Chapter 8 Summary
Reactions As Collisions

Recall from before that according to collision theory:

$$r_{A-BC} = Z_{ABC} P_{\text{reaction}}$$

(Equation 7.10)

Today advanced collision theory:

Method

- simulate the collisions
- Integrate using statistical mechanics

$$r_{A\to BC} = \iiint\iiint r_{A\to BC}(v_{A\to BC}, E_{BC}, \phi, b_{A\to BC}, \mathbb{R}, v_{BC}) \times D(v_{A\to BC} E_{BC}, \phi, b_{A\to BC}, \mathbb{R}_{BC}, v_{BC})\, dv_{A\to BC}\, dE_{BC}\, d\phi\, db_{A\to BC}\, d\mathbb{R}_{BC}\, dv_{BC}$$

(Equation 8.20)

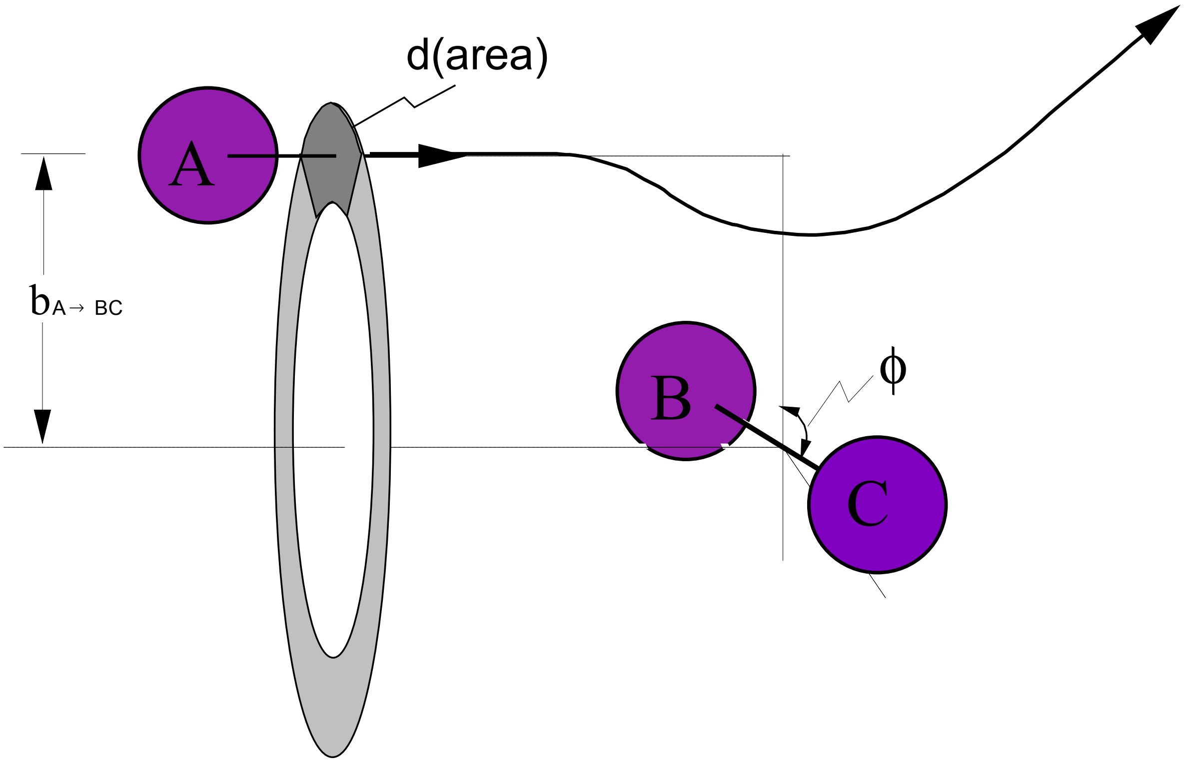

Figure 8.2 A typical trajectory for the collision of an A atom with a BC molecule as calculated by the methods in section 8.3.2.

$$dr_{A\rightarrow BC}=C_{A}C_{BC}V_{A\rightarrow BC}P_{reaction}\,d(area)$$

(Equation 8.23)

$$r_{A\rightarrow BC} = C_{A}C_{BC}\iiint\iiint P_{reaction}(v_{A\rightarrow BC}, E_{BC}, b_{A\rightarrow BC}, \phi, \mathbb{R}_{BC}, v_{BC})v_{A\rightarrow BC} \times D(v_{A\rightarrow BC}, E_{BC}, \mathbb{R}_{BC}, v_{BC})dv_{A\rightarrow BC}dE_{BC}(b_{A\rightarrow BC}db_{A\rightarrow BC})d\phi\, d\mathbb{R}_{BC}dv_{BC}$$

(Equation 8.24)

$$k_2 = \iiint\iiint P_{reaction}(v_{A\to BC}, E_{BC}, b_{A\to BC}, \phi, \mathbb{R}_{BC}, v_{BC})\, v_{A\to BC} \times$$
$$D(v_{A\to BC}, E_{BC}, \mathbb{R}_{BC}, v_{BC})\, dv_{A\to BC}\, dE_{BC}\, (b_{A\to BC}\, db_{A\to BC}\, d\phi)\, d\mathbb{R}_{BC}, dv_{BC}$$

(Equation 8.25)

If we can calculate reaction probabilities can calculate rates

Molecular dynamics as a way of calculating reaction probabilities

Idea:

- Treat atoms as billiard balls moving in the force field created by all of the other atoms
- Assume molecules start moving toward each other.
- Solve Newton's equation of motion (F=ma) to calculate the motion of the atoms during the collision

See if reaction occurs

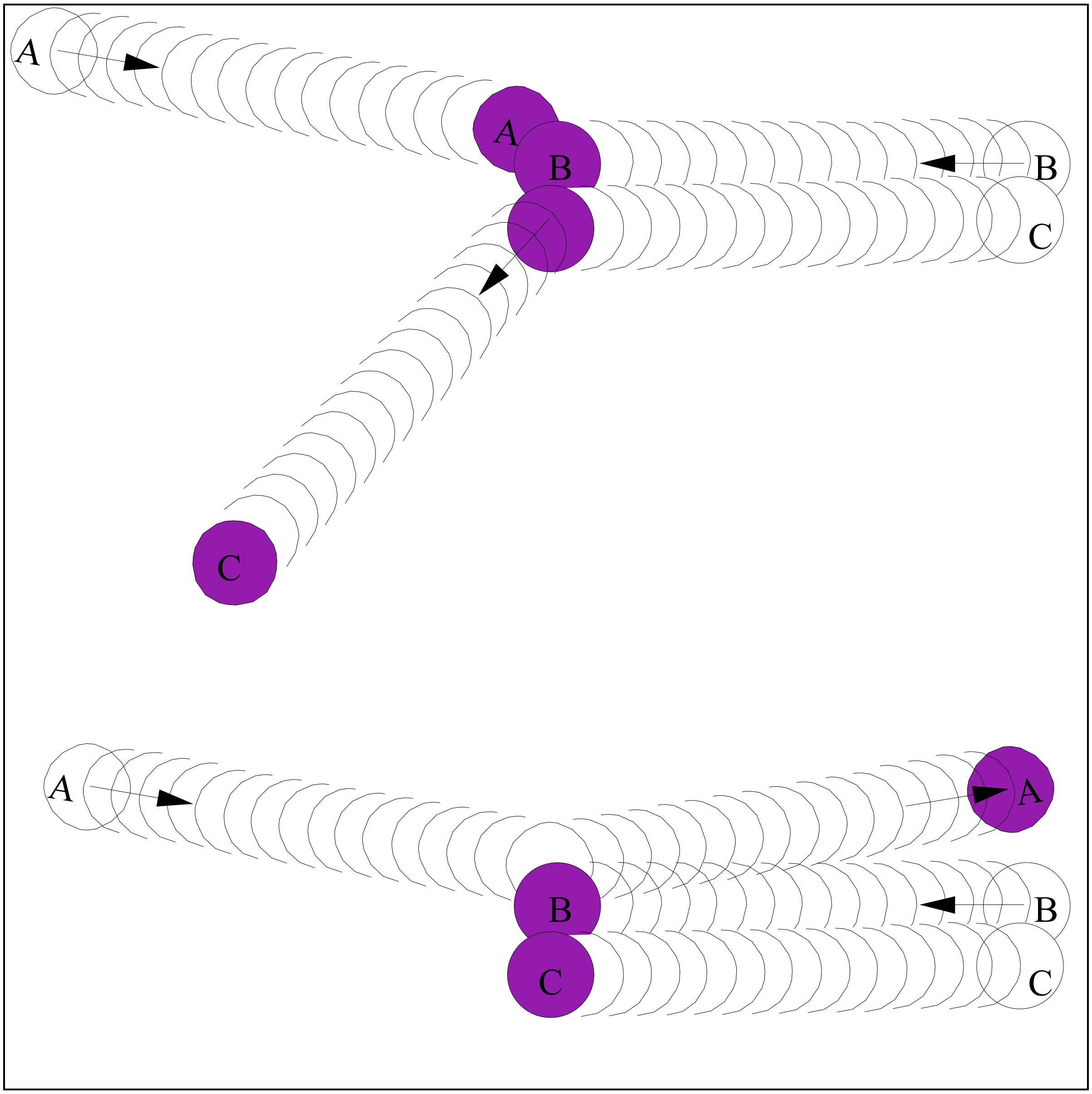

Figure 8.1 A typical collision between A and BC.

Do simulation

Next set up the background to do the simulation

What do we need to do the simulations?

- Need to know intermolecular forces
- Need to have a way to integrate equation of motion (already have one from chapter 4)

Intermolecular forces

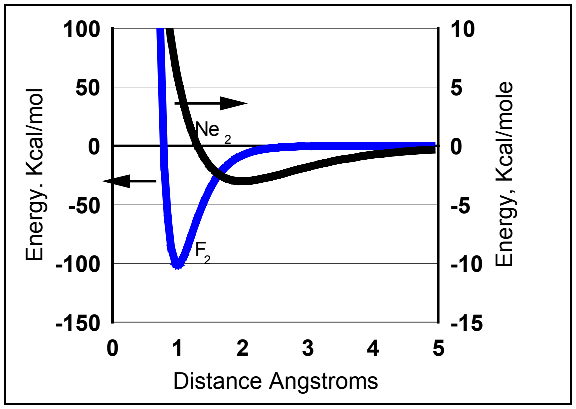

Figure 8.3 A neon-neon and a fluorine-fluorine potential.

$$F_{Ne} = -\frac{\partial V}{\partial \mathbb{R}_{NeNe}}$$

(Equation 8.34)

Where do these plots come from

Types of intermolecular forces:

- Dispersion Forces
- Forces due to Electron Exchange and Bonding
- Pauli Repulsions
- Nuclear Repulsions

Dispersion forces

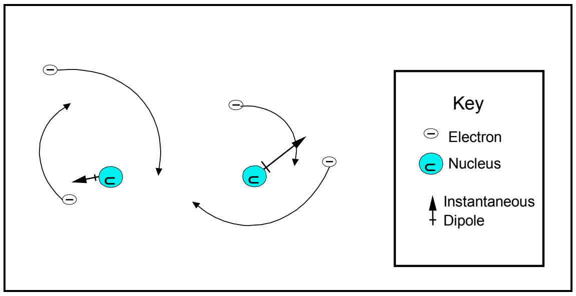

Figure 8.4 The interaction between two neon atoms.

Pauli repulsions:

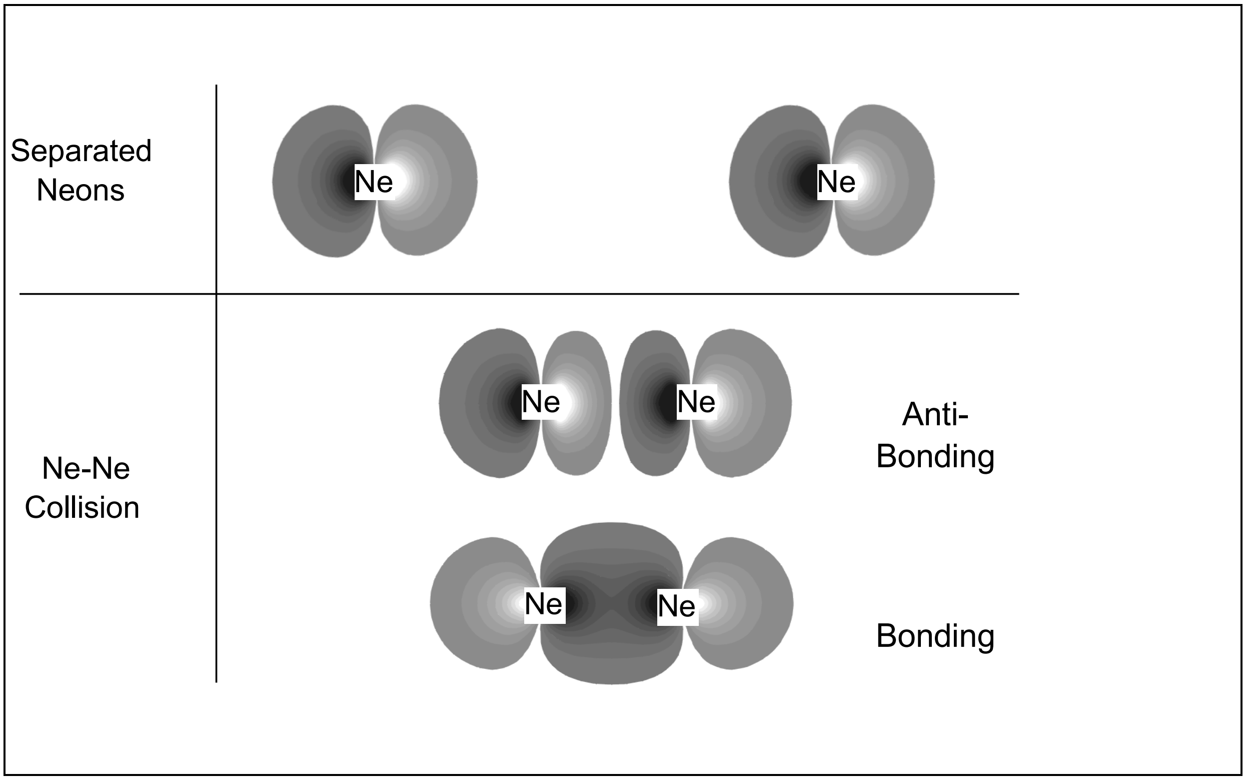

Figure 8.5 The changes in the homo of Ne_2 as the neon atoms move together.

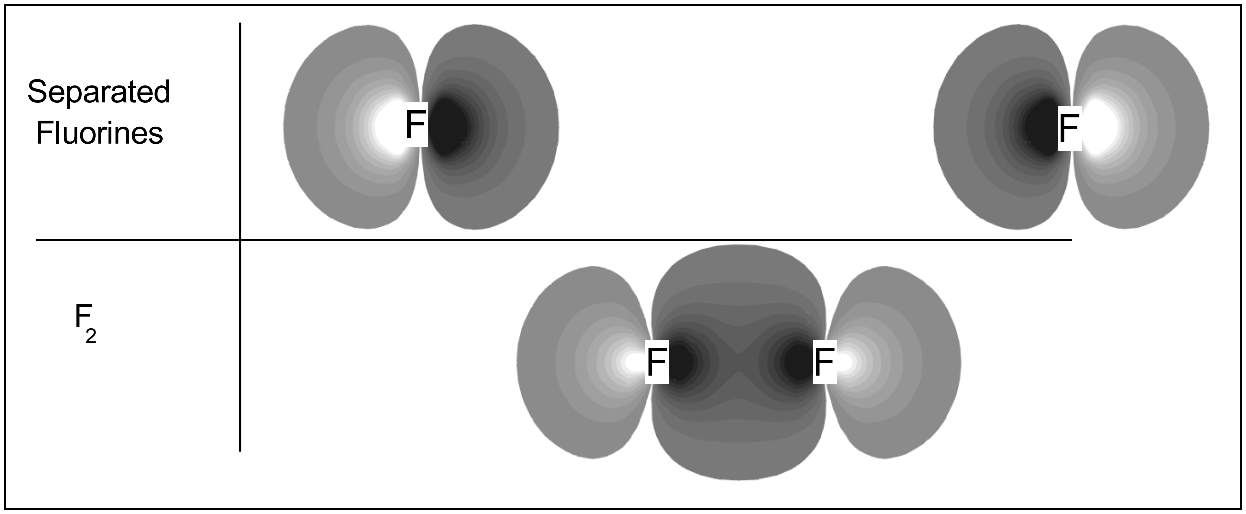

Figure 8.6 The changes in the highest occupied molecular orbital when two fluorines come together.

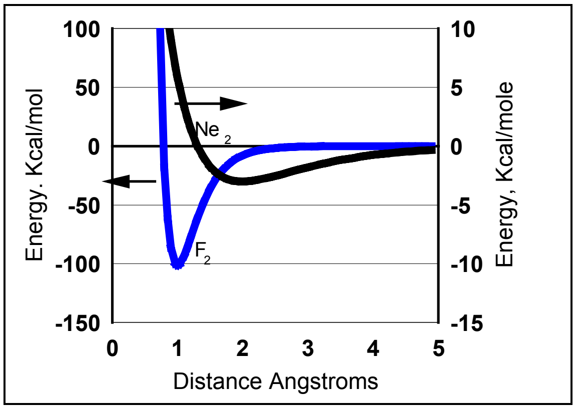

Figure 8.3 A neon-neon and a fluorine-fluorine potential.

Reactive potentials

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

(Equation 8.37)

$$Cl + {}^{18}F - {}^{19}F \rightarrow Cl^{18}F + {}^{19}F$$

(Equation 8.39)

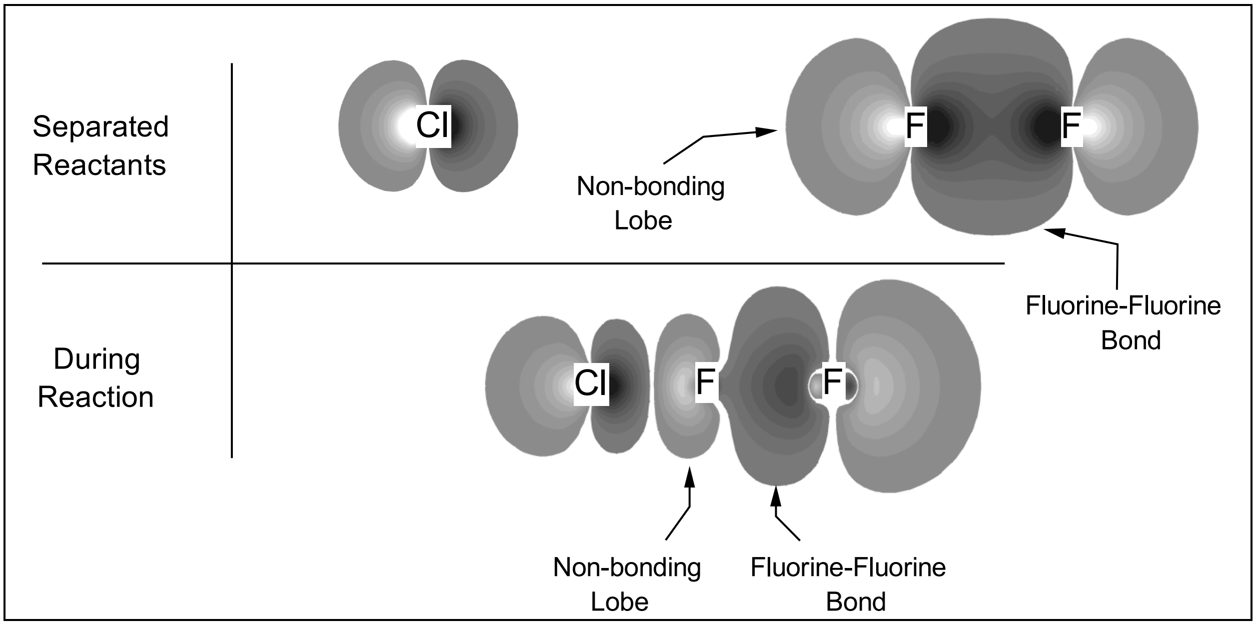

Figure 8.7 The changes in the $3A_{1g}$ orbital when a chlorine approaches a F_2.

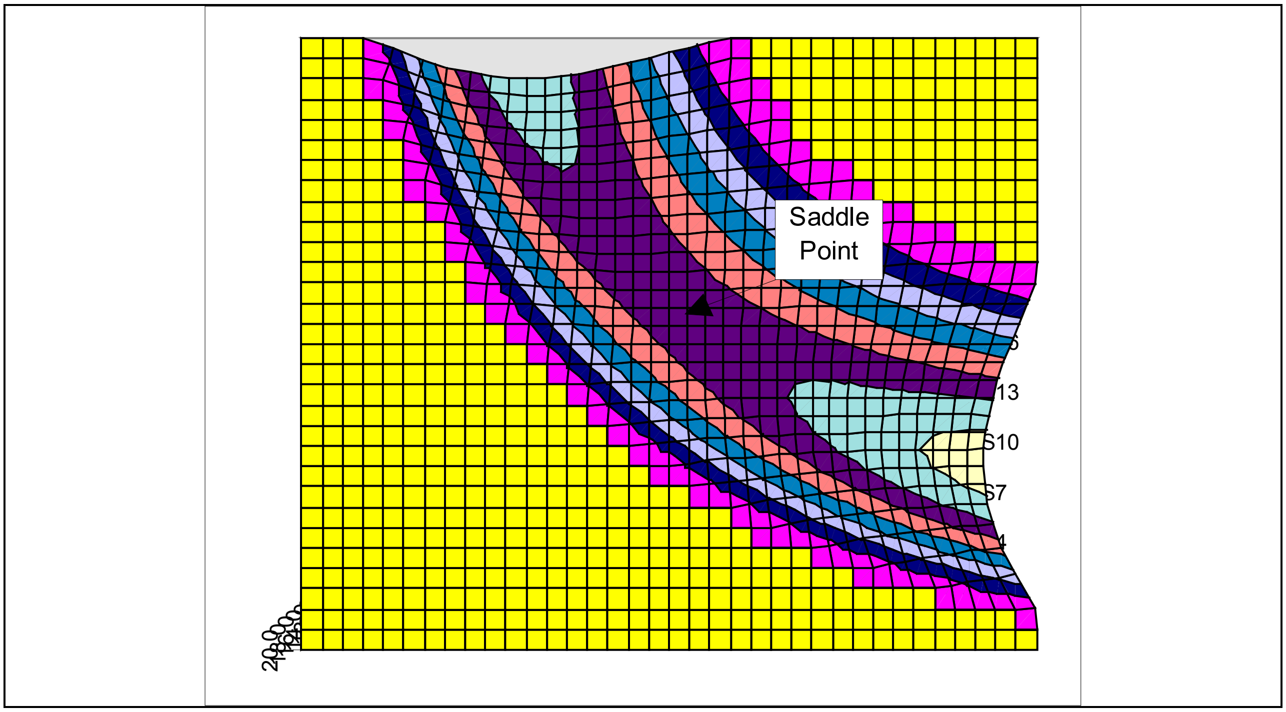

Figure 7.G.2 A side view of the potential in figure 7.G.1. Elevation=0, rotation= 90 perspective=30, chart depth=100

(Figure 7.G.2 replaced - Figure 8.9 A potential energy surface for reaction)

Ways to visualize motion

- as a trajectory in space where all the atoms move
- as a trajectory on the potential energy surface in Figure 8.9 where the bond lengths evolve
- as a plot of the motion of the atoms versus time

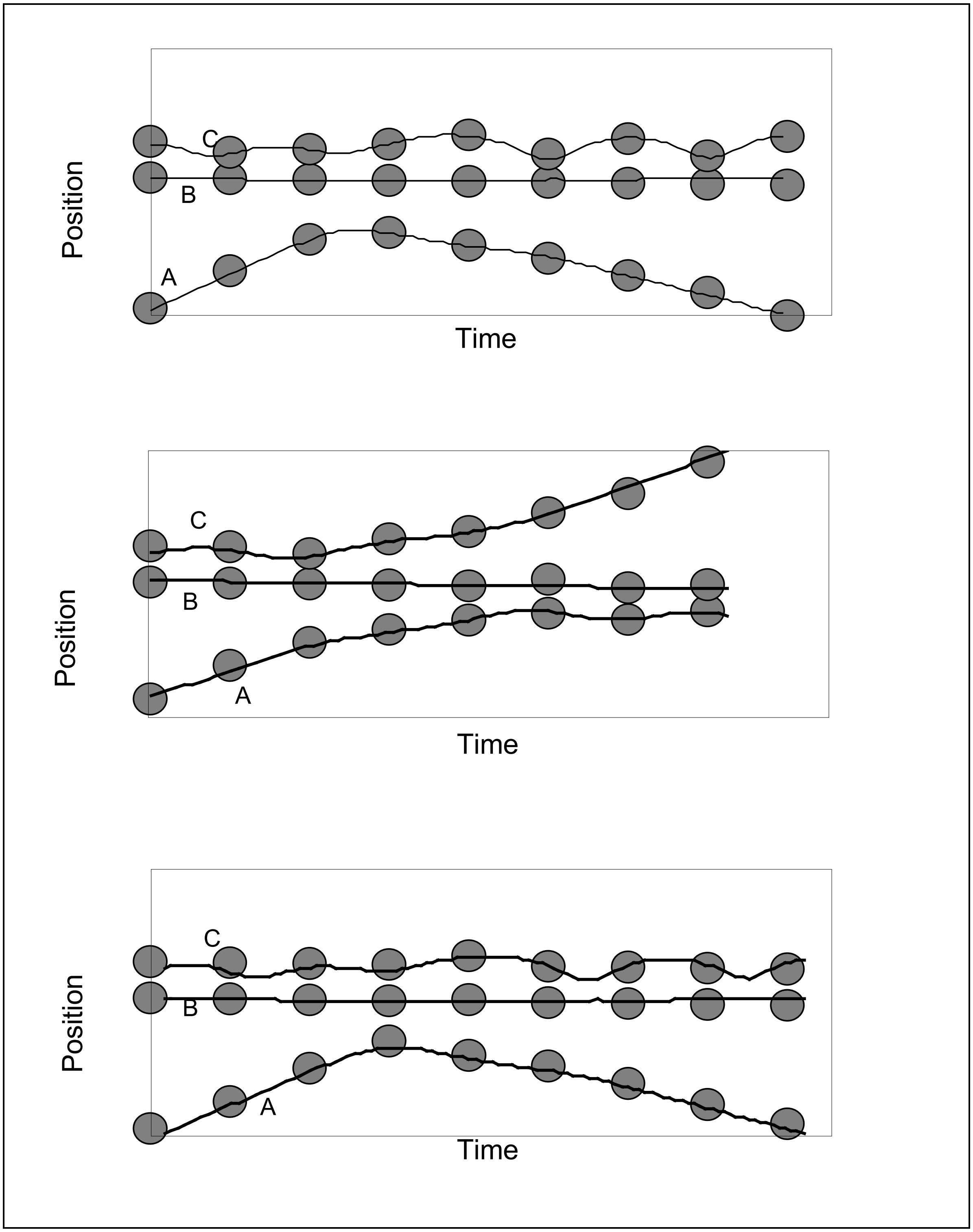

Figure 8.10 A series of trajectories during the reaction A+BC→AB+C, with $M_A = M_C = 1$, $M_B = 19$, and various initial reactant configurations.

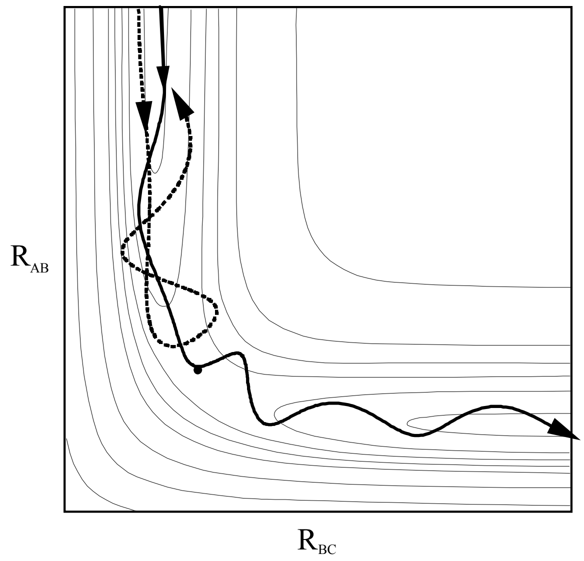

Figure 8.11 A series of typical trajectories for motion over a potential energy contour.

Consider exchange reactions

$$\mathrm{A + BC \rightarrow AB + C}$$

(8.45)

$$\mathrm{D\bullet + CH_3CH_3 \rightarrow DH + \bullet CH_2CH_3}$$

(8.46)

$$\mathrm{F\bullet + CH_3Cl \rightarrow FCH_3 + Cl\bullet}$$

(8.47)

$$\mathrm{HO\bullet + CH_3CH_2CH_3 \rightarrow HOCH_3 + \bullet CH_2CH_3}$$

(8.48)

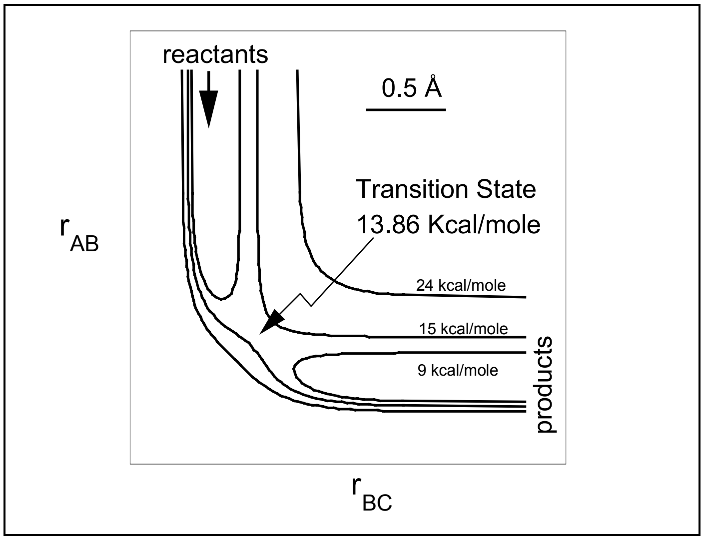

Figure 8.12 An idealized potential energy surface for the reaction A + BC → AB + C.

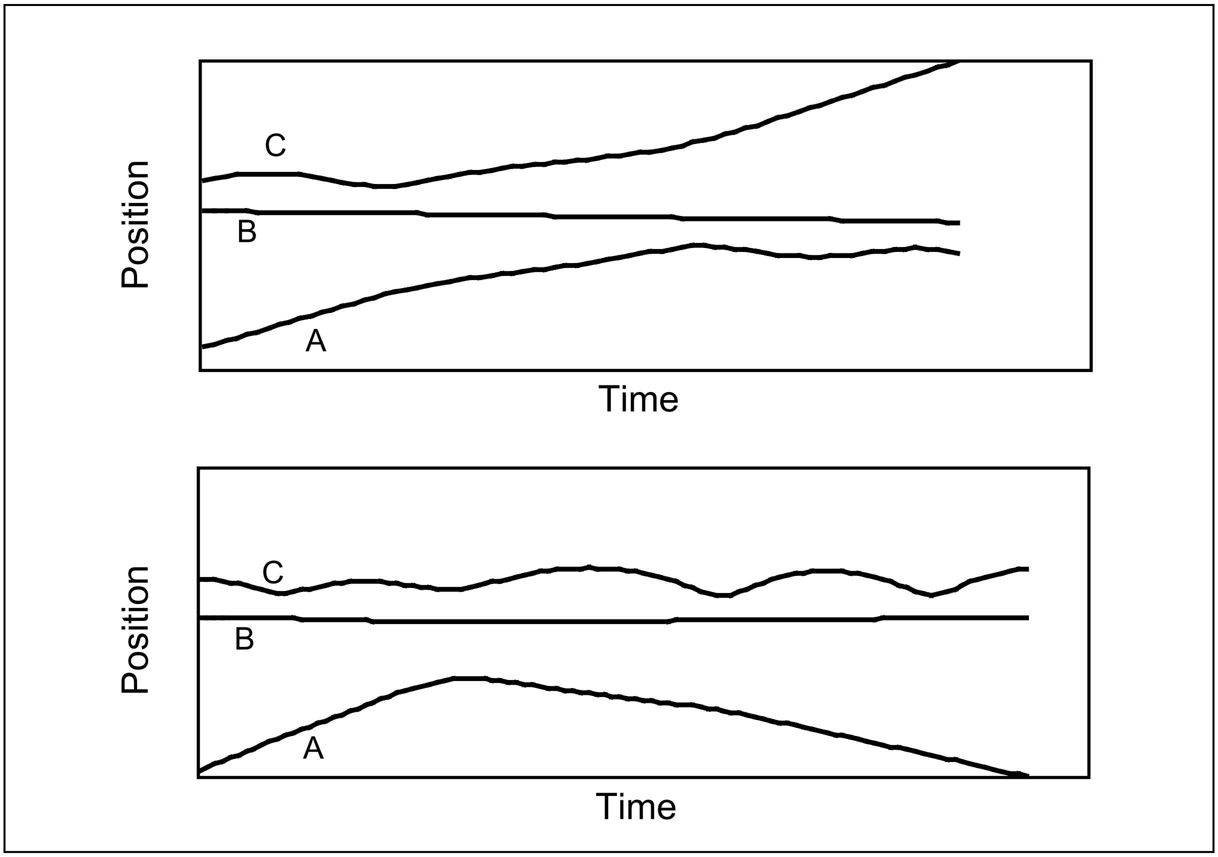

Figure.1 Two typical trajectories A series of trajectories for the reaction A + BC ⇒AB + C, with M_A=M_C=1, M_C=19, E_{total}=18kcal/mole (E_{trans}=14kcal/mole, E_{tot}=0kcal/mole, E_{vib}=4kcal/mole. Reaction occurs in the top trajectory but not in the bottom trajectory.

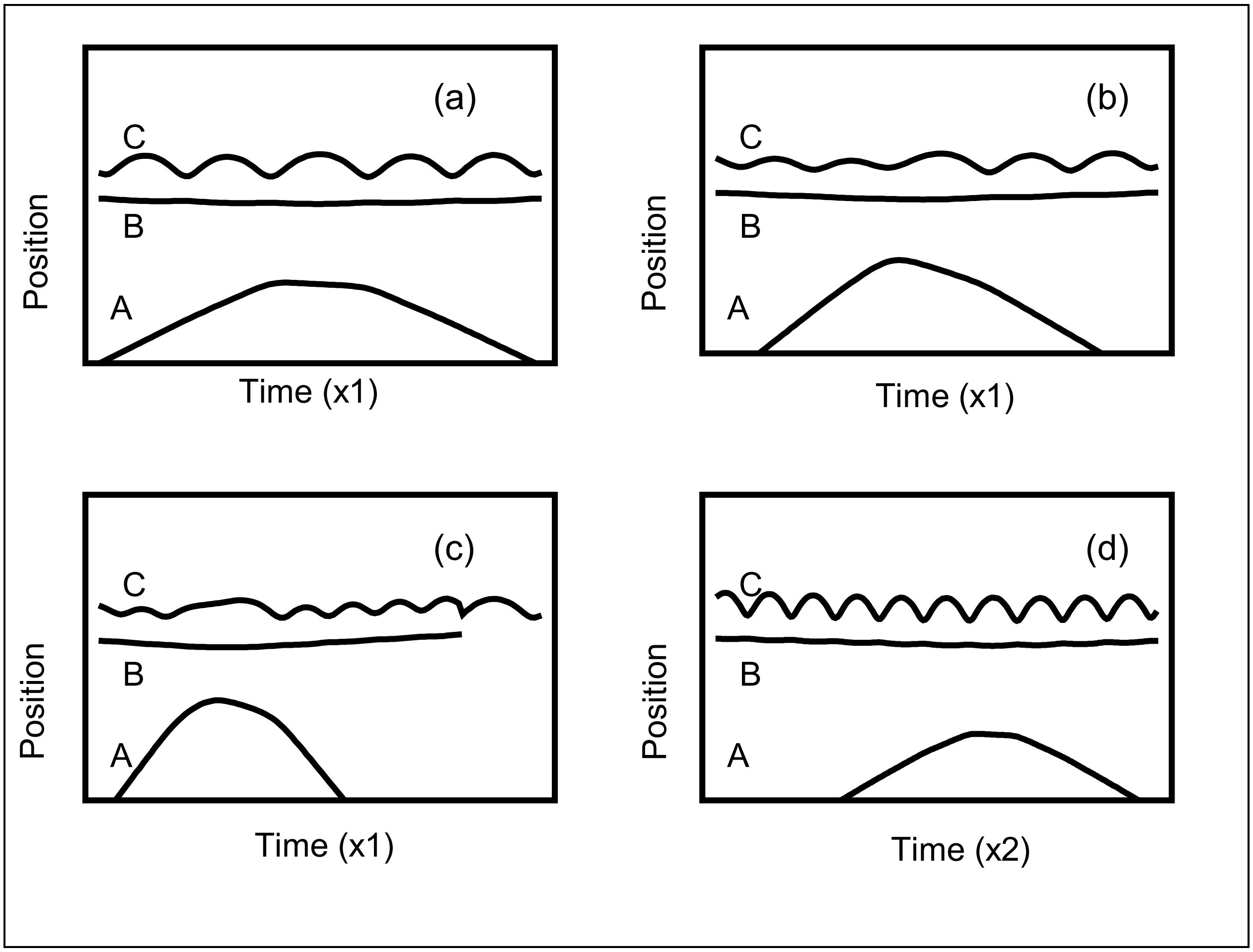

Figure 8.14 A sampling of the trajectories taken by putting a total of 13.8 kcal/mole into the reactants, choosing random initial positions for the atoms, putting a random amount of rotational energy into the BC bond. Choosing the initial velocity at A toward BC so that the total energy was 13.8 kcal/mole and then integrating the equations of motion to see whether reaction occurs. In this example, the barrier is 13.88 kcal/mole so no reaction occurs.

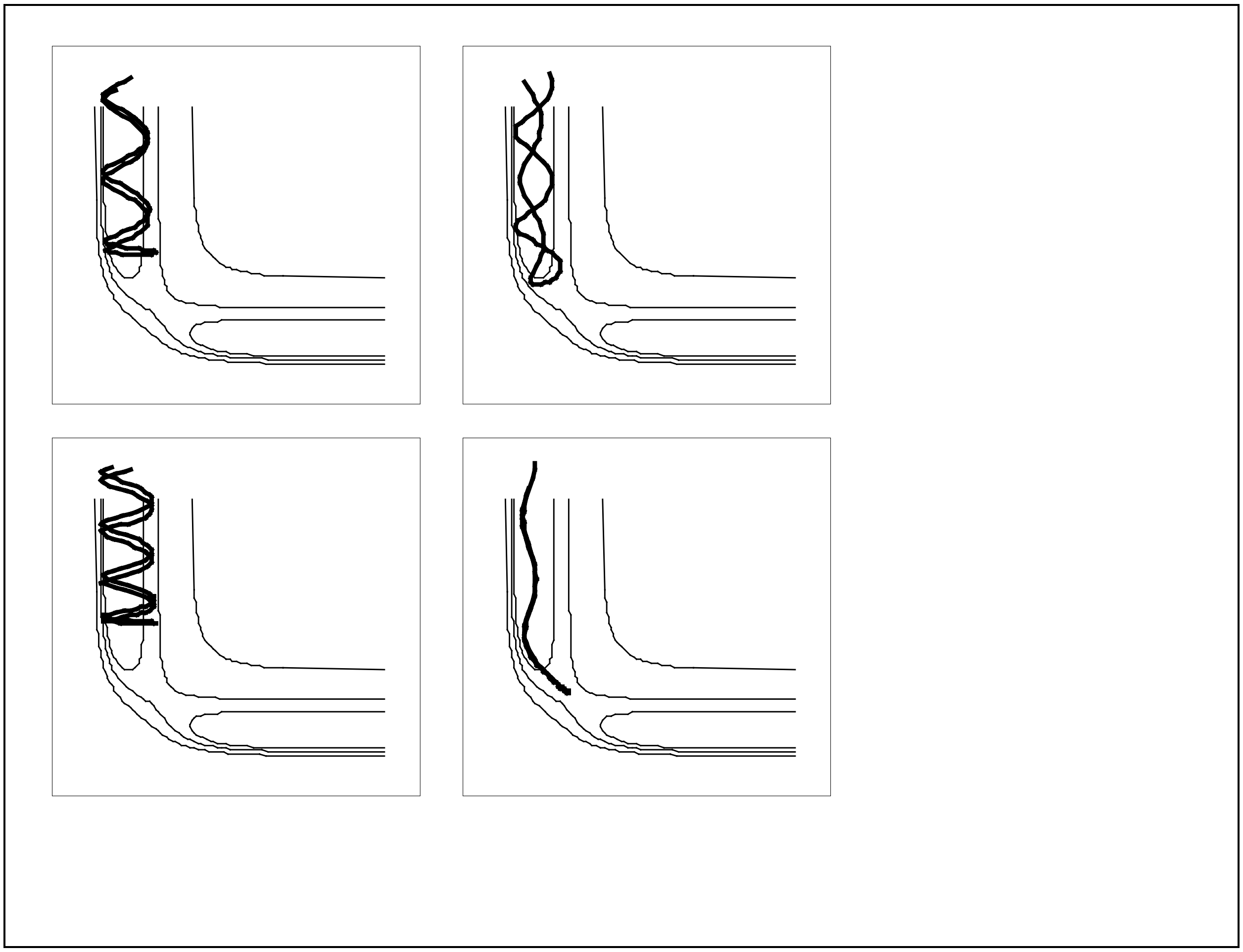

Figure 8.15 A replot of the data from Figure 8.14 on a potential energy surface.

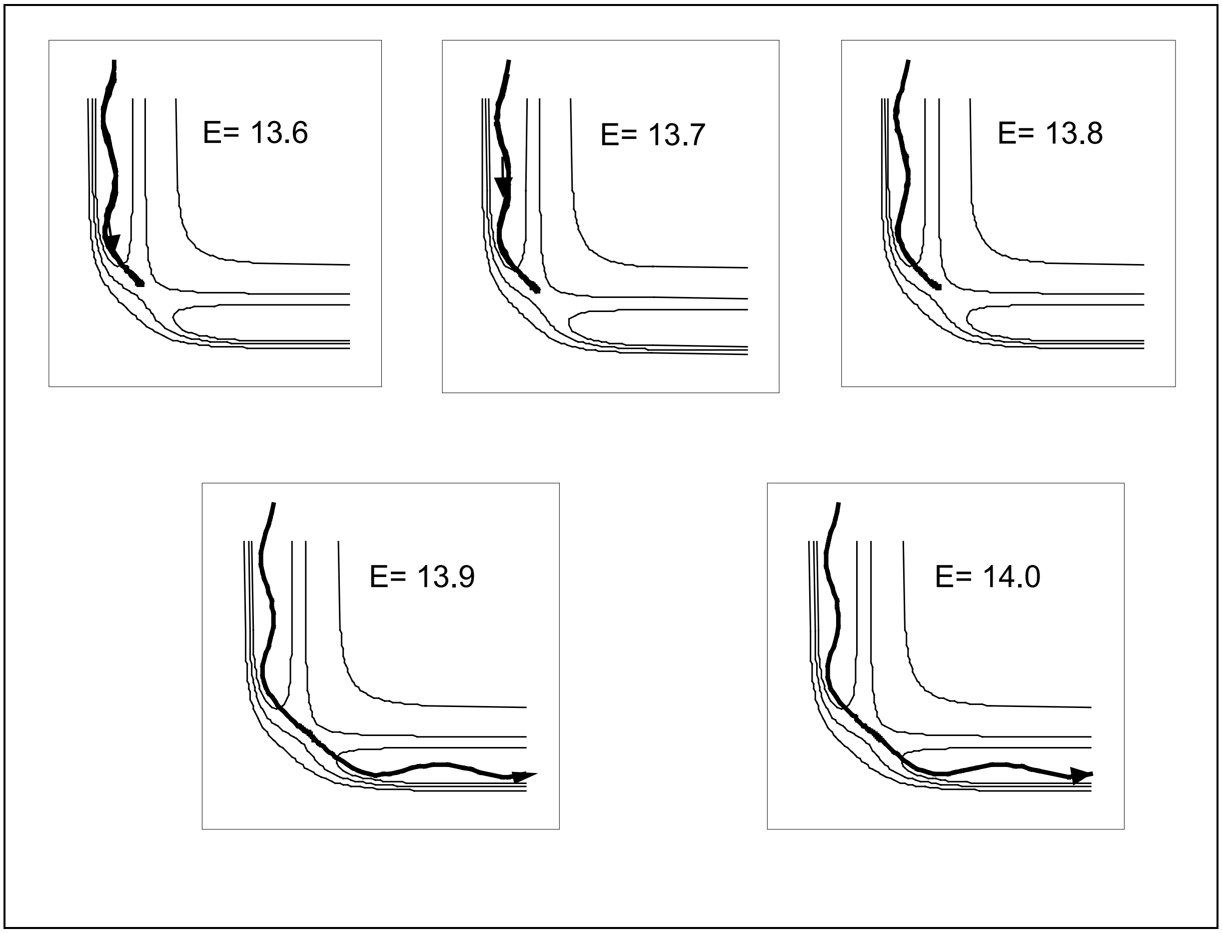

Figure 8.16 A series of trajectories calculated by fixing the total energy of the reactants and then optimizing all of the other parameters. The barrier is 13.88 kcal/mole for this example.

If the system has enough energy to make it over the saddle point, reaction can occur!

Not every collision makes it though.

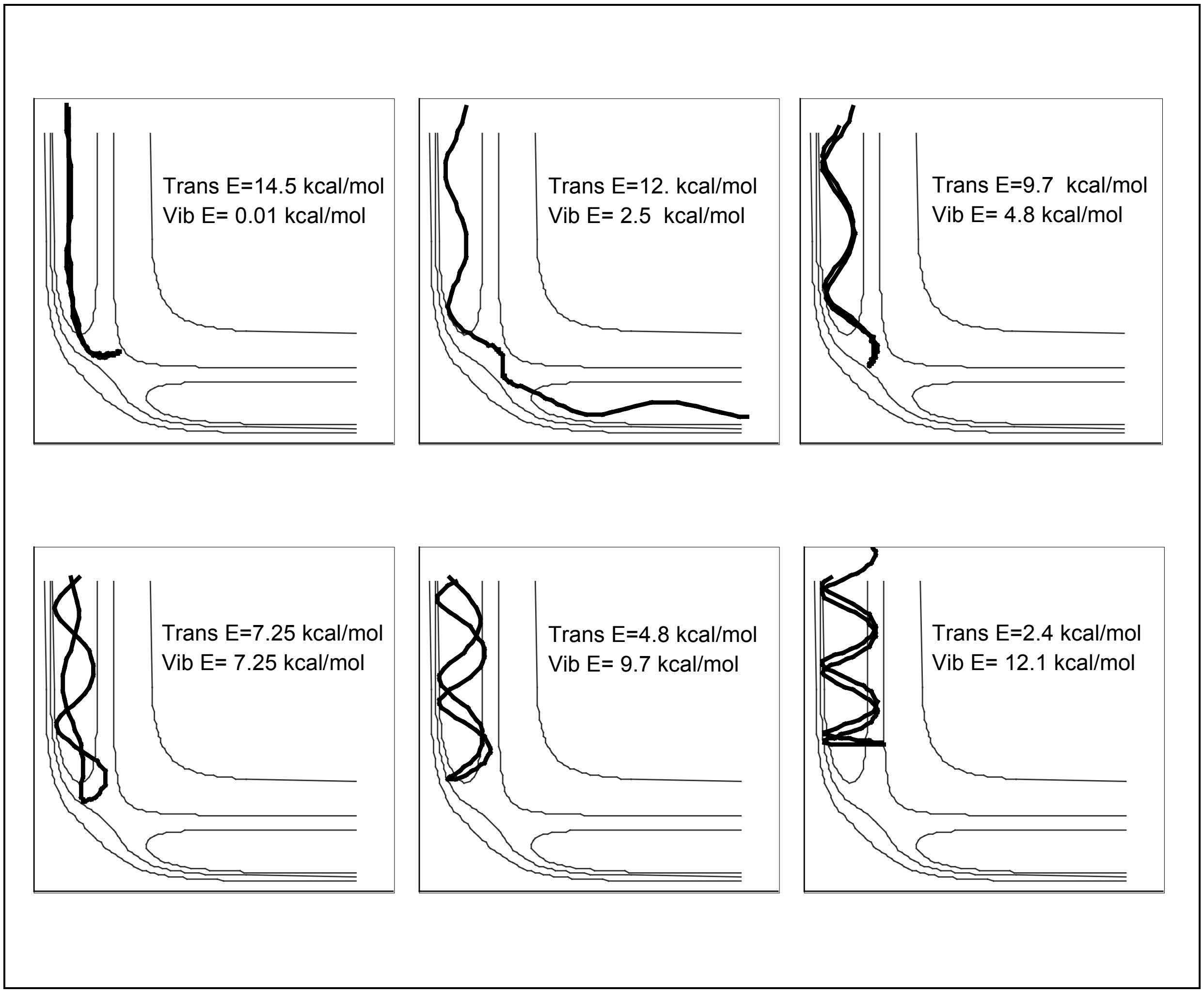

Figure 8.21 A series of cases where the molecules have enough energy to get over the barrier. Notice that some of the molecules do not make it, because the partitioning the energy between translation and rotation is incorrect.

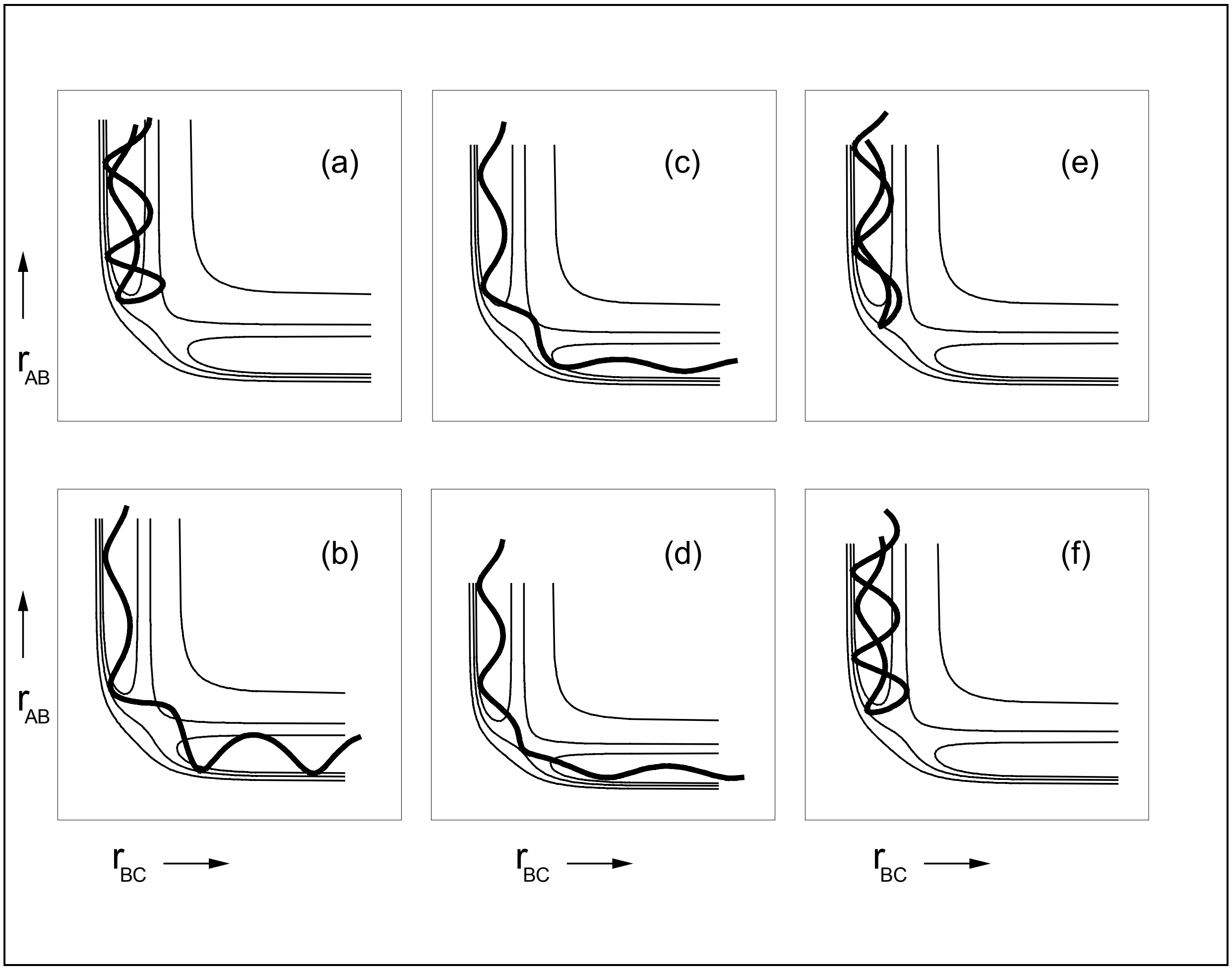

Figure 8.20 A replot of the results in Figure 8.19 on a potential energy surface.

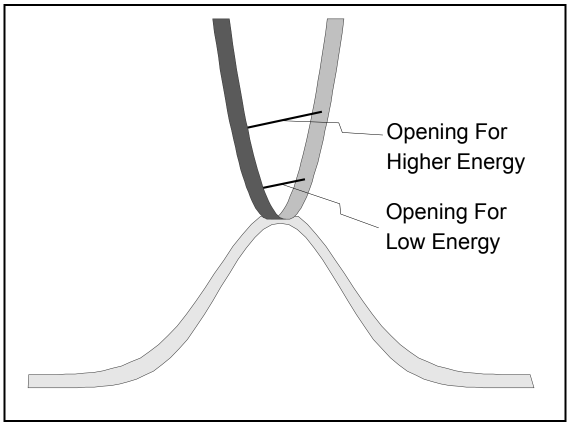

Figure 8.17 A blow up of the top of the barrier.

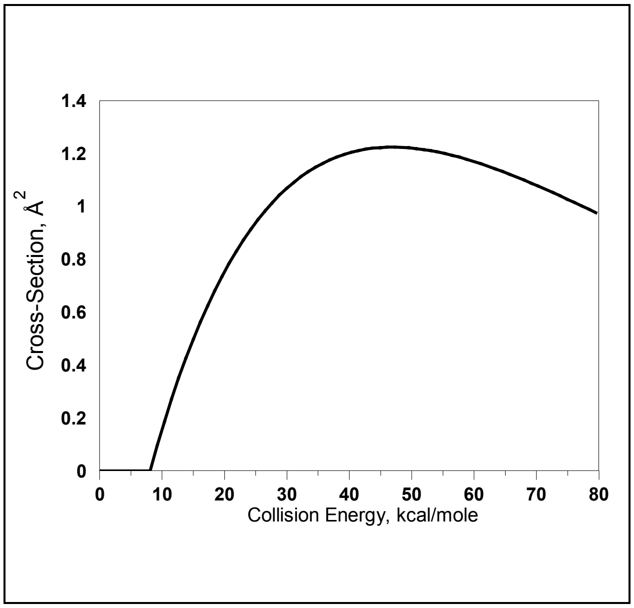

Figure 8.18 The cross section for reaction $H+H_2 \rightarrow H_2+H$. Adapted from Tsukiyariu et. al. [1986] and Levine and Bernstein[1987].

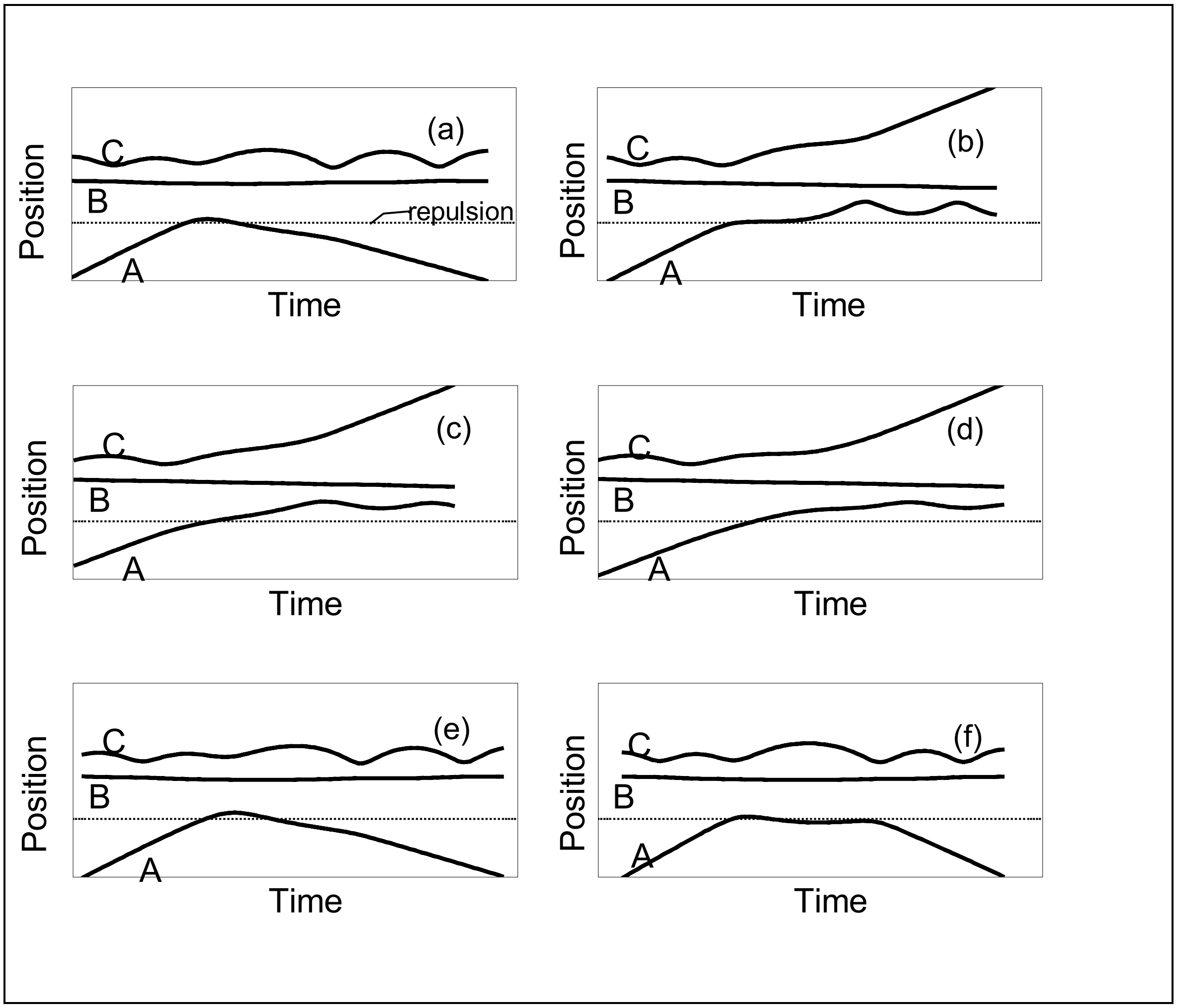

Figure 8.19 A series of cases calculated by fixing free energy at 18 kcal/mole, fixing the vibrational energy at 6 kcal/mole and varying whether A hits when C is vibrating in toward B or out away from B.

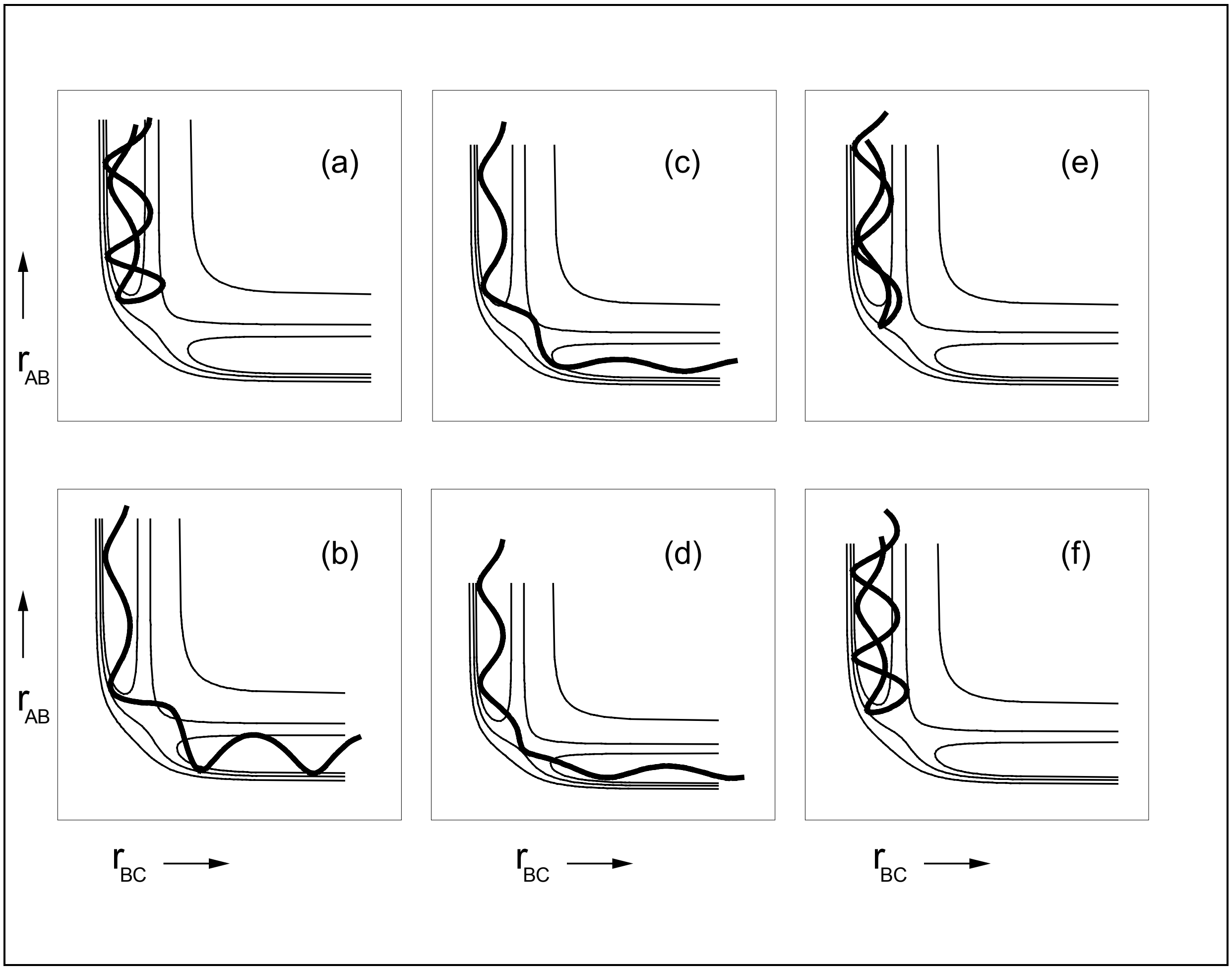

Figure 8.20 A replot of the results in Figure 8.19 on a potential energy surface.

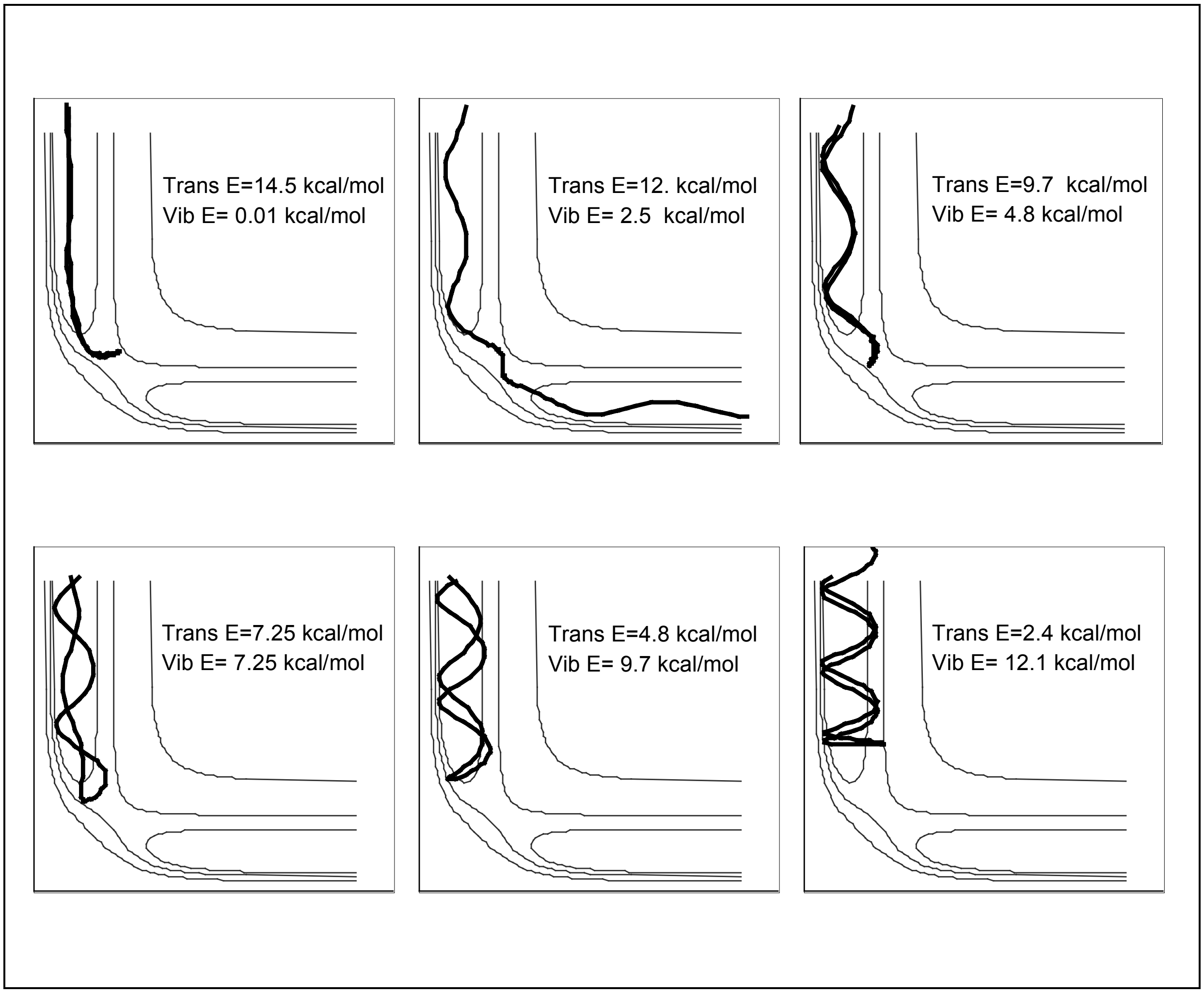

Figure 8.21 A series of cases where the molecules have enough energy to get over the barrier. Notice that some of the molecules do not make it, because the partitioning the energy between translation and rotation is incorrect.

What do we need to get reaction - linear case?

Need enough energy to get over the barrier

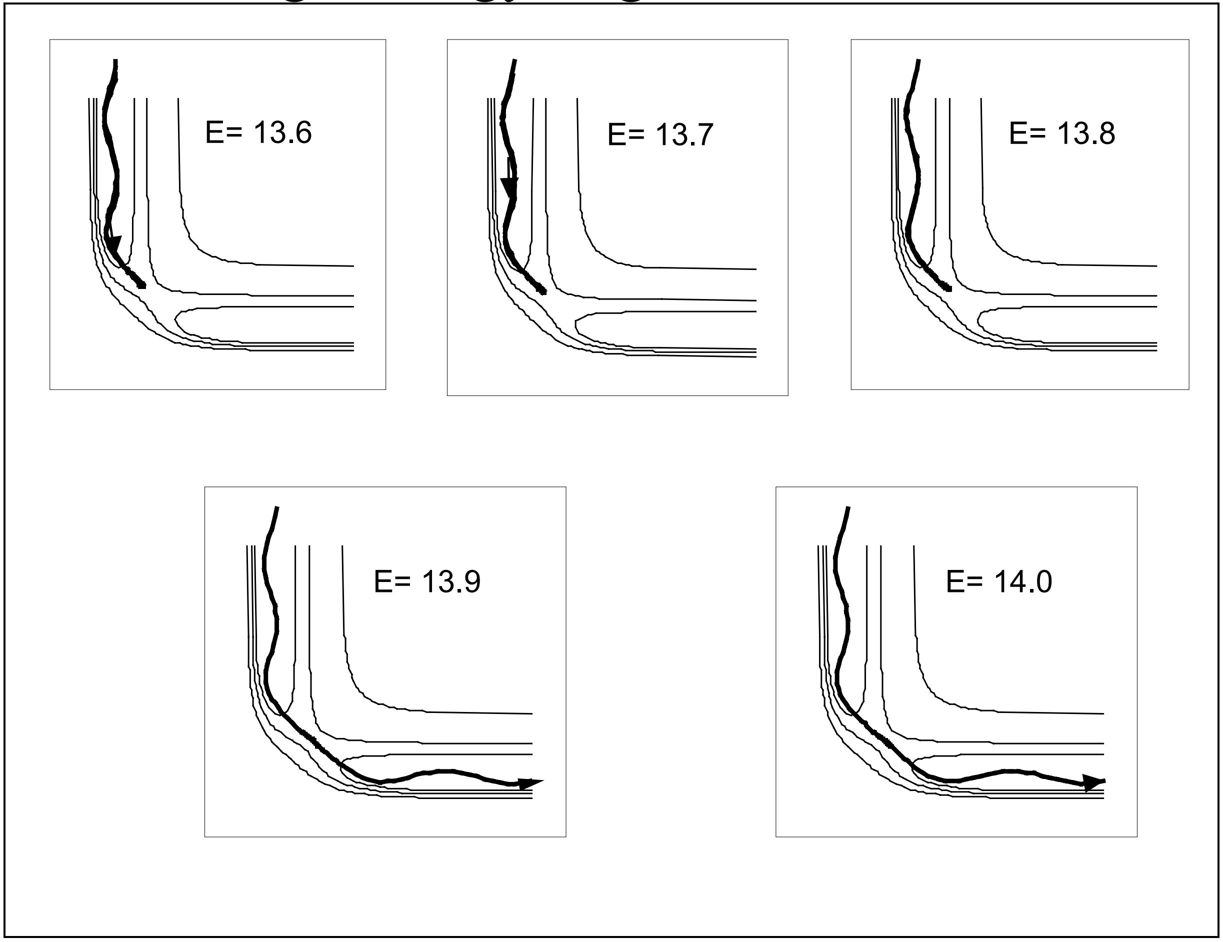

Figure 8.16 A series of trajectories calculated by fixing the total energy of the reactants and then optimizing all of the other parameters. The barrier is 13.88 kcal/mole for this example.

Not every collision makes it though.

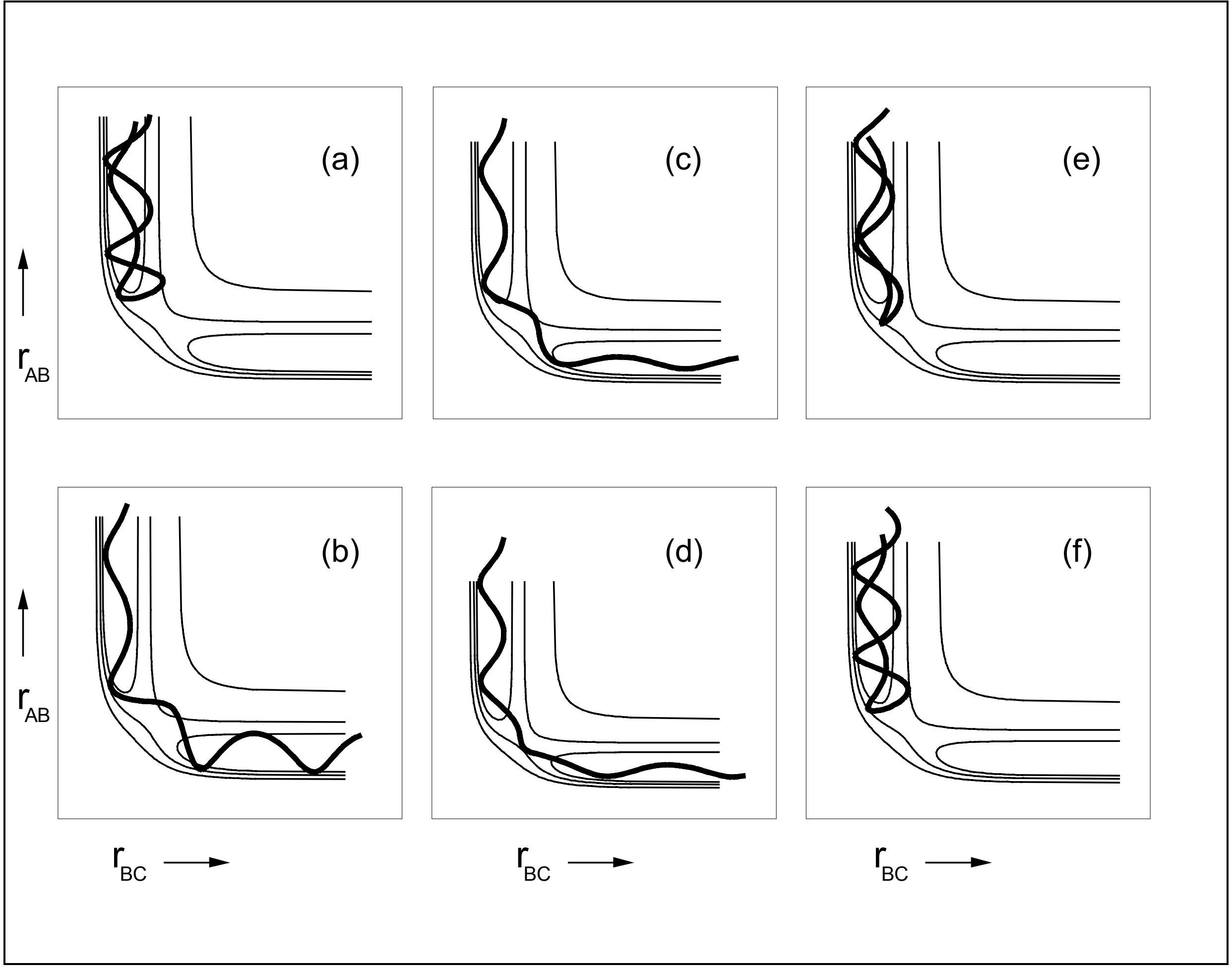

Figure 8.20 A replot of the results in Figure 8.19 on a potential energy surface.

Need sequential motion of the atoms:

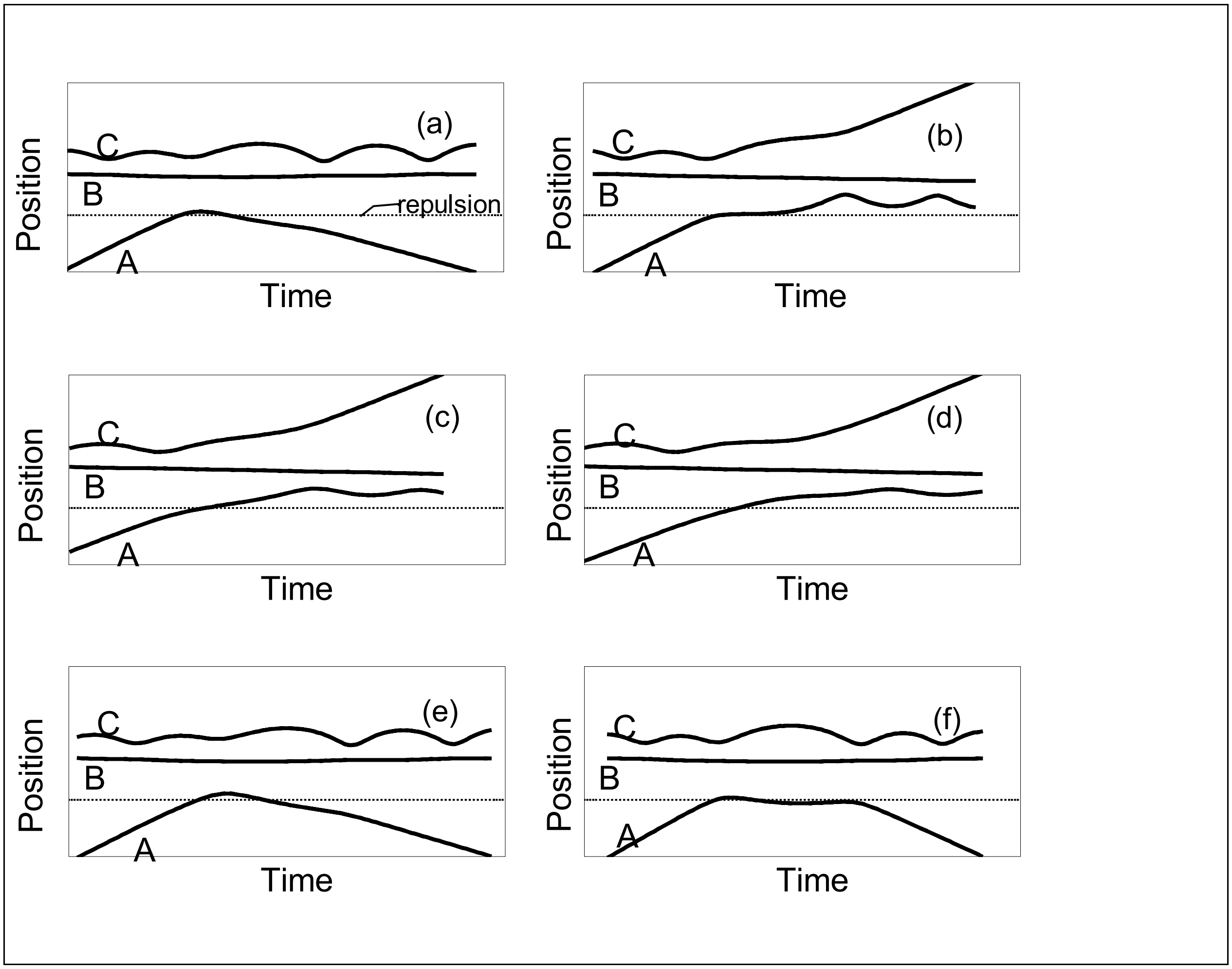

Figure 8.20 A series of cases calculated by fixing free energy at 18 kcal/mole, fixing the vibrational energy at 6 kcal/mole and varying whether A hits when C is vibrating in toward B or out away from B.

Turning analogy

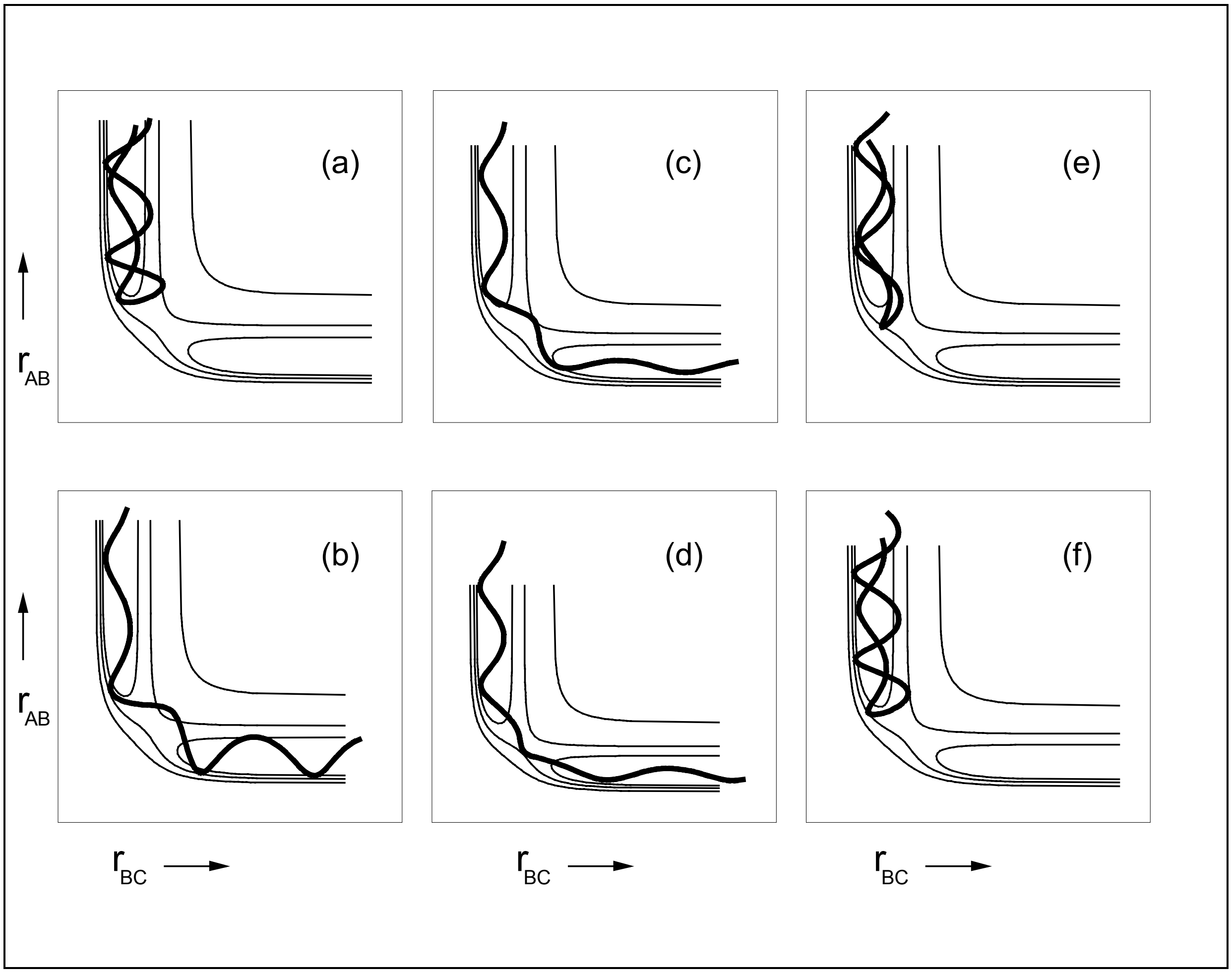

Figure 8.20 A replot of the results in Figure 8.19 on a potential energy surface.

Also need correct distribution between translation and vibration:

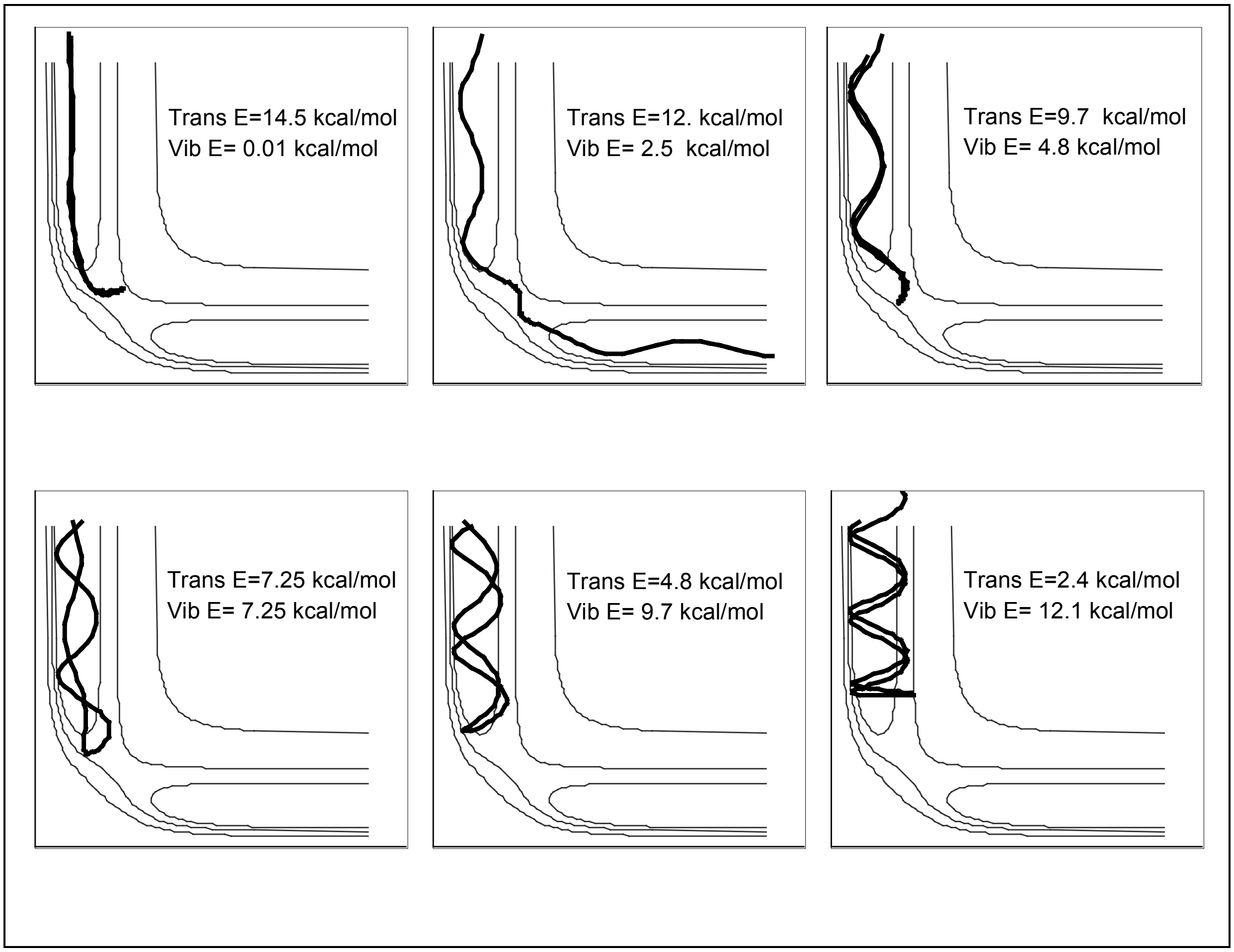

Figure 8.21 A series of cases where the molecules have enough energy to get over the barrier, but they do not make it, unless partitioning the energy between translation and rotation is correct.

Again turning analogy important

Polanyi rules:

Can use vibration/translation to probe structure of transition state:

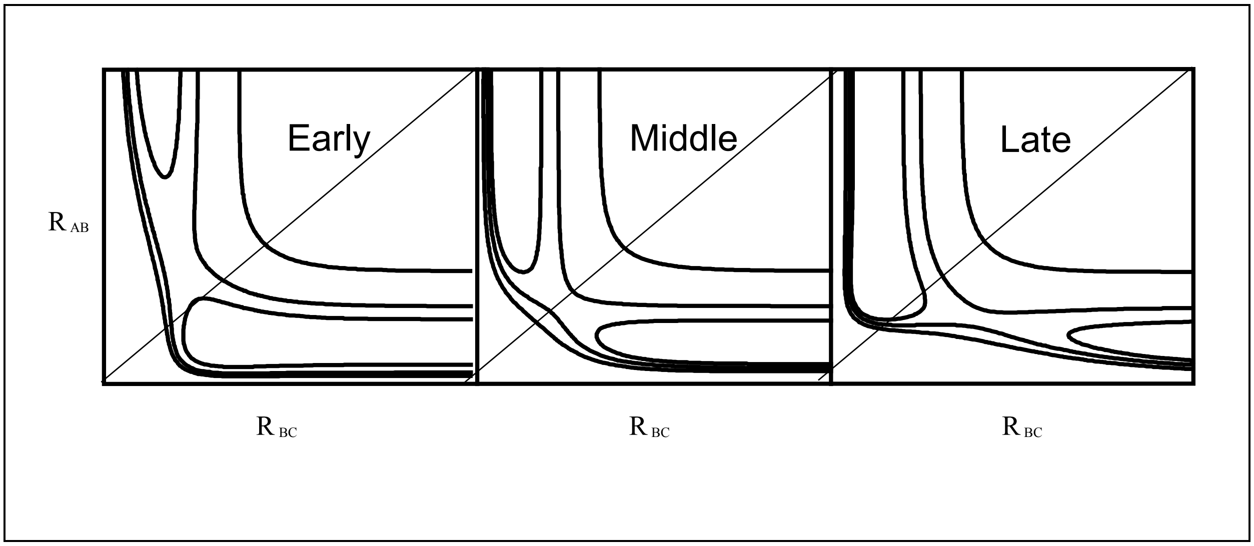

Figure 8.24 Potential energy surfaces with early, middle and late transition states.

Leads to excess energy in product:

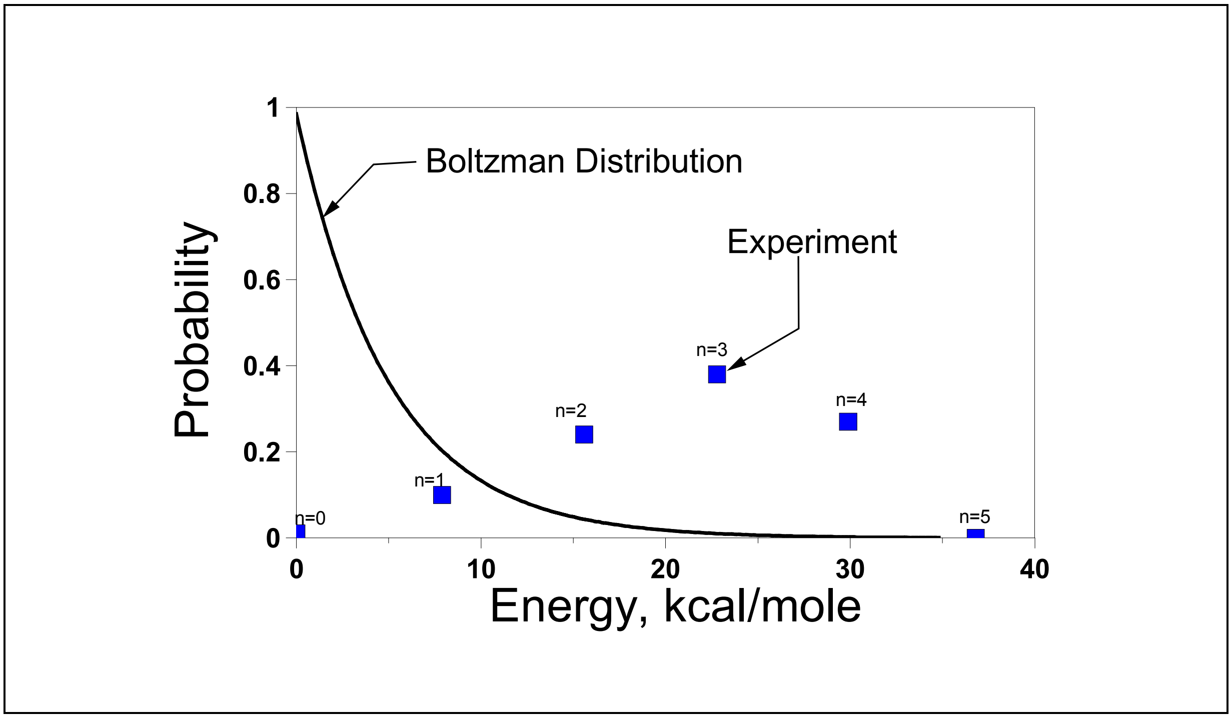

Figure 8.25 The distribution of vibrational energy produced during the reaction $F+H_2 \rightarrow HF+H$. Results of Polayni and Woodall [1972].

Summary of linear collisions

can treat the collision of two molecules as a collision between two classical particles following Newton’s equations of motion.

The reactants have to have enough total energy to get over the transition state (or Col) in the potential energy surface.

It is not good enough for the molecules to just have enough energy. Rather, the energy needs to be correctly distributed between vibration and transition.

Coordinated motions of the atoms are needed. In particular, it helps to have C moving away from B when A collides with BC.

We also find that we need to localize energy and momentum into the B-C bond for reaction to happen.

The detailed shape of the potential energy surface has a large influence on the rate.

These effects mean that the system has very complex behavior. Note, however, that the latter four effects only cause perhaps a factor of 10 or 100 in rate. There are always some trajectories which make it over the barrier, even though the molecules have barely enough energy to cross the barrier. If 1% of the trajectories make it those trajectories will have an important effect on the rate.

Next: Non- linear case:
Different because reaction probability varies with the impact parameter

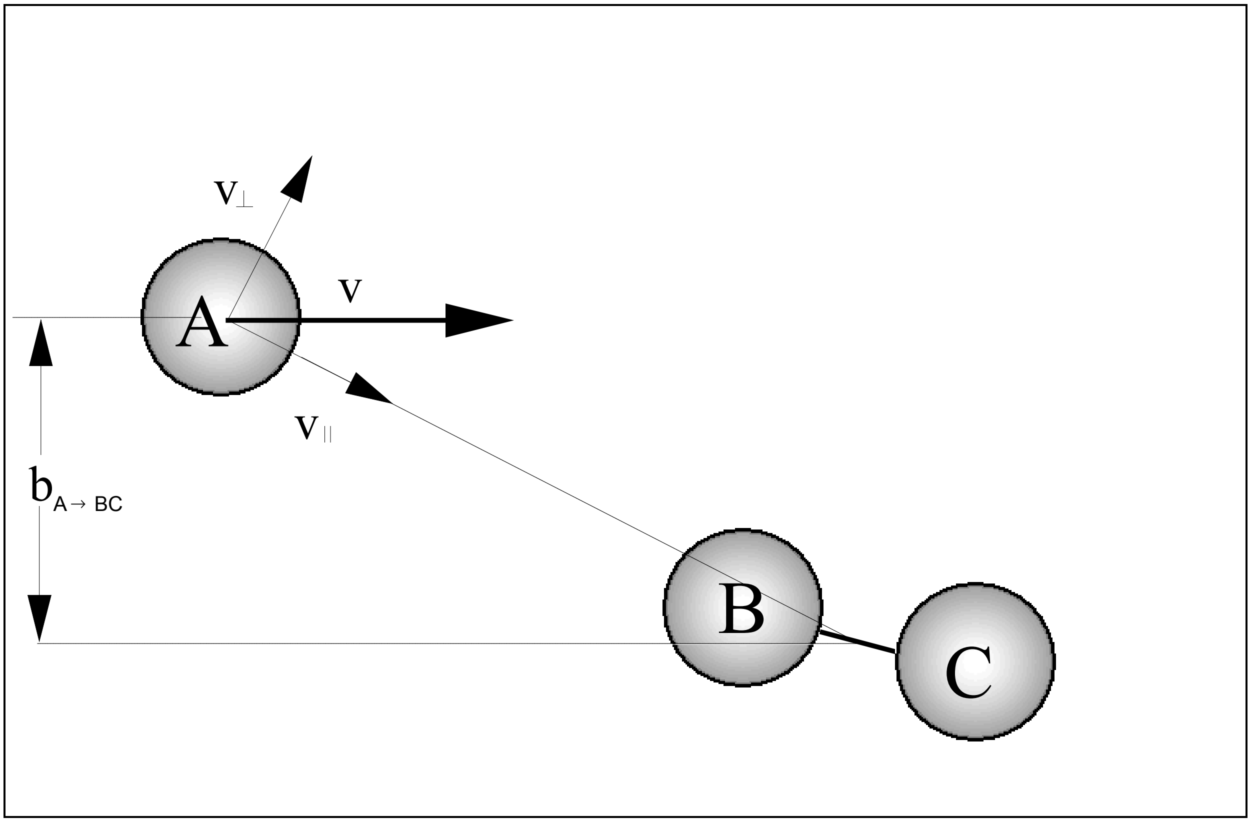

Figure 8.27 The typical trajectory for the collision of an A atom with a BC molecule.

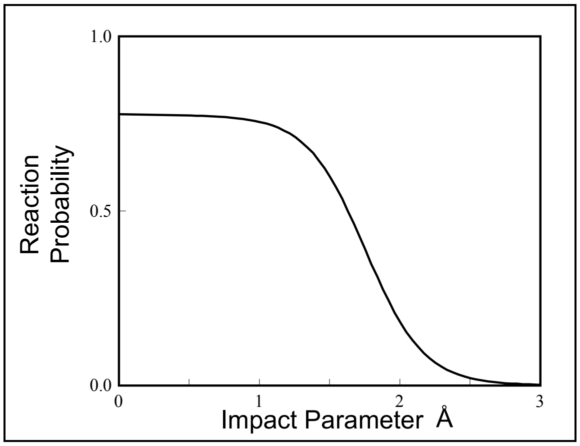

Figure 8.26 The variation in $P_{A\rightarrow BC}$ with changing impact parameter.

Extra barrier to non-linear collisions:

- Component of velocity caries reactants apart
- Must overcome that velocity component for reaction to occur

Book derives and equation for the the Angular Momentum Barrier to Reaction

The derivation starts by looking at the classical equations of motion of A and B.

$$m_A \frac{d^2 \mathbb{R}_A}{dt^2} = \vec{F}_A = -\nabla_A V(\mathbb{R}_A, \mathbb{R}_B)$$

(8.81)

Pages of Algebra

$$E = \frac{1}{2}\mu_{AB}\left(\frac{d\mathbb{R}_{AB}}{dt}\right)^2 + \left[\frac{E_{AB} b^2}{\mathbb{R}_{AB}^2} + V(\mathbb{R}_{AB})\right]$$

(8.130)

It is useful to define an effective potential, V_{eff}, by:

Result: atom moves in effective potential:

$$V_{eff}(\mathbb{R}_{AB}) = \frac{E_{AB} b^2}{\mathbb{R}_{AB}^2} + V(\mathbb{R}_{AB})$$

(8.131)

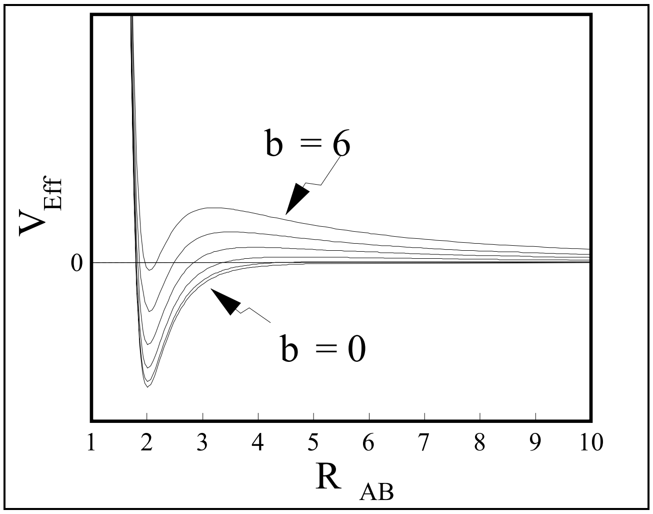

Figure 8.28 A plot of the effective potential as a function of $\mathbb{R}_{AB}$ for a modified Lennard Jones Potential with $b_{A \to BC}$ =0, 1, 2, 3, 4, 5, 6.

The angular momentum barrier prevents reactions from occurring when molecules approach with large impact parameters. As a result, no reaction occurs unless the reactants get close to each other.

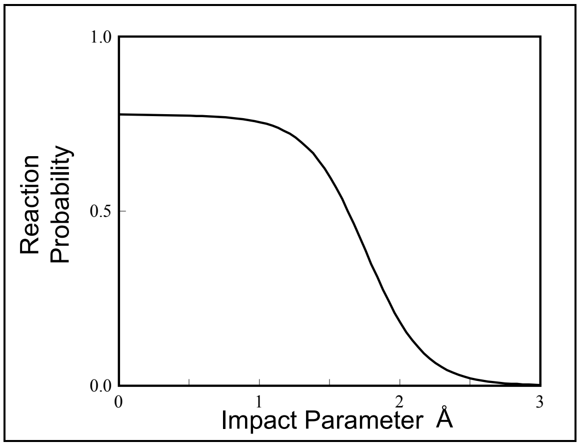

Figure 8.26 The variation in $P_{A \rightarrow BC}$ with changing impact parameter.

Quantifying the effects:

Let’s define $P_{reaction}$ as the probability that a given A molecule reacts with a given BC molecule if the two molecules collide. One can show that the reaction probability varies with:

- $v_{A \to BC}$, the velocity that the A molecule approaches the BC molecule;
- E_{BC}, the internal state (i.e., vibrational, rotational energy) of the BC molecule before collision occurs;
- the “impact parameter” $b_{A \to BC}$, which is a measure of how closely A collides with BC;
- “the angle of approach” where ϕ is a measure of the angle of the collision
- the initial position $\mathbb{R}_{BC}$ and velocity v_{BC} of B relative to C when collision occurs.

$$\frac{1}{\mu_{AB}} = \frac{1}{M_A} + \frac{1}{M_B}$$

(8.57)

$$\sigma_{A \to BC}(v_{A \to BC}, E_{BC}) = \iint\iint P_{reaction}(v_{A \to BC}, E_{BC}, b_{A \to BC}, \phi, \mathbb{R}_{BC}, v_{BC}) \times$$
$$D_1(\mathbb{R}_{BC}, v_{BC}) b_{A \to BC}, db_{A \to BC} d\phi d\mathbb{R}_{BC} dv_{BC}$$

(8.58)

$$\sigma^r_{A \to BC}(v_{A \to BC}, E_{BC}) = 2\pi \int P_{A \to BC}(b_{A \to BC}, v_{A \to BC}, E_{BC}) b_{A \to BC} db_{A \to BC}$$

(8.59)

Example 8.E Calculating the Cross Section

A program called ReactMD is available from Dr. Masel's website. Assume you used the program to calculate the reaction probability as a function of impact parameter, and the data in Table 8.E.1 were obtained. Calculate the cross section for the reaction.

Table 8.E.1

$b_{A\to BC}$,Å	P(b)	$b_{A\to BC}$,Å	P(b)
0	.84	1.2	.80
.2	.83	1.4	.83
.4	.85	1.6	.72
.6	.78	1.8	.21
.8	.80	2.0	.10
1.0	.75	2.2	0

Solution: The cross section is given by:

$$\sigma = 2\pi \int_0^\infty P(b)\,b\,db$$

We can integrate using the trapezoid rule.

Here is a spreadsheet to do the calculations:

	A	B	C
03	b	P(b)	
04	0	0.84	=A4*B4
05	0.2	0.83	=A5*B5
06	0.4	0.85	=A6*B6
07	0.6	0.78	=A7*B7
08	0.8	0.8	=A8*B8
09	1	0.75	=A9*B9
10	1.2	0.8	=A10*B10
11	1.4	0.83	=A11*B11
12	1.6	0.72	=A12*B12
13	1.8	0.21	=A13*B13
14	2	0.1	=A14*B14
15	2.2	0	=A15*B15
16			
17		integral=	=0.5*(C4+C15)+SUM(C5:C14)
18		σ=	=2*PI()*C17

Here are the results:

	A	B	C
03	b	P(b)	
04	0	0.84	0
05	0.2	0.83	0.166
06	0.4	0.85	0.34
07	0.6	0.78	0.468
08	0.8	0.8	0.64
07	1	0.75	0.75
10	1.2	0.8	0.96
11	1.4	0.83	1.162
12	1.6	0.72	1.152
13	1.8	0.21	0.378
14	2	0.1	0.2
15	2.2	0	0
16			
17		integral=	6.216
18		σ=	39.05628

Example 8.D: Calculating the rate constant using equation 8.60

Figure 8.17 shows some data for the cross section for the reaction $H + H_2 \rightarrow H_2 + H$ as a function of E_T, the translational energy of H approaching H_2. The energy is measured in center of mass coordinates as described in section 8.9.

Assume that the cross section follow:

$$\sigma^{r}_{A\rightarrow BC} > 0 \text{ for } E_T \leq 0.35\text{eV}$$

$$\sigma^{r}_{A\rightarrow BC} = 12(\text{Å})^2\left(1-\exp\left(0.35\text{eV} - E_T\right)/\left(5.08\text{eV}\right)\right)\times$$

$$\exp\left(-E_T/2\text{eV}\right) \qquad \text{for } E_T \geq 0.35\text{eV}$$

(8.D.2)

where E_T is the translational energy. Calculate the rate constant for the reaction at 300K.

According to equation 8.60, if there is no E_{BC} dependence

$$k_{A\rightarrow BC} = \int_0^{\infty} v_{A\rightarrow BC}\, \sigma^{r}_{A\rightarrow B}\, D(v_{A\rightarrow BC})\, dv_{A\rightarrow BC}$$

(8.D.3)

According to results in Example 6.2:

$$D(v_{A\rightarrow BC}) = \frac{\left(v_{A\rightarrow BC}\right)^2 \exp\left(-\frac{\mu_{ABC}}{2\,ķ_B\,T}(v_{A\rightarrow BC})^2\right)}{\int_0^{\infty}(v_{A\rightarrow BC})^2 \exp\left(-\frac{\mu_{ABC}}{2}(v_{A\rightarrow BC})^2\right)}$$

(8.D.4)

where μ_{ABC} is the reduced mass of ABC, $ķ_B$ is Boltzman’s constant and T is the temperature. Looking up the integral in the CRC yields:

$$D(v_{A\rightarrow BC}) = \frac{4}{\sqrt{\pi}}\left(\frac{\mu_{ABC}}{2\,ķ_B\,T}\right)^{3/2}(v_{A\rightarrow BC})^2 \exp\left(-\frac{\mu_{ABC}}{2\,ķ_B\,T}(v_{A\rightarrow BC})^2\right)$$

(8.D.5)

Combining equations (8.D.3) and 8.D.5) and substituting $E_T = \frac{1}{2}\mu_{ABC}(v_{A\to BC})^2$ yields:

$$k_{A\to BC} = \sqrt{\frac{8\,k_B\,T}{\pi\mu_{AB}}}\int_0^\infty (E_T / k_B T)\sigma^{r}{}_{A\to BC}\exp(-E_T / k_B T)\ d(E_T / k_B T)$$

(8.D.6)

Note:

$$\sqrt{\frac{8\,k_B\,T}{\pi\mu_{AB}}} = \bar{v}_{A\to BC} \qquad (8.D.7)$$

Therefore,

$$k_{A\to BC} = \bar{v}_{A\to BC}\int_0^\infty (E_T / k_B T)\sigma^{r}_{A\to BC}\exp(-E_T / k_B T)d(E_T / k_B T)$$

(8.D.8)

For future reference, it is useful to define an average cross section, $I_{A\to BC}$ by

$$I_{A\to BC} = \int_0^\infty (E_T / k_B T)\sigma^{r}_{A\to BC}\exp(-E_T / k_B T)d(E_T / k_B T)$$

(8.D.9)

Equation 8.D.8 becomes:

$$k_{A\to BC} = \bar{v}_{A\to BC} I_{A\to BC} \qquad (8.D.10)$$

Let’s define a new variable W by:

$$W = \left(E_T - 0.35\text{eV}\right) / k_B T \qquad (8.D.11)$$

Substituting equation (8.D.6) into equation (8.D.5) yields:

$$k_{A\to BC} = \bar{v}_{A\to BC} e^{-0.35\text{eV}/k_B T} \times$$
$$\int_{-0.35\text{eV}/k_B T}^{\infty} \left(W k_B T + 0.35\text{eV} / k_B T\right) \sigma^r{}_{A\to BC} \exp(-W) dW$$
$$(8.D.12)$$

For future reference, it is useful to note:

$k_B T$ = 0.6 kcal/mole = 0.026 eV/molecule (8.D.13)

$$\frac{1}{\mu_{ABC}} = \frac{1}{2\text{AMU / mole}} + \frac{1}{1\text{AMU / mole}} = \frac{1.5}{\text{AMU}}$$

(8.D.14)

According to equation (7.A.4):

$$\bar{v}_{A \rightarrow BC} = \left(2.4 \times 10^{13}\,\text{Å} / \sec\right)\left(\frac{T}{300K}\right)^{1/2}\left(\frac{1AMU}{\mu}\right)^{1/2}$$

$$= \left(2.4 \times 10^{13}\,\text{Å} / \sec\right)\left(\frac{300K}{300K}\right)^{1/2}\left(\frac{1AMU}{1AMU / 1.5}\right)^{1/2}$$

(8.D.15)

$$= 2.94 \times 10^{13}\,\text{Å} / \sec$$

Substituting equation 8.D.10 into 8.D.8 and adding the appropriate conversion factors yields:

$$k_{A \rightarrow BC} = 2.94 \times 10^{13}\,\text{Å} / \sec \exp\left(-0.35eV / ķ_B T\right)$$

$$\int_{-0.35eV/ķ_B T}^{\infty} \left(W + 0.35eV / ķ_B T\right) \sigma^r{}_{A \rightarrow BC} \exp\left(-W\right) dW$$

(8.D.16)

Note: $\sigma = 0$ for $E_T < 0.35\text{eV}$.

Therefore,

$$k_{A\rightarrow BC} = \frac{2.94\times 10^{13}\,\text{Å}}{\text{molecule - sec}}\exp\left(-\,0.35\text{eV}/k_B T\right)\times$$
$$\int_{-o.}^{\infty}\left(W + 0.35\text{eV}/k_B T\right)\sigma^{r}{}_{A\rightarrow BC}\exp\left(-\,W\right)dW$$

(8.D.17)

Let's define $I_{A\rightarrow BC}$ and F(W) by:

$$I_{A\rightarrow BC} = \int_{o.}^{\infty}\left(W + 0.35\text{eV}/k_B T\right)\sigma^{r}{}_{A\rightarrow BC}\exp\left(-\,W\right)dW$$

(8.D.18)

$$F(W) = \left(W + 0.35\text{eV}/k_B T\right)\sigma^{r}_{A\rightarrow BC}$$

(8.D.19)

Combining equations (8.D.16) and 8.D.17) yields:

$$I_{A\rightarrow BC} = \int_{o.}^{\infty}F(W)\quad\exp\left(-\,W\right)dW$$

(8.D.20)

One can conveniently integrate equation 8.D.18 using the Laguere integration formula:

$$\int_{o.}^{\infty} F(W) \exp(-W) dW = \sum_{i} B_i F(W_i)$$

(8.D.21)

where the B_i and W_i's are given in the spreadsheet below.

Here is a spreadsheet for the calculations:

	A	B	C	D	E	F
02	kbT=	=D$_2$*0.00198/23.05	T=	300		
03					I=	=SUM(F5:F10)
04	W	Et	s	F(w)	B$_i$	term in sum
05	0.22285	=A5*kbT+0.35	=12*(1-EXP((0.35-$B5)/5.08))*EXP(-$B5/2)	=$B5*$C5/kbt	0.458964	=D5*E5
06	1.118893	=A6*kbT+0.35	=12*(1-EXP((0.35-$B6)/5.08))*EXP(-$B6/2)	=$B6*$C6/kbt	0.417	=D6*E6
07	2.99273	=A7*kbT+0.35	=12*(1-EXP((0.35-$B7)/5.08))*EXP(-$B7/2)	=$B7*$C7/kbt	0.113373	=D7*E7
08	5.77514	=A8*kbT+0.35	=12*(1-EXP((0.35-$B8)/5.08))*EXP(-$B8/2)	=$B8*$C8/kbt	0.0103991	=D8*E8
09	9.83747	=A9*kbT+0.35	=12*(1-EXP((0.35-$B9)/5.08))*EXP(-$B9/2)	=$B9*$C9/kbt	0.000261017	=D9*E9
10	15.98287	=A10*kbT+0.35	=12*(1-EXP((0.35-$B10)/5.08))*EXP(-$B10/2)	=$B10*$C10/kbt	8.98547e-7	=D10*E10

Here are the results:

	A	B	C	D	E	F
02	kbT=	0.02577	T=	300		
03					I=	0.747826
04	W	Et	s	F(w)	Bi	term in sum
05	0.22285	0.355743	0.011349	0.156665	0.458964	0.071904
06	1.118893	0.378834	0.056199	0.826153	0.417	0.34506
07	2.99273	0.427123	0.146036	2.420454	0.113373	0.274414
08	5.77514	0.498826	0.26998	5.225937	0.010399	0.054345
09	9.83747	0.603512	0.43199	10.11683	2.61E-04	0.002641
10	15.98287	0.76188	0.6385	18.87694	8.99E-07	1.7E-5

Therefore,

$$I_{A\rightarrow BC} = 0.748\text{Å}^2 \tag{8.D.23}$$

$$k_{A\rightarrow BC} = 2.94\times10^{13}\,\frac{\text{Å}}{\text{sec}}\times\left(0.748\text{Å}^{2}\right)\exp\left(-0.35\text{eV}/k_{B}T\right)$$

(8.D.24)

$$k_{A\rightarrow BC} = 2.2\times10^{13}\,\frac{\left(\text{Å}\right)^{3}}{\text{molecule}-\text{sec}}\exp\left(-0.35\text{eV}/k_{B}T\right)$$

(8.D.25)

Notice that the activation barrier is about 0.35 eV (i.e., the minimum energy to get reaction) even though the reaction probability is small below 0.5eV. It is not exactly 0.35eV though. In the problem set, we ask the reader to calculate the rate constant at other temperatures. $\bar{v}_{A\rightarrow BC}$ and $I_{A\rightarrow BC}$ are temperature dependent. If you make an Arrhenius plot of the data, you find that the activation barrier is not exactly 0.35eV, but close to 0.35eV, even though the reaction probability is negligible at $E = 0.35$eV.

Discussion Problem:

The reaction probability A+BC → AB+C is given below. Calculate the cross section.

b,Å	**P(b)**
0	0.95
0.25	0.93
0.5	0.92
1.0	0.91
1.5	0.50
2.0	0.0