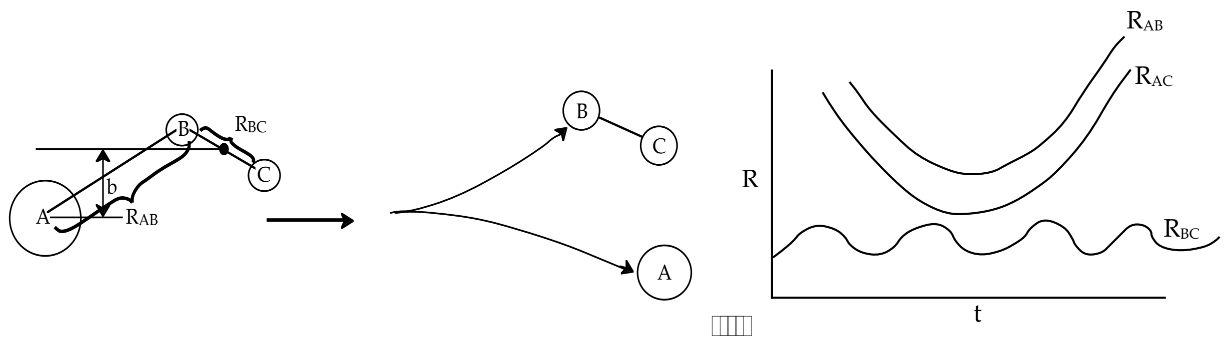
Molecular Dynamics

Abbreviated Notes

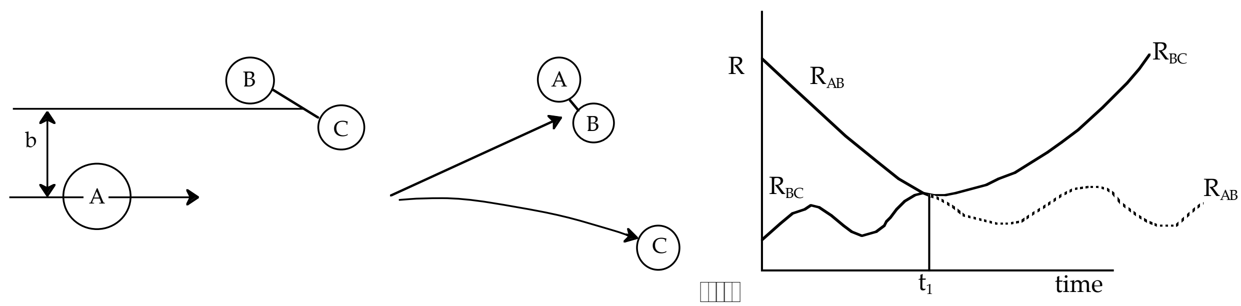
Part I

$$A + BC \longrightarrow AB + C$$

<u>Nonreactive Trajectory</u>



<u>Reactive Trajectory</u>



To trace the trajectories we simply solve for R as a function of time

$$F = ma = m\frac{dV}{dt} = \frac{d(mV)}{dt} = \frac{dP}{dt} \qquad (1)$$

$$K.E. = \frac{1}{2}mV^2 = \frac{1}{2m}P^2 \qquad (2)$$

$$F = -\frac{d\tilde{V}(x)}{dx}$$

$$\tilde{V}(R_{AB}, R_{AC}, R_{BC})$$

$$\tilde{V} = D_{AB}\left[1 - e^{\square}\right]$$ See page 10 of notes.

Solution Procedure

Equating Equations (1) and (2)

$$\frac{dP_x}{dt} = -\frac{d\tilde{V}}{dx}$$

Integrating

$$P_x = P_{xo} + \int -\frac{d\tilde{V}}{dx}\,dt = P_{xo} + \overline{\left(-\frac{d\tilde{V}}{dx}\right)}\Delta t$$

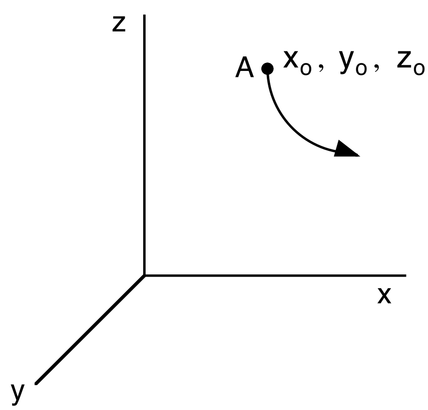
$$P_y = P_{yo} + \overline{\left(-\frac{d\tilde{V}}{dy}\right)}\Delta t$$

$$P_z = P_{zo} + \overline{\left(-\frac{d\tilde{V}}{dz}\right)}\Delta t$$

$$\frac{dx}{dt} = \frac{1}{m_A} P_x \Rightarrow x = x_0 + \frac{1}{m_A}\bar{P}_x \Delta t$$

$$\frac{dy}{dt} = \frac{1}{m_A} P_y \Rightarrow y = y_0 + \frac{1}{m_A}\bar{P}_y \Delta t$$

$$\frac{dz}{dt} = \frac{1}{m_A} P_z \Rightarrow z = z_0 + \frac{1}{m_A} P_z \Delta t$$



We can trace out a trajectory

$$H = KE + P.E. = \frac{1}{2m_A}\left[P_x^2 + P_y^2 + P_z^2\right] + \tilde{V}$$

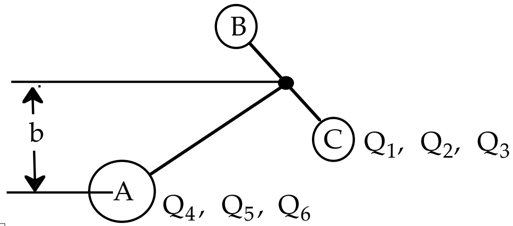
$$\frac{\partial H}{\partial P_x} = \frac{1}{2m_A} 2P_x = \frac{P_x}{m_A} = \frac{mV}{m} = V = \frac{dx}{dt}$$

$$\frac{dx}{dt} = \frac{\partial H}{\partial P_x}$$

We really don't care where we are in space, what we care about is location of molecules with regard to one another. Define a new coordinate system – affine transformation.

Carry Out Trajectory Calculations

The equations of motion used to calculate the trajectories in order to obtain the internuclear distances R_{AB}, R_{AC}, and R_{BC} are



$$\frac{\partial Q_j}{\partial t} = \frac{P_j}{\mu}$$

$$\frac{\partial P_j}{\partial t} = -\frac{\partial \tilde{V}(R_{BC}, R_{AB})}{\partial Q_j}$$

where P is the momentum and $\tilde{V}$ (R_{AB}, R_{BC}, R_{AC}) is the potential energy surface.

Q_1, Q_2, Q_3 {Location of C with B as the origin.

Q_4, Q_5, Q_6 {Location of A with the center of mass of BC as the origin.

$$H = \frac{1}{2\mu_{BC}} \sum_1^3 P_i^2 + \frac{1}{2\mu_{A,BC}} \sum_4^6 P_i^2 + \tilde{V}(R_{AB}, R_{BC}, R_{AC})$$

$$\frac{1}{\mu_{BC}} = \frac{1}{m_B} + \frac{1}{m_C}, \quad \frac{1}{\mu_{A,BC}} = \frac{1}{m_A} + \frac{1}{m_B + m_C}$$

i = 1, 2, 3

$$\frac{\partial Q_i}{\partial t} = \frac{\partial H}{\partial P_i} = \frac{1}{\mu_{BC}} P_i$$

$$Q_i(t) = Q_{io} + \int_0^t P_i dt$$

i = 1, 2, 3

$$\frac{\partial Q_j}{\partial t} = \frac{\partial H}{\partial P_i} = \frac{1}{\mu_{BC}} P_i$$

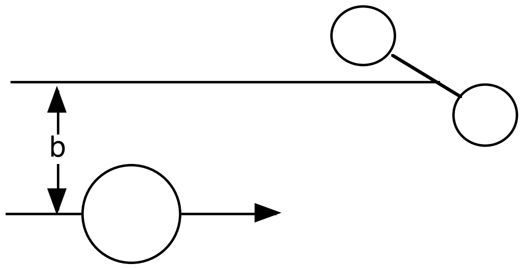
$$Q_i(t) = Q_i(0) + \int_0^t P_i dt$$

i = 4, 5, 6

$$\frac{\partial Q_i}{\partial t} = \frac{1}{\mu_{A,BC}} P_i$$

$$\frac{\partial P_i}{\partial t} = -\frac{\partial V}{\partial Q_i} \qquad P_i(t) = P_{io} + \int_0^t \left(-\frac{\partial V}{\partial Q_i}\right) dt$$

Let's Begin

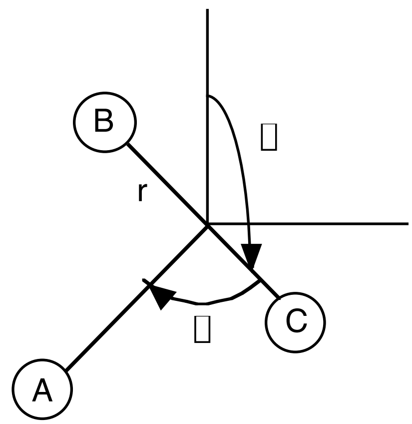


We Specify	Monte Carlo Chooses
b	R_{BC} ($R < R < R_+$)
V_R	□ presentation of BC molecule
□	□ relative to A
J	□ angular momentum of molecule (i.e., which derivation is it turning)

Part II

$$\frac{dP_x}{dt} = -\frac{d\tilde{V}}{dx}$$

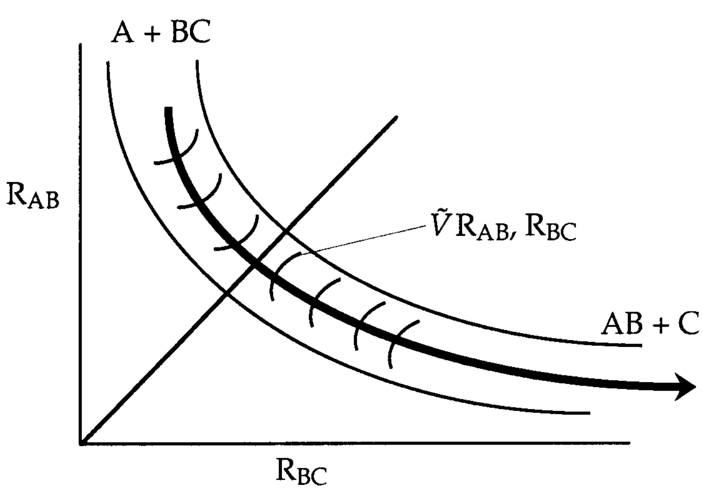
$$\frac{dx}{dt} = \frac{1}{m_A} P_x$$



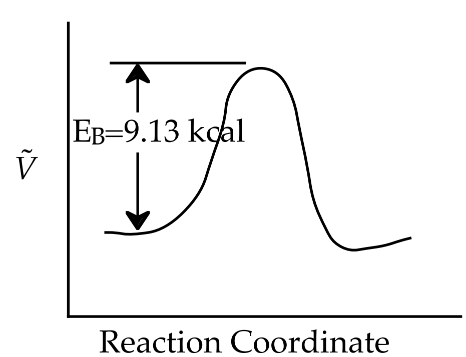
$i = 1, 2, 3$ $$\frac{dQ_i}{dt} = \frac{1}{\mu_{BC}} P_i \qquad Q_i = Q_{io} + \int_0^t P_i dt$$

$i = 4, 5, 6$ $$\frac{dQ_i}{dt} = \frac{1}{\mu_{A,BC}} P_i$$

$$\frac{\partial P_i}{\partial t} = -\frac{\partial \tilde{V}}{\partial Q_i} \qquad P_i = P_{io} + \int_0^t -\frac{\partial \tilde{V}}{\partial Q_i} dt$$



Sectional view along the bold trajectory.



We Specify	Monte Carlo Chooses
b	R – distance between B and C ($R_- < R < R_+$)
U_R	θ, φ orientation of the BC molecule to A ($0 < \theta < \pi$, $0 < \phi < 2\pi$)
J	
ψ	ψ angular momentum of BC, the direction the BC pair is turning

When θ rotates π degrees the H–H molecule, i.e., (BC) is the same as it was θ = 0. However, φ rotates the C molecule towards and away from T. A molecule, therefore it can rotate 2π.

Initial conditions, A and the center of mass of BC lie x–y plane and A approaches along z axis.

For the (C) with regard to (B)

$Q_1 = R_{BC} \, \text{Sin}\, \theta \, \text{Cos}\, \phi$

$Q_2 = R_{BC} \, \text{Sin}\, \theta \, \text{Sin}\, \phi$

$Q_3 = R_{BC} \, \text{Cos}\, \theta$

$P_1 = -P\, (\text{Sin}\, \phi \, \text{Cos}\, \psi + \text{Cos}\, \theta \, \text{Cos}\, \phi \, \text{Sin}\, y)$

$P_2 = -P\, (\text{Cos}\, \phi \, \text{Cos}\, \psi - \text{Cos}\, \theta \, \text{Sin}\, \phi)$

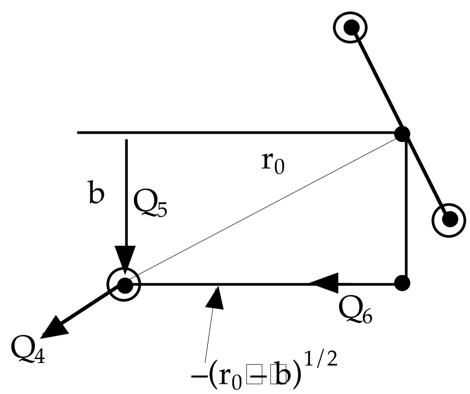
$P_3 = -P\, \text{Sin}\, \theta, \text{Sin}\, \psi$

$P = \sqrt{J(J+1)}\, \hbar / R_+$ (R_+ is the out turning radius)

$P_4 = 0$

$P_5 = 0$

$P_6 = \mu_{A,BC}\, U_R$



For (A) with regard to the center of the mass of BC

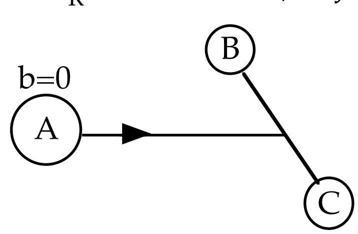
$Q_4 = 0$

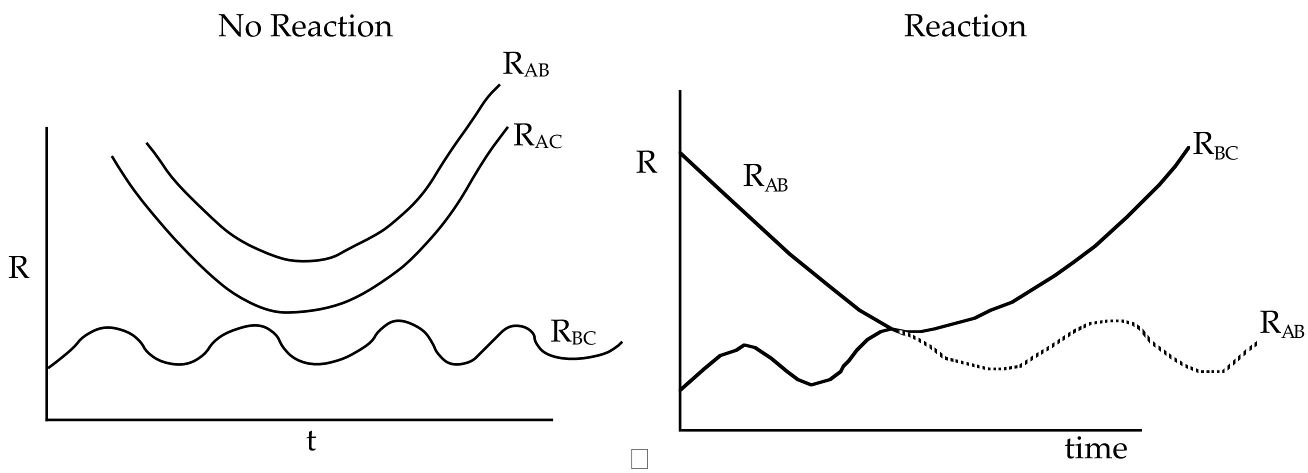
$Q_5 = b$

$Q_6 = -\left(r_o^2 - b^2\right)^{1/2}$

Let's begin to calculate the trajectories to find to whether or not we will have a reaction.

Set $b = 0$ $V_R = 1.17\ 10^6$ cm/s $J = 0, \psi = 0$





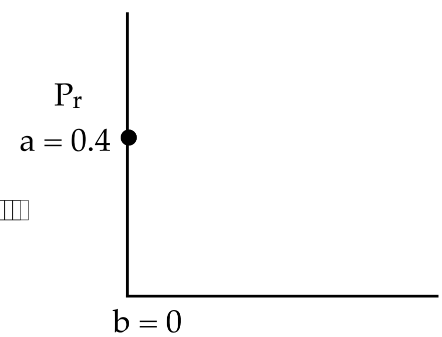
Now count up the number of reactions and the number of trials

Trials   ~~||||~~ ||| Pr = Probability Reaction

Reactions |||| $\Pr = \frac{4}{8} = 0.5$

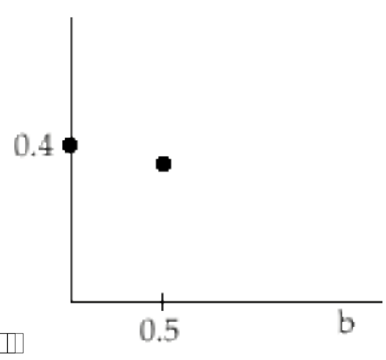
$$\Pr = \frac{\text{Number of trajectories that resulted in reaction}}{\text{Total number of trajectories (trials) carried out}}$$

$$P_r = \lim_{N_T \to \infty} \frac{N_{RXS}}{N_{Trials(T)}}$$

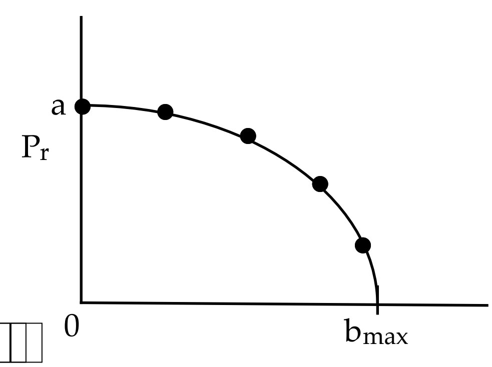


Now set b = 0.5 and again count up the number of reactions and trials to find P_r at this value of b.

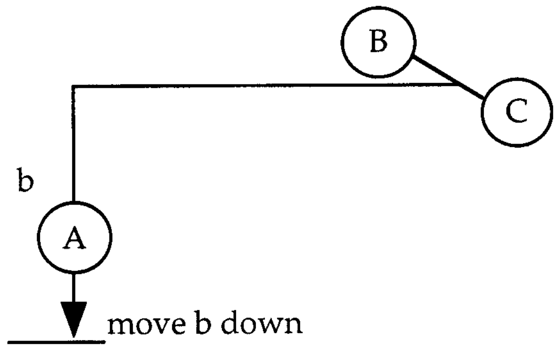
$$P_r = \frac{N_r}{N_T}$$

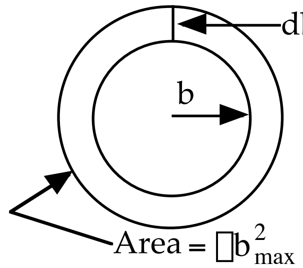


Again → Vary b



Now let's calculate the reaction cross section





The differential reaction cross section is

$$dS_r = P_r(b, U, J, \theta) 2\pi b db$$

integrating

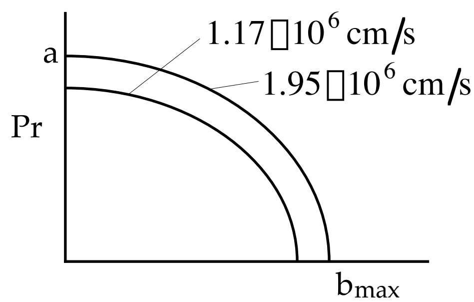
$$S_r = \int_0^{b_{max}} P_r(b, U, J, \theta) 2\pi b db$$

If we approximate Pr = a cos $\left[\frac{\pi b}{2 b_{max}}\right]$

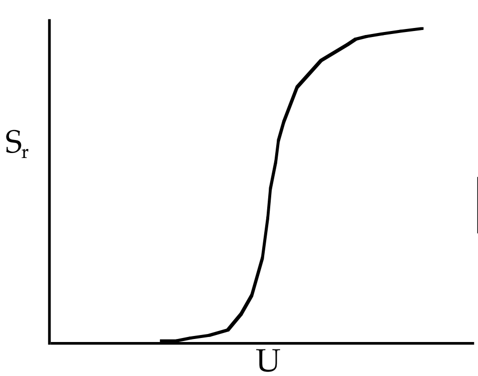
then

$$S_r = (U_r, J, \theta) = 1.45 \ a \ b_{max}^2 \ (a.u)^2$$

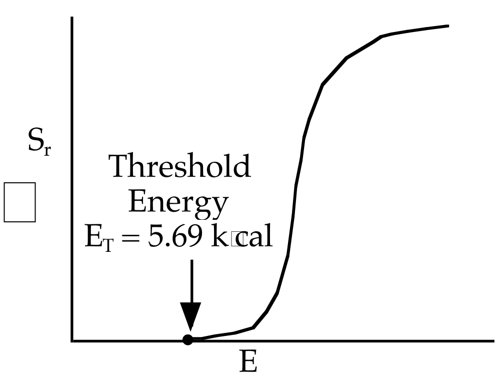
Now increase U_R to $U = 1.95 \times 10^6$ cm/s. We find both "b_{max}" and "a" both increase



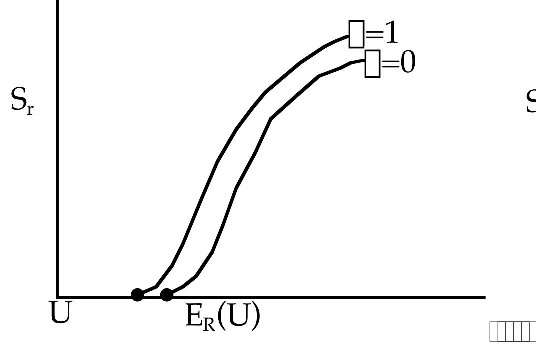
Now plot the reaction cross sections as a function of velocity and energy

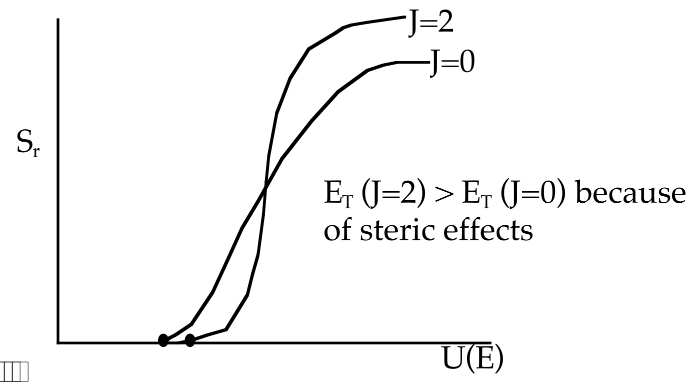


$$\left[E = \frac{1}{2\mu} U^2 \right]$$

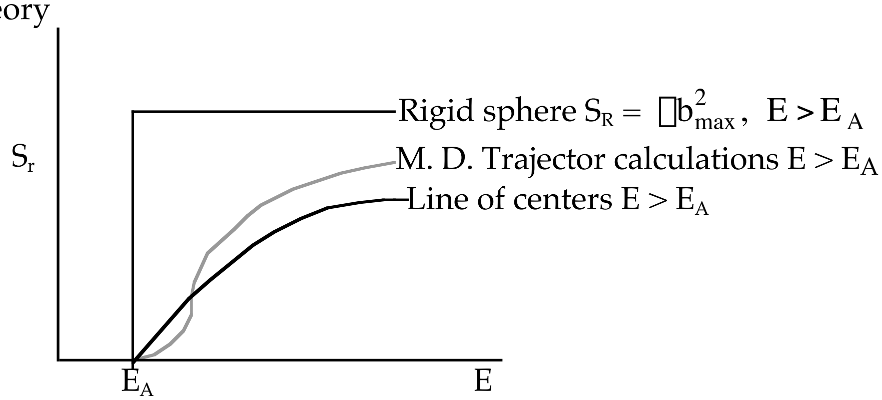


The threshold kinetic energy, E_T, below which no reaction will occur for $\nu = 0$ and $J = 0$ is 5.69 kcal





Let's compare S_r versus E from Molecular Dynamics (MD) with that obtained from collision theory



$$\vec{V}_R = \vec{V}_A - \vec{V}_{BC}$$

$$U_R = V_A - V_{BC}$$

From Collision Theory we had

$$-r_A = \underbrace{\left[\int_0^\infty S_r U f(U) dU\right]}_{k} C_A C_{BC}$$

by analogy we have

$$-r_A(\nu,J) = \underbrace{\left[F_{BC}(J,\nu)\int_0^\infty \int_0^\infty U_r S_r(\nu,J,U_r) f_A dV_A f_{BC} dV_{BC}\right]}_{k(\nu,J)} C_A C_{BC}$$

where $F_{BC}(\nu,J)$ is fraction of BC molecules in rotation state, J, and vibration state ν.

$$-r_A(\nu,J) = k(\nu,J) C_A C_{BC}$$

The total reaction rate is found by summing over all quantum states ν and J.

$$-r_A = \sum_{\nu} \sum_{J} k(\nu,J) C_A C_{BC} = k C_A C_{BC}$$

From first principles we evaluate all the parameters to calculate k at 300K and 1000K to compare with experimental observation.

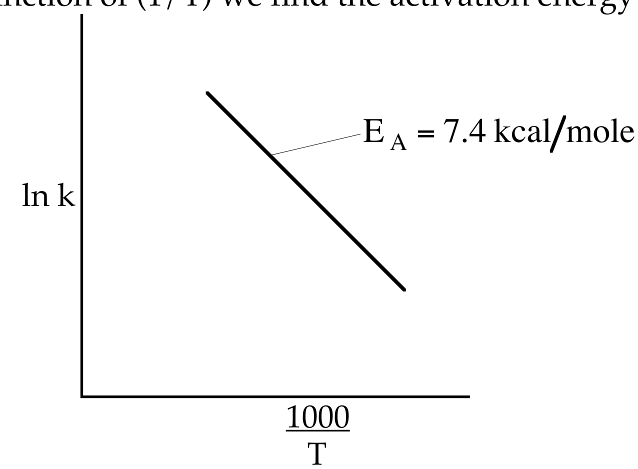
	$k\left(cm^2/mol \bullet s\right)$	
Temperature	Theory	Exp
300	0.00185	0.0017 0.006
1000	11.5	11 22

From the Arrhenius equation we know

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

$$\ln k = \ln A - \left(\frac{E}{R}\right)\left(\frac{1}{T}\right)$$

Plotting (ln k) as a function of (1/T) we find the activation energy to be T.4 kcal/mole.



Comparison of Energies

$$E_V + E_T = 6.2 + 5.89 = 11.89 \text{ kcal}$$

$$E_B = 9.13 \text{ kcal}$$

$$E_A = 7.4 \text{ kcal}$$

$$E_T = 5.69 \text{ kcal}$$

$$E_R = 5.35 \text{ kcal} \quad J = 5$$

$$E_R = 0.35 \text{ kcal} \quad J = 1$$