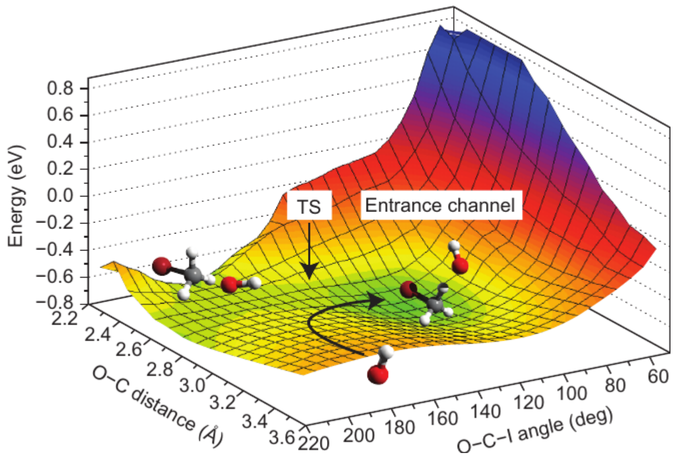
assignment 4 - solns.

(due before class on 10 Nov 2020)

1. Shown below is a PES for the reaction $OH^- + CH_3I \rightarrow$ products.



(a) What are the likely products?

(b) The curved arrow indicates how a co-linear approach starting at large distances is steered towards the non-co-linear entrance channel complex. Explain how this statement can be derived from the figure.

(c) What are the magnitudes of O-C distance and O-C-I angle after the system has landed in in the exit valley? If the C-I distance was monitored as the reaction progressed, what is its likely value in the exit valley?

(d) Estimate the activation energy for the reaction from the graph.

Ans. (a) It is a S_N2 reaction.

$OH^- + CH_3I \rightarrow CH_3OH + I^-$

(b) colinearlty $\implies \angle$O-C-I $= \pi$

The figure shows that the entrance at $\angle$O-C-I $= \pi$ is at roughly -0.3eV of potential energy and the system is taken away to a lower energy zone (-0.8 eV) of $\angle$O-C-I $\lesssim \frac{2\pi}{3}$. The energy estimate is based on the assumption that the minimum shown is at the bottom of the scale.

(c) In the exit valley O-C distance must be the smallest (~ 2.2Å).

It is seen from the figure that at this point $\angle$O-C-I $= \pi$

(d) There are two activation energies here - the first one is from the colinear entry to the minimum at $\angle$O-C-I $\lesssim \frac{2\pi}{3}$. This is an almost barrier less transition, so for this step $E_a \approx 0$.

The second one is from the minimum at $\angle$O-C-I $\lesssim \frac{2\pi}{3}$ to the products. Assuming that the minimum shown is at the bottom of the scale (-0.8 eV) and with a visual estimate of TS at (-0.6 eV, $E_a \approx -0.6 - (-0.8) = 0.2eV\approx 4.6$ kcal/mol

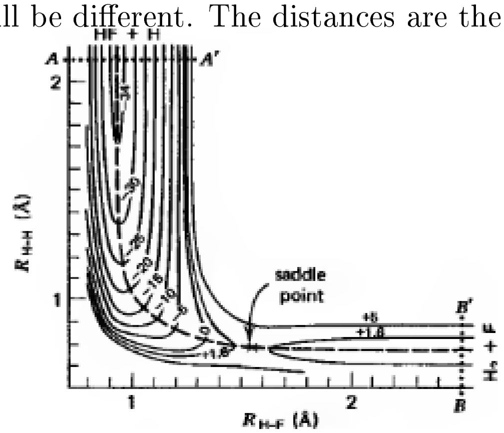
2. For a reaction A+B_2 $\rightarrow$AB+B, the following parameters are reported:

Dissociation energy, $D_{A-B} = 591.1$kJ/mol; $D_{B-B} = 458.2$kJ/mol;

equilibrium distance, $R_{A-B} = 0.917$Å ; $R_{B-B} = 0.742$Å

Using this data and activation energy= 300 kJ/mol, draw the contour diagram for the variation of potential energy with distances between atoms.

Ans. This is similar to the F+H_2 $\rightarrow$HF+H reaction with A as the F atom and B as the H atom. You may refer to the contour diagram as shown below except that the numbers for energy will be different. The distances are the same.



3. Derive expressions for $\frac{d(\ln k)}{d(\frac{1}{T})}$ for the rate constant from the Arrhenius equation and from collision theory and compare the two. Comment on the difference.

Ans. Arrhenius equation : $k = A.e^{-\frac{E_a}{RT}}$

$\implies \ln k = \ln A - \frac{E_a}{RT}$

$\therefore \frac{d(\ln k)}{d(\frac{1}{T})} = -\frac{E_a}{R}$ (assuming A to be a constant w.r.t. temperature)

collision theory : $k = \text{const.}\sqrt{T}.e^{-\frac{E_a}{RT}}$

$\implies \ln k = const + \frac{1}{2}\ln T - \frac{E_a}{RT}$

$\therefore \frac{d(\ln k)}{d\left(\frac{1}{T}\right)} = -\frac{1}{2}T - \frac{E_a}{R}$

The difference is due to the fact that in Arrhenius equation, T dependence of the pre-exponential factor is not explicitly stated.

4. Rutherford scattering experiment : For the case of classical scattering of two particles with a repulsive Coulomb potential, $V(r) = \frac{B}{r}$,

scattering angle, $\chi(E, b) = 2\csc^{-1}\left[1 + \left(\frac{2bE}{B}\right)^2\right]^{\frac{1}{2}}$.

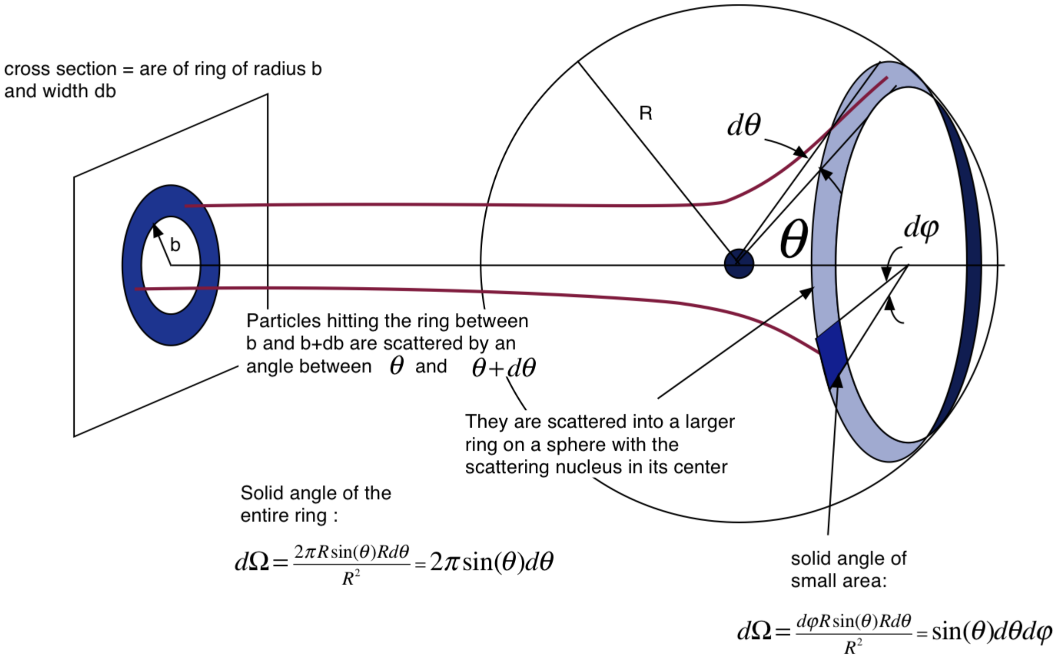
Show that the differential scattering cross-section,

$\frac{d\sigma}{d\Omega}(E, \chi) = \left(\frac{B}{4E}\right)^2 \csc^4\left(\frac{\chi}{2}\right)$

Ans. Let us say, we have a trajectory with impact parameter $b \to b + db$ that scatters into the solid angle $\Omega \to \Omega + d\Omega$ with differential cross-section $\frac{d\sigma}{d\Omega}$

Conservation of particle flux implies that the total number of particles passing through an annular ring of radius $b \to b + db$ must be equal to the total number of particles scattered with scattering angle $\chi \to \chi + d\chi$ in all azimuthal directions taken together. The number of such particles passing through a given area per unit time is the product of the flux density and the area element.

In the picture below, read θ as χ.



Assuming azimuthal symmetry (i.e., identical environment for all values of the angle ϕ : $(0,\, 2\pi)$
, we have,

flux$\times 2\pi b db =$ flux$\times 2\pi \frac{d\sigma}{d\Omega}.\sin\chi.d\chi$ (similar to writing $d\Omega = \sin\theta d\theta d\phi$; here ϕ is integrated out as 2π)

or, $\frac{d\sigma}{d\Omega} = \frac{b}{\sin\chi}\left|\frac{db}{d\chi}\right|$

for Rutherford scattering, cosec$\frac{\chi}{2} = [1+ab^2]^{\frac{1}{2}}$, where $a = \left(\frac{2E}{B}\right)^2$

or, $1+ab^2 = \csc^2\frac{\chi}{2}$

or, $2abdb = -2\text{csc}\frac{\chi}{2}.\frac{1}{2}\cot\frac{\chi}{2}.\csc\frac{\chi}{2}d\chi$

$\therefore \frac{d\sigma}{d\Omega} = \frac{b}{\sin\chi}\left|\frac{db}{d\chi}\right| = \frac{1}{2a\sin\chi}.\cot\frac{\chi}{2}.\csc^2\frac{\chi}{2} = \frac{1}{4a\sin\frac{\chi}{2}\cos\frac{\chi}{2}}.\frac{\cos\frac{\chi}{2}}{\sin\frac{\chi}{2}}.\csc^2\frac{\chi}{2} = \left(\frac{B}{4E}\right)^2\csc^4\frac{\chi}{2}$

Sometimes differential scattering cross-section is written as σ. Be careful, when you are looking at a text book.