

INTRODUCTION TO REACTION RATE THEORY

PRÉCIS

So far in this book, we have been discussing what is called classical kinetics: rate laws for chemical reactions and how those rate laws arise from the mechanism of the reaction. In the next several chapters, we will be changing topics and starting to discuss how reactions happen on a molecular level. Our objective will be to formulate an expression for the rate of reaction in terms of the rates of all of the elementary processes that occur during reaction and the forces on all of the molecules. This is a large topic. There are two parts: predicting the preexponentials and predicting the activation barriers. The object of Chapter 7 is to provide a brief overview of the prediction of preexponentials with collision theory, transition state theory, and the RRKM model so that the reader can get an introduction to the material. Chapters 8–11 will fill in the details.

7.1 INTRODUCTION

In this chapter, we will be discussing what is called *reaction rate theory*. The objective of reaction rate theory is to relate the rate constants for reactions to the properties of the reactants, products, and transient intermediates.

The earliest work on reaction rate theory came from Arrhenius (1889). Arrhenius was interested in why activation barriers arose in chemical reactions. Arrhenius considered a simple reaction:



and 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).

Equation (7.6) is equivalent to

$$k_1 = k_0 e^{-(E_a/k_B T)} \quad (7.7)$$

with

$$k_0 = K_0 e^{(\Delta S^\ddagger/k_B)} \quad (7.8)$$

In equation (7.6), k_1 is the rate constant for a reaction (7.1), 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 temperature.

Equation (7.7) was Arrhenius' key result. At the time this work was done, there were many empirical rules to predict how rates vary with temperature. Arrhenius was the first person to derive a theoretical expression. When the expression was found to fit data, Arrhenius' expression, which was renamed *Arrhenius' law*, was universally adopted in kinetics.

Arrhenius' law was one of the early successes of physical chemistry. It applied to both the behavior of chemical reactions and the growth and reproduction of plants and simple animals as described in Chapter 2. Consequently, Arrhenius' law was an important advance.

7.2 COLLISION THEORY

Arrhenius never was able to provide a model for k_0 in equation (7.8). Fortunately, Trautz (1918) and Lewis (1918) independently proposed the collision theory of reactions. The idea in the original version of collision theory was that molecules need to collide if the molecules are going to react. Figure 7.2 shows a few trajectories that we have calculated using a program from Chapter 8. In the top case, A comes in to hit BC, then A flies away again. According to Trautz and Lewis, this would be an unreactive collision. In the second case, A comes in and hits B-C, and C flies away. That is a reactive collision. Trautz and Lewis proposed that one could calculate the reaction rate by looking at how many collisions occurred and multiplying by a reaction probability that is a function of energy. As a result, one can calculate the reaction rate from the number of times that the hot molecules collide.

Trautz and Lewis then used the kinetic theory of gases to calculate a collision rate. If one assumes that all hot molecules react when they collide, then one can show that the rate of the reaction



$$r_{A-BC} = Z_{ABC} P_{\text{reaction}} \quad (7.10)$$

where Z_{ABC} is the rate of collisions between A and BC in units of molecules/(Å³·second) and P_{reaction} is the probability of reaction once the molecules collide.

Arrhenius noted that there is a distribution of molecular velocities as indicated in Figure 7.1. Most of the molecules are too cold to react. However, there are a few molecules in the tail of the Boltzmann distribution that *can* react.

Arrhenius then derived an equation for the rate of reaction. The derivation assumed that equilibrium was maintained between the reactive and unreactive A molecules. We reproduce the arguments below.

Recall that at equilibrium, the concentration of molecules of A that have the right properties to react, C_A^\ddagger , is related to the overall concentration of the unreactive A molecules by

$$C_A^\ddagger = C_A^u e^{-(\Delta G^\ddagger/k_B T)} \quad (7.2)$$

where C_A^u is the concentration of the unreactive A molecules and ΔG^\ddagger is the free energy change (kJ/molecule) when one converts an unreactive A molecule into a reactive one. Normally, most of the A molecules will be unreactive. Consequently, $C_A^u \cong C_A$, where C_A is the total concentration of A molecules. If it is then assumed that the reactive molecules react via a first-order rate law, one can show

$$r_A = -k_0 C_A^\ddagger = -k_0 C_A e^{-(\Delta G^\ddagger/k_B T)} \quad (7.3)$$

where k_0 is the rate constant for the reaction of the reactive A molecules. According to equation (7.3), the rate constant for the overall reaction is given by

$$k_1 = k_0 e^{-(\Delta G^\ddagger/k_B T)} \quad (7.4)$$

Note:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (7.5)$$

where ΔH^\ddagger is the average enthalpy to convert an unreactive A molecule into a reactive one, and ΔS^\ddagger is the entropy of the same process. Substituting equation (7.5) into equation (7.4) yields

$$k_1 = \left(k_0 e^{(\Delta S^\ddagger/k_B)} \right) e^{-(\Delta H^\ddagger/k_B T)} \quad (7.6)$$

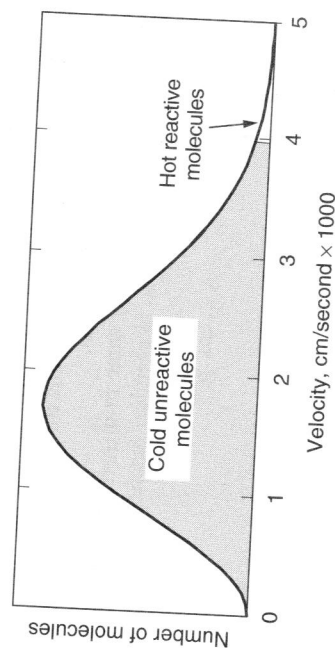


Figure 7.1 The Boltzmann distribution of molecular velocities.

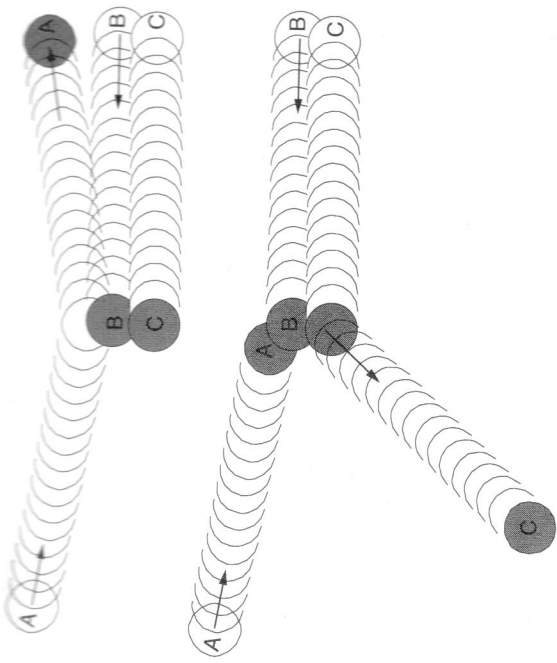


Figure 7.2 A collision between an A molecule and BC molecules.

Using Arrhenius' model in Section 7.1, we write

$$P_{\text{reaction}} = e^{-\Delta G^\ddagger / k_B T} \tag{7.11}$$

Combining equations (7.10) and (7.11) shows

$$\Gamma_{A \rightarrow BC} = Z_{ABC} e^{-\Delta G^\ddagger / k_B T} \tag{7.12}$$

Next, let's derive an equation for Z_{ABC} . First consider the reaction between the molecules A and BC. To simplify the analysis, we will treat the molecules as two billiard balls. Figure 7.3 shows some of the possible collisions between the billiard balls. In the figure, A is moving toward BC. A starts at the upper left, and the motion of A is indicated as a series of circles. In the top case, a hot A molecule approaches a hot BC but it misses. In the second case, the hot A just misses B-C. In the third case, the hot A collides with the hot BC. Trautz and Lewis assumed that in the first two cases, no reaction occurs, but in the third case, reaction happens with unity probability, provided the molecules have a minimum energy E_T^\ddagger .

Notice that any A molecule that gets within a distance b_{coll} of the BC molecule will collide with the BC molecule. Therefore the collision diameter becomes a distance. Any collisions with a distance less than b_{coll} react.

Next, we will derive an expression for the rate of molecular collisions. For the purposes of derivation, consider the motion of a given BC molecule toward an A molecule as shown in Figure 7.4. During the collision BC moves toward A as shown in this figure. We will define $v_{A \rightarrow BC}$ as the velocity of A toward BC.

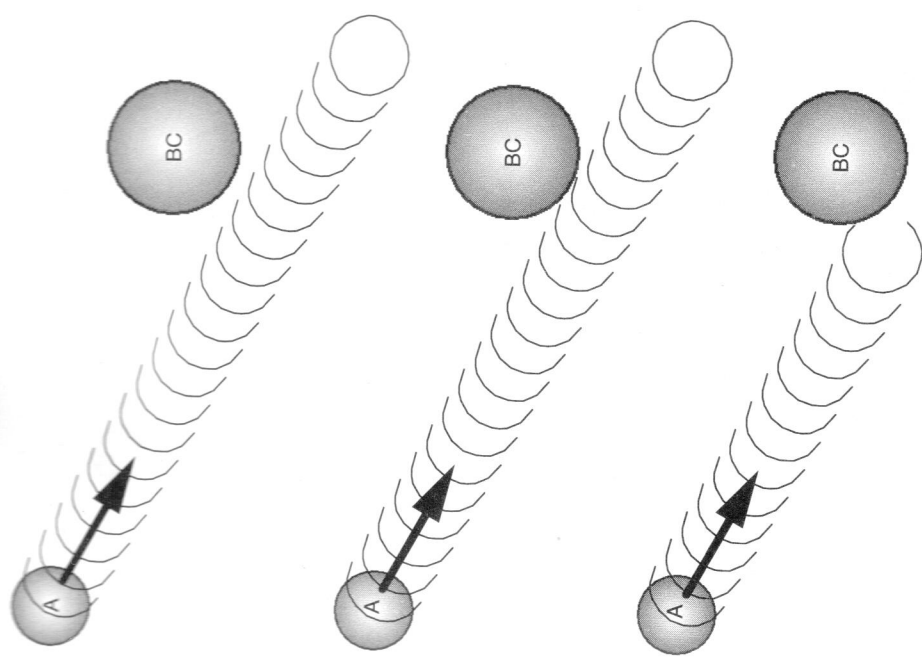


Figure 7.3 Some typical billiard ball collisions.

Now let us consider a small increment of time t_c . If we treat A as a fixed point, then during the collision BC will move a distance L_{ABC} given by

$$L_{ABC} = v_{A \rightarrow BC} t_c \tag{7.13}$$

Next, we want to note that if there is an A molecule within the cylinder in Figure 7.4, there will be a collision between A and BC sometime during the time slice t_c .

If there are two molecules within the cylinder, there will be two collisions. In general, the number of collisions will be

$$\left(\begin{matrix} \text{Number of collisions} \\ \text{of the given} \\ \text{BC molecule} \end{matrix} \right) = \left(\begin{matrix} \text{volume of} \\ \text{cylinder} \end{matrix} \right) C_A \tag{7.14}$$

where C_A is the concentration of the A molecules in the reacting mixture, measured in molecules/cm³.

The total number of collisions is

$$\left(\begin{array}{c} \text{Total number of} \\ \text{A molecules with all} \\ \text{BC molecules} \end{array} \right) = \left(\begin{array}{c} \text{number of collisions at} \\ \text{a given BC molecule} \end{array} \right) \left(\begin{array}{c} \text{number of BC} \\ \text{molecules in the} \\ \text{volume} \end{array} \right) \quad (7.20)$$

Combining equations (7.17)–(7.20) yields

$$Z_{ABC} = C_A C_{BC} \sigma_{A \rightarrow B}^c v_{A \rightarrow BC} \quad (7.21)$$

Equation (7.21) gives us the collision rate if we know the velocity of A toward BC. In a real system, there will be a distribution of velocities, so we have to average equation (7.21) over the velocity distribution. The result is

$$Z_{ABC} = \bar{v}_{A \rightarrow BC} C_A C_{BC} \sigma_{A \rightarrow BC}^c \quad (7.22)$$

Where $\bar{v}_{A \rightarrow BC}$ is the average velocity of A toward BC. Equation (7.22) gives the total rate of collisions between hot A molecules and hot BC molecules.

Substituting equations (7.5) and (7.19) into equation into equation (7.12) yields

$$\Gamma_{A \rightarrow BC} = (\bar{v}_{A \rightarrow BC} \sigma_{A \rightarrow BC}^c) (e^{-E_a/k_B T}) (e^{-\Delta H^\ddagger/k_B T}) C_A C_{BC} \quad (7.23)$$

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

Substituting equation (7.16) into (7.23) and setting $\Delta H^\ddagger = E_a$ yields

$$\Gamma_{A \rightarrow BC} = \pi d_{\text{coll}}^2 \bar{v}_{ABC} e^{-E_a/k_B T} (e^{-\Delta S^\ddagger/k_B T}) C_A C_{BC} \quad (7.24)$$

where $\Gamma_{A \rightarrow BC}$ is the rate of reaction between A and BC, \bar{v}_{ABC} is the average velocity of A toward BC, C_A and C_{BC} are the concentrations of A and BC, and d_{coll} is the collision diameter of A–BC as indicated in Figure 7.4. E_a is the average amount of energy needed to get the reaction to happen in kJ/molecule, k_B is Boltzmann's constant [1.38×10^{-23} J/(molecule·K)], T is the absolute temperature, and ΔS^\ddagger is the entropy of the molecules that react in kJ/(molecule·K).

Equation (7.23) is just a second-order rate law, with an activation barrier of ΔH^\ddagger and a preexponential, k_0 , which is given by

$$k_0 = \bar{v}_{A \rightarrow BC} \sigma_{A \rightarrow BC}^c e^{\Delta S^\ddagger/k_B} \quad (7.25)$$

Neither Trautz nor Lewis had a way to calculate ΔS^\ddagger . Consequently, they set ΔS^\ddagger to zero in equation (7.25) to obtain

$$k_0 = \bar{v}_{A \rightarrow BC} \sigma_{A \rightarrow BC}^c \quad (7.26)$$

Equation (7.26) is the key result for simple collision theory.

Trautz and Lewis also asserted that the molecular velocity in equation (7.26) should be calculated, ignoring the fact that we are considering hot molecules. We will derive an

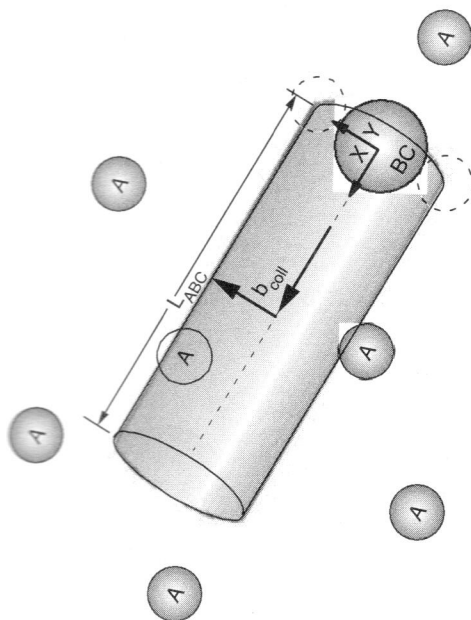


Figure 7.4 The collision of two molecules A + BC.

The volume of the cylinder is

$$\left(\begin{array}{c} \text{Volume of} \\ \text{cylinder} \end{array} \right) = \pi (b_{\text{coll}})^2 L_{ABC} \quad (7.15)$$

For the purposes of derivation, it's useful to define a new variable by

$$\sigma_{A \rightarrow BC}^c = \pi (b_{\text{coll}})^2 \quad (7.16)$$

where b_{coll} is the collision diameter combining equations (7.13)–(7.16). Then

$$\left(\begin{array}{c} \text{Number of collisions} \\ \text{of the given BC} \\ \text{molecule} \end{array} \right) \frac{1}{t_c} = v_{A \rightarrow BC} C_A \sigma_{A \rightarrow BC}^c \quad (7.17)$$

Now consider a volume v of gas. The number of BC molecules in the gas is given by

$$\text{Number of BC molecules} = v C_{BC} \quad (7.18)$$

where C_{BC} is the concentration of BC in the reacting mixture, measured in molecules/cm³. By definition

$$Z_{ABC} = \frac{\left(\begin{array}{c} \text{total number of} \\ \text{collisions at A with} \\ \text{all BCs} \end{array} \right)}{(\text{volume}) (\text{time})} = \frac{\left(\begin{array}{c} \text{total number of} \\ \text{collisions of A with} \\ \text{all BCs} \end{array} \right)}{(v) t_c} \quad (7.19)$$

equation for $\bar{v}_{A \rightarrow BC}$ is Section 8.16.4. The result is

$$\bar{v}_{A \rightarrow BC} = \left(\frac{8k_B T}{\pi \mu_{ABC}} \right)^{1/2} \quad (7.27)$$

where

$$\frac{1}{\mu_{ABC}} = \frac{1}{m_A} + \frac{1}{m_B + m_C} \quad (7.28)$$

and m_A , m_B , and m_C are respectively the masses of A, B, and C in atomic mass units (1 amu = 1.66×10^{-24} grams).

I find it convenient to rewrite equation (7.27) as

$$\bar{v}_{ABC} = 2.52 \times 10^{13} \frac{\text{\AA}}{\text{second}} \left(\frac{T}{300 \text{ K}} \right)^{1/2} \left(\frac{1 \text{ amu}}{\mu_{ABC}} \right)^{1/2} \quad (7.29)$$

For example, for the reaction $F + H_2 \rightarrow HF + H$ at 400 K

$$m_F = 19 \text{ amu}$$

$$m_{H_2} = 2 \text{ amu}$$

$$\frac{1}{\mu_{ABC}} = \frac{1}{19 \text{ amu}} + \frac{1}{2 \text{ amu}} = \frac{21}{38 \text{ amu}}$$

$$\mu_{ABC} = \frac{38}{21} \text{ amu}$$

$$\begin{aligned} \bar{v}_{ABC} &= (2.52 \times 10^{13} \text{ \AA/second}) \left(\frac{400 \text{ K}}{300 \text{ K}} \right)^{1/2} \left(\frac{1 \text{ amu}}{\frac{38}{21} \text{ amu}} \right)^{1/2} \\ &= 2.2 \times 10^{13} \text{ \AA/second} \end{aligned}$$

There is one other detail. It is not clear whether you should use van der Waal's radii, covalent radii, or some other radii in the calculation. Generally, **covalent radii give better predictions**, although Lewis' original papers suggest van der Waal's radii instead. Trautz and Lewis picked numbers for d_{coll} , but did not have a theory to predict it, so this was a limitation of their model.

7.2.1 Predictions of Collision Theory

Equations (7.23) and (7.26) were big advances. Equation (7.23) correctly predicted that an elementary reaction between two molecules would show second-order kinetics. That was quite important to people deriving rate equations. Equation (7.26) gave a numerical value for the preexponential for the first time. Again, that was quite important. Further, the numerical value was close to the experimental values.

It is interesting to put some numerical values into equation (7.26) so that we can compare to experiments. Table 7.1 shows the molecular velocities of a number of molecules computed at 273 K. Notice that most of the molecular velocities in the table are between 2×10^{12} and 1×10^{13} Å/second. If we assume an average velocity of

Table 7.1 Molecular velocities and collision diameters for a number of molecules at 273 K

Molecule	Molecular Velocity, Å/second	Collision Diameter, Å
He	1.2×10^{13}	2.2
N ₂	4.5×10^{12}	3.5
O ₂	4.2×10^{12}	3.1
H ₂ O	5.6×10^{12}	3.7
C ₂ H ₆	4.37×10^{12}	3.5
C ₆ H ₆	2.7×10^{12}	5.3

4×10^{12} Å/second and an average collision diameter of 3 Å, substitute into equation (7.16), and substitute the resultant value of σ_A^2 into equation (7.26), we predict a preexponential of about $(4 \times 10^{12} \text{ Å/second}) \times [\pi(3 \text{ Å})^2] = 1.1 \times 10^{14} \text{ Å}^3/\text{second}$.

It is useful to compare this result to the compilation of preexponentials in Table 7.2. Notice that most of the preexponentials in Table 7.2 are between 10^{12} and 2×10^{14} Å³/(molecule-second). Equation (7.26) predicts 1×10^{14} . Therefore, it seems that equation (7.26) predicts preexponentials that are usually within an order of magnitude of the experimental value.

According to equation (7.26), preexponentials for reaction are determined by two factors: the size of the molecules, as given by the cross section; and the average velocity of the molecules, as given in Table 7.1. According to equation (7.26), if everything else is equal, faster-moving molecules will react more quickly than will slower-moving ones. These trends generally agree with experiments. Equation (7.26) also predicts that bigger molecules (i.e., those with larger cross sections) will react more quickly than will smaller molecules. Again, that agrees with experiment. Collision theory also gives preexponentials that are generally within the right order of magnitude. That is quite a significant result considering that collision theory was first proposed in 1918.

Table 7.3 shows a few additional values of the preexponentials calculated from equation (7.30). Details are given in the solved examples. Generally, **collision theory tends to overestimate the preexponentials for reaction**, although the errors are often less than a factor of 10. To put this in perspective, in 1918, one could not measure preexponentials to within a factor of 10, so this was as good an approximation as the data itself.

Table 7.2 A selection of the preexponentials reported by Westley (1980)

Reaction	Preexponential, Å ³ /(molecule-second)	Reaction	Preexponential, Å ³ /(molecule-second)
H + C ₂ H ₆ → C ₂ H ₅ + H ₂	1.6×10^{14}	O + C ₂ H ₆ → OH + C ₂ H ₅	2.5×10^{13}
H + CH → H ₂ + C	1.1×10^{12}	O + C ₃ H ₈ → (CH ₃) ₂ CH + OH	1.4×10^{10}
H + CH ₄ → H ₂ + CH ₃	1×10^{14}	O ₂ + H → OH + O	1.5×10^{14}
O + H ₂ → OH + H	1.8×10^{13}	OH + OH → H ₂ O + O	1×10^{13}
O + OH → O ₂ + H	2.3×10^{13}	OH + CH ₄ → H ₂ O + CH ₃	5×10^{13}
O + CH ₄ → CH ₃ + OH	2.1×10^{13}	OH + H ₂ CO → H ₂ O + HCO	5×10^{13}
O + CH ₃ → H + CH ₃ O	5×10^{13}	OH + CH ₃ → H + CH ₃ O	1×10^{13}
O + HCO → H + CO ₂	5×10^{12}	OH + CH ₃ → H ₂ O + CH ₂	1×10^{13}

Table 7.3 Preexponentials calculated from equation (7.30) for a number of reactions compared to experimental data

Reaction	Calculated		Experimental, $\text{\AA}^3/(\text{molecule}\cdot\text{second})$
	Assuming $b_{\text{coll}} =$ van der Waals Radius, $\text{\AA}^3/(\text{molecule}\cdot\text{second})$	Preexponential Assuming $b_{\text{coll}} =$ Covalent Radius, $\text{\AA}^3/(\text{molecule}\cdot\text{second})$	
$\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{H}_2$	6.2×10^{14}	2.0×10^{14}	1.6×10^{14}
$\text{H} + \text{CH} \rightarrow \text{H}_2 + \text{C}$	4×10^{14}	2.0×10^{14}	1.1×10^{12}
$\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{OH} + \text{C}_2\text{H}_5$	1.9×10^{14}	7.6×10^{13}	2.5×10^{13}
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	1.25×10^{14}	5.8×10^{13}	1×10^{13}
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	4.0×10^{14}	2×10^{14}	1.5×10^{14}

7.2.2 Failure of Collision Theory

Unfortunately, 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 predicted from collision theory [equation (7.26)]. 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 predicted from collision theory. These are special cases. In most cases, collision theory gets about the right answer. 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 the following two reactions:



During reaction (7.32a), the oxygen reacts with the hydrogen on the propane's middle carbon. If the incoming oxygen hits the hydrogen on the middle carbon, then the reaction can occur. However, if the oxygen hits anywhere else, a $\cdot\text{CH}_2\text{CH}_2\text{CH}_3$ species 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 such as reaction (7.32a).

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.

Polanyi noted that one can approximately account for these effects by considering the ΔS^\ddagger term in equation (7.25). Recall from Chapter 6 that the entropy is a measure of how many configurations are available in the system, specifically:

$$\text{Configurations} = \exp\left(\frac{S}{k_B}\right) \quad (7.33)$$

If we look at reaction (7.32), there are many configurations of the reactants that do not lead to reaction. We can define ΔS^\ddagger by

$$\exp\left(\frac{\Delta S^\ddagger}{k_B}\right) = \frac{\text{configurations which lead to reaction}}{\text{average number of configurations of the reactants}} \quad (7.34)$$

ΔS^\ddagger is called the **entropy of activation**. Generally, $\exp(\Delta S^\ddagger/k_B)$ is less than 1.0, and it can be much less than 1 in a case such as reaction (7.32), where only special configurations lead to reaction. There are also a few cases where $\exp(\Delta S^\ddagger/k_B)$ is greater than 1, because there are more accessible configurations in the transition state than in the reactants.

Polanyi also defined **loose transition states** and **tight transition states**. Loose transition states have ΔS^\ddagger near zero, so any collision can lead to reaction. Tight transition states have negative values of ΔS^\ddagger . Tight transition states arise when a special configuration of the reactants is needed in order for a reaction to occur.

Unfortunately, in 1931, Polanyi was not able to get an expression of ΔS^\ddagger , so he could not correct collision theory to account for this effect.

Another weakness of the model is that it does not explain activation barriers. Neither Arrhenius, nor Trautz, nor Lewis was able to explain why the reactants needed to be hot in order for reaction to occur. Trautz and Lewis just assumed — without explaining this assumption — that reactions had barriers.

7.3 THE MARCELLIN-WIGNER-POLANYI MODEL

Marcellin (1914–1920), Wigner (1932), and Polanyi (1931, 1932) provided the first model that explained why reactions have barriers. Their idea was that the reactants need to cross a mountain in a potential energy surface in order for the reaction to occur. See Figure 7.5.

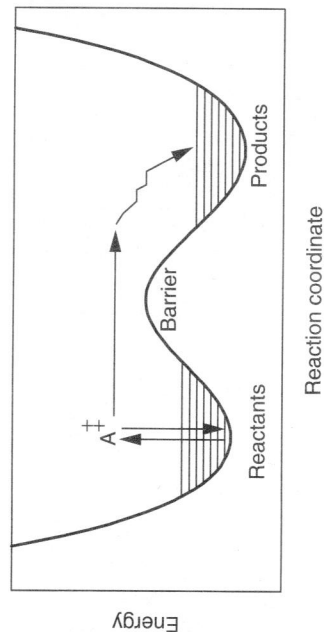


Figure 7.5 Polanyi's picture of excited molecules.

According to Marcellin, Wigner, and Polanyi, the activation barrier is associated with the energy to get over the barrier.

Figure 7.6 shows what the barrier really looks like for the reaction



There is a two-dimensional barrier in Figure 7.6 rather than the one-dimensional barrier in Figure 7.5. The two-dimensional barrier is called a *potential energy surface*. The potential energy surface looks like a gorge through the mountains with two broad valleys and a saddle point in between. Point X in the figure corresponds to the minimum in the potential at the reactants, Y is the minimum at the products, and there is a rise corresponding to the saddle point. Figure 7.7 shows the saddle point in more detail. Notice that there is a hill. The hill is the barrier to the reaction.

People usually plot the potential energy surface as a contour plot. The contour plot is shown on the right of Figure 7.6. The lines are contours of constant energy, and are

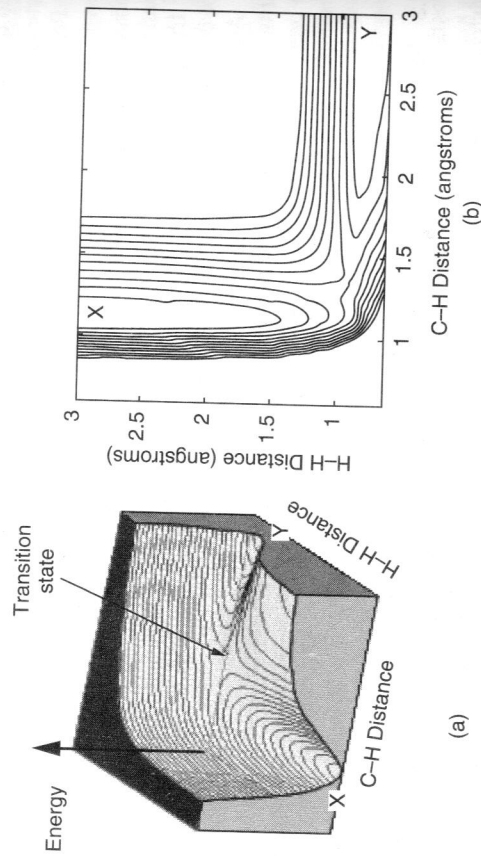


Figure 7.6 A potential energy surface for the reaction $\text{H} + \text{CH}_3\text{OH} \rightarrow \text{H}_2 + \text{CH}_2\text{OH}$ from the calculations of Blowers and Masel. The lines in the figure are contours of constant energy. The lines are spaced 5 kcal/mol apart.

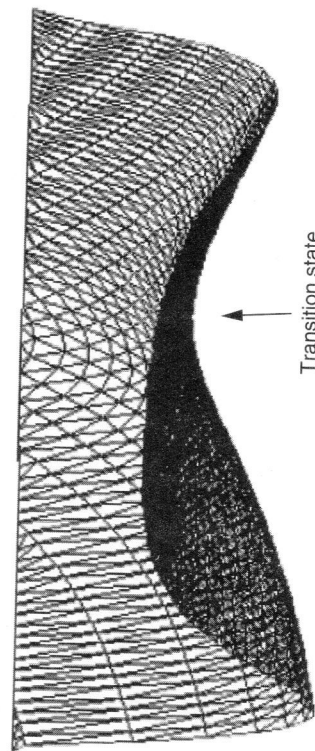


Figure 7.7 A blowup of the saddle point in Figure 7.6.

spaced 5 kcal/mol apart. Point X in the figure corresponds to the minimum in the potential at the reactants, Y is the minimum at the products, and there is a rise corresponding to the saddle point.

Examples 7.G and 8.A show more information about potential energy surfaces. Please look at these two examples before proceeding with this chapter.

Marcellin, Wigner, and Polanyi noted that molecules need to get over the rise in the potential energy surface in order for reaction to occur. Therefore, they proposed that activation barriers are associated with the rise in the potential energy surfaces. In the literature, this is called rise the **transition state**, or the **col** (saddle), in the potential energy surface. Generally, it is still believed that activation barriers are associated with the hills in the potential energy surface.

In the literature, people sometimes say that the barrier height is equal to the activation energy. In fact this is only an approximation. For example, Table 7.4 compares the activation barriers for a number of reactions to the energy of the saddle point on the potential energy surface. One sees qualitative agreement, that reactions with larger saddle point energies also have higher activation barriers. However, the activation barrier is not exactly equal to the saddle point energy.

7.3.1 Tunneling

Generally, when a hydrogen atom is being transferred during a reaction, the barrier is a little less than the saddle point because of a quantum-mechanical process called *tunneling*. In Chapter 8, we will show that quantum-mechanically an atom that does not have quite enough energy to go over a barrier still has some probability of going through that barrier. In these cases, the activation barrier is lower than the barrier in the potential energy surface because some atoms can get through the barrier.

Tunneling arises because of the uncertainty principle. Classically one might say that the reactants are just approaching the barrier. However, quantum-mechanically there is some uncertainty in the position of the molecule, and so when you think that the reactants are just approaching the barrier, the wavefunction for the molecules will have a component on the other side of the barrier as shown in Figure 7.8. This uncertainty in the atomic

Table 7.4 A comparison of the saddle point energy from accurate ab initio calculations and the activation barrier measured experimentally for a number of reactions

Reaction	Saddle Point Energy, kcal/mol	E_a , kcal/mol
$\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$	9.60	8.0
$\text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H}$	9.60	7.78
$\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$	13.5	11.9
$\text{H} + \text{CH}_3\text{CH}_3 \rightarrow \text{H}_2 + \text{C}_2\text{H}_5$	11.8	9.7
$\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$	5.8	1.7
$\text{H} + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{H}_2 + \text{C}_3\text{H}_7$	10.4	8.2
$\text{H} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}$	9.8	9.0
$\text{CH}_3 + \text{CF}_3\text{I} \rightarrow \text{CH}_3\text{I} + \text{CF}_3$	4.95	7.5

According to equation (6.7), K_{eq} , the equilibrium constant for the production of the hot reactive molecules, is

$$K_{\text{eq}} = \frac{q_{\text{ABC}}}{q_{\text{A}}q_{\text{BC}}} e^{-E^\ddagger/k_{\text{B}}T} \quad (7.37)$$

where E^\ddagger is the average energy needed to traverse the barrier, q_{ABC} is the partition function per unit volume for the hot molecules, q_{A} and q_{BC} are the partition functions per unit volume for A and BC, k_{B} is Boltzmann's constant, and T is the temperature. If we substitute equations into Arrhenius' model, assuming that the reaction probability is equal to the probability that a molecule is hot when the collision occurs, we obtain

$$k_{\text{A} \rightarrow \text{BC}} = K_0 \frac{q_{\text{ABC}}}{q_{\text{A}}q_{\text{BC}}} e^{-E^\ddagger/k_{\text{B}}T} \quad (7.38)$$

where $k_{\text{A} \rightarrow \text{BC}}$ is the rate constant for reaction (7.36), and K_0 is the rate constant for the reaction of hot molecules. Equation (7.38) is exact, but we will need an expression for K_0 . We can get it from collision theory.

First, let us define a new partition coefficient q^\ddagger , by

$$q^\ddagger = \frac{q_{\text{ABC}}}{q_{\text{A} \rightarrow \text{BC}}} \quad (7.39)$$

In equation (7.39) $q_{\text{A} \rightarrow \text{BC}}$ is the partition function for the translation of A toward BC and q^\ddagger is the partition function for all of the other modes of the reacting A-B-C complex. Combining equation (7.38) and (7.39) yields

$$k_{\text{A} \rightarrow \text{BC}} = (K_0 q_{\text{A} \rightarrow \text{BC}}^\ddagger) \frac{q^\ddagger}{q_{\text{A}}q_{\text{BC}}} e^{-E^\ddagger/k_{\text{B}}T} \quad (7.40)$$

Eyring (1935, 1937, 1944) proposed that one could replace q^\ddagger in equation (7.5) with q^\ddagger , the partition function of the transition state, and E^\ddagger the average energy of the molecules will react with E^\ddagger , the energy of the transition state. See Eyring (1944, 1980). The result is

$$k_{\text{A} \rightarrow \text{BC}} = (K_0 q_{\text{A} \rightarrow \text{BC}}^\ddagger) \frac{q^\ddagger}{q_{\text{A}}q_{\text{BC}}} e^{-E^\ddagger/k_{\text{B}}T} \quad (7.41)$$

In Chapter 9 we will use collision theory to show

$$K_0 q_{\text{A} \rightarrow \text{BC}}^\ddagger = \left(\frac{k_{\text{B}}T}{hp} \right) \quad (7.42)$$

Substituting equation (7.42) into equation (7.41) yields

$$k_{\text{A} \rightarrow \text{BC}} = \left(\frac{k_{\text{B}}T}{hp} \right) \frac{q^\ddagger}{q_{\text{A}}q_{\text{BC}}} e^{-E^\ddagger/k_{\text{B}}T} \quad (7.43)$$

where k_{B} is Boltzmann's constant, T is the temperature, h is Planck's constant, E^\ddagger is the energy of the saddle point in the potential energy surface, q_{A} and q_{BC} are the partition

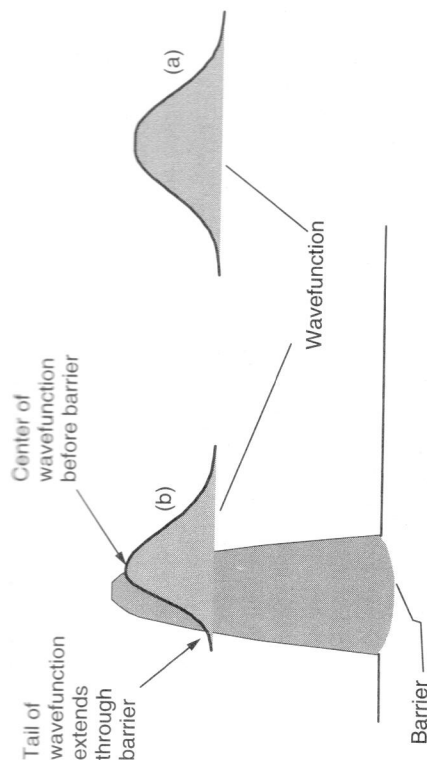


Figure 7.8 A diagram showing the extent of the wavefunction for a molecule. In (a) the molecule is by itself. In (b) the molecule is near a barrier. Notice that the wavefunction has a finite size (i.e., there is some uncertainty in the position of the molecule). As a result, when a molecule approaches a barrier, there is a component of the molecule on the other side of the barrier.

positions allows a molecule to transport through a barrier. We call the transport through the barrier tunneling.

Tunneling is most important for reactions in which a hydrogen atom is being exchanged. The effect is that activation energies for hydrogen transfer reactions are generally less than the energy of the barrier on the potential energy surface.

7.3.2 Dynamic Effect

Most ligand transfer reactions have activation energies that are slightly higher than the saddle point energies. Physically, when the reaction $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$ occurs, the BC bond needs to accumulate enough energy to break. Generally, it is easier to accumulate enough energy if there is a little excess energy in the system. Consequently, the average energy of the reacting molecule is usually slightly higher than the saddle point energy.

We will discuss tunneling and dynamic effects in detail in Chapter 8. However, the thing to remember for now is that activation energies are usually slightly different from the energy of the saddle point in the potential energy surface.

7.4 TRANSITION STATE THEORY

Marcellin was killed in World War I, and neither Wigner nor Polanyi were able to derive a simple expression for the rate. However, Eyring (1937) took an equation that appeared in Tolman (1927), and modified it using Wigner's ideas to derive what is called *transition state theory*. We will reproduce the key arguments in Chapter 9. The idea builds on Arrhenius' model described in Section 7.1. First you use statistical mechanisms to calculate an expression for K_{eq} , the equilibrium concentration of hot molecules. Then you plug back into collision theory to get the rate constant. Consider the reaction



functions for the reactants, and q_{\ddagger}^{\ddagger} is the partition function for all of the modes of transition state except the motion over the barrier.

Equation (7.43) is the key result for transition state theory. One should also memorize equation (7.43) before proceeding through the rest of this chapter.

7.4.1 Key Predictions of Transition State Theory

Transition state theory was a major advance. It provided a way to predict the magnitude of the preexponential. It also gave lots of parameters (i.e., the q values) that could be used to fit data.

It is useful to use transition state theory to get an order of magnitude for the rate constant. In Example 7.B, we show that for most first-, second-, and third-order reactions, $q_{\ddagger}^{\ddagger}/q_A q_B$ is between 0.1 and 10 in units of molecules, angstroms, and seconds, while $k_B T/h_p \sim 10^{13}$ /seconds. Consequently, transition state theory predicts

Preexponentials for elementary reactions are usually between 10^{12} and 10^{14} in units of \AA , molecules, and seconds independent of the order of the reaction or other details.

Other key predictions of transition state theory include

- Transition state theory identifies the barrier to reaction with the saddle point in the potential energy surface. Saddle point energies can be calculated exactly as described in Chapter 11, which then allows activation barriers to be calculated.
- Transition state theory allows you to calculate b_{coll} in equation (7.16) rather than guess it. In Chapter 9, we will show that for a simple collision b_{coll} is just the distance between the reactants at the transition state.
- Transition state theory suggests that $P_{\text{reactions}}$ can be less than $e^{-E_{\ddagger}^{\ddagger}/k_B T}$. For example, in the reaction



the incoming deuterium has to hit the hydrogen atom for reaction to occur. Transition state theory accounts for that by saying that the transition state must be a linear CHD molecule.

- Transition state theory also predicts that small changes in the shape of the potential energy surface produce large changes in q_{\ddagger}^{\ddagger} , which, in turn, changes the rate.

We work out solutions in Examples 7.B–7.E. One should read those examples before proceeding with this chapter.

Transition state theory was a major advance. It gave an equation that could be used to make practical calculations before the days of computers. It gave an explanation of barriers to reactions that could be explained to college freshmen. The model contained lots of parameters (i.e., the q terms) that could be fit to data. When these ideas were first proposed, no one knew what potential energy surfaces for reactions were like. Transition state theory allowed people to fit their data to an empirical model, and so transition state theory explained a lot of data that had not been explained before.

Transition state theory has dominated our thinking about reactions since the early 1950s, so it was quite an important advance.

7.4.2 Relationship between Transition State Theory and Collision Theory

One of the details is that transition state theory is closely related to collision theory. Next, we will show that transition state theory and collision theory are identical for the collision of structureless particles. Let's assume that the transition state for the reaction is the hard-sphere collision in Figure 7.4. Next, we will obtain expressions for q_A , q_{BC} , and q_{\ddagger}^{\ddagger} .

A only has translational motion. According to Table 6.6

$$q_A^3 = \frac{(2\pi m_A k_B T)^{3/2}}{h_p^3} \quad (7.44)$$

where q_A is a translational partition function, m_A is the mass of A, k_B is Boltzmann's constant, T is the temperature, and h_p is Planck's constant.

Similarly, BC is a hard-sphere that can translate. There is also a BC vibration, but we will ignore rotation of the BC molecule. Therefore

$$q_{BC} = \frac{(2\pi(m_B + m_C)k_B T)^{3/2}}{h_p^3} q_{v,BC} \quad (7.45)$$

where m_B and m_C are the masses of B and C, respectively, and $q_{v,BC}$ is the partition function for the BC vibration.

The transition state can translate and rotate. There is also a partition function for the B–C vibration. Collision theory ignores changes in the BC vibration. Therefore

$$q_{\ddagger}^{\ddagger} = (q_{\ddagger}^{\ddagger})^3 (q_{\ddagger}^{\ddagger})^2 q_{v,BC} \quad (7.46)$$

where q_{\ddagger}^{\ddagger} is the translational partition function of the transition state, q_{\ddagger}^{\ddagger} is its rotational partition function, and $q_{v,BC}$ is the partition function for the BC vibration. From the above we have

$$(q_{\ddagger}^{\ddagger})^3 = \frac{(2\pi(m_A + m_B + m_C)k_B T)^{3/2}}{h_p^3} \quad (7.47)$$

According to the results in Chapter 6

$$(q_{\ddagger}^{\ddagger})^2 = \frac{8\pi^2 I k_B T}{h_p^2} \quad (7.48)$$

with

$$I = \mu_{ABC} (b_{\text{coll}})^2 \quad (7.49)$$

Substituting all of the q values into equation (7.43), we obtain

$$k_{A \rightarrow BC} = \frac{k_B T}{h_p} \frac{h_p^3}{(2\pi(m_A + m_B + m_C)k_B T)^{3/2}} \frac{h_p^3}{(2\pi m_A k_B T)^{3/2} (2\pi(m_B + m_C)k_B T)^{3/2}} \times \left(\frac{q_{v,ABC}}{q_{v,ABC}} \right) \frac{8\pi^2 \mu_{ABC} (b_{\text{coll}})^2 k_B T}{h_p^2} e^{-(E_{\ddagger}^{\ddagger}/k_B T)} \quad (7.50)$$

Crossing out like terms yields

$$k_{A \rightarrow BC} = (k_B T)^{1/2} \left(\frac{m_A + m_B + m_C}{m_A(m_B + m_C)} \right)^{1/2} \mu_{ABC} \times (b_{\text{coll}})^2 \left(\frac{8}{\pi} \right)^{1/2} e^{-E_{\ddagger}^{\ddagger}/k_B T} \quad (7.51)$$

Note that according to equation (7.28)

$$\mu_{ABC} = \frac{1}{\frac{1}{m_A} + \frac{1}{m_B + m_C}} = \frac{(m_A)(m_B + m_C)}{m_A + m_B + m_C} \quad (7.52)$$

Substituting equation (7.52) into (7.51) yields

$$k_{A \rightarrow BC} = (k_B T)^{1/2} \frac{1}{\mu_{ABC}^{1/2}} \left(\frac{8}{\pi} \right)^{1/2} \pi (b_{\text{coll}})^2 \exp^{-E_{\ddagger}^{\ddagger}/k_B T} \quad (7.53)$$

Further rearrangements yields

$$k_{A \rightarrow BC} = \left(\frac{8k_B T}{\pi \mu_{ABC}} \right)^{1/2} \pi (b_{\text{coll}})^2 e^{-E_{\ddagger}^{\ddagger}/k_B T} \quad (7.54)$$

According to equation (7.27)

$$\left(\frac{8k_B T}{\pi \mu_{ABC}} \right)^{1/2} = \bar{v}_{A \rightarrow BC} \quad (7.55)$$

Substituting (7.55) into (7.54) yields

$$k_{A \rightarrow BC} = \bar{v}_{A \rightarrow BC} \pi (b_{\text{coll}})^2 e^{-E_{\ddagger}^{\ddagger}/k_B T} \quad (7.56)$$

Notice that equation (7.56) is identical to equation (7.26) (collision theory). Therefore, transition state theory reduces to collision theory when the transition state geometry is a hard-sphere.

Transition state theory differs from collision theory in two key ways:

- One can actually make a calculation. With transition state theory the problem with collision theory is that one never knows b_{coll} in equation (7.16) and thus one cannot make any detailed calculations. Transition state theory replaces b_{coll} with d_{coll} . The distance between the reactants is calculated using transition state geometry. In Chapter 11 we will show that one can use ab initio methods to calculate the transition state geometry. Therefore d_{coll} can be calculated exactly.
- Transition state theory allows you to consider reactions like reaction (7.32a) where only special configurations lead to the desired products. In such a case the partition function for the transition state will be reduced since fewer configurations lead to reaction. See equation (7.34).

7.4.3 Limitations of Transition State Theory

Unfortunately, transition state theory also makes errors, so one has to be careful when using it. For example, Figure 7.9 gives a plot of the experimental values of the rate constant divided by $k_B T/h_p$ for a number of reactions versus the value of the same quantity calculated from transition state theory. Notice that there is very little correlation between transition state theory and the experiment. Physically, Figure 7.9 tests whether the $q_{\ddagger}^{\ddagger}/q_A q_{BC}$ term in equation (7.43) is correctly modifying the rate as the shape of the potential energy surface changes. The figure shows that transition state theory is not quite getting the right answer.

Transition state theory does not work because transition state theory assumes that the reactants remain at a pseudoequilibrium as the reactants traverse the potential energy surface and that tunneling can be ignored. A typical A + BC collision might last only 10^{-12} seconds. There is no time for all of the normal modes to reach thermal equilibrium. As a result, there are some dynamical corrections to the rate equation. When the reaction



occurs, one has to get energy into the B–C bond to break the bond. One also has to transfer momentum into C to carry C away. It happens that the energy and momentum transfer rates play a significant role in reactions. Those influences are ignored in transition state theory.

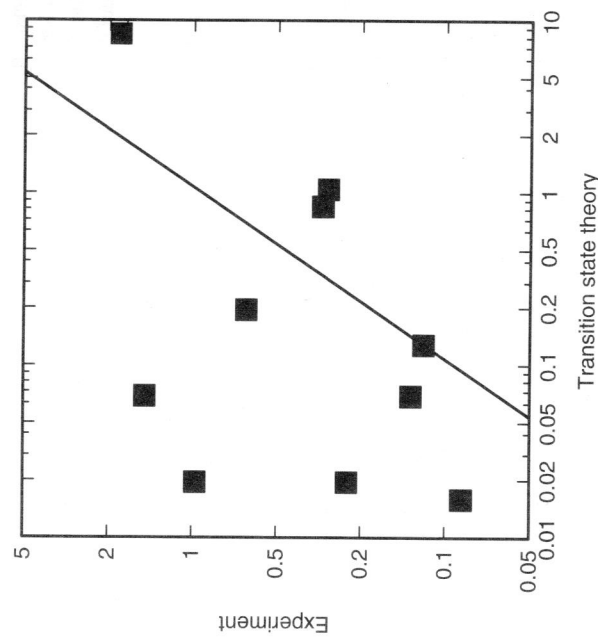


Figure 7.9 A comparison of the $kh/k_B T$ measured experimentally for the reactions in Table 7.4 to the transition-state approximation of the same quantities.

There is a simple way to think about this process. Consider a hypothetical reaction such as that shown in Figure 7.2. During reaction, the molecules collide with one another as shown in Figure 7.2. A comes in and then collides with BC. Then C flies away. Marcellin showed that one can view the process as a trajectory on a potential energy surface, where R_{AB} , the distance from A to B, and R_{BC} , the distance from B to C, change with time. Figure 7.10 shows a typical trajectory. Notice that the trajectory needs to go around a sharp turn on the potential energy surface in order for reaction to happen. The sharp turn corresponds to converting momentum from the A-B motion to B-C motion. Consequently, one needs to have enough momentum transfer and sidewise motion to get a reaction to happen.

Sidewise motion comes from vibrational energy of the BC molecule. In Chapter 8, we will find that one has to carefully balance the translational energy from the incoming A molecule with the vibrational energy in the B-C molecule in order for the reaction to happen. If there is too little vibrational energy, the reactants never make it around the turn in the potential energy surface. If there is too little translational energy, the reactants never make it up the hill. All of these effects can be explored by computing the trajectories of molecules over potential energy surfaces, as described in Chapter 8.

At present, in general, there are no simple ways to predict a rate of reaction when energy transfer is important. People discuss the effect by rewriting equation (7.43) as

$$k_{A \rightarrow BC} = \left(\frac{k_B T}{h} \right) \kappa(T) \left(\frac{q^\ddagger}{q_A q_{BC}} \right) e^{-E^\ddagger/k_B T} \quad (7.58)$$

where $\kappa(T)$ is called the *transmission factor*. Physically, $\kappa(T)$ accounts for the fact that some collisions with enough total energy do not make it over the transition state. $\kappa(T)$ also accounts for the fact that some molecules can go through the barrier rather than over the barrier due to a tunneling process as discussed in Section 7.3.1. It is possible to do complex calculations to look at each state of the system and use an approximation to

estimate the probability that the molecules react. The calculations are complicated, but in principle one can calculate $\kappa(T)$.

In practice, κ is often treated as a "fudge" factor. It is temperature-dependent and can be greater than 1 when tunneling is important. Generally, it is hard to predict κ accurately, which limits the utility of equation (7.58). Accurate Methods to calculate κ will be discussed in Chapter 9.

7.5 RICE-RAMSPERGER-KASSEL-MARCUS (RRKM) THEORY

NEXT, we want to change topics and start to discuss unimolecular isomerization reactions. Unimolecular isomerizations are reactions in which a single molecule rearranges to form stable products. They can be written in general as



Examples of unimolecular reactions include



where $h\nu$ is a photon and the asterisks (*) represent excited species. Unimolecular reactions are different from ligand exchange reactions. Recall that an elementary reaction



is impossible. Instead, we need a collision partner X to get the reaction to occur. In Chapter 5, we wrote the reaction with a collision partner as



Equation (7.63) is an approximation. It says that the collision partner collides with the reactant to immediately produce the product. Lindemann, (1922) however, found that the process does not occur immediately. Instead, it was better to think about the reaction as occurring in following two steps:



First the collision partner collides with the reactant A, to form A^* , an excited A molecule. Then the excited A decomposes to yield products.

Next it is useful to calculate a rate equation for reaction (7.64). The derivation follows that in Chapter 4. First one writes equations for the rate of formation of all the species,

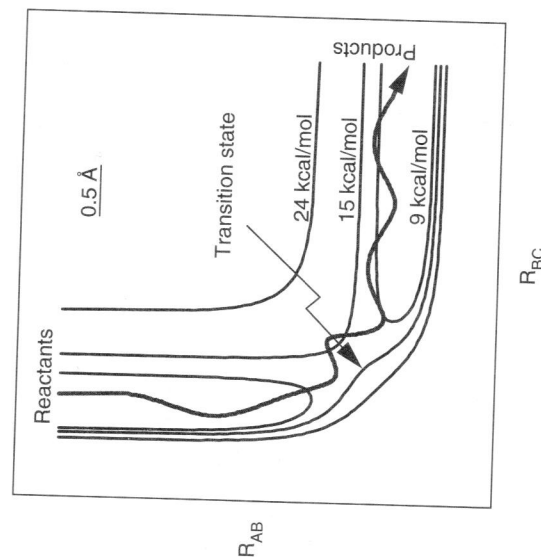


Figure 7.10 A trajectory on a potential energy surface.

collide once, and if they do react during the collision, the reactants fly apart. In a unimolecular reaction, though, reactants cannot fly apart. Instead, the reacting atoms bump against each other multiple times. In effect, you get multiple collisions. That increases the rate.

Kassel (1928a,b,c), Rice, and Ramsperger (1927, 1928) worked out a classical equation for the rate of reaction for cases where the molecules stay hot for a long time. Transition state theory assumes that reaction occurs only when there is enough energy in the A → BC translation to carry the reactants over the transition state. However, Rice, Ramsperger, and Kassel assumed that the activation energy could be distributed over a vibrational modes and one would still get reaction. They then asserted that the rate would be enhanced by a factor of

$$\frac{\text{Number of ways to put an energy } E_a \text{ in } s \text{ modes}}{\text{Number of ways to put an energy of } E_a \text{ in one mode}}$$

They then counted the modes, assuming that the spacing at the vibrational levels was much smaller than $k_B T$ to estimate the enhancement. After some algebra, they obtained

$$k_3 = \left(\frac{k_B T}{h_p} \right) \frac{1}{(s-1)!} \left(\frac{E_a}{k_B T} \right)^{s-1} \frac{q^\ddagger}{q_A q_{BC}} e^{-E_a/k_B T} \quad (7.68)$$

where s is the number of modes that can store energy. According to equation (2.34), E_a is on the order of 20. Methylisocyanide (CH₃NC) has 12 vibrational modes, and if we arbitrarily assume that six of them contribute to reaction, then according to equation (7.68), the rate will be enhanced by a factor of

$$\frac{1}{(6-1)!} (20)^{6-1} = 26,667 \quad (7.69)$$

Physically, if one can store up energy in all of the modes, the rate will be faster than if all of the energy needs to be deposited in the breaking bond during a single collision. As a result, the rate constant for a unimolecular reaction tends to be bigger than the rate constant for a bimolecular reaction.

If one tests equation (7.68) in detail, one finds that it explains why the k_3 in the Lindemann model is so large, but it does not explain the errors in the Lindemann model at medium pressures. The reasons for the errors are

- The rate constant varies according to how much energy is put in the molecule. If you use a laser to put considerable excess energy in the reactants, the reactants react more quickly than if there is only a small amount of excess energy.
- There are quantum effects, the assumption that the level spacing is less than $k_B T$ is not accurate for vibrations.

Marcus derived a modification of the Rice-Ramsperger-Kassel theory for that case. According to the model, the rate of reaction for an molecule excited with an energy E^* is given by

$$\tau_{A \rightarrow B} = \frac{q_M^\ddagger}{h p q_A} \quad (7.70)$$

Then one applies the steady-state approximation to A^* . The result is the following approximation to the rate equation:

$$r_B = \frac{k_1 k_3 [A][X]}{k_3 + k_2 [X]} \quad (7.65)$$

Equation (7.65) is Lindemann's approximation to the rate of a unimolecular reaction.

In order to understand equation (7.65), we will consider the special case that the only collision partners are other reactants so that $[X] = [A]$. Equation (7.65) becomes

$$r_B = \frac{k_1 k_3 [A]^2}{k_3 + k_2 [A]} \quad (7.66)$$

According to equation (7.66), the reaction should be second-order at low pressure and first-order at high pressure (i.e., when $k_2[A] \gg k_3$). Figure 7.11 shows a log-log plot of the rate data for the reaction



and indeed the log-log plot is second-order at low pressure (i.e., slope = 2) and first-order at high pressures (slope = 1).

If one compares to the Lindemann model in detail, one finds that it fits very well at high and low pressures, but that there are some small deviations at intermediate pressures. Also, the value of k_3 that you need to fit the data is way too large. In Figure 7.9, we used $k_3 = 10^{17}$ /second, while according to transition state, the k_3 should be 10^{14} /second, at most.

The reason why k_3 is so large is that the excited complex lasts for a long time in comparison to usual molecular collisions. The complex might last 10^{-7} seconds, compared to 10^{-13} seconds for a transition state. With a bimolecular collision, the hot molecules

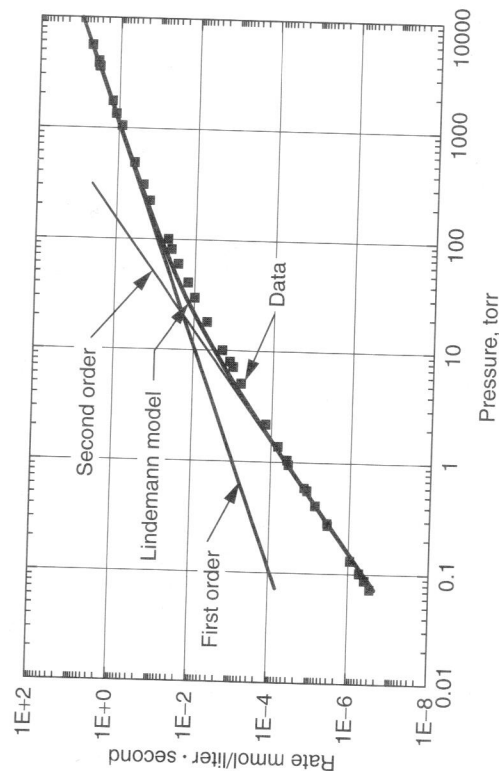


Figure 7.11 The rate of the reaction $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ as a function of pressure. (Data of Schneider and Rabinowicz (1962).)

where h_p is Planck's constant, q_A is the partition function per unit volume of the reactant A, and q_M^\ddagger is the partition function for the molecules that have accumulated enough energy to react. Note that q_M^\ddagger is different from q_T^\ddagger . q_T^\ddagger includes only states that have energy in the mode that translates over the saddle point in the potential energy surface. These are states where energy is localized in the bond that breaks during the reaction. q_M^\ddagger , on the other hand, includes all of the states of the system, which, added up together, have enough energy to cross the barrier independent of whether the energy is localized in any specific bond. The key assumption in equation (7.70) is that if the excited complex has enough energy to react, the excited complex will eventually decay into products.

Equation (7.70) is one version of the RRKM model. Figure 7.12 shows how well the model fits in the best case. It happens that in this case the RRKM model predicts that the rate should show a staircase pattern with increasing energy for reasons that are described in Chapter 9. The data seem to show the same staircase pattern. We will give other examples in Chapter 9 and will find that the theory does not always do as well as shown in Figure 7.12. Still, with unimolecular reactions, we can predict very accurate rate constants easily. One can also make accurate predictions with bimolecular reactions, but in those cases the calculations are much more elaborate.

There is one other important detail: the rate constants for unimolecular reactions change according to what collision partner is used. Table 7.5 gives examples of this. Generally, it is not uncommon for a unimolecular reaction to vary by more than an order of magnitude according to which collision partner is used. Unfortunately, there is not enough room here to describe all of the effects.

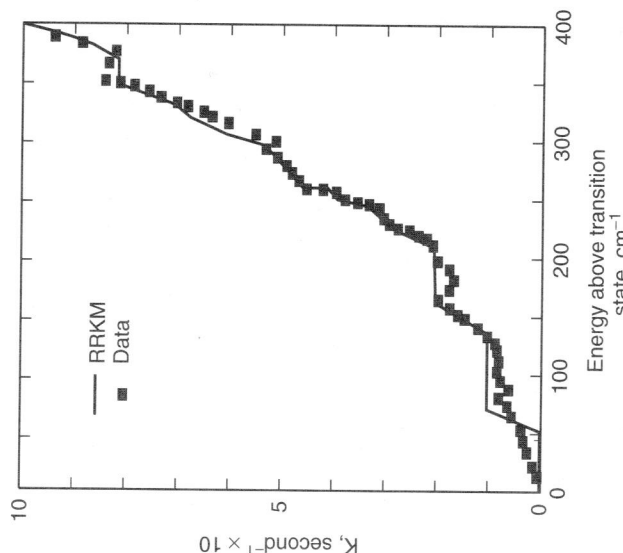


Figure 7.12 A comparison of the rate of the photolysis of ketene (CH_2CO) as a function of energy to the predictions of the RRKM model.

Table 7.5 The preexponentials [in $\text{cm}^3/(\text{mol}^2 \cdot \text{second})$] for a series of unimolecular reactions, as you change the collision partner

Reaction	k_0 When $x = \text{Argon}$	k_0 When $x = \text{Water}$	k_0 When $x = \text{N}_2$
$\text{HO}_2 + \text{X} \rightarrow \text{NO} + \text{O} + \text{X}$	1.7×10^{14}	6.7×10^{15}	1.57×10^{15}
$\text{H}_2\text{O} + \text{X} \rightarrow \text{OH} + \text{H} + \text{X}$	2.1×10^{15}	3.5×10^{17}	5.1×10^{16}
$\text{HO}_2 + \text{X} \rightarrow \text{O}_2 + \text{H} + \text{X}$	1.5×10^{15}	3.2×10^{16}	2×10^{15}
$\text{H}_2 + \text{X} \rightarrow \text{H} + \text{H} + \text{X}$	6.4×10^{17}	2.6×10^{15}	
$\text{O}_2 + \text{X} \rightarrow 2\text{O} + \text{X}$	1.9×10^{13}		1.0×10^{14}

Source: Data of Westley (1980).

7.6 SUMMARY AND PLAN FOR THE NEXT TWO CHAPTERS

In summary, in this chapter we reviewed three key methods that can be used to estimate preexponentials for reaction: collision theory, transition state theory, and the RRKM model. All three of these models are based on Arrhenius' idea that a reaction happens when two hot molecules collide with the right configuration to react. Collision theory assumes that reaction happens whenever two hot molecules collide. The assumption is made that it does not matter how the two molecules come together. For example, in the reaction $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$, collision theory assumes that the rate will be the same whether A first collides with B or A first collides with C. Transition state theory takes the opposite view and says that a reaction occurs only if the collision reaches the transition state. Transition state theory also assumes that equilibrium is manufactured throughout the collision process. The RRKM model goes back to the collision theory assumptions, and says that if you have a unimolecular reaction, a reaction will occur whenever the initial excitation of the reactant A puts enough energy into the molecule independent of where the energy is deposited. Each of these models are approximations. However, they do work in a wide variety of systems.

In the next two chapters, we will be expanding these ideas in detail. In particular, in Chapter 8, we will consider collision theory and try to understand what happens when atoms or molecules collide. We will see how one calculates the reaction probability and will provide software so that students can use the results to calculate rates. We will then use our findings to derive transition state theory, the RRKM model, and related results in Chapter 9. I divided up the discussion in this way because, when I teach the material to undergraduates, I find that I cannot get to catalysis unless I skip Chapter 8 and 9. However, I believe that collision theory is essential to our understanding of reactions. Therefore, I urge the readers to read the chapters and use the findings to learn about how molecules react.

7.7 SOLVED EXAMPLES

Example 7.A A Collision Theory Calculation Use collision theory to calculate the preexponential for the reaction



at 500 K.

Solution According to collision theory

$$k_0 = \pi d_{\text{coll}}^2 \bar{v}_{\text{ABC}} \quad (7.A.2)$$

First let us calculate \bar{v}_{ABC} . According to equation (7.26)

$$\bar{v}_{\text{ABC}} = 2.52 \times 10^{13} \text{ \AA/second} \left(\frac{T}{300 \text{ K}} \right)^{1/2} \left(\frac{1 \text{ amu}}{\mu_{\text{ABC}}} \right)^{1/2} \quad (7.A.3)$$

with

$$\mu_{\text{ABC}} = \mu \frac{1}{\frac{1}{M_A} + \frac{1}{M_B}} \quad (7.A.4)$$

For reaction (7.A.1)

$$\mu_{\text{ABC}} = \frac{1}{\frac{1}{1 \text{ amu}} + \frac{1}{30 \text{ amu}}} = 0.968 \text{ amu} \quad (7.A.5)$$

Plugging in the numbers shows that at 500 K:

$$\bar{v}_{\text{ABC}} = 2.52 \times 10^{13} \left(\frac{500 \text{ K}}{300 \text{ K}} \right)^{1/2} \left(\frac{1 \text{ amu}}{0.968 \text{ amu}} \right)^{1/2} = 3.31 \times 10^{13} \text{ \AA/second} \quad (7.A.6)$$

There is some question about what values of d_{coll} to use in the calculation. Hydrogen has a van der Waals diameter of 1.5 \AA, while ethane has a van der Waals diameter of 3.5 \AA. One approximation to d_{coll} is

$$d_{\text{coll}} = \frac{1.5 \text{ \AA} + 3.5 \text{ \AA}}{2} = 2.5 \text{ \AA} \quad (7.A.7)$$

Substituting (7.A.5) and (7.A.6) into equation (7.A.2) yields

$$k_0 = \pi \frac{(2.5 \text{ \AA})^2}{\text{molecule}} (3.31 \times 10^{13} \text{ \AA/second}) = 6.49 \times 10^{14} \frac{\text{\AA}^3}{\text{molecule}\cdot\text{second}} \quad (7.A.8)$$

Example 7.B Approximate Evaluation of $\frac{q^\ddagger}{q_A q_{\text{BC}}}$ Earlier in this chapter, we said that typically $\frac{q^\ddagger}{q_A q_{\text{BC}}}$ is within an order of magnitude or two of unity. The object of this

problem is to evaluate $\frac{q^\ddagger}{q_A q_{\text{BC}}}$ using the approximations given in Chapter 6 for a case where A, B, and C are atoms, not molecular ligands.

Solution Consider a second-order reaction $A + BC \rightarrow AB + C$. Recall from Chapter 6 that if a molecule contains n_a atoms, the molecule will have $3n_a$ total vibrational, translational, and rotational modes. All molecules can translate in three directions, so every molecule has three translational modes. A linear molecule can rotate in two directions, so

it has two rotational modes. Such a molecule will have $3n_a - 3 - 2 = 3n_a - 5$ vibrational modes. A nonlinear molecule can rotate in three directions, so it will have three rotational modes. Such a molecule will have $3n_a - 3 - 3 = 3n_a - 6$ vibrational modes.

If A contains a single atom, then the atom can only translate, not vibrate. Therefore

$$q_A = (q_t^1)^A \quad (7.B.1)$$

where q_t is a translational partition function and the parentheses designate that we are considering molecule A. The BC molecule can translate and rotate in two directions. It has six total modes. There are three translational modes and two rotational modes. Therefore, there must be one vibrational mode. Consequently

$$q_{\text{BC}} = (q_t^3 q_v q_r^2)_{\text{BC}} \quad (7.B.2)$$

where q_t is a translational partition function per unit length, q_v is a vibrational partition function, and q_r is a rotational partition function and the parens are used to designate a BC molecule.

The A-BC transition state has three atoms, so it must have $3n_a = 9$ total modes. If we treat A-BC as linear, then the molecule will have three translational modes and two rotational modes. That leaves $9 - 3 - 2 = 4$ vibrational modes. Therefore

$$q^* = (q_t^3 q_v^4 q_r^2)_{\text{TST}} \quad (7.B.3)$$

where q^* is the partition function for the transition state and the parentheses are used to indicate that this is for the transition state. The transition state approximation is to treat one of the vibrational modes as a translational mode:

$$q_A^* = (q_t^3 q_v^3 q_r^2 q_{A \rightarrow \text{BC}})_{\text{TST}} \quad (7.B.4)$$

where $q_{A \rightarrow \text{BC}}$ is the partition function for the motion of A toward BC. In transition state theory, we want q^\ddagger , not q^* . By definition

$$q^\ddagger = \frac{q^*}{q_{A \rightarrow \text{BC}}} = (q_t^3 q_v^3 q_r^2)_{\text{TST}} \quad (7.B.5)$$

Combining equations (7.B.1)–(7.B.5) yields

$$\frac{q^\ddagger}{q_A q_{\text{BC}}} = \frac{(q_t^3 q_v^3 q_r^2)_{\text{TST}}}{(q_t^1)^A (q_t^3 q_v q_r^2)_{\text{BC}}} \quad (7.B.6)$$

Now we will make the approximation that

$$(q_t)_{\text{TST}} \approx (q_t)_A \approx (q_t)_{\text{BC}} = q_t \quad (7.B.7)$$

$$(q_r)_{\text{TST}} \approx (q_r)_{\text{BC}} \quad (7.B.8)$$

$$(q_v)_{\text{TST}} \approx (q_v)_{\text{BC}} = q_v \quad (7.B.9)$$

Substituting (7.B.7)–(7.B.9) into equation (7.B.6) yields

$$\frac{q^\ddagger}{q_A q_{\text{BC}}} = \frac{q_v^3}{q_t^2} \quad (7.B.10)$$

According to Table 6.5, $q_V \approx 1$, $q_t \approx 3/\text{\AA}$. Substituting into equation (7.B.10) yields

$$\frac{q^\ddagger}{q_A q_{BC}} = \left(\frac{l^2}{(3/\text{\AA})^3} \right) = 0.037 \text{\AA}^3 \quad (7.B.11)$$

One can do the same analysis for a nonlinear transition state. The result is

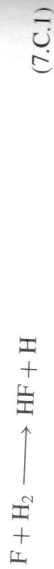
$$\frac{q^\ddagger}{q_A q_{BC}} = \frac{q_r q_t}{q_t^3} \left(\frac{l^2}{(3/\text{\AA})^3} \right) = 1.85 \text{\AA}^3 \quad (7.B.12)$$

Equations (7.B.11) and (7.B.12) are estimates of the partition functions from transition state theory.

Notice that in this chapter we saw that $q^\ddagger/q_A q_{BC}$ is between 0.1 and 10 but we got smaller values. This is an artifact that is created because we have ignored the fact that the transition state is bigger, than the reactants, so its rotational partition function is bigger, too. Also, vibrational partition functions in transition states tend to be bigger than in the reactants. Those two factors produce another factor of 5–10 in the partition function. Multiplying the results in (7.B.11) and (7.B.12) by 5 shows that $q^\ddagger/q_A q_B$ should be between 0.1 and 10 in angstrom units (\AA).

Example 7.C A True Transition State Theory Calculation

In Example 7.B, we used the approximation in equations (7.B.7)–(7.B.9) to calculate the partition functions. Here we want to do the calculation more carefully. The reaction



is one of the most heavily studied reactions in the literature. It is important in chemical lasers. Stark and Werner [1996] calculated a potential energy surface using exact methods, while Stechleretal [1985] fit a potential energy surface to the reaction, and adjusted the potential energy surface so that transition state theory fits the experimental results.

Solution In the solution here, we will first compute the rate using transition state theory with a potential energy surface that has been adjusted so that transition state theory works. Then, we will use the exact results and see how things change.

Table 7.C.1 shows the parameters used in the calculations. Generally, the adjusted potential energy surface was calculated by extending the H–F bond in the transition state by 30% and reducing the barrier by 3 kcal/mol. We also assumed a curvature of 310 cm^{-1} for the barrier, that is we assumed the barrier looks like an inverted parabola with a vibrational frequency of 310 cm^{-1} . All of the other parameters do not matter to the calculation.

According to transition state theory:

$$k_{F \rightarrow H_2} = \left(\frac{k_B T}{h_p} \right) \frac{q_{F-H_2}^\ddagger}{q_{H_2}} e^{-E^\ddagger/k_B T} \quad (7.C.2)$$

It is useful to divide up the partition functions in equation (7.C.2) into the contributions from the translation, vibration, rotation, and electronic modes:

Table 7.C.1 Parameters used to calculate the transition state theory rate constant for $F + H_2 \rightarrow HF + H$ (the exact parameters are also shown for comparison)

	Transition State			Reactants		
	Exact	Used for Transition State Calculations		F	H ₂	
l	1.34 \AA	1.602 \AA			0.7417 \AA	
l_{H-H}	0.801 \AA	0.756 \AA			4395.2 cm^{-1}	
H–H stretch	$\sim 3750 \text{ cm}^{-1}$	4007 cm^{-1}				
H–H bend	?	397.9 cm^{-1}				
H–H bend	?	397.9 cm^{-1}				
Curvature barrier	?	310 cm^{-1}				
E^\ddagger	5.6 kcal/mol	1.7 kcal/mol				
m	21 amu	21 amu		19 amu	2 amu	
I	5.48 amu· \AA^2	7.09 amu· \AA^2			0.275 amu· \AA^2	
ν	4	4		4	1	

$$k_{F \rightarrow H_2} = \frac{k_B T}{h_p} l^\ddagger \left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{trans}} \left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{vibr}} \left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{rot}} \left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{elec}} e^{-E^\ddagger/k_B T} \quad (7.C.3)$$

where l^\ddagger is an extra factor of 2 that arises because there are two equivalent transition states: one with the fluorine attacking one hydrogen and the other with one fluorine attacking the other hydrogen.

Now it is useful to use the results in Chapter 6 to calculate the various terms in equation (7.C.3). According to Table 6.7

$$q_t = \left(\frac{2\pi m k_B T}{h_p^2} \right)^{1/2} \quad (7.C.4)$$

where q_t is the translational partition function for a single translational mode of a molecule, m is the mass of the molecule, k_B is Boltzmann's constant, T is the temperature, and h_p is Planck's constant. For our particular reaction, the fluorine can translate in three directions, the H₂ can translate in three directions, and the transition state can translate in three directions. Consequently

$$\left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{trans}} = \frac{\left(\frac{2\pi m_\ddagger k_B T}{h_p^2} \right)^{3/2}}{\left(\frac{2\pi m_F k_B T}{h_p^2} \right)^{3/2} \left(\frac{2\pi m_{H_2} k_B T}{h_p^2} \right)^{3/2}} \quad (7.C.5)$$

where m_F , m_{H_2} , and m_\ddagger are the masses of fluorine, H₂, and the transition state. Performing the algebra, we obtain

$$\left(\frac{q^\ddagger}{q_F q_{H_2}} \right)_{\text{trans}} = \left(\frac{m_\ddagger}{m_F m_{H_2}} \right)^{3/2} \left(\frac{h_p^2}{2\pi k_B T} \right) \quad (7.C.6)$$

Let's calculate the last term in equation (7.C.6). Rearranging the last term shows

$$\left(\frac{h_p^2}{2\pi k_B T}\right)^{3/2} = \left(\frac{300 \text{ K}}{T}\right)^{3/2} \left(\frac{h_p^2}{2\pi k_B (300 \text{ K})}\right)^{3/2} \quad (7.C.7)$$

Substituting the numbers yields

$$\left(\frac{h_p^2}{2\pi k_B T}\right)^{3/2} = \left(\frac{300 \text{ K}}{T}\right)^{3/2} \times \left(\frac{(6.626 \times 10^{-34} \text{ kg}\cdot\text{meter}^2/\text{second})^2 \left(\frac{10^{10} \text{ \AA}}{\text{meter}}\right)^2 \left(\frac{\text{amu}}{1.66 \times 10^{-27} \text{ kg}}\right)}{2\pi(1.381 \times 10^{-23} \text{ kg}\cdot\text{meter}^2/(\text{second}^2\cdot\text{K}))(300 \text{ K})}\right)^{3/2} \quad (7.C.8)$$

Doing the arithmetic yields

$$\left(\frac{h_p^2}{2\pi k_B T}\right)^{3/2} = \left(\frac{300 \text{ K}}{T}\right)^{3/2} 1.024 \text{ \AA}^3 \cdot \text{amu}^{3/2} \quad (7.C.9)$$

Combining equations (7.C.6) and (7.C.9) yields

$$\left(\frac{q^\ddagger}{q_F q_{H_2}}\right)_{\text{trans}} = \left(\frac{M_\ddagger}{(M_F)M_{H_2}}\right)^{3/2} \left(\frac{300 \text{ K}}{T}\right)^{3/2} (1.024 \text{ \AA}^3 \cdot \text{amu}^{3/2}) \quad (7.C.10)$$

Setting $T = 300 \text{ K}$, $M_\ddagger = 21 \text{ amu}$, $M_F = 19 \text{ amu}$, $M_{H_2} = 2 \text{ amu}$ yields

$$\left(\frac{q^\ddagger}{q_F q_{H_2}}\right)_{\text{trans}} = \left(\frac{21 \text{ amu}}{(19 \text{ amu})2 \text{ amu}}\right)^{3/2} 1.024 \text{ \AA}^3 \cdot \text{amu}^{3/2} = 0.42 \text{ \AA}^3 \quad (7.C.11)$$

Next, let's calculate the ratio of the rotational partition functions. The fluorine atom does not rotate, so

$$\left(\frac{q^\ddagger}{q_{H_2} q_{F_2}}\right)_{\text{rot}} = \left(\frac{q^\ddagger}{q_{H_2}}\right)_{\text{rot}} \quad (7.C.12)$$

According to table (6.7)

$$q_r = \frac{8\pi k_B T I}{h_p^2} \quad (7.C.13)$$

where k_B is Boltzmann's constant, T is the temperature, h_p is Planck's constant, and I is the moment of inertia of the molecule. Combining (7.C.12) and (7.C.13) yields

$$\left(\frac{q^\ddagger}{q_{H_2}}\right)_{\text{rot}} = \left(\frac{8\pi k_B T I^\ddagger / h_p^3}{8\pi k_B T I_{H_2} / h_p^3}\right) = \frac{I^\ddagger}{I_{H_2}} \quad (7.C.14)$$

Substituting in the adjusted value of I^\ddagger and I_{H_2} from Table 7.C.1 yields

$$\left(\frac{q^\ddagger}{q_{H_2}}\right)_{\text{rot}} = \frac{I^\ddagger}{I_{H_2}} = \frac{7.091 \text{ amu}\cdot\text{\AA}^2}{0.275 \text{ amu}\cdot\text{\AA}^2} = 25.8 \quad (7.C.15)$$

Next, let's calculate the vibrational partition functions. According to Table 6.5

$$q_v = \frac{1}{1 - \exp\left(-\frac{h_p \nu}{k_B T}\right)} \quad (7.C.16)$$

Let's first get an expression for the exponential term in equation (7.C.16). It is easy to show

$$\frac{h_p \nu}{k_B T} = \left(\frac{h_p (1 \text{ cm}^{-1})}{(k_B)(300 \text{ K})}\right) \left(\frac{300 \text{ K}}{T}\right) \left(\frac{\nu}{1 \text{ cm}^{-1}}\right) \quad (7.C.17)$$

Plugging in values of h_p and k_B from the end of the book yields.

$$\frac{h_p \nu}{k_B T} = \frac{(2.85 \times 10^{-3} \text{ kcal}/(\text{mol}\cdot\text{cm}^{-1}))(1 \text{ cm}^{-1}) (300 \text{ K})}{(1.980 \times 10^{-3} \text{ kcal}/(\text{mol}\cdot\text{K}))(300 \text{ K})} \left(\frac{\nu}{1 \text{ cm}^{-1}}\right) \quad (7.C.18)$$

Note we actually used $h_p c / N_a$ and k_B / N_a in equation (7.C.16), and not h_p where N_a is Avogadro's number and c is the speed of light, to get the units right. Doing the arithmetic in equation (7.C.18) yields

$$\frac{h_p \nu}{k_B T} = (4.784 \times 10^{-3}) \left(\frac{300 \text{ K}}{T}\right) \left(\frac{\nu}{1 \text{ cm}^{-1}}\right) \quad (7.C.19)$$

Table 7.C.2 shows numerical values for various values of ν . The vibrational partition function ratio equals

$$\left(\frac{q^\ddagger}{q_{H_2}}\right)_{\text{vib}} = \frac{q_{HH}^\ddagger q_{\text{bend}}^\ddagger q_{\text{bend}}^\ddagger}{(q_{H-H})_{H_2}} = \frac{(1)(1.19)(1.19)}{1} = 1.42 \quad (7.C.20)$$

Next, let's calculate the ratio of the partition functions for the electronic state. Let's consider only the ground electronic state:

$$\left(\frac{q^\ddagger}{q_{H_2} q_F}\right)_{\text{elec}} = \frac{g_e^\ddagger}{(g_e)_{H_2} (g_e)_F} = \frac{4}{1 \times 4} = 1 \quad (7.C.21)$$

Finally, let's calculate $k_B T / h_p$:

$$\begin{aligned} \frac{k_B T}{h_p} &= \frac{(1.381 \times 10^{-23} \text{ kg}\cdot\text{meter}^2/(\text{second}^2\cdot\text{molecule}\cdot\text{K}))(300 \text{ K})}{6.626 \times 10^{-34} \text{ (kg}\cdot\text{meter}^2)/\text{second}} \left(\frac{T}{300 \text{ K}}\right) \\ &= 6.25 \times 10^{12} / \text{molecule}\cdot\text{second} \left(\frac{T}{300 \text{ K}}\right) \end{aligned} \quad (7.C.22)$$

Table 7.C.2 The vibrational partition function

Mode	ν , cm^{-1}	$h_p \nu / k_B T$	q_v
q_{HH}^\ddagger	4395.2	21.0	1.0
$(q_{HH})_{H_2}$	4007	19.2	1.0
q_{bend}^\ddagger	379.9	1.82	1.19

Putting this all together allows one to calculate a preexponential:

$$k_0 = I^\ddagger \left(\frac{k_B T}{h_p} \right) \left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{trans}} \left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{rot}} \left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{vib}} \left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{elec}} \quad (7.C.24)$$

Plugging in the numbers yields

$$k_0 = 2(6.25 \times 10^{12} / (\text{molecule} \cdot \text{second})) (0.42 \text{ \AA}^3) (25.8) (1.42) (1) = 1.92 \times 10^{14} \text{ \AA}^3 / (\text{molecule} \cdot \text{second}) \quad (7.C.25)$$

If one uses the actual transition state geometry, the only thing that changes significantly is the rotational term. One obtains

$$\left(\frac{q^\ddagger}{q_{H_2}} \right)_{\text{rot}} = \left(\frac{I^\ddagger}{I_{H_2}} \right)_{\text{rot}} = \frac{5.48 \text{ (amu} \cdot \text{\AA}^2)}{0.275 \text{ (amu} \cdot \text{\AA}^2)} = 19.9 \quad (7.C.26)$$

Then k_0 becomes

$$k_0 = 2(6.25 \times 10^{12} / \text{molecule} \cdot \text{second}) (0.42 \text{ \AA}^3) (19.9) (1.42) (1) = 1.46 \times 10^{14} \text{ \AA}^3 / (\text{molecule} \cdot \text{second}) \quad (7.C.27)$$

One can also calculate the preexponential via old collision theory. In collision theory, one considers the translations and rotations, but not the vibrations:

$$k_0 = I^\ddagger \left(\frac{k_B T}{h_p} \right) \left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{trans}} \left(\frac{q^\ddagger}{q_{H_2} q_F} \right)_{\text{rot}} \quad (7.C.28)$$

In equation (7.C.26), the rotational partition function should be calculated at the collision diameter, and not the transition state geometry. If we assume a collision diameter of 2.3 \AA (i.e., the sum of the van der Waals radii), we obtain

$$I^\ddagger = (r_{F-H_2})^2 (\mu_{FH_2}) = (2.3 \text{ \AA})^2 \left(\frac{(2 \text{ amu})(19 \text{ amu})}{21 \text{ amu}} \right) = 9.57 \text{ \AA}^2 \cdot \text{amu} \quad (7.C.29)$$

Substituting into equation (7.C.25) using the results given above yields

$$k_0 = 2(6.25 \times 10^{12} / (\text{mol} \cdot \text{second})) (0.42 \text{ \AA}^3) \left(\frac{9.57 \text{ \AA}^2 \cdot \text{amu}}{0.275 \text{ \AA}^2 \cdot \text{amu}} \right) = 1.8 \times 10^{14} \text{ \AA}^3 / (\text{mol} \cdot \text{second}) \quad (7.C.30)$$

Table 7.C.3 summarizes these results. In this particular example, collision theory did pretty well. Transition state theory does not improve the predictions if you use the real transition state geometry. You can fit the real data if you "adjust" the transition state geometry. Overall, transition state theory is almost the same as collision theory.

Of course, one should expect that from the calculations. Transition state theory makes two corrections to old collision theory:

Table 7.C.3 A comparison of the preexponential calculated by transition state theory and collision theory to the experimental value [in $\text{\AA}^3 / (\text{mol} \cdot \text{second})$]

k_0 transition state theory with adjusted transition state geometry	1.92×10^{14}
k_0 transition state theory with exact transition state geometry	1.46×10^{14}
k_0 collision theory	1.8×10^{14}
k_0 experiment	2.3×10^{14}

1. Transition state theory uses the transition state diameter rather than the collision diameter in the calculation.
2. Transition state theory multiplies by two extra terms: (a) the ratio of the vibrational partition function, to the electronic partition function for the transition state and (b) the reactants.

Neither of these corrections is very big, and these corrections tend to cancel one another. The result in this example was that the prediction was less reliable than collision theory. This is a typical result. Transition state theory makes small adjustments to collision theory, but ignores other key terms such as the coupling between vibrations and translations. The net result is that for many examples, transition state theory is not more accurate than collision theory in estimating preexponentials for reactions.

Example 7.D Activation Barriers for Reactions According to Transition State Theory Use transition state theory to calculate the activation barrier for reaction 7.C.1.

Solution According to transition state theory

$$E_a = E_T^\ddagger + E_0^\ddagger - E_0^{\text{H}_2} - E_0^F \quad (7.D.1)$$

where E_T^\ddagger is the energy of the transition state relative to the reactants and $E_0^{\text{H}_2}$, E_0^F are the zero-point energies of the various species. Recall that $E_0 = h_p \nu / 2$, where h_p is Planck's constant. Therefore

$$E_a = E_T^\ddagger + \frac{1}{2} h_p (\nu_{\text{HH}}^\ddagger + \nu_{\text{bend}}^\ddagger + \nu_{\text{curvature}}^\ddagger - \nu_{\text{HH}}^{\text{H}_2}) \quad (7.D.2)$$

If we use the "adjusted" potential energy surface, we obtain

$$E_a = 1.7 \text{ kcal/mol} + \frac{1}{2} (2.859 \times 10^{-3} \text{ kcal}/(\text{mol} \cdot \text{cm}^{-1})) \times (4007 \text{ cm}^{-1} + 397.9 \text{ cm}^{-1} + 397.9 \text{ cm}^{-1} - 310 \text{ cm}^{-1} - 4392 \text{ cm}^{-1}) \quad (7.D.3) \\ = 1.7 \text{ kcal/mol} + 0.14 \text{ kcal/mol} = 1.84 \text{ kcal/mol}$$

One can also calculate the activation barrier based on the exact potential energy surface. Stark and Werner [1996] et al. did not report vibrational frequencies for the bending mode, so I will assume that they are the same as in the approximate potential energy surface. In

Table 7.D.1 A comparison of the activation barrier calculated from transition state theory to the experimental value (in kcal/mol)

E_a from the exact potential energy surface	5.38
E_a from the "adjusted" potential energy surface	1.84
E_a from experiment	1.58

that case

$$E_a = 5.6 \text{ kcal/mol} + \frac{1}{2}(2.859 \times 10^{-3} \text{ kcal/(mol}\cdot\text{cm}^{-1})) \times (3750 \text{ cm}^{-1} + 397.9 \text{ cm}^{-1} + 397.9 \text{ cm}^{-1} - 310 \text{ cm}^{-1} - 4392 \text{ cm}^{-1}) \quad (7.D.4)$$

$$= 5.6 \text{ kcal/mol} - 0.22 \text{ kcal/mol} = 5.38 \text{ kcal/mol}$$

Table 7.D.1 compares these calculations to the experimental results. Again, transition state theory gets you the right order of magnitude. However, it is not exact. In this particular case, tunneling lowers the barrier and tunneling is ignored in transition state theory. One can get exact results by adjusting the potential energy surface. An alternative is to do the calculation correctly including tunneling as described in Chapter 9.

Example 7.E **Temperature dependence of the preexponential** In Example 7.C, we calculated the preexponential term at 300 K to calculate k_0 . How does the preexponential change with temperature?

Solution The principal temperature dependence comes from the $k_B T/h_p$ term and the ratio of translational partition functions in equation (7.C.24). If one substitutes equation (7.C.10) into equation (7.C.24), one finds

$$k_0 = \left(\frac{k_B 300 \text{ K}}{h_p} \right) \left(\frac{300 \text{ K}}{T} \right)^{3/2} \left(\frac{q^\ddagger}{q_{\text{H}_2} q_{\text{HF}}} \right)_{300 \text{ K}}^{\text{trans}} \left(\frac{q^\ddagger}{q_{\text{H}_2} q_{\text{HF}}} \right)_{300 \text{ K}}^{\text{rot}} \times \left(\frac{q^\ddagger}{q_{\text{H}_2} q_{\text{HF}}} \right)_{300 \text{ K}}^{\text{vib}} \left(\frac{q^\ddagger}{q_{\text{H}_2} q_{\text{HF}}} \right)_{300 \text{ K}}^{\text{elec}} \quad (7.E.1)$$

where $\left(\frac{q^\ddagger}{q_{\text{H}_2} q_{\text{HF}}} \right)_{300 \text{ K}}^{\text{trans}}$ is the translational partition function at 300 K. Comparing equations (7.D.1) and (7.C.22) shows

$$k_0 \approx k_0^{300 \text{ K}} \left(\frac{300 \text{ K}}{T} \right)^{1/2} \quad (7.E.2)$$

In the homework set, we ask the reader to look at a case where the number of rotational modes also changes. In that case, one predicts some extra temperature dependence due to the temperature dependence of the rotational partition function.

Example 7.F **Transition State Analogs** In the examples so far in this chapter, we considered exact transition state for a reaction. However, another approach is to find a

stable molecule that is an analog of the transition state. The idea is to use the following expression:

$$k_0 = Z_{\text{AB}} e^{+\Delta S^\ddagger/h_p} \quad (7.F.1)$$

where k_0 is the preexponential, k_B is Boltzmann's constant, T is the temperature, h_p is Planck's constant, and ΔS^\ddagger is the entropy of formation of the transition state.

One then estimates ΔS^\ddagger by looking at a molecular analogy of the transition state. For example, consider the reaction



The transition state for the reaction looks like



Find an analogous molecule and use it to estimate ΔS^\ddagger .

Solution Consider the stable molecule $\text{CF}_3\text{-S-CH}_3$. It has a structure like that of $\text{CF}_3 \cdots \text{Br} \cdots \text{CH}_3$. The bonds in $\text{CF}_3\text{-S-CH}_3$ are shorter than in the transition state, and the frustrated rotations have higher barriers, but $\text{CF}_3\text{-S-CH}_3$ is an analog of the transition state for reaction (7.F.2). Now consider the reaction



This reaction is similar to the reaction



where $(\text{CF}_3 \cdots \text{Br} \cdots \text{CH}_3)$ is the transition state for reaction (7.F.2), and it happens that I can look up (ΔS_A) the entropy change for reaction (7.F.4). According to the NIST tables, ΔS_A is $-41.2 \text{ cal/(mol}\cdot\text{K)}$.

Years ago people often used the approximation

$$\Delta S^\ddagger = \Delta S_A \quad (7.F.6)$$

Combining equations (7.F.1) and (7.F.6) yields

$$k_0 \geq Z_{\text{AB}} e^{+\Delta S_A/h_p} \quad (7.F.7)$$

We put a "greater than or equal to" sign in equation (7.F.4) because ΔS_A is a lower bound to ΔS^\ddagger for the reaction. Generally, the analog has a smaller rotational partition function than the transition state, so the ΔS_A for the analog is always less than ΔS^\ddagger . For example, ΔS^\ddagger for reaction (7.F.2) is $-14 \text{ cal/(mol}\cdot\text{K)}$, while the reaction



has a ΔS of $-41.2 \text{ cal/(mol}\cdot\text{K)}$. By comparison, collision theory gives an upper bound to the preexponential. The result is that one can get a range for the preexponential for the reaction.

Let us use the transition state analog to estimate k_0 for reaction (7.E.2) at 500 K. We will use the approximation

$$k_0 = Z_{AB} e^{-\Delta S_A^\ddagger/k_B} \quad (7.F.9)$$

First, we will estimate Z_{AB} following the methods in Example 7.A:

$$Z_{AB} = \pi(b_{\text{coil}})^2 \bar{v}_{ABC} \quad (7.F.10)$$

$$\mu_{ABC} = \frac{1}{\frac{1}{m_{\text{CF}_3\text{Br}}} + \frac{1}{m_{\text{CH}_3}}} = \frac{1}{\frac{1}{179 \text{ amu}} + \frac{1}{15 \text{ amu}}} = 13.8 \text{ amu} \quad (7.F.11)$$

At 500 K

$$\bar{v}_{ABC} = 2.52 \times 10^{13} \text{ \AA/second} \left(\frac{500 \text{ K}}{300 \text{ K}} \right)^{1/2} \left(\frac{1 \text{ amu}}{13.8 \text{ amu}} \right)^{1/2} = 8.8 \times 10^{12} \text{ \AA/second} \quad (7.F.12)$$

Assume a collision diameter of 2 \AA:

$$Z_{AB} = \pi(2 \text{ \AA})^2 (8.8 \times 10^{12} \text{ \AA/second}) = 1.1 \times 10^{14} \frac{\text{\AA}^3}{\text{mole}\cdot\text{second}} \quad (7.F.13)$$

Substituting into equation (7.F.9)

$$k_0 = (1.1 \times 10^{14} \text{ \AA}^3 / (\text{mole}\cdot\text{second})) \exp \left(\frac{-41.2 \text{ cal}/(\text{mol}\cdot\text{K})}{1.98 \text{ cal}/(\text{mol}\cdot\text{K})} \right) \quad (7.F.14)$$

Doing the arithmetic yields

$$k_0 = 1 \times 10^5 \text{ \AA}^3 / (\text{mole}\cdot\text{second}) \quad (7.F.15)$$

Benson (1986) also has one other good rule of thumb. If you have a transition state of the form $\text{CF}_3\text{-Br-CH}_3$, then the CF_3 and CH_3 bending and rocking models will have vibrational frequencies of about 70% of the vibrational frequency of the rocking modes in a stable molecule. That typically adds a factor of 3 to the rate. Therefore the value based on an analog is $k_n = 3 \times 10^5 \text{ \AA}^3 / (\text{mole}\cdot\text{second})$. By composition, the experimental value is $10^{12 \pm 0.5} \text{ \AA}^3 / \text{mole}\cdot\text{second}$.

In my experience, the transition state analogs grossly underestimate preexponentials. However, they provide useful lower bounds, so if you measure a lower preexponential than you calculate for the analog, you know that something is wrong.

We will see later in this book that even though transition state analogs are not that useful in predicting ΔS^\ddagger , the analogs are very useful in designing catalysts or enzymes. Catalysts and enzymes enhance rates by lowering the energy of the transition state for a reaction. One way to design a catalyst is to find a transition state analog (i.e., one with the correct ΔS_A) and then design a catalyst that strongly binds to the analog. If the catalyst binds strongly to the analog, the catalyst will usually also bind strongly to the transition state. The binding lowers ΔG^\ddagger . Transition state analogs are very useful in designing catalysts even though they are not as useful for calculating rates.

There also is the converse, that if you want to stop a catalytic reaction, then a good way to do that is to add a transition state analog to block the transition state for the formation of an undesired product. For example, there is a class of AIDS drugs, called

protease inhibitors, which work by blocking the transition state for one of the key steps in reproduction of the AIDS virus. People design the drugs by finding a transition state analog of the key step in the reproduction cycle of the virus, and then testing the transition state analog as a drug. The transition state analogs are very potent drugs. They really work!

Example 7.G Understanding Contour Plots Consider a potential v defined by:

$$\begin{aligned} v(r_1, r_2, r_0, a, w, vp, wa, hr) &= w^*(\text{Exp}(-2^*a^*(r_1 - r_0))) \\ &- 2^*\text{Exp}(-a^*(r_1 - r_0)) + (w + hr)^*(\text{Exp}(-2^*a^*(r_2 - r_0))) \\ &- 2^*\text{Exp}(-a^*(r_2 - r_0)) + vp^*\text{Exp}(-a^*(r_1 + r_2 - 2^*r_0)) + \\ &w + wa^*\text{Exp}(-4^*a^*a^*((r_1 - r_0)^2 + (r_2 - 3^*r_0)^2)) + \quad (7.G.1) \\ &wa^*\text{Exp}(-4^*a^*a^*((r_1 - 3^*r_0)^2 + ((r_2 - r_0)^2))) \\ &\text{If } (v > 20 + \text{abs}(hr)) \text{ Then} \\ &\quad v = 20 + \text{abs}(hr) \end{aligned}$$

Make contour plots for the following function of r_1 and r_2 with parameters r_0, a, w, hr, vp, wa given by

- (a) $w = 109 \text{ kcal/mol}, wa = 0, hr = 0, vp = 258 \text{ kcal/mol}, r_0 = 0.74 \text{ \AA}, a = 1.2 \text{ \AA}^{-1}$
- (b) $w = 109 \text{ kcal/mol}, wa = 0, hr = 0, vp = 218 \text{ kcal/mol}, r_0 = 0.74 \text{ \AA}, a = 1.2 \text{ \AA}^{-1}$
- (c) $w = 109 \text{ kcal/mol}, wa = 0, hr = 0, vp = 158 \text{ kcal/mol}, r_0 = 0.74 \text{ \AA}, a = 1.2 \text{ \AA}^{-1}$
- (d) $w = 109 \text{ kcal/mol}, wa = -10, hr = 0, vp = 258 \text{ kcal/mol}, r_0 = 0.74 \text{ \AA}, a = 1.2 \text{ \AA}^{-1}$
- (e) $w = 109 \text{ kcal/mol}, wa = 20, hr = 0, vp = 178 \text{ kcal/mol}, r_0 = 0.74 \text{ \AA}, a = 1.2 \text{ \AA}^{-1}$
- (f) $w = 109 \text{ kcal/mol}, wa = 0, hr = -20, vp = 233 \text{ kcal/mol}, r_0 = 0.74 \text{ \AA}, a = 1.2 \text{ \AA}^{-1}$

Solution I used microsoft excel to do the calculations. First I defined a microsoft excel module to calculate the v . My module is given in Table 7.G.1. The spreadsheet can be found in the instructors materials.

Then I set up a microsoft Excel spreadsheet to do the calculations. Table 7.G.2 shows the formulas in part of the spreadsheet. I named cell B1 w , cell B2 vp , cell D2, and cell

Table 7.G.1 The module used to calculate the function in equation (7.G.1)

Public Function v(r1,r2,r0,a,w,vp,wa,hr) As Variant
v = w*(Exp(-2*a*(r1 - r0)) - 2*Exp(-a*(r1 - r0)))
v = v + (w + hr)*(Exp(-2*a*(r2 - r0)) - 2*Exp(-a*(r2 - r0)))
v = v + vp*Exp(-a*(r1 + r2 - 2*r0))
v = v + w
v = v + wa*Exp(-4*a*a*((r1 - r0)^2 + (r2 - 3*r0)^2))
v = v + wa*Exp(-4*a*a*((r1 - 3*r0)^2 + ((r2 - r0)^2)))
If (v > 20 + Abs(hr)) Then
v = 20 + Abs(hr)
End If
End Function

D3 r0. Cell F1 was named wa, and cell I2 was named sp, where sp refers to the spacing of r1 and r2 points. I listed values of r1 in cells B3, C3, ..., AF3. I listed values of r2 in cells A4, A5, ..., A40. I then used the function defined by the module in Table 7.B.1 to calculate all of the numerical values.

I then used the three-dimensional (3D) plotting routines in Excel to produce a diagram of the potential. Excel has a 3D plotting routine. You use it by first choosing cells to be plotted, (A3 to AF40 in my example) and then choosing a 3D surface plot. I used the defaults for all of the values. I then went back and edited the vertical axis of the plot so that the major unit was 2.

Part A Figure 7.G.1 shows a diagram of the potential when $w = 109$ kcal/mol, $wa = 0$, $vp = 258$ kcal/mol, $r0 = 0.74$ Å, $a = 1.74$ Å⁻¹. The potential looks like a deep valley with a rise and then a fall. There is a saddlepoint in the middle of the potential.

Figure 7.G.2 shows a side view of the potential. Notice the rise in the potential near the saddle point.

Figure 7.G.3 shows another view of the potential in this case from above. There are a series of parabola-shaped contours leading up to the saddle point. Then there is a contour that looks somewhat like a flat body with two arms and two legs. Then there are a series of circular contours.

The parabolic contours are indicative of the potential rising in the direction of the center of the parabola. The contour with arms and legs is indicative of a saddle point. The circular contours are indicative of a potential that goes smoothly from reactants to products.

There are no connections from reactants to products below the saddle point. However, all of the contours above the saddle point connect from reactants to products.

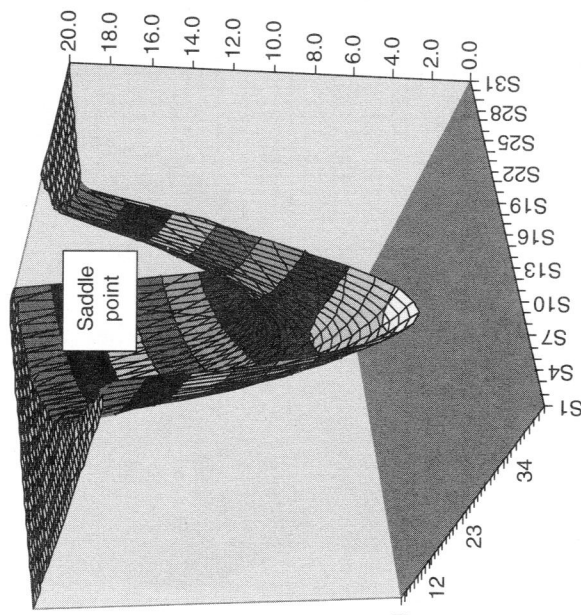


Figure 7.G.1 A diagram of the potential when $w = 109$ kcal/mol, $wa = 0$, $hr = 0$, $vp = 258$ kcal/mol, $r0 = 0.74$ Å, $a = 1.2$ Å⁻¹ (elevation = 15, rotation = 60, perspective = 30, chart depth = 100).

01	w=	109.4
02	vp=	258
03	r2\r1	0.5
04	r0=	0.74
05	=A4+sp	=v(B\$3,\$A4,r0), a,w,vp,wa,hr)
06	=A5+sp	=v(B\$3,\$A5,r0), a,w,vp,wa,hr)
07	=A6+sp	=v(B\$3,\$A6,r0), a,w,vp,wa,hr)
08	=A7+sp	=v(B\$3,\$A7,r0), a,w,vp,wa,hr)
09	=A8+sp	=v(B\$3,\$A8,r0), a,w,vp,wa,hr)
10	=A9+sp	=v(B\$3,\$A9,r0), a,w,vp,wa,hr)
11	=A10+sp	=v(B\$3,\$A10,r0), a,w,vp,wa,hr)
12	=A11+sp	=v(B\$3,\$A11,r0), a,w,vp,wa,hr)
13	=A12+sp	=v(B\$3,\$A12,r0), a,w,vp,wa,hr)
14	=A13+sp	=v(B\$3,\$A13,r0), a,w,vp,wa,hr)
15	=A14+sp	=v(B\$3,\$A14,r0), a,w,vp,wa,hr)

The actual spreadsheet extends to cell AF40.

Table 7.G.2 The formulas in part of the spreadsheet^a used to solve Example 7.G.2. A copy of this spreadsheet is available at <http://www.wiley.com/chemicalkinetics>

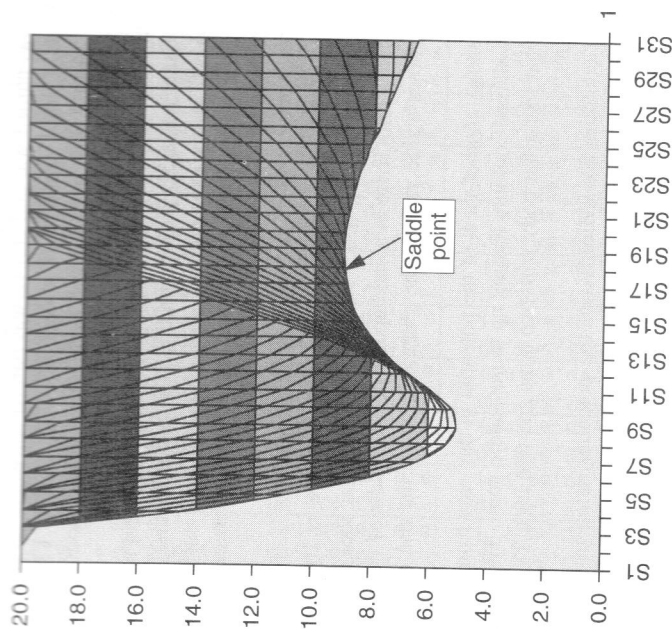


Figure 7.G.2 A side view of the potential in Figure 7.G.1 (elevation = 0, rotation = 90, perspective = 30, chart depth = 100).

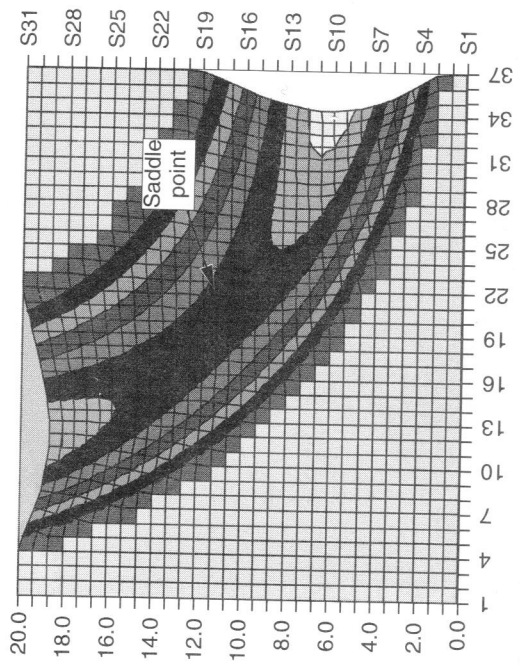


Figure 7.G.3 A top view of the potential in Figure 7.G.1 (elevation = 90, rotation = 0, perspective = 30, chart depth = 100).

It is very important that the reader be able to recognize the saddle points on these contour plots. Therefore the reader should examine these contour plots carefully before proceeding.

Part B I solved part B using the same spreadsheet that I used for part A. I changed the value of V_p and then used the same plots as with part A.

Figure 7.G.4 shows a plot of the potential. In this case, there is a deep valley, but no hills between the reactants and products.

Figure 7.G.5 shows a top view of the potential. Notice that there are the hemispherical contours, but none of the parabolic contours, and none of the areas that look like a body with arms and legs.

Part C Again this problem was solved using the spreadsheet in Table 7.G.1 and the same plotting commands. Figure 7.G.6 shows a diagram of the potential. In this case there is a valley as before, but now the potential falls, showing a well. A well corresponds to the formation of a stable molecule or molecular complex.

Figure 7.G.7 shows a top view of the potential. In this case there is a bull's-eye pattern of ellipses corresponding. The bull's-eye pattern corresponds to a stable complex or molecule.

Part D Again I used the same spreadsheet as before to calculate the potential. In this case I set $sp = 0.07$ to get a better plot, and inputted the parameters accordingly.

Figure 7.G.8 shows a top view of the potential for this case. Notice that there are two elliptical areas corresponding to complexes or intermediates and a saddle point in between.

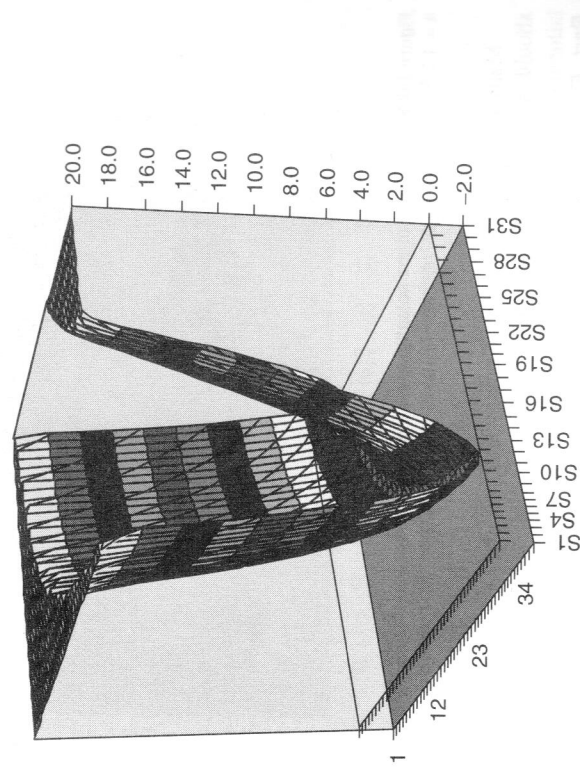


Figure 7.G.4 A diagram of the potential when $w = 109$ kcal/mol, $w_a = 0$, $v_p = 218$ kcal/mol, $r_0 = 0.774 \text{ \AA}$, $a = 1.2 \text{ \AA}^{-1}$ (elevation = 15, rotation = 60 perspective = 30, chart depth = 100).

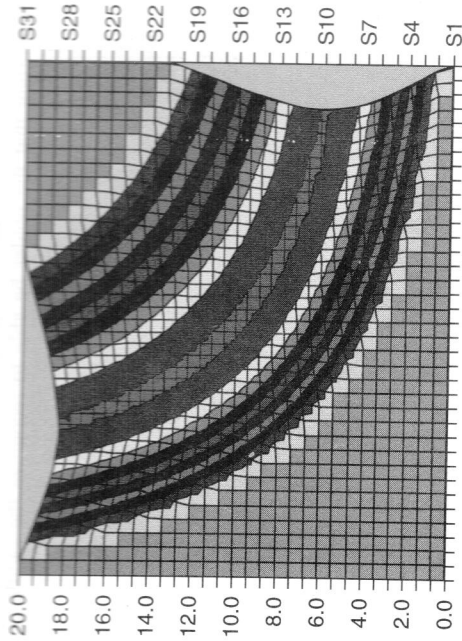


Figure 7.G.5 A top view of the potential in Figure 7.G.6 (elevation = 90, rotation = 0, perspective = 30, chart depth = 100).

Figure 7.G.7 A top view of the potential in Figure 7.G.6 (elevation = 90, rotation = 0, perspective = 30, chart depth = 100).

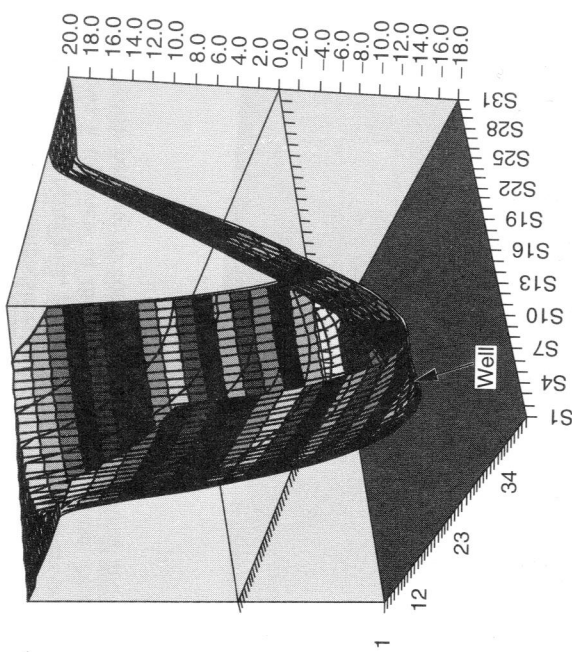


Figure 7.G.6 A diagram of the potential when $w = 109$ kcal/mol, $w_a = 0$, $v_p = 158$ kcal/mol, $r_0 = 0.74 \text{ \AA}$, $a = 1.2 \text{ \AA}^{-1}$ (elevation = 15, rotation = 60, perspective = 30, chart depth = 100).

Many reactions show potential energy surfaces like those in Figure 7.G.8, and so one should study the features carefully.

Part E I solved part E using the same spreadsheet as for part D with $sp = 0.10$. Figure 7.G.9 shows the plot. In this case, there are two saddle points and an intermediate or complex in between.

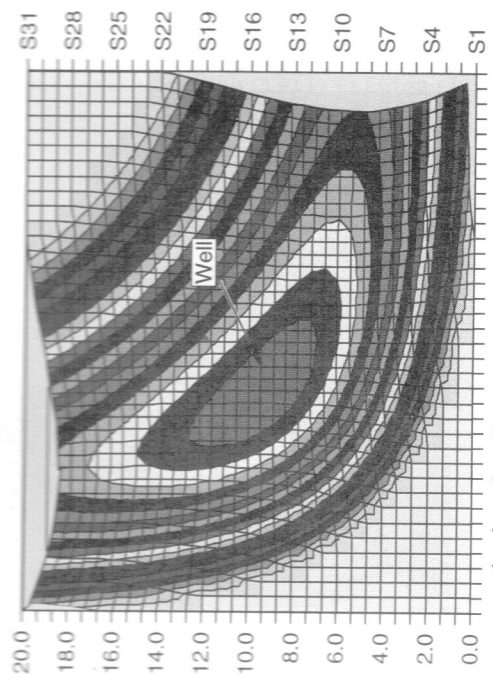


Figure 7.G.7 A top view of the potential in Figure 7.G.6 (elevation = 90, rotation = 0, perspective = 30, chart depth = 100).

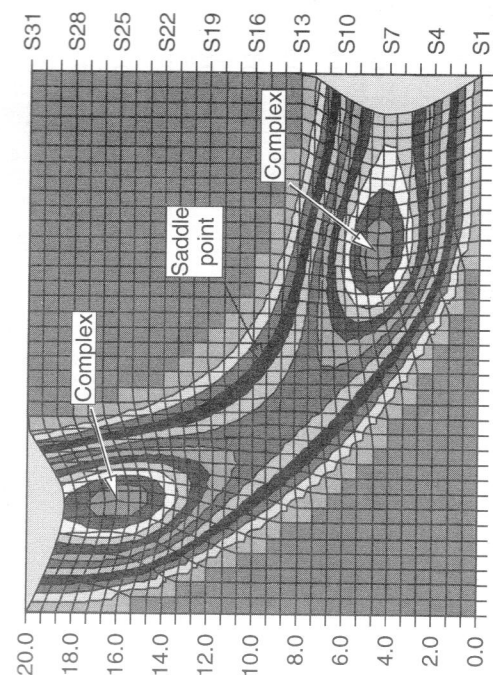


Figure 7.G.8 A top view of the potential for $w = 109$ kcal/mol, $w_a = -10$, $h_r = 0$, $v_p = 158$ kcal/mol, $r_0 = 0.74 \text{ \AA}$, $a = 1.2 \text{ \AA}^{-1}$ (elevation = 90, rotation = 0, perspective = 30, chart depth = 100).

Part F I solved part F using the same spreadsheet as for part D with $sp = 0.10$. Figure 7.G.10 shows the plot. There are parabolic contours showing that the potential is rising, but there is no transition state between reactants and products.

Readers may want to reproduce these results themselves before proceeding to the next chapter.

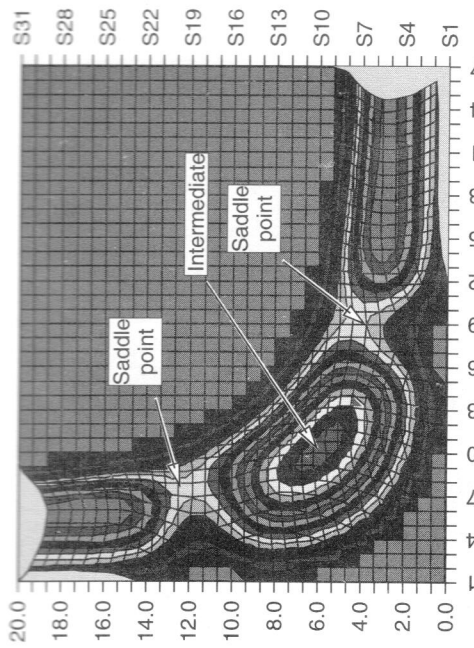


Figure 7.G.9 A top view of the potential for $w = 109$ kcal/mol, $wa = 20$, $hr = 0$, $vp = 178$ kcal/mol, $r0 = 0.74$ Å, $a = 1.2$ Å⁻¹ (elevation = 90, rotation = 0 perspective = 30, chart depth = 100).

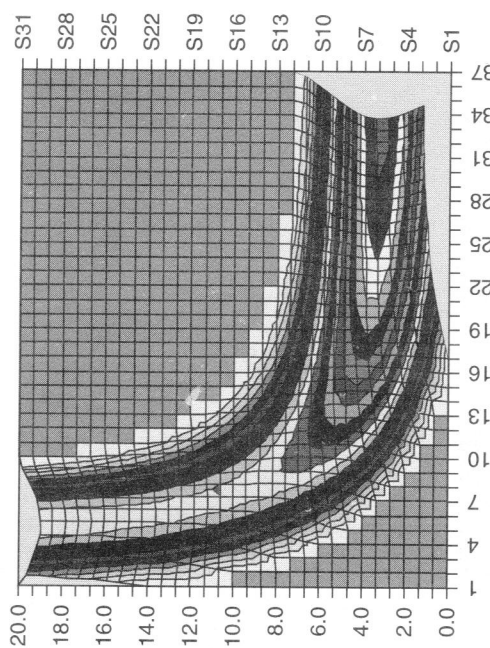


Figure 7.G.10 A top view of the potential for $w = 109$ kcal/mol, $wa = 0$, $hr = -20$, $vp = 233$ kcal/mol, $r0 = 0.74$ Å, $a = 1.2$ Å⁻¹ (elevation = 90, rotation = 0, perspective = 30, chart depth = 100, sp = 0.1).

Example 7.H Counting normal modes Consider the reaction $H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$. How many modes should you include in q^\ddagger ?

Solution Consider the transition state $H \cdots H \cdots CH_2CH_3$. The transition state has 9 atoms so it must have $3 \times 9 = 27$ normal modes. The transition is nonlinear, so it has three translational modes, three rotational modes, so it must have $27 - 3 - 3 = 21$ vibrational modes.

One of the modes is the H-H-C asymmetric stretch. That is the mode that carries the incoming hydrogen along the reaction coordinate. That mode is already included in the $(h_0 V/h_0)$ term in transition state theory so we should not include it in q^\ddagger . That leaves $21 - 1 = 20$ vibrational modes. Therefore, the transition state must have 3 translational modes, three rotational modes and 20 vibrational modes.

7.0 SUGGESTIONS FOR FURTHER READING

Other elementary discussions of transition state theory and collision theory can be found in:

K. J. Laidler, *Chemical Kinetics*, 3rd ed., Harper & Row, New York, 1987.

Additional suggestions for further reading are given in Chapters 8 and 9.

7.0 PROBLEMS

7.1 Define the following terms:

- (a) Arrhenius' theory
- (b) Collision theory
- (c) Transition state theory
- (d) RRKM model
- (e) Lindemann model
- (f) Transmission coefficient
- (g) Wigner and Polanyi's model
- (h) Tunneling
- (i) Entropy of activation
- (j) Saddle point energy
- (k) Potential energy surface
- (l) Reduced mass
- (m) Collision partner
- (n) Partition function
- (o) Moment of inertia
- (p) Transition state
- (q) Col
- (r) Loose transition state
- (s) Tight transition state
- (t) Transition state analog

7.2 In Section 7.4.1 we noted that transition state theory predicts that a bimolecular collision has a preexponential in the order of 10^{13} Å³/(molecule-second). Calculate a typical value of the preexponential in units of (a) cm³/(mol-second), (b) liter/(mol-second), (c) liter/(mol-hour), (d) dm³/(mol-second).

7.3 Compare and contrast: collision theory, transition state theory, and the RRKM model. What are the key assumptions in each model? What are the key predictions of each model? Where do the models fail? How is transition state theory different from Wigner and Polanyi's model?

7.4 Describe in your own words why the preexponentials for unimolecular reactions are so large. Where does the large term come into the RRKM model? How large is the term?

7.5 What lead Arrhenius to propose that the rate varied exponentially with temperature? That is, what in Figure 7.1 and equation (7.2) leads to an exponential temperature dependence?

7.6 One of the ways that enzymes work is by binding to the transition state of a reaction. Assume that you have an enzyme that forms a 10-kcal/mol bond to the

reactants (i.e., $\Delta G = 10$ kcal/mol), a 12-kcal/mol bond to the products, and a 28-kcal/mol bond to the transition state. By how much will the rate of reaction increase at 310 K in the presence of the enzyme?

7.7 Table 7.4 compares the saddle point energy to the activation barrier for a number of reactions.

- Plot the measured versus calculated activation barrier. Do you see any pattern?
- Why are the barriers lower than the saddle energy for hydrogen transfer reactions?
- How do the other barriers compare?

7.8 Figure 7.6a shows a potential energy surface for the reaction



Make a copy of the figure. Start with the picture on the left of the figure and identify

- The minimum energy of the reactants when the reactants are far apart. (*Hint*: When the reactants are far apart, the H–H distance is large.)
- The minimum energy of the products.
- The vibrational well of the reactants.
- The vibrational well of the products.
- The transition state.
- What does the C–H potential look like when the H–H distance is large?
- What does the H–H potential look like when the C–H distance is large?
- What does the potential look like near the transition state?
- Repeat all of the questions on the contour plot on Figure 7.6b. Can you see the C–H and H–H potentials? Can you see the shape of the transition state?

7.9 In Section 7.4, we discussed the Lindemann model. We assumed that a unimolecular reaction $A \Rightarrow B$ followed



and stated that

$$r_{\text{B}} = \frac{k_1[\text{A}][\text{X}]}{k_2[\text{X}] + 1} \quad (\text{P7.9.1})$$

- Use the steady-state approximation to derive equation (P7.9.1).
- Now let $[\text{X}] = [\text{A}]$. Convert equation (P7.9.1) to a linear form. Two linear forms are possible: one based on the Lineweaver–Burke transformation (see Example 3.A), and another based on the Eadie–Hofstee transformation. Derive an equation for both of them.
- Table P3.17 page 149 shows some data for the reaction $\text{HNC} \Rightarrow \text{HCN}$. How well do each of the lines fit?

7.10 Why do the lines look so poor when Figure 7.10 shows that equation P7.9.1 fits the data quite well? *Hint*: look back to the discussion of errors in Example 3.A.

Use transition state theory to calculate the temperature dependence of the rate constant for

- The reaction $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$, where A, B, and C are atoms. Assume a linear transition state.
- $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$, where A, B, and C are atoms. Assume a nonlinear transition state.
- $\text{AB} + \text{CD} \rightarrow \text{ABC} + \text{D}$, where A, B, C, and D are atoms. Assume a linear transition state.
- $\text{AB} + \text{CD} \rightarrow \text{ABC} + \text{D}$, where A, B, C, and D are atoms. Assume a nonlinear transition state.
- Estimate the value of the preexponential at 500 K in all cases.

7.11 Example 7.G showed values of the potential given by equation (7.G.1).

Set up the spreadsheet yourself and verify the findings. The original spreadsheet is posted at <http://www.wiley.com/chemcalc/kinetics>.

- Print out the numerical values of the spreadsheet for $w = 100$ kcal/mol, $wa = 0$, $hr = 0$, $vp = 230$ kcal/mol, $r_0 = 0.74 \text{ \AA}$, $a = 1.2 \text{ \AA}^{-1}$.
- Consider the reaction $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$, with r_1 = the AB distance and r_2 = the BC distance. Find the place corresponding to the reactants and the products. (*Hint*: Examine Example 8.A—this is similar except r_1 and r_2 are reversed.)
- Trace a path from the reactants to products as indicated in Example 8.A.
- Identify the saddle point on your plot.
- Show that your point is really a saddle point.
- What is the energy of the transition state?

7.12 Example 7.G showed values of the potential given by equation (7.G.1).

Set up the spreadsheet yourself and verify the findings. The original spreadsheet is posted at <http://www.wiley.com/chemcalc/kinetics>.

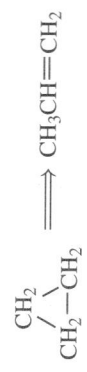
Make contour plots (i.e., top views) of the potential for the following parameters:

- $w = 100$ kcal/mol, $wa = 0$, $hr = 0$, $vp = 218$ kcal/mol, $r_0 = 0.74 \text{ \AA}$, $a = 1.2 \text{ \AA}^{-1}$
- $w = 100$ kcal/mol, $wa = 0$, $hr = -20$, $vp = 218$ kcal/mol, $r_0 = 0.74 \text{ \AA}$, $a = 1.2 \text{ \AA}^{-1}$
- $w = 100$ kcal/mol, $wa = 0$, $hr = 20$, $vp = 218$ kcal/mol, $r_0 = 0.74 \text{ \AA}$, $a = 1.2 \text{ \AA}^{-1}$
- $w = 100$ kcal/mol, $wa = 5$, $hr = 0$, $vp = 218$ kcal/mol, $r_0 = 0.74 \text{ \AA}$, $a = 1.2 \text{ \AA}^{-1}$
- $w = 100$ kcal/mol, $wa = 0$, $hr = 0$, $vp = 188$ kcal/mol, $r_0 = 0.74 \text{ \AA}$, $a = 1.2 \text{ \AA}^{-1}$
- $w = 100$ kcal/mol, $wa = -5$, $hr = 0$, $vp = 218$ kcal/mol, $r_0 = 0.74 \text{ \AA}$, $a = 1.2 \text{ \AA}^{-1}$

Use $sp = 0.1$ in all cases

- (c) In each case label the reactants, products, transition states, or complexes on your plots following Problem 7.11(c).
- (d) Which of the reactions are activated in the forward direction? [Hint: The reaction will be activated if (1) there is a saddle point with an energy above the reactants or (2) if the reaction is endothermic so that the system must go uphill to products.]
- (e) Which of the reactions are activated in the reverse direction?

7.13 The reaction



- has an activation barrier of 66 kcal/mol.
- (a) Use the Kassel-Rice-Ramsperger model to estimate the preexponential for the reaction at 1000 K. (Assume that you are working in the high-pressure limit so that $k = k_3$.)
- (b) Estimate the rate constant at 1000 K.
- (c) Estimate the temperature dependence of the preexponential for the reaction.

7.14 D. R. Hershbach, et al. (1956), reported preexponentials for a number of reaction. Most were near 10^{13} Å³/(molecule-second), but some were not. Table P7.14 gives a few examples where the preexponential differs substantially from 10^{13} . Go through each of the examples and tell us what you know about the transition state.

- (a) Is it a loose (i.e., hard-sphere-like) or tight (i.e., have a very specific geometry)?
- (b) Diagram a likely transition state from the data given.
- (c) Estimate the preexponential for your transition state. Can you find a transition state with a small enough preexponential?

7.15 The preexponentials for surface reactions can be very different from 10^{13} . Consider the reaction



Table P7.14 A selection of reactions that show preexponentials well below 10^{13}

Reaction	E_a , kcal/mol	$\log(k_0)$, Å ³ /(molecule-second)
$\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$	2.6	11.1
$\text{NO} + \text{O}_3 \longrightarrow \text{NO}_3 + \text{O}$	7	12
$\text{NO}_2 + \text{F}_2 \longrightarrow \text{NO}_2\text{F} + \text{F}$	10.4	11.4
$\text{NO}_2 + \text{CO} \longrightarrow \text{CO} + \text{CO}_2$	31.5	12.3
$2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$	26.5	11.5
$\text{NO} + \text{NO}_2\text{Cl} \longrightarrow \text{NOCl} + \text{N}_2\text{O}$	6.4	11.1
$2\text{NOCl} \rightleftharpoons 2\text{NO} + \text{Cl}_2$	20.3	12.2
$\text{F}_2 + \text{ClO}_2 \longrightarrow \text{FClO}_2 + \text{F}$	8.5	9.7
$2\text{ClO} \rightleftharpoons \text{Cl}_2 + \text{O}_2$	0	10.0

(a) Assume that the transition state is a surface complex that does not translate, vibrate, or rotate. Estimate the preexponential for the reaction. Hint: Be careful with units. When you replace a translational with a vibrational partition function you replace q_T with q_V . However q_L (not q_T) appears in equation (7.B.3).

(b) Now assume that the preexponential can translate in two dimensions and rotate around one axis. How would the preexponential change?

7.16 The objective of this problem is to calculate the rate of formation of NO from the air in your bedroom. Assume that the main reaction is



with an activation barrier of 85 kcal/mol.

- (a) What is the collision rate of N_2 with O_2 in air at 300 K and 1 atm?
- (b) What fraction of the collisions have at least 85 kcal/mol?
- (c) Assume that there are 2000 liters of air in your bedroom. Use collision theory to estimate the NO production rate in molecules/per hour.
- (d) NO is poisonous. Will you ever produce enough NO to poison you? Be sure to consider the equilibrium concentration of NO.

7.17 Use transition state theory and collision theory and the data in Table P7.17 to estimate the rate of the reaction



- at 300, 400, 500, 600, 700, 800, 900, and 1000 K.
- (a) Estimate the preexponentials at each temperature
- (b) Make an Arrhenius plot of the rate constant as a function of temperature to estimate a preexponential. How well does your preexponential fit agree with the results in (a)?
- (c) How well does your activation barrier compare to E^\ddagger ?

Table P7.17 Data for the transition state of reaction (P7.17.1)

	Linear Transition State	Reactants	
		H	HBr
r_{HH}	1.5 Å	—	1.414 Å
r_{HBr}	1.42 Å	—	—
$\nu_{\text{H-Br}}$	2340 cm ⁻¹	—	2650 cm ⁻¹
$\nu_{\text{HBr bend}}$	460 cm ⁻¹	—	—
$\nu_{\text{HBr bend}}$	460 cm ⁻¹	—	—
Curvature	320 cm ⁻¹	—	—
I	10.4 amu·Å ²	—	1.99 amu·Å ²
E^\ddagger	1.21 kcal/mol	—	—
g_c	4	1	4

(d) How do the preexponentials compare to the experimental value of $4.2 \times 10^{13} \text{ \AA}^3/(\text{molecule}\cdot\text{second})$?

More Advanced Problems

7.18 The objective of this problem is to use collision theory and transition state theory to model adsorption. Consider a simple chemical reaction:



where a CO molecule reacts with a surface site, S. Masel (1996) shows that one can model the rate via collision theory:

$$R_{\text{ad}} = (0.25v_{\text{CO}})\sigma_s C_{\text{CO}} P_{\text{stick}} \quad (\text{P7.18.2})$$

where R_{ad} is the rate of adsorption in molecules/cm², v_{CO} is the average molecular velocity of the CO, C_{CO} is the gas-phase CO concentration in molecules/cm³, σ_s is the concentration of surface sites, σ_s is the surface area taken up by one surface site, and P_{stick} is the probability that the CO sticks when it hits the surface. Notice that we use $0.25v_{\text{CO}}$ in equation (P7.18.2) rather than v_{CO} . If all the CO would impinge perpendicularly to the surface, then v_{CO} would have been the correct term. However, in reality, the COs impinge from all directions, and it works out that the correct velocity is $0.25v_{\text{CO}}$.

- (a) Calculate the rate of adsorption of CO in molecules/(cm²·second) at 300 K and 1 atm pressure. Assume that P_{stick} is 0.5, and that $C_s = 10^{15}$ sites/cm².
- (b) How long will it take for all of the surface sites to be filled with gas?
- (c) In reality, P_{stick} decreases as the surface coverage increases because gas cannot stick to sites that are filled with gas. Calculate how long it will take to fill 99% of the surface with gas assuming that $P_{\text{stick}} = 0.5(1 - \theta_{\text{CO}})$, where θ_{CO} is the fraction of the surface covered by CO.
- (d) How low of a pressure do you need to reach to slow down the adsorption process, so that the adsorption process takes 100 seconds?
- (e) The calculations so far in this problem assumed that the sticking probability was 0.5. Use transition state theory to get a “better” value. Assume that there is no barrier to adsorption (i.e., $E_a = 0$). Also assume that at the transition state, the CO is stuck to the surface, so it does not translate or rotate. Instead the transition state vibrates, with vibrational frequencies of 45, 49, 130, 133, and 2085 cm⁻¹.

7.19 In this chapter we have been examining chemical reactions, but the equations in the chapter are also useful for nuclear reactions. Consider the simple nuclear reaction:



where n is a neutron.

(a) Derive an equation for the rate of reaction as a function of the concentration of neutrons and lead atoms, the average velocity of the neutron and the lead atoms,

and the crosssection for neutron capture. Note the crosssection $\sigma_x = \pi(b_{\text{coll}})^2$, where b_{coll} is the collision diameter.

- (b) Assume that you have a nuclear reactor producing 1-eV neutrons. Calculate the rate constant of the reaction. Assume a crosssection of 0.37 barn/lead atom (1 barn = 10^{-20} \AA^2). [Hint: First calculate the velocity of the neutrons from $E_n = \frac{1}{2}m_n(v_n)^2$, where E_n is the energy of the neutron, m_n is the mass of the neutron, and v_n is the velocity of the neutron].
- (c) Show that the reaction is first-order in the neutron concentration.
- (d) Now consider shooting neutrons through a flat plate. Show that if you start the neutrons moving through the plate at time, $t = 0$, the concentration of neutrons will obey

$$\frac{dC_n}{dt} = \sigma_x v_n C_n C_{\text{Pb}} \quad (\text{P7.19.1})$$

where C_n is the neutron concentration, C_{Pb} is the concentration of lead atoms, v_n is the neutron’s velocity, and σ_x is the cross section.

- (e) Do a shell balance to show that the concentration of neutrons at any distance x from the front of the plate obeys
- $$\frac{dC_n}{dx} = \sigma_x C_n C_{\text{Pb}} \quad (\text{P7.19.2})$$

(f) Integrate equation (P7.19.2) to derive an equation for the fraction of the neutrons that are captured in passing through a lead plate as a function of the thickness of the plate. Assume that the plate is 22% ²⁰⁷Pb and that the other lead isotopes have small neutron cross sections.

(g) How thick of a lead plate do you need to capture 99.999% of the neutrons? Berry and Marshall (1918) studied the reaction



They obtained the results in Table P7.20 (see also Figure P7.20). The objective of this problem is to use transition state theory to obtain a rate constant for the reaction.

(a) How many translational, vibrational, and rotational modes are there in the reactants, products, and transition state?

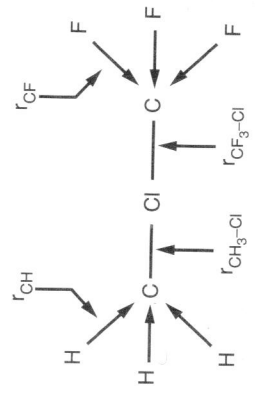


Figure P7.20 Transition state geometry for Problem 7.20.

Table P7.20 Data for Problem 7.20

	CH ₃ (planar)	CICF ₃	TST
r _{CH}	1.078 Å		1.085 Å
r _{CF}		1.335 Å	1.331 Å
r _{CF₃-Cl}		1.749 Å	2.014 Å
r _{CH₃-Cl}			2.031 Å
Angle H-C-Cl			104.1°
Angle Cl-C-F		110.4°	109.2°
E [‡]			19.4 kcal/mol
Vibrations	384 cm ⁻¹	337 cm ⁻¹	14 cm ⁻¹
	1407 cm ⁻¹	332 cm ⁻¹	79 cm ⁻¹
	1477 cm ⁻¹	402 cm ⁻¹	79 cm ⁻¹
	3061 cm ⁻¹	531 cm ⁻¹	242 cm ⁻¹
	3240 cm ⁻¹	531 cm ⁻¹	242 cm ⁻¹
	3240 cm ⁻¹	752 cm ⁻¹	274 cm ⁻¹
		1095 cm ⁻¹	483 cm ⁻¹
		1220 cm ⁻¹	483 cm ⁻¹
		1220 cm ⁻¹	647 cm ⁻¹
			755 cm ⁻¹
			755 cm ⁻¹
			951 cm ⁻¹
			1131 cm ⁻¹
			1190 cm ⁻¹
			1190 cm ⁻¹
			1379 cm ⁻¹
			1379 cm ⁻¹
			2909 cm ⁻¹
			3052 cm ⁻¹
			3052 cm ⁻¹
Curvature			101 cm ⁻¹

(d) Calculate the position of the center of mass from

$$X_{cm} = \sum_i m_i X_i$$

$$Y_{cm} = \sum_i m_i Y_i$$

$$Z_{cm} = \sum_i m_i Z_i$$

(e) Next, calculate the three moments of inertia.

(f) Plug into transition state theory to calculate the rate constant for the reaction at 800 K.

7.21

One of the key steps in the reproduction cycle of the HIV-1 virus is for the virus to produce an enzyme protease that catalyzes the hydrolysis of a protein in your blood cells. The enzyme produces fragments that act as the building block for the production of more viruses. One class of AIDS drugs work by mimicking the transition state for the reaction and binding to the active site on the enzyme. *Erickson and Wlodawer, (1993)* describe the findings.

(a) Explain how the transition state analogs block the transition state.

(b) Look up the structure of Indinavir, Saquinavir, and Ritonavir. How are they similar or different?

(c) Look up how each of these drugs bind to the enzyme.

(d) What do these findings tell you about the transition state for the reaction on the protease?

(b) Next, you need to calculate the three moments of inertia for each of the species. Recall from freshman physics that

$$I_X = \sum_{\text{atoms}} m_i (X_i - X_{cm})^2$$

$$I_Y = \sum_{\text{atoms}} m_i (Y_i - Y_{cm})^2$$

$$I_Z = \sum_{\text{atoms}} m_i (Z_i - Z_{cm})^2$$

where X_i, Y_i, and Z_i are respectively the X, Y, and Z positions of atoms i; and X_{cm}, Y_{cm}, and Z_{cm} are the positions of the center of mass.

(c) Pick one of the carbon atoms as the origin, then calculate the X, Y, and Z positions of all of the other atoms in the reactants, products, and transition state.