Professional Reference Shelf

A. Collision Theory

Overview – Collision Theory

In Chapter 3, we presented a number of rate laws that depended on both concentration and temperature. For the elementary reaction

\[ A + B \rightarrow C + D \]

the elementary rate law is

\[ -r_A = k C_A C_B = A e^{-E_A / RT} C_A C_B \]

We want to provide at least a qualitative understanding of why the rate law takes this form. We will first develop the collision rate, using collision theory for hard spheres of cross section \( S_r \), \( \pi \sigma_{AB}^2 \). When all collisions occur with the same relative velocity, \( U_R \), the number of collisions between A and B molecules, \( \tilde{Z}_{AB} \), is

\[ \tilde{Z}_{AB} = S_r U_R \tilde{C}_A \tilde{C}_B \quad \text{[collisions/s/molecule]} \]

Next, we will consider a distribution of relative velocities and only consider those collisions that have an energy of \( E_A \) or greater in order to react to show

\[ -r_A = A e^{-E_A / RT} C_A C_B \]

where

\[ A = \pi \sigma_{AB}^2 \left( \frac{8 k_B T}{\pi \mu_{AB}} \right)^{1/2} N_{Avo} \]

with \( \sigma_{AB} \) = collision radius, \( k_B \) = Boltzmann’s constant, \( \mu_{AB} \) = reduced mass, \( T \) = temperature, and \( N_{Avo} \) = Avogadro’s number. To obtain an estimate of \( E_A \), we use the Polanyi Equation

\[ E_A = E_A^0 + \gamma_P \Delta H_{Rx} \]

Where \( \Delta H_{Rx} \) is the heat of reaction and \( E_A^0 \) and \( \gamma_P \) are the Polanyi Parameters. With these equations for \( A \) and \( E_A \) we can make a first approximation to the rate law parameters without going to the lab.
HOT BUTTONS

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References for Collision Theory, Transition State Theory, and Molecular Dynamics

As a shorthand notation, we will use the following references nomenclature:

This nomenclature means that if you want background on the principle, topic, postulate, or equation being discussed, go to the specified page of the referenced text.

I. FUNDAMENTALS OF COLLISION THEORY

The objective of this development is to give the reader insight into why the rate laws depend on the concentration of the reacting species (i.e., \(-r_A = kC_AC_B\)) and why the temperature dependence is in the form of the Arrhenius law, \(k= Ae^{-E/RT}\).

To achieve this goal, we consider the reaction of two molecules in the gas phase

\[ A + B \rightarrow C + D \]

We will model these molecules as rigid spheres.
A. Rigid Spheres

Species A and B are modeled as rigid spheres of radius $\sigma_A$ and $\sigma_B$, respectively.

![Figure R3.A-1](image)

Figure R3.A-1 Schematic of molecules A and B.

We shall define our coordinate system such that molecule B is stationary wrt molecule A so that molecule A moves towards molecule B with a relative velocity, $U_R$. Molecule A moves through space to sweep out a collision volume with a collision cross section, $\pi \sigma_{AB}^2$, illustrated by the cylinder shown in Figure R3.A-2.

![Figure R3.A-2](image)

Figure R3.A-2 Schematic of collision cross-section.

The collision radius is $\sigma_{AB}$.

\[
\sigma_{AB} = \sigma_A + \sigma_B
\]

If the center of a “B” molecule comes within a distance of $\sigma_{AB}$ of the center of the “A” molecule they will collide. The collision cross section of rigid spheres is $S_r = \pi \sigma_{AB}^2$. As a first approximation, we shall consider $S_r$ constant. This constraint will be relaxed when we consider a distribution of relative velocities. The relative velocity between gas molecules A and B is $U_R$.

\[
U_R = \left(\frac{8k_B T}{\pi \mu_{AB}}\right)^{1/2}
\]

(R3.A-1)

where

\[
k_B = \text{Boltzmann’s constant} = 1.381 \times 10^{-23} \text{ J/K/molecule} = 1.381 \text{ kg m}^2/\text{s}^2/\text{K/molecule}
\]

\[\uparrow\] This equation is given in most physical chemistry books, e.g., see Moore, W. J. Physical Chemistry, 2nd Ed., Englewood Cliffs, NJ: Prentice Hall, p.187.
m_A = mass of a molecule of species A (gm)
m_B = mass of a molecule of species B (gm)
\( \mu_{AB} = \text{reduced mass} = \frac{m_A m_B}{m_A + m_B} \) (g), [Let \( \mu = \mu_{AB} \)]

\[ M_A = \text{Molecular weight of A (Daltons)} \]
\[ N_{Avo} = \text{Avogadro’s number} 6.022 \text{ molecules/mol} \]
\[ R = \text{Ideal gas constant} 8.314 \text{ J/mol} \cdot \text{K} = 8.314 \text{ kg} \cdot \text{m}^2/\text{s}^2/\text{mol} \cdot \text{K} \]

We note that \( R = N_{Avo} k_B \) and \( M_A = N_{Avo} \cdot m_A \), therefore we can write the ratio \( (k_B/\mu_{AB}) \) as

\[
\frac{k_B}{\mu_{AB}} = \sqrt[3]{\frac{R}{M_A M_B}} \frac{1}{M_A + M_B} \]  

(R3.A-2)

An order of magnitude of the relative velocity at 300 K is \( U_R \approx 3000 \text{ km/hr} \), i.e., ten times the speed of an Indianapolis 500 Formula 1 car. The collision diameter and velocities at 0°C are given in Table R3.A-1.

**Table R3.A-1 Molecular Diameters**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Average Velocity, (meters/second)</th>
<th>Molecular Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>1687</td>
<td>2.74</td>
</tr>
<tr>
<td>CO</td>
<td>453</td>
<td>3.12</td>
</tr>
<tr>
<td>Xe</td>
<td>209</td>
<td>4.85</td>
</tr>
<tr>
<td>He</td>
<td>1200</td>
<td>2.2</td>
</tr>
<tr>
<td>N(_2)</td>
<td>450</td>
<td>3.5</td>
</tr>
<tr>
<td>O(_2)</td>
<td>420</td>
<td>3.1</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>560</td>
<td>3.7</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>437</td>
<td>5.3</td>
</tr>
<tr>
<td>C(_4)H(_6)</td>
<td>270</td>
<td>3.5</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>593</td>
<td>4.1</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>518</td>
<td>4.4</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>412</td>
<td>4.7</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>361</td>
<td>4.6</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>361</td>
<td>4.7</td>
</tr>
<tr>
<td>NO</td>
<td>437</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Consider a molecule A moving in space. In a time \( \Delta t \), the volume \( \Delta V \) swept out by a molecule of A is

\[ \Delta V = (U_R \Delta t) \pi \sigma_{AB}^2 \]

Figure R3.A-3 Volume swept out by molecule A in time \( \Delta t \).

The bends in the volume represent that even though molecule A may change directions upon collision the volume sweep out is the same. The number of collisions that will take place will be equal to the number of B molecules, \( \Delta V \tilde{C}_B \), that are in the volume swept out by the A molecule:

\[
[\tilde{C}_B \Delta V = \text{No. of B molecules in } \Delta V]
\]

where \( \tilde{C}_B \) is in \([\text{molecules/dm}^3]\) rather than \([\text{moles/dm}^3]\)

In a time \( \Delta t \), the number of collisions of this one A molecule with many B molecules is \( U_R \tilde{C}_B \pi \sigma_{AB}^2 \Delta t \). The number of collisions of this one A molecule with all the B molecules per unit time is

\[
\dot{Z}_{1A \cdot B} = \pi \sigma_{AB}^2 \tilde{C}_B U_R
\]

(R3.A-3)

However, we have many A molecules present at a concentration, \( \tilde{C}_A \) (molecule/dm\(^3\)). Adding up the collisions of all the A molecules per unit volume, \( \tilde{C}_A \), then the number of collisions \( \dot{Z}_{AB} \) of all the A molecules with all B molecules per time per unit volume is

\[
\dot{Z}_{AB} = \pi \sigma_{AB}^2 U_R \tilde{C}_A \tilde{C}_B = S_t U_R \tilde{C}_A \tilde{C}_B
\]

(R3.A-4)

Where \( S_t \) is the collision cross section (\( \text{Å} \))^2. Substituting for \( S_t \) and \( U_R \)

\[
\dot{Z}_{AB} = \pi \sigma_{AB}^2 \left( \frac{8 k_B T}{\pi \mu} \right)^{1/2} \tilde{C}_A \tilde{C}_B \text{[molecules/time/volume]} \]

(R3.A-5)

If we assume all collisions result in reactions, then

\[
-\dot{r}_A = \dot{Z}_{AB} = \pi \sigma_{AB}^2 \left( \frac{8 k_B T}{\pi \mu} \right)^{1/2} \tilde{C}_A \tilde{C}_B \text{[molecules/time/volume]} \]

(R3.A-6)

Multiplying and dividing by Avogadro's number, \( N_{Avo} \), we can put our equation for the rate of reaction in terms of the number of moles/time/vol.

\[
\begin{align*}
\left( \frac{-\dot{r}_A}{N_{Avo}} \right) N_{Avo} &= \pi \sigma_{AB}^2 \left( \frac{8 k_B T}{\pi \mu} \right)^{1/2} \frac{\tilde{C}_A}{C_A} \frac{\tilde{C}_B}{C_B} N_{Avo}^2
\end{align*}
\]

(R3.A-7)
\[ -r_A = \pi \sigma_{AB}^2 \left( \frac{8\pi k_B T}{\mu \pi} \right)^{1/2} N_{Avo} C_A C_B \text{ [moles/time/volume]} \]  
(R3.A-8)

where \( A \) is the frequency factor

\[ A = \sigma_{AB}^2 \left( \frac{8\pi k_B T}{\mu_{AB}} \right)^{1/2} N_{Avo} \]  
(R3.A-9)

\[ -r_A = A C_A C_B \]  
(R3.A-10)

**Example**

Calculate the frequency factor \( A \) for the reaction

\[ H + O_2 \rightarrow OH + O \]

at 273K.

Additional information:

Using the values in Table R3.A-1

Collision Radii

- Hydrogen H \( \sigma_H = 2.74 \, \text{Å}/4 = 0.68 \, \text{Å} = 0.68 \times 10^{-10} \, \text{m} \)
- Oxygen \( O_2 \) \( \sigma_{O_2} = \frac{3.1}{2} \, \text{Å} = 1.55 \, \text{Å} = 1.5 \times 10^{-10} \, \text{m} \)

\[ R = 8.31 \, \text{J/mol/K} = 8.314 \, \text{kg m}^2/\text{s}^2/\text{K/mol} \]

**Solution**

\[ A = S_r U_R N_{Avo} \]  
(R3.A-E-1)

\[ A = \pi \sigma_{AB}^2 U_R N_{Avo} = \pi \sigma_{AB}^2 \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} N_{Avo} \]  
(R3.A-9)

The relative velocity is

\[ U_R = \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \]  
(R3.A-1)

Calculate the ratio \( k_B / \mu_{AB} \) (Let \( \mu = \mu_{AB} \))

\[ \frac{k_B}{\mu} = \frac{R}{M_A M_B} \left( \frac{1 \, \text{g/mol}}{1 \, \text{g/mol}} \right) \left( \frac{32 \, \text{g/mol}}{32 \, \text{g/mol}} \right) = \frac{8.314 \, \text{kg m}^2/\text{s}^2/\text{K/mol}}{0.97 \, \text{g/mol} \times \frac{1 \, \text{kg}}{1000 \, \text{g}}} \]
\[ \frac{k_B}{\mu} = 8571 \text{ m}^2/\text{s}^2/\text{K} \]

Calculate the relative velocity

\[ U_R = \left[ \frac{(8)(273K)(8571) \text{ m}^2/\text{s}^2/\text{K}}{3.14} \right]^{1/2} = 2441 \text{ m/s} = 2.44 \times 10^{13} \text{ Å/s} \]  \hspace{1cm} (R3.A-E-2)

\[ S_r = \pi \sigma_{AB}^2 = \pi \left[ \sigma_A + \sigma_B \right]^2 = \pi \left[ 0.68 \times 10^{-10} \text{ m} + 1.55 \times 10^{-10} \text{ m} \right]^2 \]

\[ = 15.6 \times 10^{-20} \text{ m}^2/\text{molecule} \]

Calculate the frequency factor \( A \)

\[ A = \frac{15.6 \times 10^{-20} \text{ m}^2}{\text{molecule}} \left[ 2441 \text{ m/s} \left[ 6.02 \times 10^{23} \text{ molecule/mol} \right] \right] \]  \hspace{1cm} (R3.A-E-3)

\[ A = 2.29 \times 10^8 \text{ m}^3/\text{mol} \cdot \text{s} = 2.29 \times 10^{11} \text{ dm}^3/\text{mol} \cdot \text{s} \]  \hspace{1cm} (R3.A-E-4)

\[ A = 2.29 \times 10^6 \text{ m}^3/\text{mol} \cdot \text{s} \times \frac{1\text{mol}}{6.02 \times 10^{23} \text{ molecule}} \left( \frac{10^{10} \text{ Å}}{\text{m}} \right)^3 \]

\[ A = 3.81 \times 10^{14} \text{ (Å)}^3/\text{molecule/s} \]  \hspace{1cm} (R3.A-E-5)

The value reported in Masel\(^\dagger\) from Wesley is

\[ A = 1.5 \times 10^{14} \text{ (Å)}^3/\text{molecule/s} \]

Close, but no cigar, as Groucho Marx would say.

For many simple reaction molecules, the calculated frequency factor \( A_{\text{calc}} \) is in good agreement with experiment. For other reactions, \( A_{\text{calc}} \) can be an order of magnitude too high or too low. In general, collision theory tends to overpredict the frequency factor \( A \)

\[ 10^8 \text{ dm}^3/\text{mol} \cdot \text{s} < A_{\text{calc}} < 10^{11} \text{ dm}^3/\text{mol} \cdot \text{s} \]

Terms of cubic angstroms per molecule per second the frequency factor is

\[ 10^{12} \text{ Å}^3/\text{molecule/s} < A_{\text{calc}} < 10^{15} \text{ Å}^3/\text{molecule/s} \]

There are a couple of things that are troubling about the rate of reaction given by Equation (R3.A-10), i.e.

\(^\dagger\)M1p367.
\[ r_A = AC_A C_B \]  \hspace{1cm} \text{(R3.A-10)}

First and most obvious is the temperature dependence. \( A \) is proportional to the square root of temperature and, therefore, is \( -r_A \):

\[ r_A \sim A \sim \sqrt{T} \]

However we know that the temperature dependence of the rate of chemical reaction on temperature is given by the Arrhenius equation

\[ r_A = Ae^{-E/RT}C_A C_B \]  \hspace{1cm} \text{(R3.A-11)}

or

\[ k = Ae^{-E/RT} \]  \hspace{1cm} \text{(R3.A-12)}

Next, we will discuss this shortcoming of collision theory, along with the assumption that all collisions result in reaction.

\section*{II. SHORTCOMINGS OF COLLISION THEORY}

A. The collision theory outlined above does not account for orientation of the collision, front-to-back and along the line-of-centers. That is, molecules need to collide in the correct orientation for reaction to occur. Figure R3.A-4 shows molecules colliding whose centers are offset by a distance \( b \).

![Figure R3.A-4 Grazing collisions.](image)

B. Collision theory does not explain activation barriers. Activation barriers occur because bonds need to be stretched or distorted in order to react and these processes require energy. Molecules must overcome electron-electron repulsion in order to come close together\(^\dagger\)

C. The collision theory does not explain the observed temperature dependence given by Arrhenius equation

\[ k = Ae^{E/RT} \]

D. Collision theory assumes all \( A \) molecules have the same relative velocity, the average one.

\[ U_R = \left( \frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2} \]  \hspace{1cm} \text{(R3.A-1)}

However, there is a distribution of velocities \( f(U,T) \). One distribution most used is the Maxwell-Boltzmann distribution.

\(^\dagger\) Masel, 1p
### III. MODIFICATIONS OF COLLISION THEORY

We are now going to account for the fact that we have (1) a distribution of relative velocities \( U_R \) and (2) that not all collisions only those collisions with an energy \( E_A \) or greater result in a reaction--the goal is to arrive at

\[
k = A e^{-E_A/RT}
\]

#### A. Distribution of Velocities

We will use the Maxwell-Boltzmann Distribution of Molecular Velocities (A6p.26). For a species of mass \( m \), the Maxwell distribution of velocities (relative velocities) is

\[
f(U,T)\,dU = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mU^2/2k_BT} \, U^2 \, dU \quad (R3.A-13)
\]

A plot of the distribution function, \( f(U,T) \), is shown as a function of \( U \) in Figure R3.A-5.

![Figure R3.A-5 Maxwell-Boltzmann distribution of velocities.](image)

Replacing \( m \) by the reduced mass \( \mu \) of two molecules A and B

\[
f(U,T)\,dU = 4\pi \left( \frac{\mu}{2\pi k_B T} \right)^{3/2} e^{-\mu U^2/2k_BT} \, U^2 \, dU
\]

The term on the left side of Equation (R3.A-13), \( [f(U,T)dU] \), is the fraction of molecules with velocities between \( U \) and \( (U + dU) \). Recall from Equation (R3.A-4) that the number of A-B collisions for a reaction cross section \( S_r \) is

\[
\tilde{Z}_{AB} = \frac{S_r(U)U}{\tilde{k}(U)} \tilde{C}_A \tilde{C}_B \quad (R3.A-14)
\]

except now the collision cross-section is a function of the relative velocity.

Note we have written the collision cross section \( S_r \) as a function of velocity \( U \): \( S_r(U) \). Why does the velocity enter into reaction cross section, \( S_r \)? Because not all collisions are head on, and those that are not will not react if the energy \( (U^2/2\mu) \) is not sufficiently high. Consequently, this functionality, \( S_r = S_r(U) \), is reasonable because if two molecules collide with a very very low relative velocity it is unlikely that such a small transfer of kinetic energy is likely to activate the internal vibrations of the molecule to cause the breaking of bonds. On the other hand, for collisions with large relative velocities most collisions will result in reaction.
We now let \( \tilde{k}(U) \) be the specific reaction rate for a collision and reaction of A-B molecules with a velocity \( U \).

\[
\tilde{k}(U) = S_r(U) U \left[ \text{m}^3/\text{molecule/s} \right] \quad \text{(R3.A-15)}
\]

Equation (R3.A-15) will give the specific reaction rate and hence the reaction rate for only those collisions with velocity \( U \). We need to sum up the collisions of all velocities. We will use the Maxwell-Boltzmann distribution for \( f(U,T) \) and integrate over all relative velocities.

\[
\tilde{k}(T) = \int_0^\infty k(U)f(U,T)dU = \int_0^\infty f(U,T) S_r(U) UdU \quad \text{(R3.A-16)}
\]

Maxwell distribution function of velocities for the A/B pair of reduced mass \( \mu_{AB} \) is\(^1\)

\[
f(U,T) = 4\pi \left( \frac{\mu}{2\pi k_B T} \right)^{3/2} U^2 e^{-\frac{\mu U^2}{2k_BT}} \quad \text{(R3.A-17)}
\]

Combining Equations (16) and (17)

\[
\tilde{k}(T) = \int_0^\infty S_r U 4\pi \left( \frac{\mu}{2\pi k_B T} \right)^{3/2} U^2 e^{-\frac{\mu U^2}{2k_BT}} dU \quad \text{(R3.A-18)}
\]

For brevity, we let \( S_r = S_r(U) \), we will now express the distribution function in terms of the translational energy \( \varepsilon_T \).

We are now going to express the equation for \( \tilde{k}(T) \) in terms of kinetic energy rather than velocity. Relating the differential translational kinetic energy, \( \varepsilon \), to the velocity \( U \):

\[
\varepsilon_t = \frac{\mu U^2}{2}
\]

Multiplying and dividing by \( \frac{2}{\mu} \) and \( \mu \), we obtain

\[
d\varepsilon_t = \mu UdU
\]

and hence, the reaction rate

\[
\tilde{k}(T) = 4\pi \left( \frac{\mu}{2\pi k_B T} \right)^{3/2} \int_0^\infty S_r \frac{2}{\mu} \frac{\mu U^2}{2} e^{-\frac{\mu U^2}{2(k_BT)}} \left( \frac{1}{\mu} \right) \frac{\mu UdU}{d\varepsilon_t} e^{-\varepsilon_t/k_BT} d\varepsilon_t
\]

Simplifying

\[
= 4\pi \left( \frac{\mu}{2\pi k_B T} \right)^{3/2} \frac{2}{\mu^2} \int_0^\infty S_r \varepsilon_t e^{-\varepsilon_t/k_BT} d\varepsilon_t
\]

\(^1\)2p185, A5p36
\[ \tilde{k}(T) = \left[ \frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \int_0^\infty S_r \left[ \frac{\epsilon_t}{k_B T} \right]^3 \left[ \frac{e^{-\frac{\epsilon_t}{k_B T}}}{\epsilon_t} \right] \mathrm{d}\epsilon_t \left[ \text{m}^3/\text{s/molecule} \right] \] (R3.A-19)

\[ \tilde{k}(T) = \left[ \frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \int_0^\infty S_r(\epsilon_t) e^{-\frac{\epsilon_t}{k_B T}} \mathrm{d}\epsilon_t \]

Multiplying and dividing by \( k_B T \) and noting \( (\epsilon_t/k_B T) = (E/RT) \), we obtain

\[ \tilde{k}(T) = \left[ \frac{8k_B T}{\pi \mu} \right]^{1/2} \int_0^\infty S_r(E) \frac{E e^{-E/RT}}{RT} \left( \frac{dE}{RT} \right) \] (R3.A-20)

Again, recall the tilde, e.g., \( \tilde{k}(T) \), denotes that the specific reaction rate is per molecule (dm\(^3\)/molecule/s). The only thing left to do is to specify the reaction cross-section, \( S_r(E) \), as a function of kinetic energy \( E \) for the A/B pair of molecules.

**B. Collisions that Result in Reaction**

We now modify the hard sphere collision cross section to account for the fact that not all collisions result in reaction. Now we define \( S_r \) to be the reaction cross section defined as

\[ S_r = P_r \pi \sigma_{AB}^2 \]

where \( P_r \) is the probability of reaction. In the first model we say the probability is either 0 or 1. In the second model \( P_r \) varies from 0 to 1 continuously. We will now insert each of these modules into Equation (R3.A-20).

**B.1 Model 1**

In this model, we say only those hard collisions that have kinetic energy \( E_A \) or greater will react. Let \( E = \epsilon_t \). That is, below this energy, \( E_A \), the molecules do not have sufficient energy to react so the reaction cross section is zero, \( S_r = 0 \). Above this kinetic energy all the molecules that collide react and the reaction cross-section is \( S_r = \pi \sigma_{AB}^2 \)

\[ P_r = 0 \quad \therefore \quad S_r[E,T] = 0 \quad \text{for} \quad E < E_A \] (R3.A-21)

\[ P_r = 1 \quad \therefore \quad S_r[E,T] = \pi \sigma_{AB}^2 \quad \text{for} \quad E \geq E_A \] (R3.A-22)
Integrating Equation (R3.A-20) by parts for the conditions given by Equations (R3.A-21) and (R3.A-22) we obtain

\[ \tilde{k} = \left( \frac{8}{\pi \mu} T \right)^{1/2} \left[ 1 + \frac{E_A}{RT} \right] e^{-E_A/RT} \pi \sigma_{AB}^2 \]  

(R3.A-23)

\[ = U_R \pi \sigma_{AB}^2 \left[ 1 + \frac{E_A}{RT} \right] e^{-E_A/RT} \]

Derive

\[(\text{Click Back 1})\]

\[\tilde{k}(T) = \left[ \frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \int_{0}^{\infty} S_r(\varepsilon_T) e^{-\varepsilon_T/k_B T} \varepsilon_T \, d\varepsilon_T \]

\[S_r = 0 \quad \varepsilon < \varepsilon^* \]

\[S_r = \pi \sigma_{AB}^2 \quad \varepsilon \geq \varepsilon^* \]

\[\tilde{k}(T) = \left[ \frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \pi \sigma_{AB}^2 \int_{\varepsilon^*}^{\infty} e^{-\varepsilon_T/k_B T} \varepsilon_T \, d\varepsilon_T \]

\[= \pi \sigma_{AB}^2 \left[ \frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \left( k_B T \right)^2 \int_{E_A}^{\infty} \frac{E}{k_B T} \, e^{-E/k_B T} \, dE \frac{1}{RT} \]

\[X = \frac{\varepsilon_T}{k_B T}, \quad dX = \frac{d\varepsilon_T}{k_B T}, \quad X = \frac{E}{RT}, \quad \frac{\varepsilon_T}{k_B T} = \frac{E}{RT} \]

Figure R3.A-6 Reaction cross section for Model 1.
\[
\tilde{k}(T) = \pi \sigma_{AB}^2 \left( \frac{8k_B^2 T}{\mu \pi} \right)^{1/2} \int_{E_A/RT}^\infty \frac{X}{u} e^{-X} \frac{dX}{dv} = -X e^{-X} \bigg|_{E_A/RT}^{\infty} - \int_{E_A/RT}^\infty e^{-X} dX
\]

\[
= \pi \sigma_{AB}^2 \left( \frac{8k_B^2 T}{\mu \pi} \right)^{1/2} \left[ \frac{E_A}{RT} e^{-E_A/RT} + e^{-E_A/RT} \right]
\]

\[
= \pi \sigma_{AB}^2 \left( \frac{8k_B^2 T}{\mu \pi} \right)^{1/2} \left[ \frac{E_A}{RT} + 1 \right] e^{-E_A/RT}
\]

\[
\frac{E_A}{RT} > 1
\]

\[
k(T) = N_{Avo} \tilde{k}(T) = \pi \sigma_{AB}^2 \left( \frac{8k_B^2 T}{\mu \pi} \right)^{1/2} N_{Avo} \frac{E_A}{RT}
\]

\[
= A \frac{E_A}{RT}
\]

Over predicts the frequency factor

\[
S_r = P_r \pi \sigma_{AB}^2
\]

Generally, \( \frac{E_A}{RT} >> 1 \), so

\[
\tilde{k} = \frac{U_R \pi \sigma_{AB}^2 E_A}{RT} \frac{e^{-E_A/RT}}{A'}
\]

Converting \( \tilde{k} \) to a per mole basis rather than a per molecular basis we have

\[
A' = \left( \frac{E_A}{RT} \right) \sigma_{AB}^2 \left( \frac{\pi 8k_B^2 T}{\mu_{AB}} \right)^{1/2} N_{Avo} = \frac{E_A}{RT} A
\]

\[
k = A' e^{-E_A/RT} = \frac{E_A}{RT} A e^{-E_A/RT}
\]

We have good news and bad news. This model gives the correct temperature dependence but predicted frequency factor \( A' \) is even greater than \( A \) given by Equation (R3.A-9) (which itself is often too large) by a factor \( (E_A/RT) \). So we have solved one problem, the correct temperature dependence, but created another problem, too large a frequency factor. Let’s try Model 2.
B.2 Model 2

In this model, we again assume that the colliding molecules must have an energy $E_A$ or greater to react. However, we now assume that only the kinetic energy directed along the line of centers $E_{\parallel}$ is important. So below $E_A$ the reaction cross section is zero, $S_r=0$. The kinetic energy of approach of A toward B with a velocity $U_R$ is $E = \mu_{AB} \left( U_R^2 \right)$. However, this model assumes that only the kinetic energy directly along the line of centers contributes to the reaction. (Click Back 2)

Here, as $E$ increases above $E_A$ the number of collisions that result in reaction increases. The probability for a reaction to occur is†

$$P_r = \frac{E - E_A}{E} \quad \text{for} \quad E > E_A \quad \text{(R3.A-24)}$$

and

$$S_r(E,T) = 0 \quad \text{for} \quad E \leq E_A \quad \text{(R3.A-25)}$$

$$S_r = \pi \sigma_{AB}^2 \frac{(E - E_A)}{E} \quad \text{for} \quad E > E_A \quad \text{(R3.A-26)}$$

The impact parameter, $b$, is the off-set distance of the centers as they approach one another. The velocity component along the lines of centers, $U_{LC}$, can be obtained by resolving the approach velocity into components.

At the point of collision, the center of B is within the distance $\sigma_{AB}$.

The energy along the line of centers can be developed by a simple geometry argument

$$\sin \theta = \frac{b}{\sigma_{AB}} \quad (1)$$

The component of velocity along the line of centers

$$U_{LC} = U_R \cos \theta \quad (2)$$

The kinetic energy along the line of centers is

$$E_{LC} = \frac{U_{LC}^2}{\mu_{AB}} = \frac{U_R^2}{\mu_{AB}} \cos^2 \theta = E \cos^2 \theta \quad (3)$$

The minimum energy along the line of centers necessary for a reaction to take place, $E_A$, corresponds to a critical value of the impact parameter, $b_{crit}$. In fact, this is a way of defining the impact parameter and corresponding reaction cross section

$$S_r = \pi b_{crit}^2 \quad (5)$$

Substituting for $E_A$ and $b_{crit}$ in Equation (4)

$$E_A = E \left(1 - \frac{b_{crit}^2}{\sigma_{AB}^2}\right) \quad (6)$$

Solving for $b_{crit}^2$

$$b_{crit}^2 = \sigma_{AB}^2 \left(1 - \frac{E_A}{E}\right) \quad (7)$$

The reaction cross section for energies of approach, $E > E_A$, is

$$S_r = \pi b_{crit}^2 = \pi \sigma_{AB}^2 \left(1 - \frac{E_A}{E}\right) \quad (8)$$

The complete reaction cross section for all energies $E$ is

$$S_r = \begin{cases} 0 & E \leq E_A \\ \pi \sigma_{AB}^2 \left(1 - \frac{E_A}{E}\right) & E > E_A \end{cases} \quad (9)$$

$$E = \mu_{AB} \frac{U_R^2}{2} \quad (10)$$

A plot of the reaction cross section as a function of the kinetic energy of approach
is shown in Figure R3.A-7.

![Figure R3.A-7](Reaction cross section for Models 1 and 2.)

Recalling Equation (20)

$$\tilde{k}(T) = \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \int_0^{\infty} ES_r(E)e^{-E/RT} dE \tag{R3.A-20}$$

Substituting for $S_r$ in Model 2

$$\tilde{k}(T) = \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \int_{E_A}^{\infty} \pi \sigma_{AB}^2 (E - E_A) e^{-E/RT} dE \tag{R3.A-27}$$

Integrating gives

$$\tilde{k}(T) = \pi \sigma_{AB}^2 \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} e^{-E_A/RT} \quad \text{(Derive)}$$

<table>
<thead>
<tr>
<th>Click Back 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E \leq E_A$</td>
</tr>
<tr>
<td>$E &gt; E_A$</td>
</tr>
</tbody>
</table>

$$\tilde{k}(T) = \left[\frac{8}{\pi \mu (k_B T)^3}\right]^2 \pi \sigma_{AB}^2 \int_{E_A}^{\infty} \left(1 - \frac{\varepsilon^*}{\varepsilon}\right) \varepsilon e^{-\varepsilon/kT} d\varepsilon$$

$$= \pi \sigma_{AB}^2 \left[\frac{8}{\pi \mu (k_B T)^3}\right]^{1/2} (kT)^3 \int_{\varepsilon^*/kT}^{\infty} \frac{\varepsilon}{kT} e^{-\varepsilon/kT} d\varepsilon - \varepsilon^* \int_{\varepsilon^*/kT}^{\infty} e^{-\varepsilon/kT} d\varepsilon$$

CD/CollisionTheory/ProfRef.doc
\frac{\varepsilon}{k_B T} = \frac{E}{RT}

= \pi \sigma_{AB}^2 \left[ \frac{8k_B T}{\pi \mu} \right]^{1/2} \left[ \frac{E_A}{RT} + 1 - \frac{E_A}{RT} \right] e^{-E_A/RT}

= \pi k(T) = \pi \sigma_{AB}^2 \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} e^{-E_A/RT}

Multiplying both sides by \( N_{Avo} \)

\tilde{k}(T) = A e^{-E_A/RT}

Multiplying by Avogadro’s number

k(T) = \tilde{k}(T) N_{Avo}

\begin{align*}
-r_A &= \pi \sigma_{AB}^2 U_R N_{Avo} e^{-E_A/RT} C_A C_B \\
&= \pi \sigma_{AB}^2 \left( \frac{8k_B T}{\mu} \right)^{1/2} N_{Avo} e^{-E_A/RT} C_A C_B
\end{align*}

This is similar to the equation for hard sphere collisions except for the term \( e^{-E_A/RT} \)

Bingo!

\begin{align*}
k(T) &= \sigma_{AB}^2 \left( \frac{8 \pi k_B T}{\mu} \right)^{1/2} N_{Avo} e^{-E_A/RT} \\
&= \sigma_{AB}^2 \left( \frac{8 \pi k_B T}{\mu} \right)^{1/2} N_{Avo} e^{-E_A/RT}
\end{align*}

This equation gives the correct Arrhenius dependence and the correct order of magnitude for \( A \).

\begin{align*}
-r_A &= A e^{-E/RT} C_A C_B \\
&= A e^{-E/RT} C_A C_B
\end{align*}

**Effect of Temperature on Fraction of Molecules Having Sufficient Energy to React**

Now we will manipulate and plot the distribution function to obtain a qualitative understanding of how temperature increases the number of reacting molecules. Figure R3.A-8 shows a plot of the distribution function given by Equation (R3.A-17) after it has been converted to an energy distribution.

We can write the Maxwell-Boltzmann distribution of velocities

\[ f(U, T) dU = 4\pi \left( \frac{\mu}{2\pi k_B T} \right)^{3/2} U^2 e^{-\frac{\mu U^2}{k_B T}} dU \]

in terms of energy by letting \( \varepsilon = \frac{\mu U^2}{2} \) to obtain
Derive

\[ f(U,T) dU = 4\pi \left( \frac{\mu}{2\pi k_B T} \right)^{3/2} U^2 e^{-\frac{\mu U^2}{2k_B T}} dU \]

\[ f(\varepsilon, T) d\varepsilon = \frac{2}{\pi^{1/2} (k_B T)^{3/2}} \varepsilon^{1/2} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon \]

where \( f(\varepsilon, T) d\varepsilon \) is the fraction of molecules with kinetic energies between \( \varepsilon \) and \( (\varepsilon + d\varepsilon) \). We could further multiply and divide by \( k_B T \).

\[ f(\varepsilon, T) d\varepsilon = \frac{2}{\pi^{1/2} (k_B T)^{3/2}} \varepsilon^{1/2} e^{-\frac{\varepsilon}{k_B T}} \frac{d\varepsilon}{k_B T} \]

Recalling \( \frac{\varepsilon}{k_B T} = \frac{E}{RT} \)

\[ f(E, T) dE = \frac{2}{\pi^{1/2} (RT)^{1/2}} e^{-E/RT} \frac{dE}{RT} \]

\[ f(E, T) = \frac{2}{\pi^{1/2} (RT)^{1/2}} e^{-E/RT} \frac{E}{RT} \]

\[ \text{Fraction of molecules with energy } E_A \text{ or greater} \]

By letting \( X = \frac{E}{RT} \), we could have put the distribution in dimensionless form

\[ f(X, T) dX = \frac{2}{\pi^{1/2}} X^{1/2} e^{-X} dX \]

\( f(X, T) dX \) is the fraction of molecules that have energy ratios between \( \frac{E}{RT} \) and \( \frac{E + dE}{RT} \)

\[ f(E, T) dE = \frac{2}{\pi^{1/2} (RT)^{1/2}} e^{-E/RT} \frac{dE}{RT} \]

Derive

Fraction of collisions that have \( E_A \) or above

\[ = \int_{E_A}^{\infty} \left[ \frac{4}{\pi(RT)^3} \right]^{1/2} E^{1/2} e^{-E/RT} dE \]
This integral is shown by the shaded area on Figure R3.A-8.

![Graph showing Boltzmann distribution of energies with shaded areas representing fractions of collisions at different energies.]

**Figure R3.A-8** Boltzmann distribution of energies.

As we just saw, only those collisions that have an energy $E_A$ or greater result in reaction. We see from Figure R3.A-10 that the higher the temperature the greater number of collision result in reaction.

However, this Equations (R3.A-9) and (R3.A-11) cannot be used to calculate $A$ for a number pf reactions because of steric factors and because the molecular orientation upon collision need to be considered. For example, consider a collision in which the oxygen atom, O, hits the middle carbon in the reaction to form the free radical on the middle carbon atom $\text{CH}_3\dot{\text{C}}\text{HCH}_3$

$$\text{CH}_2$$

$$\text{O} \rightarrow \text{CH}_3 \rightarrow \text{CH}_3 \dot{\text{CH}} \text{CH}_3 + \cdot\text{OH}$$

$$\text{CH}_2$$

Otherwise, if it hits anywhere else (say the end carbon) $\text{CH}_3 \dot{\text{C}} \text{H \ CH}_3$ will not be formed$^\dagger$

$$\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 \leftrightarrow \text{CH}_3\dot{\text{C}}\text{HCH}_3$$

$$\rightarrow \cdot\text{CH}_3\text{CH}_2\text{CH}_2 + \cdot\text{OH}$$

Consequently, collision theory predicts a rate 2 orders of magnitude too high for the formation of $\text{CH}_3\dot{\text{C}}\text{HCH}_3$.

**IV. OTHER DEFINITIONS OF ACTIVATION ENERGY**

We will only state other definitions in passing, except for the energy barrier concept, which will be discussed in transition state theory.

$^\dagger$M1p.36.
A. Tolman’s Theorem

\[ E_a = E^* - \left( E^* - e^* \right) \]

\[ \varepsilon_a = \frac{\text{Average Energy of Molecules Undergoing Reaction}}{\text{Average Energy of Colloiding Molecules}} + \frac{1}{2} kT \]

The average transitional energy of a reactant molecule is \( \frac{3}{2} kT \).

B. Fowler and Guggenheim

\[ E_a = \frac{\text{Average Energy of Molecules Undergoing Reaction}}{\text{Average Energy of Reactant Molecules}} + \frac{1}{2} kT \]

C. Energy Barrier

The energy barrier concept is discussed in transition state theory, Ch3, Profession Reference Shelf B.

\[ A + BC \rightarrow AB + C \]

For simple reactions, the energy, \( E_A \), can be estimated from computational chemistry programs such as Cerius² or Spartan, as the heat of reaction between reactants and the transition state

\[ E_A = H_{ABC}^{\#} - H_A^* - H_{BC}^* \]

V. ESTIMATION OF ACTIVATION ENERGY FROM THE POLYANI EQUATION

A. Polyani Equation

The Polyani equation correlates activation energy with heat of reaction. This correlation

\[ E_A = \gamma_p \Delta H_{Rx} + c \]  \hspace{1cm} (R3.A-33)

works well for families of reactions. For the reactions

\[ R + HR' \rightarrow RH + R' \]

where \( R = OH, H, CH_3 \), the relationship is shown in Figure R3.A-10.
For this family of reactions

\[ E_A = 12 \text{ kcal/mol} + 0.5 \Delta H_R \]  

(R3.A-34)

For example, when the exothermic heat of reaction is

\[ \Delta H_{Rx} = -10 \text{ kcal/mol} \]

The corresponding activation energy is

\[ E_a = 7 \text{ cal/mol} \]

To develop the Polyan equation, we consider the elementary exchange reaction

\[ A + BC \rightarrow AB + C \]

We consider the superposition of two attraction/repulsion potentials, \( V_{BC} \) and \( V_{AB} \), similar to the Lennard-Jones 6-12 potential. For the molecules BC, the Lennard-Jones potential is

\[ V_{BC} = 4\varepsilon_{LJ} \left[ \left( \frac{r_0}{r_{BC}} \right)^{12} - \left( \frac{r_0}{r_{BC}} \right)^6 \right] \]  

(R3.A-35)

where \( r_{BC} \) = distance between molecules (atoms) B and C.

In addition to the Lennard-Jones 6-12 model, another model often used is the Morse potential, which has a similar shape

\[ V_{BC} = D \left[ e^{-2\beta(r_{BC} - r_0)} - 2e^{-\beta(r_{BC} - r_0)} \right] \]  

(R3.A-36)

When the molecules are far apart the potential \( V \) (i.e., Energy) is zero. As they move closer together, they become attracted to one another and the potential energy reaches a minimum. As they are brought closer together, the BC molecules

\footnote{After R. I. Masel (Loc cit).}
begin to repel each other and the potential increases. Recall that the attractive force between the B and C molecules is

$$F_{BC} = -\frac{dV_{BC}}{dx}$$  \hspace{1cm} (R3.A-37)

The attractive forces between the B–C molecules are shown in Figure R3.A-11.

A potential similar to atoms B and C can be drawn for the atoms A and B. The F shown in figures a and b represents the attractive force between the molecules as they move in the distances shown by the arrows. That is the attractive force increase as we move toward the well ($r_o$) from both directions, $r_{AB}>r_o$ and $r_{AB}<r_o$.

![Figure R3.A-11](image)

**Figure R3.A-11** Potentials (Morse or Lennard-Jones).

One can also view the reaction coordinate as a variation of the BC distance for a fixed AC distance, $\ell$

For a fixed AC distance as B moves away from C, the distance of separation of B from C, $r_{BC}$ increases as N moves closer to A. See point 2 in Figure R3.A-11. As $r_{BC}$ increases, $r_{AB}$ decreases and the AB energy first decreases and then increases as the AB molecules become close. Likewise, as B moves away from A and toward C, similar energy relationships are found. E.g., as B moves toward C from A, the energy first decreases due to attraction and then increases due to repulsion of the AB molecules as they come close together at point 2 in Figure R3.A-11. The overlapping Morse potentials are shown in Figure R3.A-11. We now superimpose the potentials for AB and BC to form Figure R3.A-12.
Let $S_1$ be the slope of the BC line between $r_1$ and $r_{BC}=r_{AB}$. Starting at $E_{1R}$ at $r_1$, the energy $E_1$ at a separation distance of $r_{BC}$ from $r_1$ can be calculated from the product of the slope $S_1$ and the distance from $E_{1R}$. The energy, $E_1$, of the BC molecule at any position $r_{BC}$ relative to $r_1$ is

$$E_1 = E_{1R} + S_1 (r_{BC} - r_1) \quad \text{(R3.A-38)}$$

[e.g., $E_1 = -50 \text{kJ} + \frac{10 \text{kJ}}{\text{nm}} \times [5 - 2] \text{nm} = -20 \text{kJ}$.]

Let $S_2$ be the slope of the AB line between $r_2$ and $r_{BC}=r_{AB}$. Similarly for AB, starting on the product side at $E_{2P}$, the energy $E_2$ at any position $r_{AB}$ relative to $r_2$ is

$$E_2 = E_{2P} + S_2 (r_{AB} - r_2) \quad \text{(R3.A-39)}$$

[e.g., $E_2 = -80 \text{kJ} + \left(-\frac{20 \text{kJ}}{\text{nm}}\right) \times (7 - 10) \text{nm} = -20 \text{kJ}$.]

At the height of the barrier

$$E_1^* = E_2^* \text{ at } r_{BC}^* = r_{AB}^* \quad \text{(R3.A-40)}$$

Substituting for $E_1^*$ and $E_2^*$

$$E_{1R} + S_1 (r_{BC}^* - r_1) = E_{2P} + S_2 (r_{AB}^* - r_2) \quad \text{(R3.A-41)}$$

Rearranging

$$S_1 (r_{BC}^* - r_1) = \frac{E_{2P} - E_{1R}}{\Delta H_{R_s}} + S_2 (r_{AB}^* - r_2) \quad \text{(R3.A-42)}$$
\[ r_{BC} = r_{AB} = r^{*} \]

\[ S_1 \left( r^{*} - r_1 \right) = \Delta H_{Rx} + S_2 \left( r^{*} - r_2 \right) \]

Solving for \( r^{*} \) and substituting back into the Equation

\[ E_a = E_1^* - E_{1R} = S_1 \left( r^{*} - r_1 \right) \]

yields

\[ E_a = E_1^* + \gamma_p \Delta H_{Rx} \]

(Derive) (see p.19) (R3.A-44)

Equation (8) gives the Polyani correlation relating activation energy and heat of reaction. Values of \( E_a^* \) and \( \gamma_p \) for different reactions can be found in Table 5.4 on page 254 of Masel. One of the more common correlations for exothermic and endothermic reactions is given on page 73 of Laidler.

1) Exothermic Reactions

\[ E_a = 48.1 + 0.25(\Delta H_{Rx}) \text{ kJ/mol} \]

If \( \Delta H_{Rx} = -100 \text{kJ/mol} \),

then

\[ E_a = 48.1 + 0.25(-100 \text{kJ/mol}) \]

\[ E_a = 23.1 \text{ kJ/mol} \]

2) Endothermic Reactions

\[ E_a = 48.1 + 0.75(\Delta H_{Rx}) \text{ kJ/mol} \]

\[ E_a = 48.1 + 0.75(100 \text{kJ/mol}) = 129 \text{ kJ/mol} = 29 \text{ kcal/mol} \]

Also see R. Masel *Chemical Kinetics and catalysis*, p603 to calculate the activation energy from the heat of reaction.

Szabo proposed an extension of Polyani equation

\[ E_a = \Sigma D_j \text{(Breaking)} - \alpha \Sigma D_j \text{(Forming)} \]

(Derive) (Click back)

\[ D_i = \text{Dissociation Energies} \]

\[
\begin{align*}
S_1 \left( r^{*} - r_1 \right) &= \Delta H_{Rx} + S_2 \left( r^{*} - r_2 \right) \quad \text{(A)} \\
\text{Rearranging} \\
(S_1 - S_2) r^{*} &= \Delta H_{Rx} + S_1 r_1 - S_2 r_2 \\
\text{Solving for } r^{*} \\
r^{*} &= \frac{\Delta H_{Rx}}{(S_1 - S_2)} + \frac{S_1 r_1 - S_2 r_2}{S_1 - S_2} \quad \text{(C)}
\end{align*}
\]
Recalling Equation (R3.A-43)

\[ E_a = E_1^* - E_1R = S_1(r^* - r_1) \]  \hspace{1cm} (R3.A-43)

Substituting Equation (C) for \( r^* \) in Equation (R3.A-43)

\[ E_a = S_1 \left[ \frac{\Delta H_{Rx}}{S_1 - S_2} + \frac{S_1 r_1 - S_2 r_2}{S_1 - S_2} \right] - S_1 r_1 \]  \hspace{1cm} (E)

Rearranging

\[ E_a = \left( \frac{S_1}{S_1 - S_2} \right) \Delta H_{Rx} + S_1 \left[ \frac{S_1 r_1 - S_2 r_2}{S_1 - S_2} - r_1 \right] \]  \hspace{1cm} (F)

\[ = \left( \frac{S_1}{S_1 - S_2} \right) \Delta H_{Rx} + S_1 \left[ \frac{S_1 r_1}{S_1 - S_2} - S_2 r_1 + S_2 r_2 \right] \]  \hspace{1cm} (G)

Finally, collecting terms we have

\[ E_a = \left( \frac{S_1}{S_1 - S_2} \right) \Delta H_{Rx} + \left( \frac{S_1 S_2}{S_1 - S_2} \right) \left[ r_1 - r_2 \right] \]  \hspace{1cm} (H)

Note: \( S_1 \) is positive, \( S_2 \) is negative, and \( r_2 > r_1 \); therefore, \( E_a^* \) is positive, as is \( \gamma_p \).

\[ E_a = E_a^* + \gamma_p \Delta H_{Rx} \]

B. Marcus Extension of the Polanyi Equation

In reasoning similar to developing the Polanyi Equation, Marcus shows (see Masel, pp. 584-586)

\[ E_A = \left( 1 + \frac{\Delta H_{Rx}}{4E_{A0}} \right)^2 E_{A0} \]

C. Blowers-Masel Relation

The Polanyi Equation will predict negative activation energies for highly exothermic reactions. Blowers and Masel developed a relationship that compares quite well with experiments throughout the entire range of heat of reaction for the family of reactions

\[ R + HR' \rightarrow RH + R' \]

as shown in Figure R3.A-13.
We see the greatest agreement between theory and experiment is found with the Blowers-Masel model.

VI. CLOSURE

We have now developed a quantitative and qualitative understanding of the concentration and temperature dependence of the rate law for reactions such as

$$A + B \rightarrow C + D$$

with

$$-r_A = k C_A C_B$$

We have also developed first estimates for the frequency factor, $A$, from collision theory

$$A = S_r U_R N_{Avo} = \pi \Theta_{AB}^2 \left( \frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2} N_{Avo}$$

and the activation energy, $E_A$, from the Polanyi Equation.

$$E_A = E_A^* + \gamma_P \Delta H_{Rx}$$

These calculated values for $A$ and $E_A$ can be substituted in the rate law to determine rates of reaction.

$$-r_A = k C_A C_B = Ae^{-E_A/RT}$$
VI. OTHER STUFF

Potential Energy Surfaces and the barrier height $\varepsilon_{hb}$

![Reaction coordinates](image)

The average transitional energy of a molecule undergoing collision is $2k_B T$. The molecules with a higher energy are more likely to collide.

A. How to Calculate Barrier Height

1. *Ab Initio* calculations. No adjustment of parameters or use of experimental data.
   
   Solve Schrödinger's Equation
   
   $E_b = \text{Barrier Height} = \varepsilon_{hb}$
   
   $E_b = 40 \text{ kJ/mol}$ for the $\text{H} + \text{H}_2$ exchange reaction

2. *Semiempirical*
   
   Uses experimental measurements (spectroscopic).
   
   Adjustments are made to get agreement.

3. *London-Eyring-Polanyi (LEP) Method*
   
   Use spectroscopic measurement in conjunction with the Morse potential equation
   
   
   $E = D \left[ e^{-2\beta(r-r_0)} - 2 e^{-\beta(r-r_0)} \right]$  
   
   $D = \text{dissociation energy}$
   
   $r_0 = \text{equilibrium internuclear distance}$
   
   $\beta = \text{constant}$

Model B3 Stored Energy

This third method considers vibrational and translation energy in addition to translational energy. Even though this approach is oversimplified, it is satisfying because it gives a qualitative feel for the Arrhenius temperature dependence. In this approach, we say the fraction of molecules that will react are those that have acquired an energy $E_A$.  

\[27\]
Maxwell-Boltzmann Statistics for \( n \) Degrees of Freedom

Here, energy can be stored in the molecule by different modes. For \( n \) degrees of freedom (transitional, vibrational, and rotational) \((L3p76)\)

\[
f(\varepsilon, T) = \frac{1}{\left(\frac{1}{2n-1}\right)!} \left(\frac{\varepsilon}{k_B T}\right)^{n-1} \frac{1}{k_B T} \ e^{-\varepsilon/k_B T}
\]

\((R3.A-30)\)

d\(F = f(\varepsilon, T) d\varepsilon\) = fraction of molecules with energy between \( \varepsilon \) and \( (\varepsilon + d\varepsilon) \)

For methane, there are 3 transitional, 3 rotational, and 9 vibrational degrees of freedom, \( n = 15 \). Because Equation (31) is awkward, the two dimension equation is often used, with \( n = 2 \) and the distribution function is

\[
f(\varepsilon, T) = \frac{e^{-\varepsilon/k_B T}}{k_B T}
\]

\((R3.A-31)\)

Activation Energy

From the Maxwell-Boltzmann distribution of velocities we obtain the distribution of energies of the molecules as shown below. Here, fd\(\varepsilon\) is the fraction, d\(F\), of molecules between \( \varepsilon \) and \( \varepsilon + d\varepsilon \).

\[
dF = f(\varepsilon, T) d\varepsilon
\]

We now say only those molecules that have an energy, \( E_A \) or greater, will react. Integrating between the limits \( E^* \) (i.e., \( E_A \)) and infinity, we find the fraction of molecules colliding with energy \( E_A \) or greater

\[
F = \frac{1}{k_B T} \int_{E^*}^{\infty} e^{-\varepsilon/k_B T} \ d\varepsilon
\]

Multiplying and dividing by \( k_B T \) and noting again \( \frac{\varepsilon}{k_B T} = \frac{E}{RT} \)

\[
dF = \int_{E_A}^{E^*} e^{-E/RT} dE
\]

Integrating

\[
F = e^{-E_A/RT}
\]

\((R3.A-32)\)

We now say that this is the fraction of collisions that have energy, \( E_A \) or greater, and can react. Multiplying this fraction times the number of collisions, e.g., Equation \((R3.A-10)\), gives

\[
-r_A = A e^{-E_A/RT} C_A C_B
\]

which gives the Arrhenius Equation

\[
k = A \ e^{-E_A/RT} = A \ e^{-E^*/kT}
\]