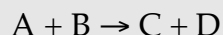## Professional Reference Shelf

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

$$-r_A = kC_A C_B = Ae^{-E/RT}C_A C_B$$

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

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

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

$$-r_A = Ae^{-E_A/RT}C_A C_B$$

where

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

with σ_{AB} = collision radius, k_B = Boltzmann's constant, μ_{AB} = reduced mass, T = temperature, and N_{Avo} = Avogadro's number. To obtain an estimate of E_A, we use the Polyani Equation

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

Where ΔH_{Rx} is the heat of reaction and E_A° and γ_P are the Polyani 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.

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HOT BUTTONS

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

P. Atkins, *Physical Chemistry*, 6th ed. (New York: Freeman, 1998)
P. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994).
G. D. Billing and K. V. Mikkelsen, *Introduction to Molecular Dynamics and Chemical Kinetics* (New York: Wiley, 1996).
P.W. Atkins, *The Elements of Physical Chemistry*, 2nd ed. (Oxford: Oxford Press, 1996).
K. J. Laidler, *Chemical Kinetics*, 3rd ed. (New York: Harper Collins, 1987).
G. Odian, *Principles of Polymerization*, 3rd ed. (New York: Wiley 1991).
R. I. Masel, *Chemical Kinetics and Catalysis* (New York: Wiley Interscience, 2001).

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

A6p701 <u>means</u> Atkins, P. W., *Physical Chemistry*, 6th ed. (1998) page 701.
L3p208 <u>means</u> Laidler, K. J., *Chemical Kinetics*, 3rd,ed. (1987) page 208.

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, $k=Ae^{-/RT}$. To achieve this goal, we consider the reaction of two molecules in the gas phase

$$A + B \longrightarrow C + D$$
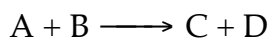
We will model these molecules as rigid spheres.

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A. Rigid Spheres

Species A and B are modeled as rigid spheres of radius σ_A and σ_B, respectively.
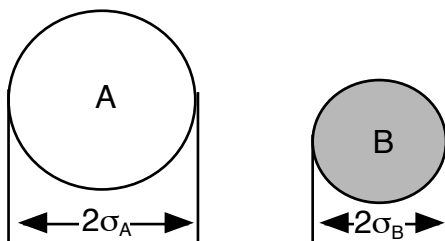

Figure R3.A-1 Schematic of molecules A and B.

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.
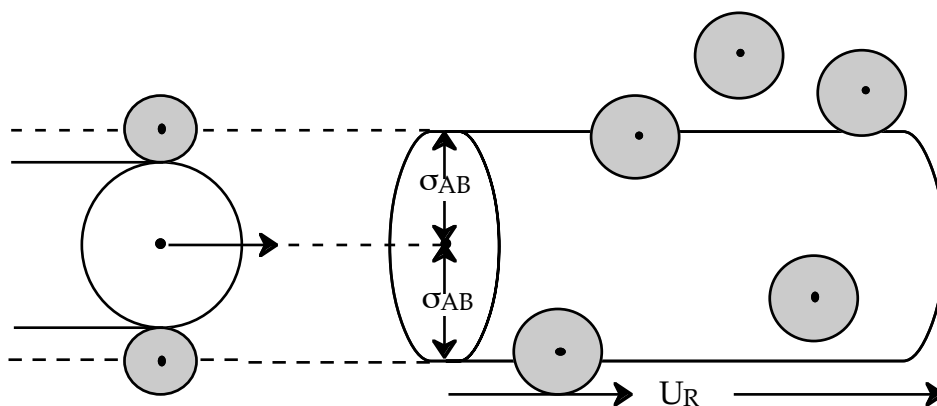

Figure R3.A-2 Schematic of collision cross-section.

The collision radius is σ_{AB}.

$$\sigma_{AB} = \sigma_A + \sigma_B$$

If the center of a "B" molecule comes within a distance of σ_{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.[†]

$$U_R = \left(\frac{8k_B T}{\pi\mu_{AB}}\right)^{1/2} \tag{R3.A-1}$$

where

k_B = Boltzmann's constant = 1.381×10^{-23} J/K/molecule
= 1.381 kg m^2/s^2/K/molecule

[†] 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.

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m_A = mass of a molecule of species A (gm)

m_B = mass of a molecule of species B (gm)

μ_{AB} = reduced mass = $\dfrac{m_A m_B}{m_A + m_B}$ (g), [Let $\mu \equiv \mu_{AB}$]

M_A = Molecular weight of A (Daltons)

N_{Avo} = Avogadro's number 6.022 molecules/mol

R = Ideal gas constant 8.314 J/mol•K = 8.314 kg • m^2/s^2/mol/K

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

$$\frac{k_B}{\mu_{AB}} = \left(\frac{R}{\dfrac{M_A M_B}{M_A + M_B}} \right) \qquad (R3.A-2)$$

An order of magnitude of the relative velocity at 300 K is $U_R \cong 3000$ 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[†]

Molecule	Average Velocity, (meters/second)	Molecular Diameter (Å)
H_2	1687	2.74
CO	453	3.12
Xe	209	4.85
He	1200	2.2
N_2	450	3.5
O_2	420	3.1
H_2O	560	3.7
C_2H_6	437	5.3
C_6H_6	270	3.5
CH_4	593	4.1
NH_3	518	4.4
H_2S	412	4.7
CO_2	361	4.6
N_2O	361	4.7
NO	437	3.7

Consider a molecule A moving in space. In a time Δt, the volume ΔV swept out by a molecule of A is

---

[†] Courtesy of J. F. O'Hanlon, *A User's Guide to Vacuum Technology* (New York: Wiley, 1980).

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$$\Delta V = \underbrace{\left(U_R \Delta t \right)}_{\Delta \ell} \pi \sigma_{AB}^2$$
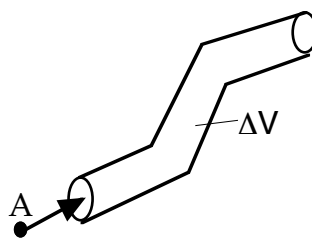
Figure R3.A-3 Volume swept out by molecule A in time Δt.

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:

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

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

In a time Δt, 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 <u>one</u> A molecule with all the B molecules *per unit time* is

$$\tilde{Z}_{1A \bullet B} = \pi \sigma_{AB}^2 \tilde{C}_B U_R \qquad (\text{R3.A-3})$$

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 $\tilde{Z}_{AB}$ of all the A molecules with all B molecules per time per unit volume is

$$\tilde{Z}_{AB} = \overbrace{\pi \sigma_{AB}^2}^{S_r} U_R \tilde{C}_A \tilde{C}_B = S_r U_R \tilde{C}_A \tilde{C}_B \qquad (\text{R3.A-4})$$

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

$$\boxed{\tilde{Z}_{AB} = \pi \sigma_{AB}^2 \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} \tilde{C}_A \tilde{C}_B} \quad [\text{molecules}/\text{time}/\text{volume}] \qquad (\text{R3.A-5})$$

If we assume all collisions result in reactions, then

$$-\tilde{r}_A = \tilde{Z}_{AB} = \pi \sigma_{AB}^2 \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} \tilde{C}_A \tilde{C}_B \quad [\text{molecules}/\text{time}/\text{volume}] \qquad (\text{R3.A-6})$$

Multiplying and dividing by Avogadrós number, N_{Avo}, we can put our equation for the rate of reaction in terms of the number of moles/time/vol.

$$\underbrace{\left(\frac{-\tilde{r}_A}{N_{Avo}} \right)}_{-r_A} N_{Avo} = \pi \sigma_{AB}^2 \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} \underbrace{\frac{\tilde{C}_A}{N_{Avo}}}_{C_A} \underbrace{\frac{\tilde{C}_B}{N_{Avo}}}_{C_B} N_{Avo}^2 \qquad (\text{R3.A-7})$$
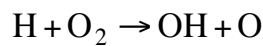
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$$-r_A = \pi\sigma_{AB}^2 \underbrace{\left(\frac{8\pi k_B T}{\mu\pi}\right)^{1/2} N_{Avo}}_{A} \; C_A C_B \quad [\text{moles/time/volume}] \qquad (R3.A\text{-}8)$$

where A is the frequency factor

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

$$-r_A = A C_A C_B \qquad (R3.A\text{-}10)$$

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 $\quad \sigma_H = 2.74 \text{ Å}/4 = 0.68\text{Å} = 0.68 \times 10^{-10}m$

Oxygen O_2 $\quad \sigma_{O_2} = \dfrac{3.1}{2} \text{ Å } 1.55\text{Å} = 1.5 \times 10^{-10}m$

$$R = 8.31\,J/mol/K = 8.314 \;\; kg\,m^2/s^2/K/mol$$

Solution

$$A = S_r U_R N_{Avo} \qquad (R3.A\text{-}E\text{-}1)$$

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

The relative velocity is

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

Calculate the ratio k_B/μ_{AB} (Let $\mu \equiv \mu_{AB}$)

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

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$$\frac{k_B}{\mu} = 8571\, m^2/s^2/K$$

Calculate the relative velocity

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

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

$$= 15.6 \times 10^{-20}\, m^2/\text{molecule}$$

Calculate the frequency factor A

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

$$\boxed{A = 2.29 \times 10^8\, \frac{m^3}{mol \cdot s} = 2.29 \times 10^{11}\, \frac{dm^3}{mol \cdot s}} \qquad \text{(R3.A-E-4)}$$

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

$$\boxed{A = 3.81 \times 10^{14}\, \left(\text{Å}\right)^3/\text{molecule}/s} \qquad \text{(R3.A-E-5)}$$

The value reported in Masel[†] from Wesley is

$$A = 1.5 \times 10^{14}\, \left(\text{Å}\right)^3/\text{molecule}/s$$

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

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

$$\boxed{10^8\, \frac{dm^3}{mol \bullet s} < A_{calc} < 10^{11}\, \frac{dm^3}{mol \bullet s}}$$

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

$$\boxed{10^{12}\, \text{Å}^3/\text{molecule}/s < A_{calc} < 10^{15}\, \text{Å}^3/\text{molecule}/s}$$

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

[†] M1p367.

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$$-r_A = AC_A C_B \qquad (R3.A\text{-}10)$$

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

$$-r_A = Ae^{-E/RT} C_A C_B \qquad (R3.A\text{-}11)$$

or

$$k = Ae^{-E/RT} \qquad (R3.A\text{-}12)$$

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

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.
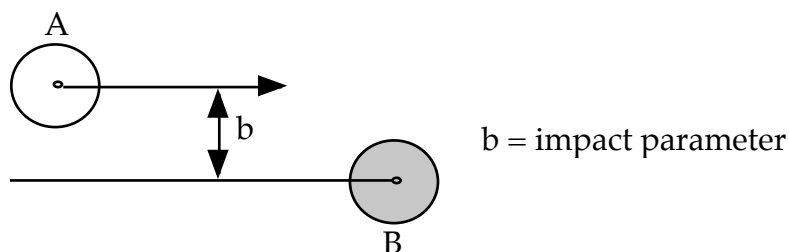

Figure R3.A-4 Grazing collisions.

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[†]

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.

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

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

[†] Masel, 1p

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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

$$k = Ae^{-E_A/RT}$$

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

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

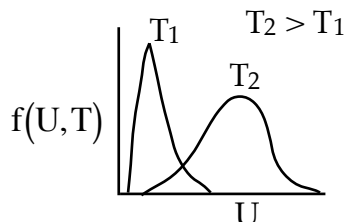A plot of the distribution function, f(U,T), is shown as a function of U in Figure R3.A-5.

Figure R3.A-5 Maxwell-Boltzmann distribution of velocities.

Replacing m by the reduced mass μ of two molecules A and B

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

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

$$\tilde{Z}_{AB} = \underbrace{S_r(U)U}_{\tilde{k}(U)} \ \tilde{C}_A \tilde{C}_B \qquad \text{(R3.A-14)}$$

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.

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We now let $\tilde{k}(U)$ be the specific reaction rate for a collision and reaction of A-B molecules with a velocity U.

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

Equation (R3.A-15) will give the specific reaction rate and hence the reaction rate for <u>only</u> 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.

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

Maxwell distribution function of velocities for the A/B pair of reduced mass μ_{AB} is[†]

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

Combining Equations (16) and (17)

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

For brevity, we let $S_r = S_r(U)$, we will now express the distribution function in terms of the translational energy ε_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, ε , to the velocity U:

$$\varepsilon_t = \frac{\mu U^2}{2}$$

Multiplying and dividing by $\dfrac{2}{\mu}$ and μ, we obtain

$$d\varepsilon_t = \mu\ UdU$$

and hence, the reaction rate

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

Simplifying

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

[†] 2p185, A5p36

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

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

Multiplying and dividing by $k_B T$ and noting $\left(\varepsilon_t/k_B T\right) = \left(E/RT\right)$, we obtain

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

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

$$\boxed{S_r = P_r\pi\sigma_{AB}^2}$$

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 $E \equiv \varepsilon_t$. 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 $S_r = \pi\sigma_{AB}^2$

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

$$P_r = 1 \qquad S_r\left[E,T\right] = \pi\sigma_{AB}^2 \qquad \text{for } E \geq E_A \qquad \text{(R3.A-22)}$$
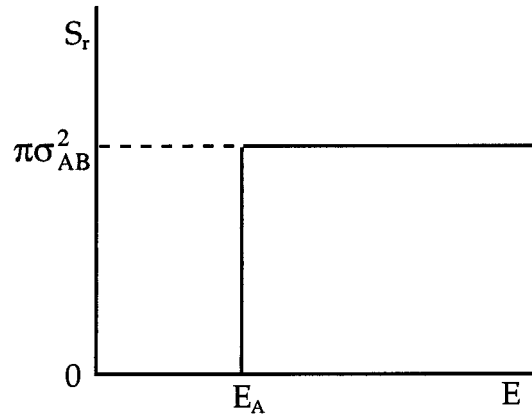
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Figure R3.A-6 Reaction cross section for Model 1.

Integrating Equation (R3.A-20) by parts for the conditions given by Equations (R3.A-21) and (R3.A-22) we obtain

$$\tilde{k} = \left(\frac{8\ k_B T}{\pi\mu}\right)^{1/2}\left[1+\frac{E_A}{RT}\right]\ e^{-E_A/RT}\pi\sigma_{AB}^2 \qquad\text{(R3.A-23)}$$

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

(Click Back 1)

(Click Back 1)

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

$$S_r = 0 \qquad\qquad \varepsilon < \varepsilon*$$

$$S_r = \pi\sigma_{AB}^2 \qquad \varepsilon \geq \varepsilon*$$

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

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

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

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

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(Click Back 1 cont'd)

$$\int \mathrm{u}\,\mathrm{dv} = \mathrm{uv} - \int \mathrm{v}\,\mathrm{du}$$

$$\tilde{k}(T) = \pi\sigma_{AB}^2 \left(\frac{8k_B T}{\mu\pi}\right)^{1/2} \int_{E_A/RT}^{\infty} \underbrace{X}_{u} \underbrace{e^{-X}dX}_{dv} = -Xe^{-X}\Big]_{E_A/RT}^{\infty} - \int_{E_A/RT}^{\infty} e^{-X}dX$$

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

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

$$\frac{E_A}{RT} > 1$$

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

$$= A\frac{E_A}{RT} \qquad \qquad \underline{\text{Over predicts the}}$$
$$\underline{\text{frequency factor}}$$

$$S_r = P_r \ \pi\sigma_{AB}^2$$

Generally, $\dfrac{E_A}{RT} >> 1$, so

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

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

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

$$k = A'e^{-E_A/RT} = \frac{E_A}{RT}Ae^{-E_A/RT}$$

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.

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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 $E_{<<}$ 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.

<div align="right">(Click Back 2)</div>

Here, as E increases above E_A the number of collisions that result in reaction increases. The probability for a reaction to occur is[†]
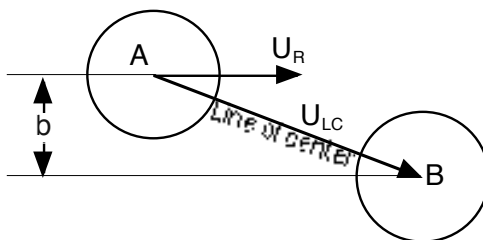
$$P_r = \left[\frac{E - E_A}{E}\right] \text{ for } E > E_A \tag{R3.A-24}$$
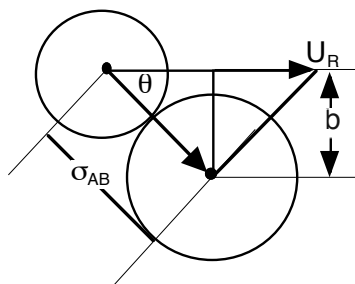
and

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

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

(Click Back 2)

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 σ_{AB}.

[†] Courtesy of J. I. Steinfeld, J. S. Francisco, and W. L. Hayes, *Chemical Kinetics and Dynamics*, (Englewood Cliffs NJ: Prentice Hall, 1989, p.250); Mp483.

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(Click Back 2 cont'd)

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

$$\sin \theta = \frac{b}{\sigma_{AB}} \tag{1}$$

The component of velocity along the line of centers

$$U_{LC} = U_R \cos \theta \tag{2}$$

The kinetic energy along the line of centers is

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

$$E_{LC} = E\left[1 - \sin^2 \theta\right] = E\left[1 - \frac{b^2}{\sigma_{AB}^2}\right] \tag{4}$$

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

$$S_r = \pi b_{crit}^2 \tag{5}$$

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

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

Solving for b_{crit}^2

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

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

$$S_r = \pi b_{crit}^2 = \pi \sigma_{AB}^2\left(1 - \frac{E_A}{E}\right) \tag{8}$$
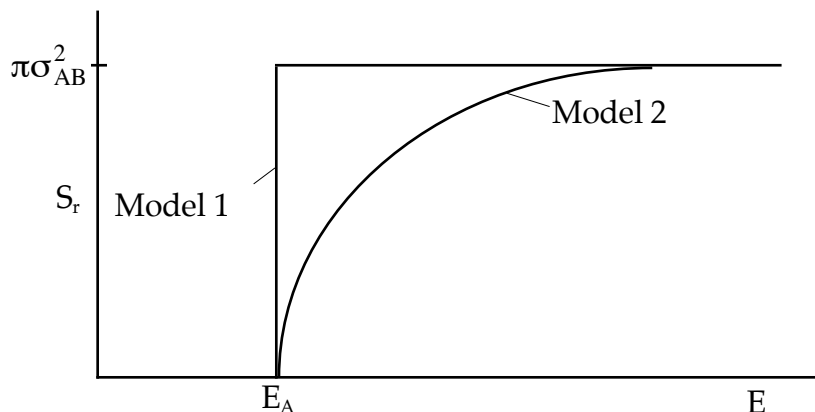
The complete reaction cross section for all energies E is

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

$$\tag{9}$$
$$\tag{10}$$

A plot of the reaction cross section as a function of the kinetic energy of approach

$$E = \mu_{AB} \frac{U_R^2}{2}$$

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is shown in Figure R3.A-7.

Figure R3.A-7 Reaction cross section for Models 1 and 2.

Recalling Equation (20)

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

Substituting for S_r in Model 2

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

Integrating gives

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

(Click Back 3)

(Click Back 3)

$$E \le E_A \qquad P_r = 0 \qquad\qquad S_r = 0$$

$$E > E_A \qquad P_r = 1 - \frac{\varepsilon^*}{\varepsilon} \qquad S_r = \pi\sigma_{AB}^2 \left(1 - \frac{E_A}{E}\right)$$

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

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

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(Click Back 3 cont'd)

$$\frac{\varepsilon}{k_B T} = \frac{E}{RT}$$

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

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

Multiplying both sides by N_{Avo}

$$\tilde{k}(T) = Ae^{-E_A/RT}$$

Multiplying by Avogodro's number

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

$$-r_A = \pi\sigma^2_{AB}U_R N_{Avo}e^{-E_A/RT}C_A C_B \qquad (R3.A\text{-}28)$$

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

Bingo!

$$\boxed{k(T) = \sigma^2_{AB}\left(\frac{8\pi k_B T}{\mu}\right)^{1/2} N_{Avo}\; e^{-E_A/RT}} \qquad (R3.A\text{-}29)$$

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

$$-r_A = Ae^{-E/RT}C_A C_B \qquad (R3.A\text{-}11)$$

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 $\varepsilon = \dfrac{\mu U^2}{2}$ to obtain

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

$$f(\varepsilon_t, T)d\varepsilon = \frac{2}{\pi^{1/2} (k_B T)^{3/2}} \varepsilon^{1/2} \ e^{-\frac{\varepsilon}{k_B T}} d\varepsilon_t$$
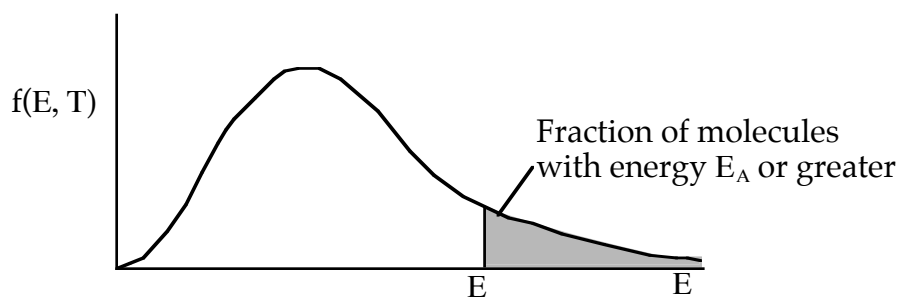
where $f(\varepsilon, T)\, d\varepsilon$ is the fraction of molecules with kinetic energies between ε and $(\varepsilon + d\varepsilon)$. We could further multiply and divide by $k_B T$.

$$f(\varepsilon, T)dE = \frac{2}{\pi^{1/2}} \left(\frac{\varepsilon}{k_B T} \right)^{1/2} e^{-E/RT} \frac{d\varepsilon}{k_B T}$$

Recalling $\dfrac{\varepsilon}{k_B T} = \dfrac{E}{RT}$

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

$$f(E,T) = \frac{2}{\pi^{1/2}} \left(\frac{E}{RT} \right)^{1/2} \frac{e^{-E/RT}}{RT}$$

Fraction of molecules with energy E_A or greater

By letting $X = \dfrac{E}{RT}$, 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 $\dfrac{E}{RT}$ and $\dfrac{E+dE}{RT}$
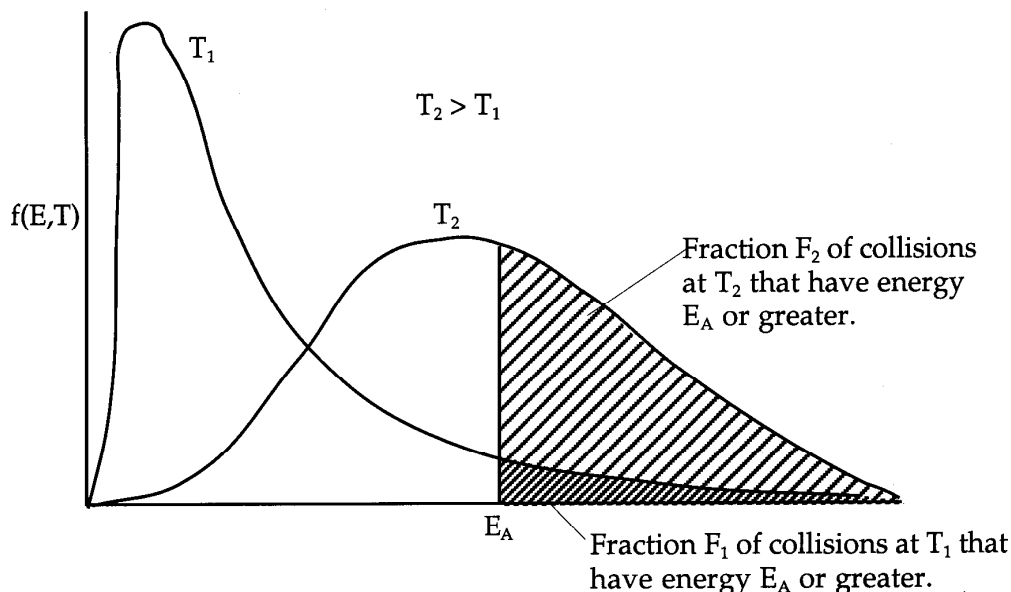
$$f(E,T)dE = \frac{2}{\pi^{1/2}} \left(\frac{E}{RT} \right)^{1/2} e^{-E/RT} \frac{dE}{RT}$$

Fraction of collisions that have E_A or above

$$= \int_{E_A}^{\infty} \left[\frac{4}{\pi (RT)^3} \right]^{1/2} E^{1/2} \ e^{-E/RT} dE$$

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This integral is shown by the shaded area on Figure R3.A-8.

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 $CH_3\dot{C}HCH_3$

$$
\begin{array}{c}
CH_2 \\
| \\
O \rightarrow CH_3 \rightarrow CH_3 \ \dot{C}H \ CH_3 + \bullet OH \\
| \\
CH_2
\end{array}
$$
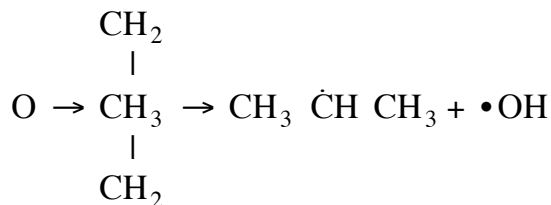
Otherwise, if it hits anywhere else (say the end carbon) $CH_3 \ \dot{C}H \ CH_3$ will not be formed[†]

$$
O \rightarrow CH_3CH_2CH_3 \ \nrightarrow \ CH_3\dot{C}HCH_3
$$
$$
\longrightarrow \bullet CH_3CH_2CH_2 + \bullet OH
$$
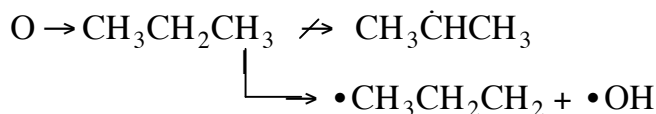
Consequently, collision theory predicts a rate 2 orders of magnitude too high for the formation of $CH_3\dot{C}HCH_3$.

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.

[†] M1p.36.

A. Tolman's Theorem $E_a = E^*$ $\quad \left(E^* \equiv e^*\right)$

$$\varepsilon_a = \begin{bmatrix} \text{Average Energy} \\ \text{of Molecules} \\ \text{Undergoing} \\ \text{Reaction} \end{bmatrix} - \begin{bmatrix} \text{Average Energy} \\ \text{of Colloiding} \\ \text{Molecules} \end{bmatrix} + \frac{1}{2}kT$$
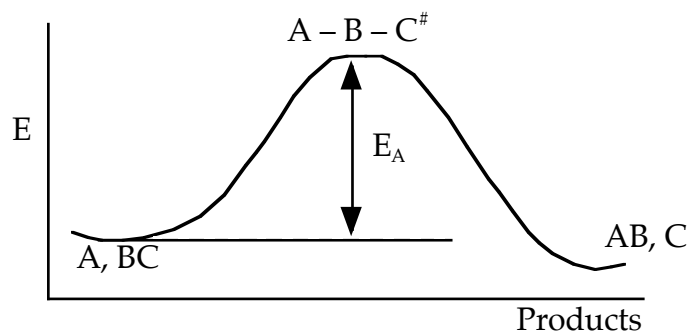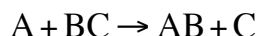
The average transitional energy of a reactant molecule is $\frac{3}{2}kT$.

B. Fowler and Guggenheim

$$\varepsilon_a = \begin{bmatrix} \text{Average Energy} \\ \text{of Molecules} \\ \text{Undergoing} \\ \text{Reaction} \end{bmatrix} - \begin{bmatrix} \text{Average Energy} \\ \text{of Reactant} \\ \text{Molecules} \end{bmatrix}$$

C. Energy Barrier

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

$$A + BC \rightarrow AB + C$$

$$A - B - C^{\#}$$

Figure R3.A-9 Reaction coordinate diagram.

For simple reactions, the energy, E_A, can be estimated from computational chemistry programs such as Cerius^2 or Spartan, as the heat of reaction between reactants and the transition state

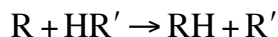$$E_A = H_{ABC}^{\#} - H_A^{\circ} - H_{BC}^{\circ}$$

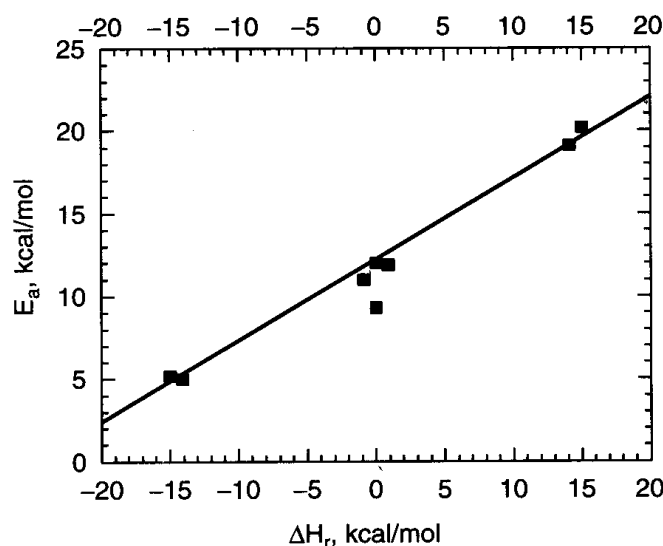## V. ESTIMATION OF ACTIVATION ENERGY FROM THE POLYANI EQUATION

A. Polyani Equation

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

$$E_A = \gamma_P \Delta H_{Rx} + c \qquad\qquad\qquad \text{(R3.A-33)}$$

works well for families of reactions. For the reactions

$$R + HR' \rightarrow RH + R'$$

where R = OH, H, CH3, the relationship is shown in Figure R3.A-10.

Figure R3.A-10 Experimental correlation of E_A and ΔH_{Rx}. Courtesy of R. I. Masel, *Chemical Kinetics and Catalysis* (New York: Wiley Interscience, 2001).

For this family of reactions

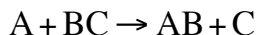$$E_A = 12 \ \text{kcal/mol} + 0.5 \ \Delta H_R \qquad \text{(R3.A-34)}$$

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 Polyani 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

$$V_{BC} = 4\varepsilon_{LJ}\left[\left(\frac{r_0}{r_{BC}}\right)^{12} - \left(\frac{r_0}{r_{BC}}\right)^{6}\right] \qquad \text{(R3.A-35)}$$

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

$$V_{BC} = D\left[e^{-2\beta(r_{BC} - r_0)} - 2e^{-\beta(r_{BC} - r_0)}\right] \qquad \text{(R3.A-36)}$$

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

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[†] After R. I. Masel (Loc cit).

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begin to repel each other and the potential increases. Recall that the attractive force between the B and C molecules is

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

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 $r_{AB} < r_o$.
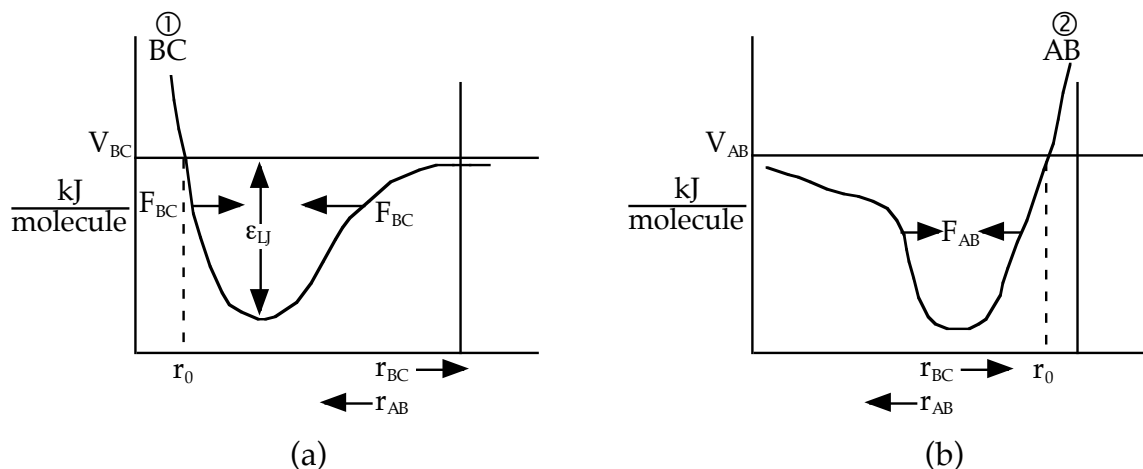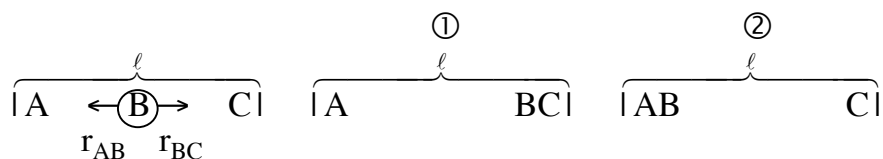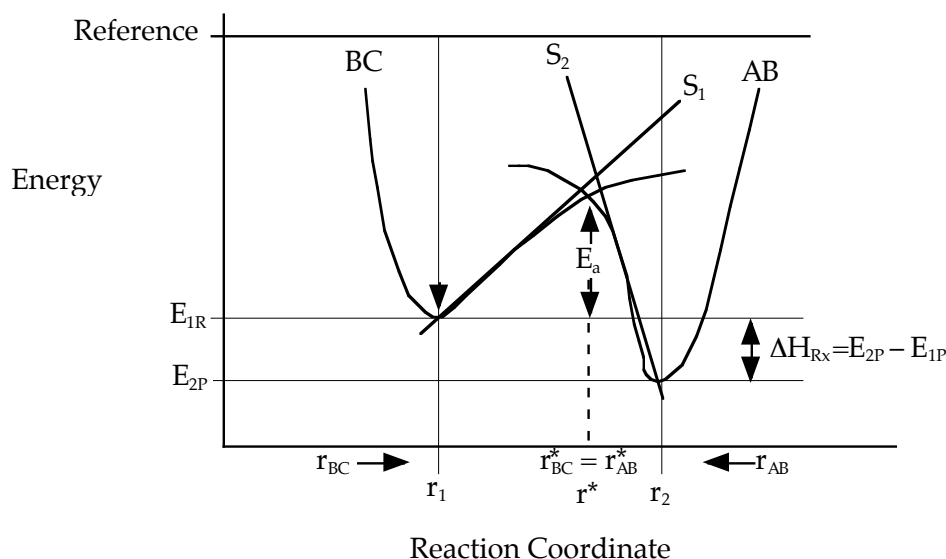

Figure R3.A-11 Potentials (Morse or Lennard-Jones).

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

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.

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Figure R3.A-12 Overlap of potentials (Morse or Lennard-Jones).

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

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

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

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

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

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

At the height of the barrier

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

Substituting for E_1^* and E_2^*

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

Rearranging

$$S_1\left(r_{BC}^* - r_1\right) = \underbrace{\left(E_{2P} - E_{1R}\right)}_{\Delta H_{Rx}} + S_2\left(r_{AB}^* - r_2\right) \tag{R3.A-42}$$

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$$r^*_{BC} = r^*_{AB} = r^*$$

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

Solving for r* and substituting back into the Equation

$$E_a = E_1^* - E_{1R} = S_1\left(r^* - r_1\right) \tag{R3.A-43}$$

yields

$$\boxed{E_a = E_a^* + \gamma_P \Delta H_{Rx}} \qquad \boxed{\text{Derive}} \quad \begin{array}{c}\text{(click back)}\\ \text{(see p.19)}\end{array} \tag{R3.A-44}$$

Equation (8) gives the Polyani correlation relating activation energy and heat of reaction. Values of E_a° and γ_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

$$E_a = 48.1 + 0.25\left(\Delta H_{Rx}\right) \ \text{kJ/mol} \tag{R3.A-45}$$

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

$$E_a = 48.1 + 0.75\left(\Delta H_{Rx}\right) \ \text{kJ/mol} \tag{R3.A-46}$$

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

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

$$E_a = \sum D_j\left(\text{Breaking}\right) - \alpha \sum D_j\left(\text{Forming}\right) \tag{R3.A-47}$$

$$D_i = \text{Dissociation Energies}$$

$\boxed{\text{Derive}}$ (Click back)

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

Rearranging

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

Solving for r*

$$r^* = \frac{\Delta H_{Rx}}{\left(S_1 - S_2\right)} + \frac{S_1 r_1 - S_2 r_2}{S_1 - S_2} \tag{C}$$

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Recalling Equation (R3.A-43)

$$E_a = E_1^* - E_{1R} = S_1\left(r^* - r_1\right) \tag{R3.A-43}$$

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

$$E_a = S_1\left[\frac{\Delta H_{Rx}}{S_1 - S_2} + \frac{S_1 r_1 - S_2 r_2}{S_1 - S_2}\right] - S_1 r_1 \tag{E}$$

Rearranging

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

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

Finally, collecting terms we have

$$E_a = \underbrace{\left(\frac{S_1}{S_1 - S_2}\right)}_{\gamma_P}\Delta H_{Rx} + \underbrace{\left(\frac{S_1 S_2}{S_1 - S_2}\right)\left[r_1 - r_2\right]}_{E_a^*} \tag{H}$$

Note: S_1 is positive, S_2 is negative, and $r_2 > r_1$; therefore, E_a^* is positive, as is γ_P.

$$\boxed{E_a = E_a^* + \gamma_p \Delta H_{Rx}}$$

## B. Marcus Extension of the Polyani Equation

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

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

C. Blowers-Masel Relation

The Polyani 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.

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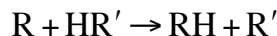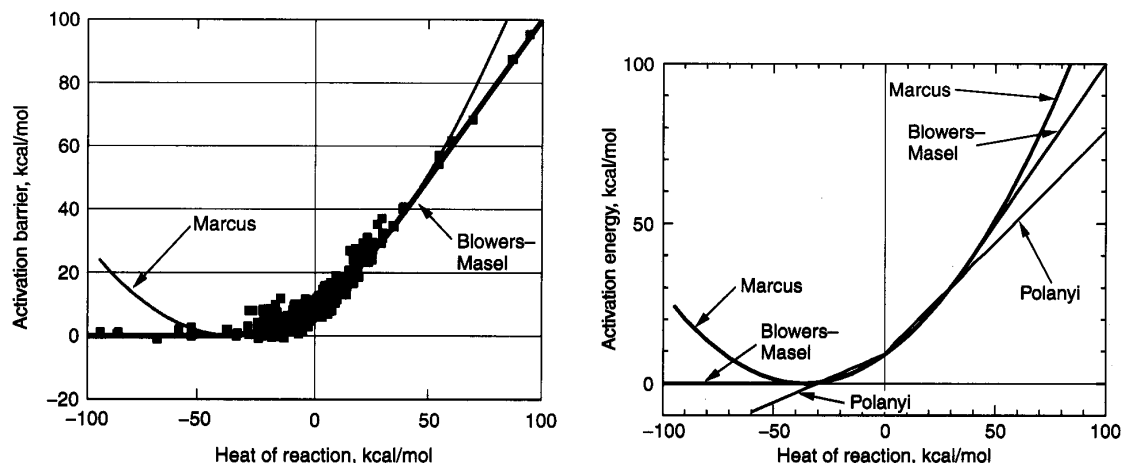
Figure R3.A-13 Comparison of models with data. Courtesy of R. I. Masel, *Chemical Kinetics and Catalysis* (New York: Wiley Interscience, 2001).

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

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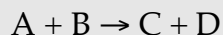
with

$$-r_A = k\, C_A C_B$$

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

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

and the activation energy, E_A, from the Polyani Equation.

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

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

$$-r_A = kC_A C_B = Ae^{-E_A/RT}$$

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VI. OTHER STUFF

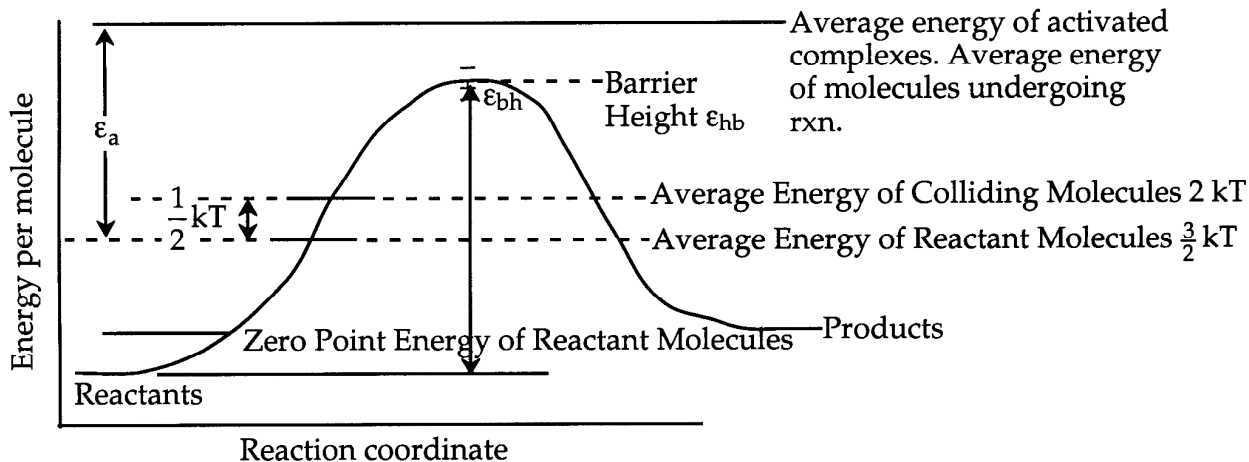### Potential Energy Surfaces and the barrier height ε_{hb}

Figure R3.A-14 Reaction coordinates.

The average transitional energy of a molecule undergoing collision is $2k_BT$. 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
$$E_b = \text{Barrier Height} \equiv \varepsilon_{hb}$$
$E_b = 40 \text{ kJ/mol}$ for the $H + H_2$ exchange reaction

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

(3) *London-Eyring-Polanyi (LEP) Method*

(LEP) Surface

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 = dissociation energy
r_o = equilibrium internuclear distance
β = 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.

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)

$$f(\varepsilon, T) = \frac{1}{\left(\frac{1}{2}n - 1\right)!} \left(\frac{\varepsilon}{k_B T}\right)^{\frac{n}{2} - 1} \frac{1}{k_B T} e^{-\varepsilon/kT} \tag{R3.A-30}$$

$dF = f(\varepsilon, T)d\varepsilon$ = fraction of molecules with energy between ε 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

$$f(\varepsilon, T) = \frac{e^{-\varepsilon/k_B T}}{k_B T} \tag{R3.A-31}$$

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, dF, of molecules between ε 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

$$F = \frac{1}{k_B T} \int_{\varepsilon^*}^{\infty} e^{-\varepsilon/k_B T} \, d\varepsilon$$

Multiplying and dividing by $k_B T$ and noting again $\dfrac{\varepsilon}{k_B T} = \dfrac{E}{RT}$

$$dF = \int_{E_A}^{\beta_\infty} e^{-E/RT} dE$$

Integrating

$$\boxed{F = e^{-E_A/RT}} \tag{R3.A-32}$$

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

$$-r_A = Ae^{-E_A/RT} C_A C_B$$

which gives the Arrhenius Equation

$$k = A \; e^{-E_A/RT} = A \; e^{-\varepsilon^*/kT}$$

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