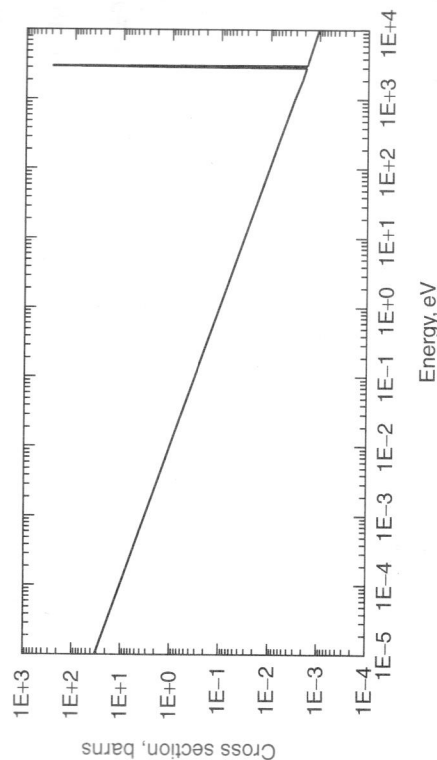


Figure P8.20 The cross section for the reaction $n + {}^{207}\text{Pb} \rightarrow {}^{208}\text{Pb}$ as a function of the energy of the neutron.

(e) Assume that the cross section for the inelastic collisions is 1000 barns independent of energy. How important will the inelastic collisions be in slowing down the 20-keV neutrons so that the neutrons are more easily trapped?

8.21 Salazart et al. (1997) measured the cross section for the reaction:



and the following data in Table P8.21 were obtained.

- (a) Use the procedure in Example 8.D to estimate the activation barrier and preexponential for the reaction at 200, 300, 400, 500, 600, and 700 K.
- (b) How does a plot of the cross section versus energy compare to that in Figure 8.29?
- (c) On the basis of the results, what is the barrier to the reaction?
- (d) Make an Arrhenius plot of the rate constant versus $1/\text{temperature}$ to estimate the activation barrier for the reaction.
- (e) Why didn't the wiggles in the plot of σ versus E affect the activation barrier or preexponential?

8.22 Knott, Proch and Kompa, *J. Chem. Phys.*, **108**, 527 (1998) measured the cross section for the reaction



For energies between 10^{-2} and 5 eV, the cross section followed

$$\sigma = \frac{18.2 \text{ \AA}^2 (\text{eV})^{0.37}}{(E_T)^{0.37}} \quad (\text{P8.22.2})$$

- (a) Make a plot of the cross section versus energy.
- (b) On the basis of these results, what is the barrier to the reaction?
- (c) Use the procedure in Example 8.D to integrate the rate equation to calculate the preexponential and activation energy at 100, 200, 300, 400, and 500 K.
- (d) Why is the preexponential so big?

Table P8.21 The rate of reaction (P8.21.1) estimated from the results of Salazar (1997)

Energy, kJ/mol	σ	Energy kJ/mol	σ	Energy kJ/mol	σ
$E_T < 19.5$	0	23.4	0.50	26.7	0.45
20.5	0.39	23.7	0.47	27.0	0.44
20.7	0.81	24.0	0.48	27.3	0.44
21.0	1.00	24.3	0.50	27.6	0.43
21.3	0.78	24.6	0.50	27.9	0.43
21.6	0.51	24.9	0.48	28.2	0.43
21.9	0.42	25.2	0.47	28.5	0.42
22.2	0.48	25.5	0.46	28.8	0.42
22.5	0.59	25.8	0.46	29.1	0.41
22.8	0.61	26.1	0.46	29.4	0.41
23.1	0.56	26.4	0.45	29.7	0.41

- (e) Are the reactants large enough to account for the large cross section?
- (f) Are there strong enough attractions between the reactants to pull the hydrogen in so that the cross section is huge? (answer yes!)
- (g) Make an Arrhenius plot of the data.
- (h) Why does the Arrhenius plot show a barrier when the reaction is barrierless?

8.23 The program ReactMD is available from Dr. Masel's Website and in the instructions materials. Choose the reaction $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$ and the case "choose random trajectories".

- (a) What does the potential energy surface look like? How does it compare to Figure 8.9?
- (b) Use the print command at the end of the trajectories. Make a plot of the potential energy surface. Identify the reactants, products, and transition state.
- (c) On your plot, label the trajectories that lead to reaction.
- (d) Calculate the reaction probability for the trajectories on your plot.
- (e) Now rerun the cases again, resizing the plots so that you can see the animation and the motion on a potential energy surface side by side. Find a trajectory where C is moving away from B when A hits. What does that trajectory look like on the potential energy surface? What does that trajectory look like on a plot of position versus time?
- (f) Use your results in (e) to explain why we say that "in order for a reaction to happen, C must be moving away from B when A hits."
- (g) Now compare the plots on a simple potential energy surface and on mass-weighted coordinates. How are the trajectories the same or different?

8.24 This problem also uses ReactMD available from Dr. Masel's Website. Choose the reaction $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$ and the case "choose random trajectories".

- (a) Run trajectories, record the energy of the trajectory, and determine whether the trajectory lead to reaction.
- (b) What is the highest energy you used where no reaction happened? What is the lowest energy? Where did you see a reaction?
- (c) How do you rationalize your results given that the barrier is only 13.80 kcal/mol?
- (d) Use your data to calculate the reaction probability versus energy. Divide up the energy scale into 0.5 kcal/mol increments (e.g., 13–13.5 kcal/mol, 13.5–14.0 kcal/mol) and calculate the reaction probability versus energy.
- (e) An additional file, Does it react. TXT, is available from Dr. Masel's Website and in the instructions materials. Repeat your results in (d) using the data in this file.
- (f) The calculations use a one-dimensional potential. Assume that you can convert to three-dimensions using $\sigma_x^3 = 3 \text{ \AA}^2 P_{\text{reaction}}(E_T)$.
- (g) Make a plot of σ_x^3 versus E_T . How does it compare to Figure 8.26?
- (h) Fit your data to Equation 8.D.1.
- (i) Follow the procedure in Example 8.D to calculate the preexponential and activation barrier at 500 K. (Note: You may have to interpolate to estimate a cross section.)

- (d) Repeat (g) for $t > 300, 700, 900,$ and 1100 K. Make an Arrhenius plot of your data. How do the preexponential and the activation barrier estimated from the slope of the plot compare to your result?
- 8.25** This example also uses ReactMD from Dr. Masel's Website. Pick the reaction $A + BC \rightarrow AB + C$.
- Choose the case "vary incident energy, optimize other parameters", and run trajectories. What is the minimum energy that leads to reaction? How does that compare to the barrier height? Plot out your results you will need them later in the problem.
 - Now choose the case "vary incident energy, do not optimize." How do your results differ?
 - Look carefully at the trajectories to see how the reactive trajectories differ from the unreactive trajectories. First determine how much the trajectory vibrates. How much vibrational energy is there in the "optimal" trajectories? How much vibrational energy is there in the trajectories that do not react?
 - Next, look at when the trajectory turns on the potential energy surface. When does the optimal trajectory turn? When do the nonreactive trajectories turn?
 - Relate the turning motion to coordinated motion. Look carefully at the coordinated motion by cascading and resizing the windows so that you can see the animation at the same time that you see the trajectory on the potential energy surface.
- 8.26** This example also uses ReactMD from Dr. Masel's Website. Choose the reaction $A + BC \rightarrow AB + C$ and the case "vary the timing of the collision."
- Run the case and see how the reactive trajectories differ from the unreactive trajectories. Look particularly at when the trajectory turns on the potential energy surface. When do the reactive trajectories turn? When do the unreactive trajectories turn?
 - Now vary the position of the transition state from an early transition state to a late transition state. How do your results change?
 - Repeat (a) and (b) for a late transition state.
- 8.27** This example also uses ReactMD from Dr. Masel's Website. Choose the reaction $A + BC \rightarrow AB + C$ and the case "vary the partitioning between translation and vibration."
- Run the case and look at the trajectories. What happens if you have no vibrational energy? What happens if you have too much vibrational energy and too little translational energy?
 - Now change to an early transition state. How does the answer in (a) change?
 - Now change to a late transition state. How does the answer in (a) change?
 - How do your results compare to the Polanyi rules?
- 8.28** This problem uses ReactMD, available from Dr. Masel's Website, to calculate a rate constant for the reaction $A + BC \rightarrow AB + C$.
- First, in order to learn how to use the "fix the energy vary the initial conditions" option, the program calculates the reaction probability of an energy of 14.0 kcal/mol.
- (b) Now assume that you want to calculate a rate constant following the procedure in Example 8.D. Set up an expression for $I_{A \rightarrow BC}$ following the procedure in Example 8.D. Assume that the cross section is zero for $E < 13.88$ kcal/mol.
- (c) In order to use Laguerre integration, you will need the cross section at a series of energies. Follow the procedure in Example 8.D to calculate those energies. (*Hint*: If you calculated things correctly, the first energy point should be 14.0 kcal/mol.)
- (d) Use ReactMD to calculate the reaction probability at each energy. You will need at least 2000 trajectories of each energy to get an accurate answer.
- (e) An additional file, reactionprob.TXT, is available from Dr. Masel's Website. Repeat your results in (d) using the data in this file.
- (f) Assume $\sigma_A^* = (1 \text{ \AA})^2 \times P_{\text{reaction}}$. Integrate equation (8.D.7) to calculate a rate constant assuming $\bar{v}_{ABC} = 1 \times 10^{13} \text{ \AA} / \text{second}$.
- 8.29** Problems 8.24–8.28 assumed a collision where the reactants were confined to a line. Now consider a nonlinear collision.
- Use the "vary the impact parameter" option in ReactMD to see how the reaction probability varies with impact parameter. What do you find?
 - Look carefully at the animation. How do the nonlinear collisions differ from the linear collisions? Do you see any "weird" trajectories, where the incoming A molecule inserts directly into the B–C bond?
 - What do the "weird" trajectories look like when plotted on a potential energy surface?
 - What does a trajectory with a large-impact parameter look like on a potential energy surface?
 - Can you see evidence that atoms are hitting the angular momentum barrier to reaction? Describe what you see.
 - Now try varying the angle of approach. How do the trajectories change?
- 8.30** The objective of this problem is to use ReactMD to calculate the collisional cross section. The procedure will closely follow Example 8.E. First you will use ReactMD to calculate the reaction probability. Then you will integrate equation 8.E.1 to calculate the cross section.
- Use ReactMD to calculate the reaction probability at several values of b for an energy of 10 kcal/mol.
 - Integrate equation (8.D.4) to calculate the cross section.
 - What would you need to do to calculate a rate constant from these results?
- 8.31** The objective of this problem is to understand how trajectories change as you change properties. Consider the reaction $A + BC \rightarrow AB + C$ confined to a plane.
- Assume that A starts with an impact parameter at 3 \AA , and moves past BC. For the purposes of the problem we will assume

$$X_A = 3 \text{ \AA}$$

$$Y_A = (10^{12} \text{ \AA} / \text{second})t - 10 \text{ \AA}$$

$$X_B = X_C = 0$$

$$Y_B = 1 \text{ \AA} + 0.1 \text{ \AA} \sin 10^{13} / \text{second } t$$

$$Y_C = 1 \text{ \AA} - 0.1 \text{ \AA} \sin 10^{13} / \text{second } t$$

where t = time and $X_A, X_B, X_C, Y_A, Y_B,$ and Y_C are the X and Y positions of $A, B,$ and C .

- (b) Show that these equations satisfy Newton's equations of motion, with $B-C$ a harmonic oscillator. Assume that A does not interact with BC .
- (c) Use a spreadsheet to plot $X_A, Y_A, X_B, Y_B,$ and X_C, Y_C versus time.
- (d) Next, use the spreadsheet to plot R_{AB} versus R_{BC} .
- (e) Why does R_{AB} decrease then increase again given that there is no interaction between A and BC ?
- (f) Why are there all of the wiggles in the trajectories?

More Advanced Problems

- 8.32** The objective of this problem is to use collision theory to make some predictions about film growth. Assume that you are designing an evaporator (see Figure P8.32) to deposit copper. The evaporator works by heating copper in a crucible. The copper sublimates, filling the crucible with copper vapor.
- (a) Use collision theory to estimate how many copper molecules will escape from a 1-cm^2 hole at the top of the crucible. Assume that the copper pressure inside the crucible is 10^{-9} Atm, and the temperature is 1500 K.
- (b) Assume that the copper is being deposited on a 10-inch wafer and that all of the copper that leaves the crucible makes it onto the wafer. How long will it take to deposit a $10\text{-}\mu\text{m}$ thick layer of copper?
- 8.33** Example 8.A used the routine ODEINT to integrate the trajectories. However, ODEINT may not be available at your university. Convert the program so that it can use the IMSL subroutine IVPK. What do the trajectories look like using IPAK?
- 8.34** In the examples in this chapter, we used trajectory calculations to model the reactions of two simple molecules. The objective of this problem is to decide what would change if the molecules are big, such as proteins.

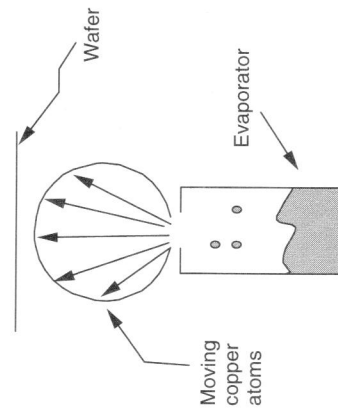


Figure P8.32 A rough diagram of the evaporator.

- (a) How would the equations of motion change? Would the same equations of motion apply?
- (b) How would the forces be different? Would the forces still be determined by path repulsions, or would other forces be important?
- (c) How would the collisions be different? Would molecules just bounce, or would they stick together for a long time? Could you use the same computer codes to simulate the reactions?

8.35

The Materials Processing Simulation Center at Cal Tech (California Institute of Technology, Pasadena) has posted a number of simulations of the changes in the orbital shapes during Diels-Alder reactions. The URL [universal (also uniform) resource locator] address is <http://www.wag.caltech.edu/gallery/gallery-quantum.html>.

- (a) Download the simulations and look at them.
- (b) How do the Orbital distortions compare to those described in this chapter?
- (c) What will the potential energy surface for a Diels-Alder reaction be like?
- (d) What will you use as coordinates for a plot of the potential energy surface?

8.36

Get a copy of the following articles and write a three page description of the findings.

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PRÉCIS

In Chapter 8, we showed how one could calculate reaction rates exactly by keeping track of how molecules move. Often, however, it is too expensive to calculate a reaction rate exactly. Instead, one uses an approximation to estimate the rate of reaction. In this chapter, we will discuss three approximations: transition state theory, the Rice-Ramsperger-Kassel-Marcus (RRKM) model, and phase space theory. We will expand on the findings in Chapter 7 and show how these approximations can be used to estimate preexponentials for reaction to reasonable accuracy.

9.1 ARRHENIUS' MODEL AND TOLMAN'S EQUATION

The subject that we now call reaction rate theory got its start when Arrhenius wrote a series of papers showing how an activation barrier arose in chemical reactions. We presented Arrhenius' original derivation in Section 8.1. However, now it is useful to extend the arguments to the generalized reaction:



In the remainder of this section, we will provide a derivation of Tolman's equation for the rate constant for reaction (9.1):

$$k_{A \rightarrow BC} = \left(\frac{k_B T}{h p} \right) \frac{q^\ddagger}{q_A q_{BC}} \exp \left(- \frac{E^\ddagger}{k_B T} \right) \quad (9.2)$$

where $k_{A \rightarrow BC}$ is the rate constant for reaction (9.1), k_B is Boltzmann's constant, T is the absolute temperature, $h p$ is Planck's constant, q_A is the microcanonical partition function per unit volume of the reactant A, q_{BC} is the microcanonical partition function per unit