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5.62 Physical Chemistry II
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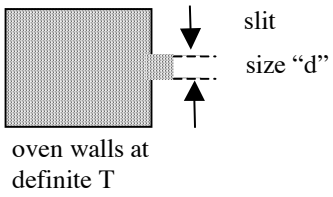
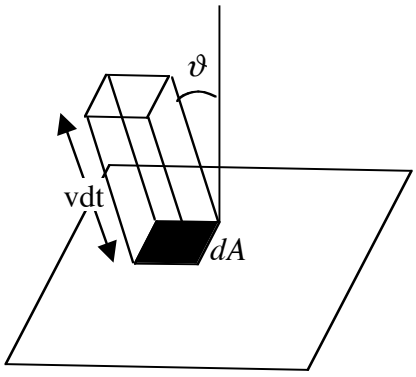
Kinetic Theory of Gases: Effusion and Collisions

EFFUSION Consider the process by which molecules escape through a hole in a vessel and into a vacuum



We assume that: (1) d is so small that the pressure in the vessel is unchanged; (2) the effusion does not perturb the velocity of the gas in the vessel; (3) there are no collisions when the molecules pass through the slit.

Molecules that would have been incident on the portion of the wall where the hole is, now pass through the hole. This creates a flux of particles defined as the number of particles per unit area per unit time that leave the vessel.



Consider a square hole of area dA. A particle that is a distance vdt from the hole moves with speed v and at angle ϑ from the surface normal toward the hole.

Draw a parallelepiped around the hole with length equal to vdt, at angle θ from the normal. All molecules within this volume moving toward the hole (i.e., with the correct ϑ, φ angle) with speed v will pass through the hole in time interval dt.

ρ = density of gas
Volume of parallelepiped = v cos ϑ dA dt
(Note that, at grazing angles, $\theta \sim \pi/2$, the volume is small)

# of molecules crossing through dA in dt = ρvcos θdAdt (number density times volume)

$$\frac{\#\,\text{molecules}}{\text{dAdt}} = \rho v \cos\vartheta = \text{FLUX}.$$

We must integrate this expression over the distribution of velocities of the gas to obtain the average flux J. The Maxwell-Boltzmann distribution (from Lecture #28) is

$$F(\vec{v})d\vec{v} = F(v,\vartheta,\varphi)v^2 dv \sin\vartheta d\vartheta d\varphi = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{kT}} v^2 \; dv \sin\vartheta d\vartheta d\varphi \; .$$

Thus, for the average flux:

$\pi/2$ rather than π to obtain forward direction only

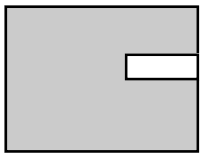
$$J = \rho\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^{\infty} e^{-\frac{mv^2}{kT}} v^3 dv \int_o^{\frac{\pi}{2}} \cos\vartheta \; \sin\vartheta d\vartheta \int_0^{2\pi} d\varphi$$

Factor of v^3: v^2 from volume element, v from flux

The result is:

$$J = \rho\left(\frac{m}{2\pi kT}\right)^{3/2}\left[\frac{1}{2}\left(\frac{2kT}{m}\right)^2\right]\left[\frac{1}{2}\right][2\pi] = \frac{\rho}{4}\left(\frac{8kT}{\pi m}\right)^{1/2} = \frac{\rho\bar{v}}{4}$$

Note : This result could have been obtained in an alternative way. Consider a volume of gas behind the hole that contains ρdV molecules. Then J simply is:

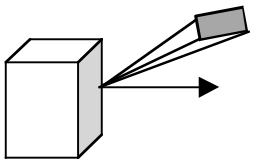


Volume
$dV = v_z dt$

$$J = \rho \int_{-\infty}^{+\infty} dv_x dv_y \int_0^{+\infty} dv_z dv_z \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}}$$

Only the molecules with $v_z > 0$ can exit the hole.

<u>Angular Distribution of Flux (or Effusing Molecules)</u> The velocity distribution of particles exiting through the hole are the same as the velocity distribution of particles hitting the hole. As a result the angular distribution and speed distribution of flux $j(v,\vartheta,\varphi)$ leaving the hole is.

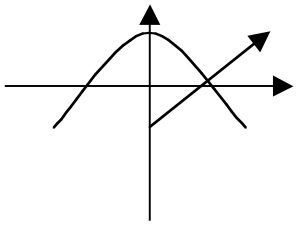


$$j(v,\vartheta,\varphi)dvd\Omega = \rho\left(\frac{m}{2kT}\right)^{\frac{3}{2}} v^3 e^{-\frac{mv^2}{2kT}} \cos\vartheta dv d\Omega$$

solid angle
$d\Omega = \sin\vartheta d\vartheta d\varphi$

The angular distribution of the flux is

cos ϑ

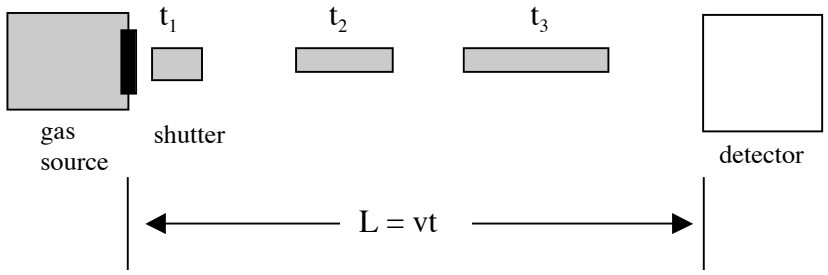


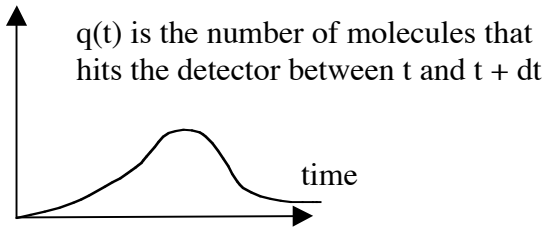
$$j_{angle}(\Omega)d\Omega = \int_0^{\infty} dv \quad j(v,\vartheta,\varphi) = \frac{\rho\bar{v}}{4\pi}\cos\vartheta d\Omega$$

$$0 < \vartheta < \frac{\pi}{2}, \quad 0 < \varphi < 2\pi$$

Effusion is an important mechanism for creating molecular beams that have practical use (for example in molecular beam epitaxy used in the manufacture of electronic devices) and for studying collisions and gas phase chemical reactions.

One important application is time of flight verification of the Maxwell Boltzmann distribution (1955!). The experiment is described in the figure below. Puffs of gas are released by opening the shutter. The gas spreads as a result of the spread in speed. {velocity distributions can also be inferred from Doppler shift measurements on spectral lines}.





There is a relation between the distribution of arrival times q(t) and the distribution of speeds h(v):

$$q(t)dt = h(v)dv\,.$$

Dynamics determines the exact relation between distance, speed, and time L=vt. Using the Dirac delta function to set this relation gives:

$$\int_0^\infty dv h(v)\delta\left(v-\frac{L}{t}\right)=h\left(\frac{L}{t}\right).$$

Thus measurement of q(t) allows us to infer the functional form of h according to:

$$h\left(\frac{L}{t}\right)=q(t)\left|\frac{dt}{dv}\right|=q(t)\frac{t^2}{L}.$$

The flux is obtained by multiplying the amplitude in the arrival time distribution at the corresponding time t with a factor t^2/L. The flux of molecules with large v arrive at the detector early and have not spread out in arrival times as much as the later arriving ones.

Molecular Collisions

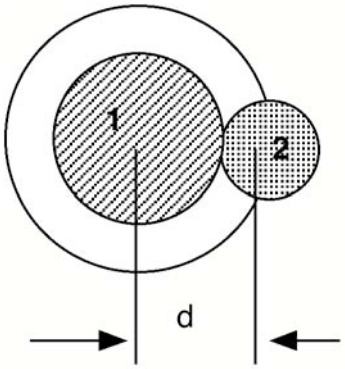
Goal: To calculate collision frequency between pairs of molecules in a gas. We begin by defining terms.

Z = average number of collisions of a single particle per unit time.

Collision event occurs when centers of 2 molecules approach within distance d.

Distance d is the hard sphere diameter

Collision cross section $\equiv \pi d^2$ =area of circle of radius d (surrounding particle 1), if the center of particle 2 enters (or touches) this circle, a collision occurs.



A collision occurs when the relative velocity permits an encounter between two particles. The relative velocity is defined as:

$$\vec{v}_r=\vec{v}_1-\vec{v}_2.$$

In a time dt, a collision volume dV is swept out by a particle. This volume is:

$$dV=\pi d^2\left|\vec{v}_r\right|dt;\qquad \left|\vec{v}_r\right|=\left[\vec{v}_r\cdot\vec{v}_r\right]^{\frac{1}{2}}.$$

The number of encounters in time dt at relative velocity v_r is ρdV. The number of encounters per unit time is

$$\#\text{ of encounters/time}=\rho\frac{dV}{dt}=\pi d^2\rho|\vec{v}_r\ |\ .$$

The collision frequency is the average of this quantity:

$$Z=\pi d^2\rho\overline{|\vec{v}_r\ |}$$

Since $|\vec{v}_r\ |=v_r$, the average of the relative velocity, is

$$\overline{v}_r=\int d\vec{v}_1\int d\vec{v}_2F(\vec{v}_1)F(\vec{v}_2)v_r$$

In this expression, we have assumed that the velocity distributions for the two molecules are independent of each other; this is true. But, at high density, intermolecular interactions will influence the spatial arrangement of the colliding pairs and this effect is not taken into account in the above expression. Thus, the average we are calculating is only valid for dilute gas conditions.

The two distribution functions have the form:

$$F(\vec{v}_1)=\left(\frac{m_1}{2\pi kT}\right)^{\frac{3}{2}}\exp\left(-\frac{m_1v_1^2}{2kT}\right)\ \text{and}\ \ F(\vec{v}_2)=\left(\frac{m_2}{2\pi kT}\right)^{\frac{3}{2}}\exp\left(-\frac{m_2v_2^2}{2kT}\right).$$

Thus the integral to be done is:

$$\overline{v}_r=\left(\frac{m_1}{2\pi kT}\right)^{\frac{3}{2}}\left(\frac{m_2}{2\pi kT}\right)^{\frac{3}{2}}\int d\vec{v}_1\int d\vec{v}_2\exp\left[-\left(\frac{m_1v_1^2+m_2v_2^2}{2kT}\right)\right]v_r$$

In order to do the integrals we must change variables from $\vec{v}_1$ and $\vec{v}_2$ to relative and center of mass velocity $\vec{U}$:

$$\vec{v}_r=\vec{v}_1-\vec{v}_2\ \ \text{and}\ \ M\vec{U}=m_1\vec{v}_1+m_2\vec{v}_2\ \ \ \text{where}\ M=m_1+m_2$$

Solving for the particle velocities gives:

$$\vec{v}_1=\vec{U}+\frac{m_2}{M}\vec{v}_r\ \ \text{and}\ \ \vec{v}_2=\vec{U}-\frac{m_1}{M}\vec{v}_r\ \ \ .$$

A bit of algebra shows that the kinetic energy term is:

$$m_1 v_1^2 + m_2 v_2^2 = (m_1 + m_2)U^2 + \frac{m_2 m_1}{m_1 + m_2} v_r^2 = MU^2 + \mu v_r^2 .$$

Here the reduced mass μ has been defined by:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 m_2}{m_1 + m_2} .$$

To proceed we need the Jacobian of the transformation for the change in variables:

$$d\vec{v}_1 d\vec{v}_2 = \begin{vmatrix} \left(\frac{\partial \vec{v}_1}{\partial \vec{U}}\right) & \left(\frac{\partial \vec{v}_2}{\partial \vec{U}}\right) \\ \left(\frac{\partial \vec{v}_1}{\partial \vec{v}_r}\right) & \left(\frac{\partial \vec{v}_2}{\partial \vec{v}_r}\right) \end{vmatrix} d\vec{U} d\vec{v}_r = \begin{vmatrix} \mathbf{1} & \mathbf{1} \\ \frac{m_2}{M}\mathbf{1} & -\frac{m_1}{M}\mathbf{1} \end{vmatrix} d\vec{U} d\vec{v}_r = d\vec{U} d\vec{v}_r$$

The Jacobian of the transformation is happily equal to unity.

The transformed integral becomes:

$$\overline{v}_r = \left(\frac{m_1}{2\pi kT}\right)^{\frac{3}{2}} \left(\frac{m_2}{2\pi kT}\right)^{\frac{3}{2}} \int d\vec{U} \int d\vec{v}_r \exp\left[-\left(\frac{MU^2 + \mu v_r^2}{2kT}\right)\right] v_r$$

$$\overline{v}_r = \left(\frac{m_1}{2\pi kT}\right)^{\frac{3}{2}} \left(\frac{m_2}{2\pi kT}\right)^{\frac{3}{2}} \int d\vec{U} \exp\left[-\left(\frac{MU^2}{2kT}\right)\right] \int d\vec{v}_r \exp\left[-\left(\frac{\mu v_r^2}{2kT}\right)\right] v_r .$$

We have no interest in the center of mass variables and can immediately integrate over these variables to obtain:

$$\overline{v}_r = \left(\frac{m_1}{2\pi kT}\right)^{\frac{3}{2}} \left(\frac{m_2}{2\pi kT}\right)^{\frac{3}{2}} \left(\frac{2\pi kT}{M}\right)^{\frac{3}{2}} \int d\vec{v}_r \exp\left[-\left(\frac{\mu v_r^2}{2kT}\right)\right] v_r$$

$$\overline{v}_r = \left(\frac{\mu}{2\pi kT}\right)^{\frac{3}{2}} \int d\vec{v}_r \exp\left[-\left(\frac{\mu v_r^2}{2kT}\right)\right] v_r .$$

Note that the Maxwell-Boltzmann distribution for the relative velocity is of the same form as the Maxwell-Boltzmann distribution for a single particle with *replacement of the particle mass by the reduced mass for the colliding pair*.

In spherical coordinates the average is:

$$\bar{v}_r = 4\pi\left(\frac{\mu}{2\pi kT}\right)^{\frac{3}{2}} \int dv_r v_r^2 \exp\left[-\left(\frac{\mu v_r^2}{2kT}\right)\right] v_r ,$$

and we obtain the final result:

$\bar{v}_r = \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}$ the average relative speed.

For like particles we have $\mu = \frac{m}{2}$ so $\bar{v}_r = \left(\frac{16kT}{\pi m}\right)^{\frac{1}{2}} = \sqrt{2}\ \bar{v}$. The average relative speed is $\sqrt{2}$ times (i.e. slightly larger than) the average speed of one of the particles. One certainly expects that $\bar{v}_r$ should be between $\bar{v}$ and $2\bar{v}$.

The average collision frequency for one particle is

$$Z = \pi d^2 \rho \bar{v}_r = \sqrt{2}\pi d^2 \rho \bar{v}$$

in a gas of like particles. The total collision frequency Z_{TOT} will be N times the one particle average collision frequency, but divided by a factor of 2 to avoid double counting. Thus the average total collision frequency per unit volume is:

$$\frac{Z_{TOT}}{V} = \frac{\sqrt{2}}{2}\rho^2 \pi d^2 \bar{v} .$$

Since collision theory is based on collisions, the average total collision frequency per unit volume is a key quantity.

Macroscopic Reaction Rates From Microscopic Properties

Part I.

Reaction rates and their corresponding rate constants are macroscopic properties determined by the microscopic properties of the individual particles that undergo reaction. Goal is to develop a theory to calculate rate constants from the molecular level properties of the reacting particles.

COLLISION THEORY

Consider $A + B \rightarrow C$

Upper limit to reaction rate d[C]/dt is the total collision frequency.

$$\frac{d[C]}{dt} = k [A] [B]$$

$$\frac{Z}{V} = \pi d_{AB}^2 \left(\frac{8kT}{\pi\mu} \right)^{1/2} \rho_A \rho_B$$

Can we describe the rate constant simply as a hard sphere collision cross section times the average speed?

$$k = \pi d_{AB}^2 \left(\frac{8kT}{\pi\mu} \right)^{1/2} = \pi d_{AB}^2 \bar{c} \qquad \bar{c} = \bar{c}_{rel}$$

But πd_{AB}^2 ≡ **collision** (as opposed to reactive) cross section! Not every collision results in a reaction. Many details are missing, e.g. do the colliding molecules have enough energy to react?

1. We want an expression for

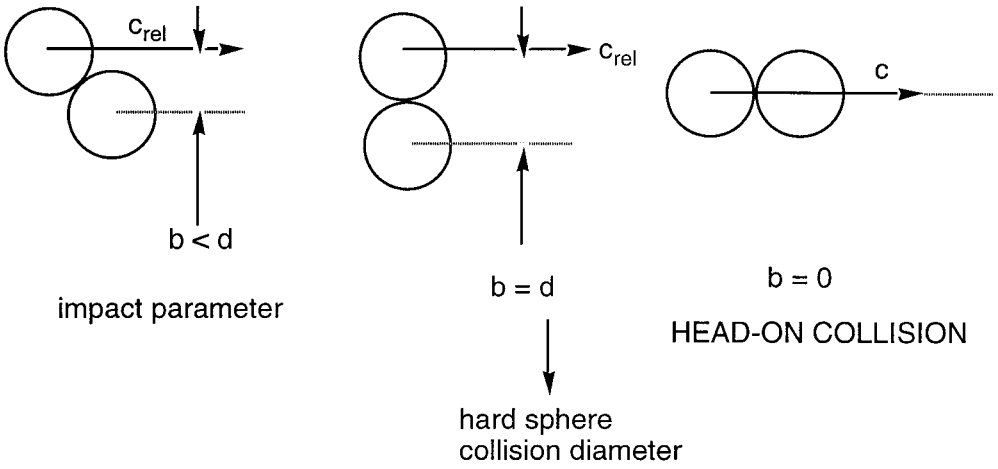
σ_R reaction cross section

Expect σ_R to have an energy dependence. *Simplest* assumption:

$\sigma_R = 0$ if $E < E_o$ and $\sigma_R = \pi d_{AB}^2$ if $E \geq E_0$

where E ≡ relative energy between colliding particles
E_0 ≡ critical energy needed to get over barrier.

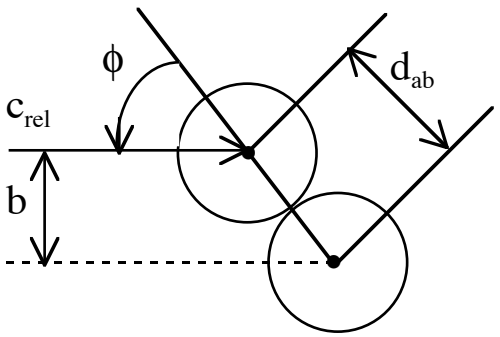
But this assumption is obviously deficient because molecules collide with different impact parameters, b.



IMPACT PARAMETER ≡ b ≡ distance between relative velocity vector and another line parallel to c_{rel} and going thru center of target atom.

We have the "intuition" that molecules that collide head-on will be more effective at reacting than molecules that experience glancing collisions (b □ d) even if the relative collision energy is the same. Propose that the critical energy, E_0, must be along the "line of centers". The line of centers is the direction of the line through the two atom centers at the instant of impact.

Calculate line-of-centers energy:



$\phi \equiv$ angle between $\underset{\sim}{c}_{rel}$ and the line of centers

$\underset{\sim}{c}_{rel} \equiv$ relative velocity vector

$c_{rel} \cos\phi \equiv$ velocity component along line of centers

$\frac{1}{2} \mu c_{rel}^2 \cos^2\phi \equiv$ translational energy component along the line of centers

$$\frac{1}{2}\mu c_{rel}^2 \cos^2\phi = \frac{1}{2}\mu c_{rel}^2\left(1-\sin^2\phi\right) \geq E_0$$

Since $\sin\phi = b/d_{AB}$ and $\frac{1}{2}\mu c_{rel}^2 = E_{rel} \equiv E$

Then the requirement for reaction is that the line of centers energy $E\left(1-\frac{b^2}{d_{AB}^2}\right) \geq E_0$

This function relates the component of the relative translational energy that provides the critical energy along the line of centers to the impact parameter of the collision.

For each E, there is some b, call it b_0, such that the line of centers energy is sufficient for reaction:

$$E\left(1-\frac{b_0^2}{d_{AB}^2}\right) = E_0$$

$b_0 \equiv$ the largest impact parameter the collision with E_{rel} can have and still have at least E_0 along line of centers

$$b_0^2 = d_{AB}^2\left(1-\frac{E_0}{E}\right)$$

For each E, all collisions with $b \leq b_0$ are effective because for these impact parameters the line of centers energy is $> E_0$

So $\sigma_R(E) = \pi b_0^2$ The reactive cross-section is a function of the relative translational energy because it includes all values of $b \leq b_0$ and b_0 is explicitly dependent on E.

$$\sigma_R = \pi b_0^2 = \pi d_{AB}^2\left(1-\frac{E_0}{E}\right) \quad \text{for } E > E_0$$

$$\sigma_R = 0 \text{ for } E \leq E_0$$

2. Calculate k by averaging over relative velocities (energies).

$$k = \sigma_R \bar{c} = \pi d_{AB}^2\left(1-\frac{E_0}{E}\right)\bar{c}$$

But, we no longer want to multiply by the average relative velocity because σ_R is now dependent on the relative energy (velocity). Want to multiply σ_R by *the* relative velocity of *the* specific collision and then want to average over all possible relative energies.

$$k = \sigma_R \bar{c} = \int \sigma_R \, c \, f(c) \, dc$$

$$= \pi d_{AB}^2 \left(1 - \frac{E_0}{E}\right) 4\pi \left(\frac{\mu}{2\pi kT}\right)^{3/2} \int c^3 \, e^{-\mu c^2/2kT} \, dc$$

Change variables to E instead of c because $\sigma_R(E)$

$$E = \frac{1}{2} \mu c^2 \qquad dE = \mu c dc$$

$$k = \pi d_{AB}^2 \int \left(1 - \frac{E_0}{E}\right) 4\pi \left(\frac{\mu}{2\pi kT}\right)^{3/2} \frac{dE}{\mu \left(\frac{2E}{\mu}\right)^{1/2}} \left(\frac{2E}{\mu}\right) e^{-E/kT} \left(\frac{2E}{\mu}\right)^{1/2}$$

$$= \frac{8\pi}{\mu^2} \left(\frac{\mu}{2\pi kT}\right)^{3/2} \pi d_{AB}^2 \int_{E_0}^{\infty} (E - E_o) \, e^{-E/kT} \, dE$$

lower limit is E_0 because $\sigma_R = 0$ if $E < E_o$

$$\text{Let } x = \frac{E - E_0}{kT} \qquad dx = \frac{dE}{kT}$$

then $e^{-E/kT} = e^{-E_0/kT} \, e^{-x}$

$$k = \frac{8\pi}{\mu^2} \left(\frac{\mu}{2\pi kT}\right)^{3/2} \pi d_{AB}^2 \, (kT)^2 \, e^{-E_0/kT} \underbrace{\int_0^{\infty} x e^{-x} dx}_{1}$$

$$k = \underbrace{\left(\frac{8kT}{\pi\mu}\right)^{1/2}}_{\text{relative speed}} \underbrace{\pi d_{AB}^2}_{\text{hard sphere cross section}} \underbrace{e^{-E_0/kT}}_{\text{fraction of collisions having necessary component of energy along line of centers } E_0}$$

COLLISION THEORY RATE CONSTANT

Collision theory result looks very much like empirical Arrhenius expression ($k = A \, e^{-E_a/kT}$) except that the collision theory preexponential factor has a $T^{1/2}$ dependence

$$k = BT^m e^{-E_0/kT} \qquad \text{where } m = 1/2$$

Most experimental measurements of k do not show a T dependent pre–exponential factor. This is because measurements of k are made over too small a temperature range to see the weak $T^{1/2}$ dependence of the pre–exponential factor in the presence of the much stronger T dependence of the exponential term. This pre-exponential $T^{1/2}$ dependence would show up as non-linearity in plot of lnk vs. 1/T.

RELATIONSHIP BETWEEN E_0 (critical line of centers energy) and E_a,
EMPIRICAL ARRHENIUS ENERGY

$$k = A\, e^{-E_a/kT}$$

$$\frac{d \ln k}{dT} = \frac{d(\ln AE_a / kT)}{dT} = \frac{E_a}{kT^2}$$

$$k^{CT} = \left(\frac{8kT}{\pi m}\right)^{1/2} \pi d_{AB}^2 \; e^{-E_0/kT}$$

$$\frac{d \ln k^{CT}}{dT} = \frac{d\left[(\ln(8k/\pi\mu)^{1/2} \pi d_{AB}^2 + \frac{1}{2}\ln T - E_0/kT)\right]}{dT}$$

$$= \frac{1}{2T} + \frac{E_0}{kT^2}$$

Now we require that

$$\frac{d \ln k}{dT} = \frac{d \ln k^{CT}}{dT} \qquad \frac{E_a}{kT^2} = \frac{1}{2T} + \frac{E_0}{kT^2}$$

Thus

$$E_a = \frac{kT}{2} + E_0$$

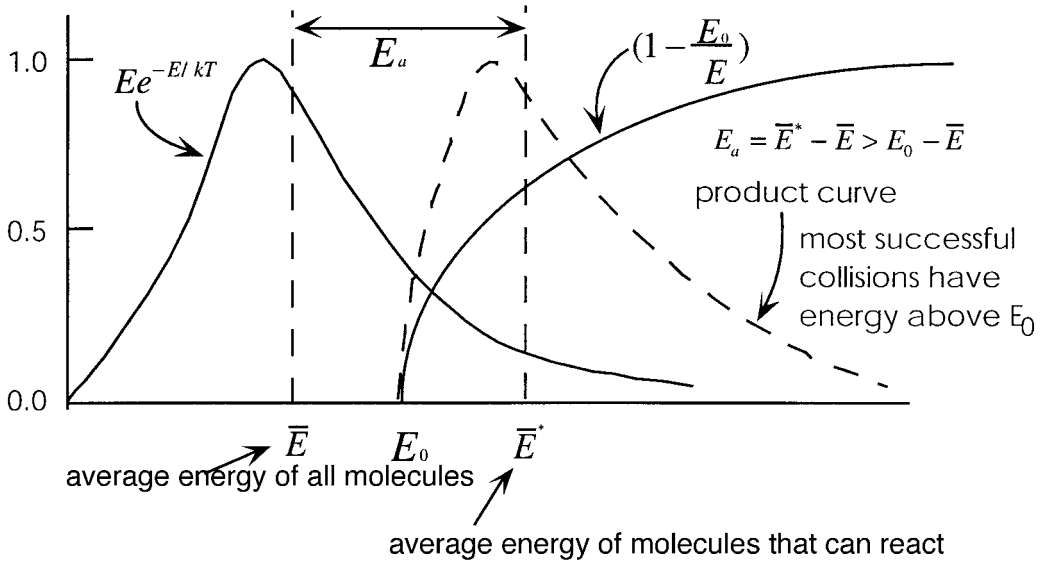
E_a must be larger than E_0. WHY?

FURTHER ANALYZE COLLISION THEORY RATE CONSTANT:

$$k^{CT} \propto \int \left(1 - \frac{E_o}{E}\right) E\, e^{-E/kT}\, dE$$

energy dependence of cross section, σ_R

distribution of relative energies



CALCULATE VALUES FOR

$$k^{CT} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \pi d_{AB}^2 \; e^{-E_0/kT} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \pi d_{AB}^2 \; e^{1/2} \, e^{-E_a/kT}$$

Get E_0 from experimental E_a since $E_0 = E_a - kT/2$

Get πd_{AB}^2 from transport data

COMPARE TO EXPERIMENT

REACTION	$\ln k^{CT}$ CALCULATED	$\ln k$ OBSERVED
$CH_3 + CH_3 \rightarrow C_2H_6$	10.6	10.5
$CF_3 + CF_3 \rightarrow C_2F_6$	10.3	10.4
$H + CCl_4 \rightarrow HCl + CCl_3$	0.83	–4.4
$Cl + H_2 \rightarrow HCl + H$	–1.4	–4.7

Conclusions: works well for simple recombination steps where the E_a is small or non-existent and where there is little steric hindrance.

does not work well for reactions with steric hindrance

— E_0 dependence may not be isotropic

— ignores effects of reactant vibrational and rotational energy in overcoming barrier.

Part II.

A "good" theory must take into account the internal degrees of freedom of the reactants and their angle of approach. An approach known as transition state theory = activated complex theory = absolute rate theory does so in an approximate way.

POTENTIAL ENERGY SURFACE

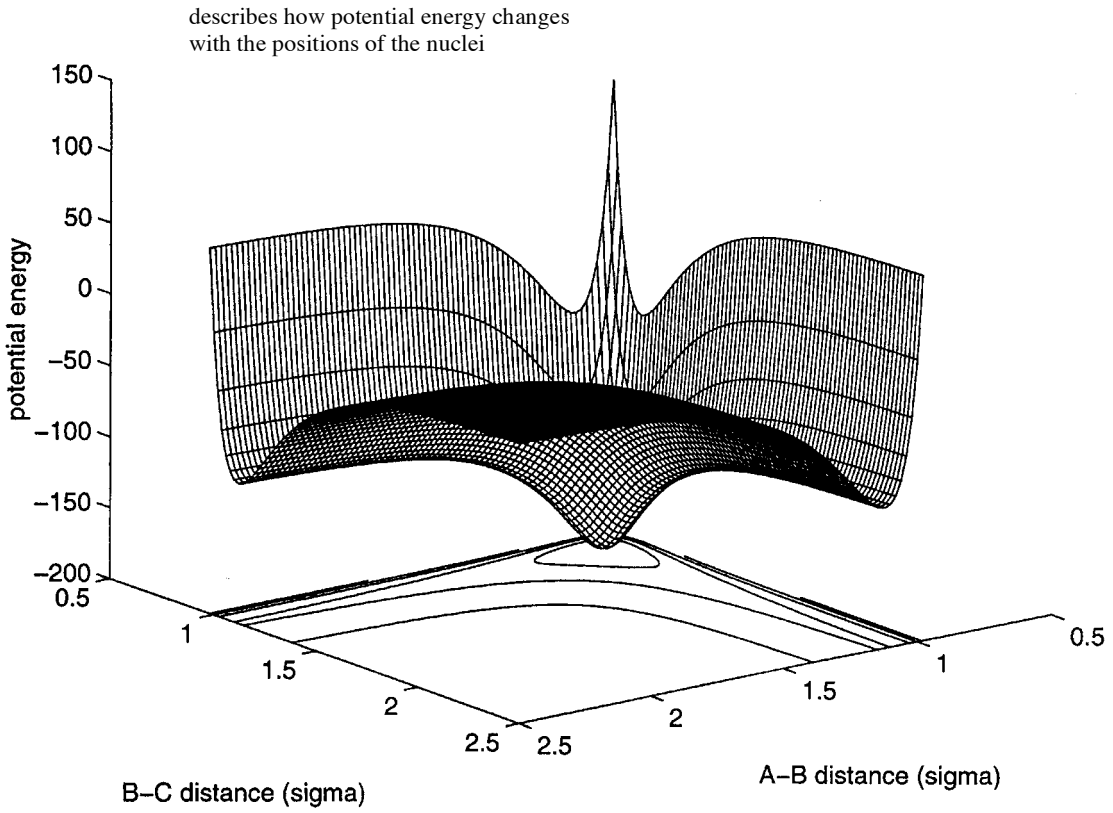
A correct theory must consider the internal structure of molecules and the forces acting on atoms in the molecules because bonds are being broken and formed during a reaction. During a reactive collision, the force on an atom depends on both intramolecular forces (forces between atoms in a molecule) and intermolecular forces (forces between molecules). Must treat the two colliding reactants as a single quantum mechanical system. This system exists only during collision process.

The system's potential energy is calculated the same way the potential energy for nuclear vibrational motion is calculated. Within the Born-Oppenheimer approximation, solve

$$H_{el}\,\Psi_{el} = E_{el}\,\Psi_{el}$$ at fixed nuclear configuration.

The resulting E_{el} is the potential energy at that nuclear configuration. Systematically vary the nuclear configuration (grid of points) to get potential energy as a function of nuclear coordinates.

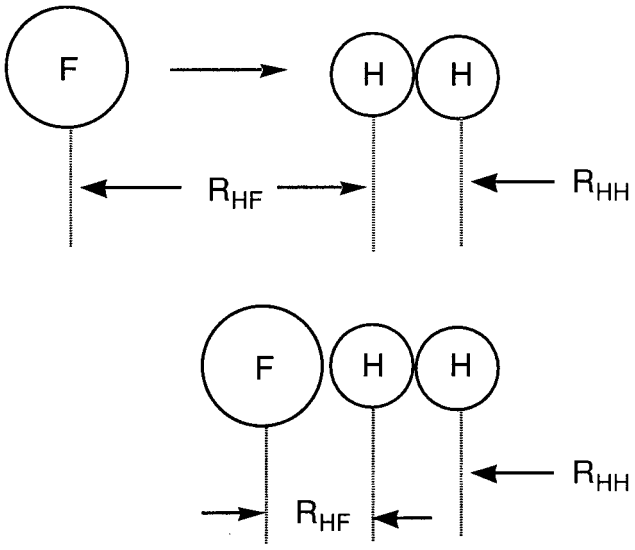
Problem: too many nuclear coordinates! Can't plot potential energy as a function of more than 2 coordinates. A plot of potential energy versus 2 coordinates is a 3-D plot where the potential energy is a SURFACE. Potential energy for more than 2 coordinates is still called a surface even though there are more than 2 coordinates.



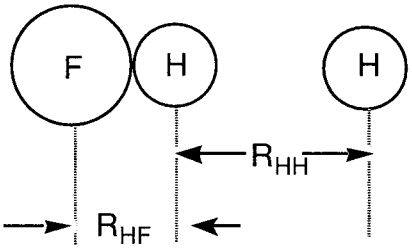
EXAMPLE: $H_2 + F \rightarrow HF + H$

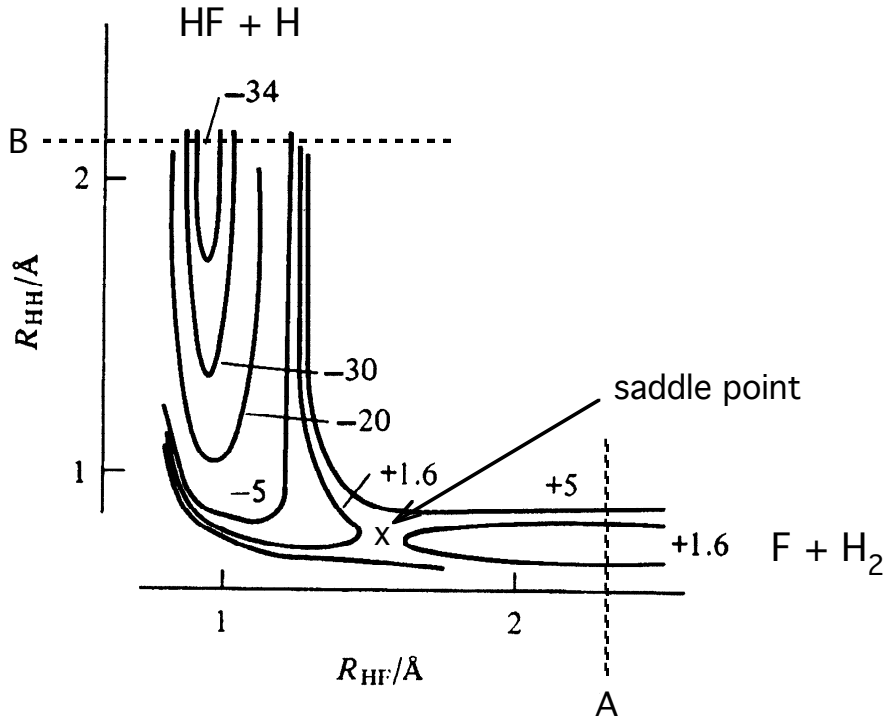
For collinear approach, there are 2 independent variables

R_{HF} and R_{HH} on which the potential depends.

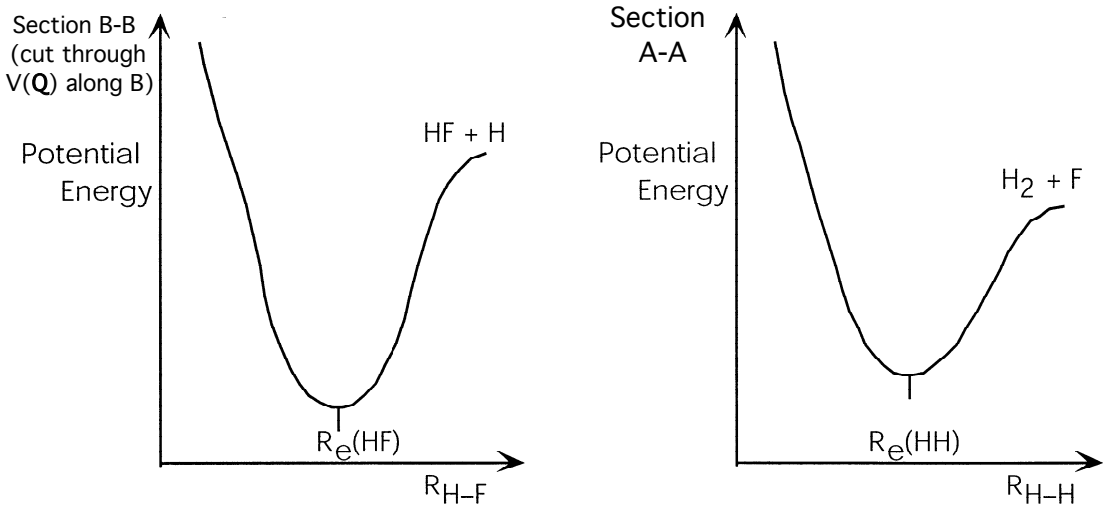


The potential energy of this system can be represented as a 3-D surface as a function of R_{HF} and R_{HH}. The 3-D surface can be represented as a 2-D contour potential energy surface.



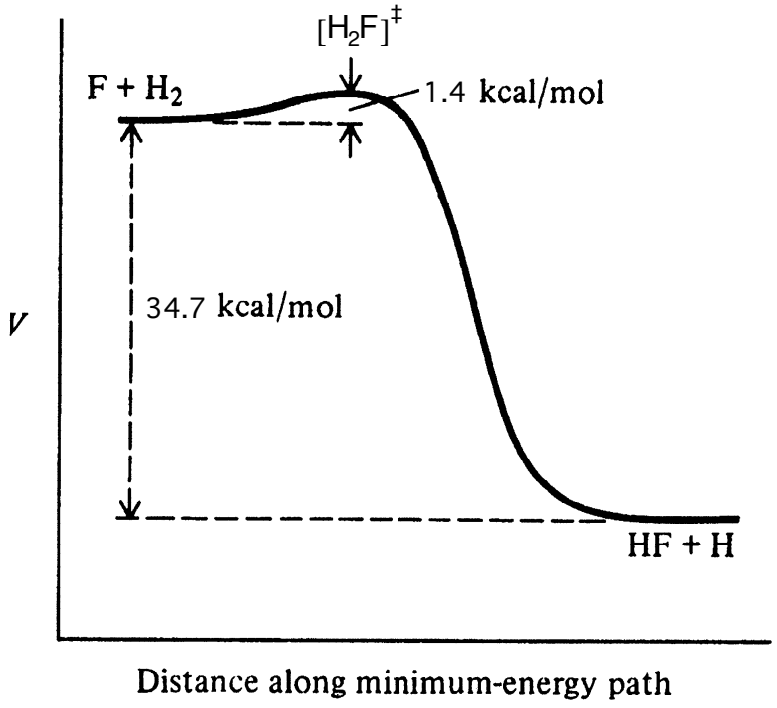


Lines on a contour map represent EQUIPOTENTIALS. Valleys correspond to initial and final states.



To go from one valley to another requires crossing a saddle point

REACTION COORDINATE FOR F + H_2



REACTION COORDINATE — *minimum energy path* along deepest part of potential energy surface

— note reaction coordinate corresponds to an antisymmetric H_2F vibration

TRANSITION STATE — transitory $[H_2F]^{\ddagger}$ complex with a definite structure
— dissociates within one half antisymmetric vibration.

TRANSITION STATE THEORY

An approach to calculating a rate constant by reducing the dynamics of the reaction to an equilibrium between the reactants and the transition state along the reaction coordinate.

$$A + B \leftrightarrow [AB]^{\ddagger} \rightarrow \text{PRODUCTS}$$

Uses statistical mechanics to treat the equilibrium. The reaction coordinate is the 1-D antisymmetric vibration of the transition state.