

# Summary Chapter 9

## Reaction Rate Theory Revisited

### Key Topics:

- Tolman's equation
- Transition state theory revisited
- RRKM theory

## Transition state theory revisited

Last time we discussed advanced collision theory:

### Method

- Use molecular dynamics to simulate the collisions
- Integrate using statistical mechanics

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

(8.20)

key finding - we need energy and momentum to be correct to get reaction to happen.

- Many molecules which are hot enough do not make it

Today how does that affect transition state theory?

Review arrhenius' model vs transition state theory.

Arrhenius's model:

- Consider two populations of molecules:
  1. Hot molecules in the right configuration to react (i.e. molecules moving toward each other with the right velocity, impact parameter etc to react)
  2. Molecules not hot enough or not moving together in the right configuration
- Assume concentration of hot reactive molecules in equilibrium with reactants
- Assume reaction occurs whenever hot molecules collide in right configuration to react

Can derive Tolman's equation

$$k_{A \rightarrow BC} = \left( \frac{k_B T}{h_p} \right) \frac{q^+}{q_A q_{BC}} \exp(-E^+ / k_B T)$$

**(9.2)**

where  $k_{A \rightarrow BC}$  is the rate constant for reaction (9.1),  $k_B$  is Boltzmann's constant;  $T$  is the absolute temperature;  $h_p$  is Planck's constant;  $q_A$  is the microcanonical partition function per unit volume of the reactant A;  $q_{BC}$  is the microcanonical partition function per unit volume for the reactant BC;  $E^+$  is the average energy of the molecules which react and,  $q^+$  is the average partition function of the molecules which react, divided by the partition function for the translation of A toward BC.

**Table 9.1** Definitions of the partition functions used in the derivation of Tolman's Equation

$q_A$	The partition function of the reactant A
$q_{BC}$	The partition function of the reactant BC
$q^*$	The partition function of the hot molecules when energies are measured relative to the reactants.
$q^{\text{Hot}}$	The partition function of the hot molecules when energies are measured relative to a molecule with energy $E^+$
$q_{A \rightarrow BC}$	The partition function for the motion of A toward BC
$q_{\text{Not } A \rightarrow BC}^{\text{Hot translation}}$	The partition function for all of the normal modes of the hot molecules except the $A \rightarrow BC$ translation. See equation (9.19).
$q^+$	Another notation for $q_{\text{Not } A \rightarrow BC}^{\text{Hot translation}}$

Tolman's equation is essentially exact.

**Table 9.2** A comparison of Tolman's equation and Transition State Theory

Equation		Definitions
Tolman's	$k_{A \rightarrow BC} = \left( \frac{k_B T}{h_p} \right) \left( \frac{q^+}{q_A q_{BC}} \right) \exp\left( -\frac{E^+}{k_B T} \right)$	$E^+$ = Average energy of the hot molecules before they react $q^+$ = partition function for the hot molecules before they react. The partition function includes all of the normal modes of the AB-C complex except the normal mode carrying the species over the barrier
TST	$k_{A \rightarrow BC} = \left( \frac{k_B T}{h_p} \right) \left( \frac{q_T^\ddagger}{q_A q_{BC}} \right) \exp\left( -\frac{E^\ddagger}{k_B T} \right)$	$E^\ddagger$ = Saddle Point energy $q_T^\ddagger$ = partition function for molecules at the saddle point in the potential energy surface. The partition function includes all of the normal modes of the AB-C complex except the normal mode carrying the species over the barrier

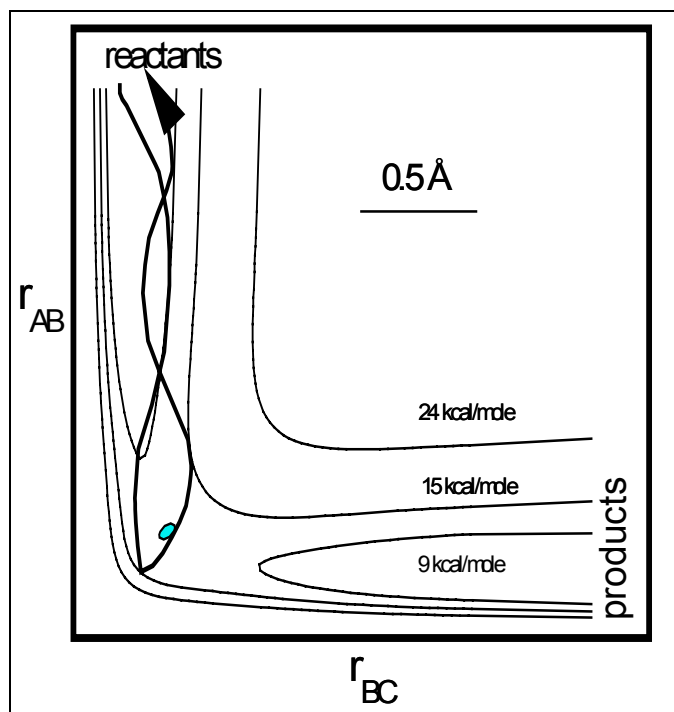
Approximate derivation of TST:

Lets go back to the statistical mechanics definition of the partition functions

$$q^{\text{Hot}} = \frac{\sum_N P_N^{\text{Hot}} g_N \exp\left(-\frac{E_N - E^\ddagger}{k_B T}\right)}{V} \quad (9.40)$$

$$q^{\text{TST}} = \frac{\sum_N P_N^{\text{TST}} g_N \exp\left(-\frac{E_N - E^\ddagger}{k_B T}\right)}{V} \quad (9.41)$$

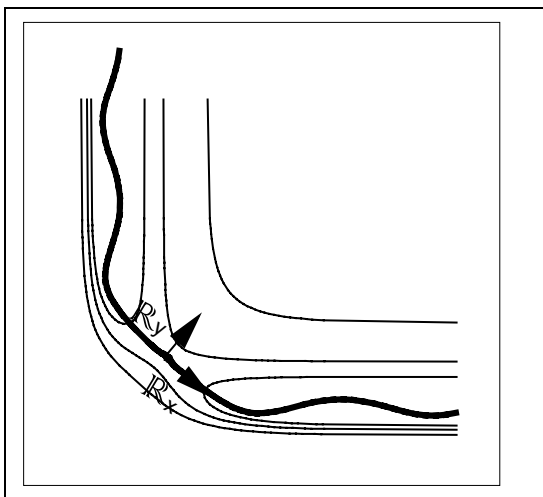
Need to assume  $P_{\text{hot}} = P_{\text{TST}}$



**Figure 9.7** A recrossing trajectory.

We also need to assume q's equal.

Let me examine the assumption that q's are equal



**Figure 9.3** The minimum energy pathway for motion over the barrier as determined by the trajectory calculations in Chapter 8.

$$q^{\text{Hot}} = q_X q_Y q_{\text{everything\_else}}$$

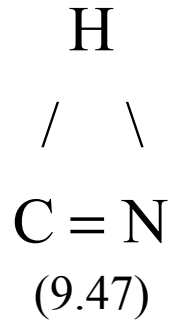
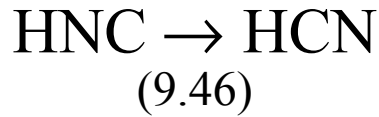
(9.38)



At this point, we have only assumed that  $P_N^{\text{Hot}} = P_N^{\text{TST}}$ .

In order to get to conventional state theory, we have to make the additional assumptions:

- All the  $P_N^{\text{Hot}}$  in equation (9.40) are 0 for states with energies below the barrier and unity for states with energy above the barrier so that  $P_N^{\text{Hot}} = P_N^{\text{TST}}$ .
- Motion along the  $\mathbb{R}_x$  direction is pure translation.
- Motion perpendicular to the  $\mathbb{R}_x$  direction is pure vibration.
- The  $P_N^{\text{Hot}}$  are determined only by the properties of the transition state; this assumption ignores the findings from chapter 8 that the reaction probability is higher when the potential energy surface is smoothly banked than when there is a sharp turn in the potential energy surface. It also ignores the fact that the vibrational levels of the reactants might not match the vibrational levels of the transition state.



$$q_{\text{HNC}} = q_t^3 q_r^2 (q_{\text{sym}})(q_{\text{asym}})(q_{\text{BendA}})(q_{\text{BendB}})$$

(9.48)

$$q_{\text{T}}^{\ddagger} = (q_t^{\ddagger})^3 (q_r^{\ddagger})^2 q_{\text{sym}}^{\ddagger} q_{\text{asym}}^{\ddagger} q_{\text{BendB}}^{\ddagger}$$

(9.50)

TST assume that the bending mode is pure translation, the other modes are pure vibration.

Cancellation of error

## Successes of Transition State Theory

- Transition state theory generally gives preexponentials of the correct order of magnitude.
- Transition state theory is able to relate barriers to the saddle point energy in the potential energy surface;
- Transition state theory is able to consider isotope effects;
- Transition state theory is able to make useful prediction in parallel reactions like reactions (7.27) and (7.29).

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Experimentally, anything one does to lower the energy of the transition state for a reaction lowers the activation energy for the reaction.

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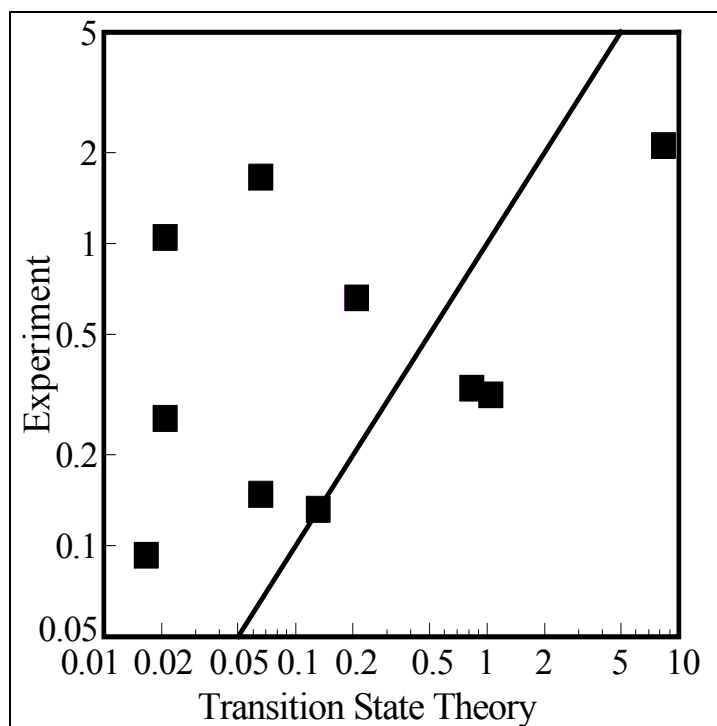
**Table 9.5** The relative rates of a series of reactions at 300K.

Reaction	Experimental Relative Rate	CTST Relative Rate
$D+H_2 \rightarrow DH+H$	6	12.3
$H+H_2 \rightarrow H_2+H$	4	6.7
$D+D_2 \rightarrow D_2+D$	2	1.7
$H+D_2 \rightarrow HD+D$	1	1

**Table 9.6** The various contributions to the relative rate of the reactions in Table 9.5 at 300K.

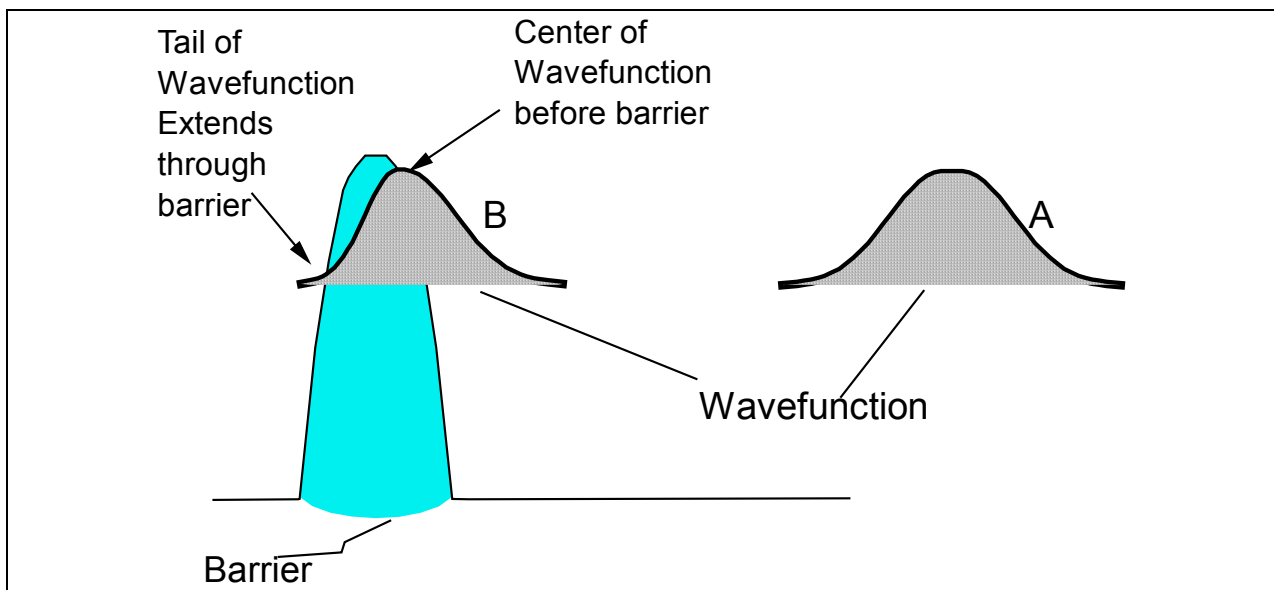
Reaction	Symmetric Stretching Frequency, $cm^{-1}$	Bending Frequency $cm^{-1}$	$\Delta$ Zero Point Energy kJ/Mole	Relative Rate 300K
$D + H_2 \rightarrow DH + H$	1732	924	4.79	12
$H + H_2 \rightarrow H_2 + H$	2012	965	6.96	6.7
$D + D_2 \rightarrow D_2 + D$	1423	683	7.60	1.7
$H + D_2 \rightarrow HD + D$	1730	737	10.16	1

## Limitations of TST



**Figure 9.6** A plot of the results in Table 9.7. If the simple formation of transition state theory with constant transmission coefficients had worked, the results should have scattered around the line in the figure.

Often gives too low of a rate due to tunneling.

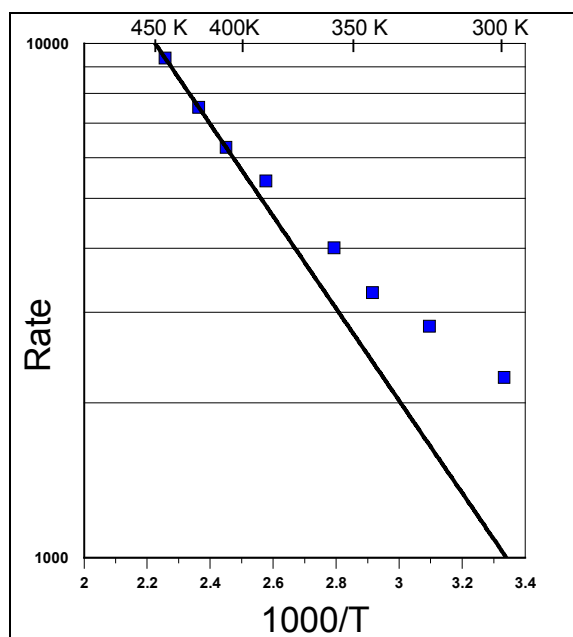


**Figure 9.9** A diagram showing the extent of the wavefunction for a molecule. In A the molecule is by itself. In B the molecule is near a barrier. Notice that the wavefunction has a finite size (i.e. there is some uncertainty in the position of the molecule.) As a result, when a molecule approaches a barrier, there a component of the molecule on the other side of the barrier.

Fail miserably for unimolecular reactions:

**Table 9.8** The preexponential for a series of unimolecular reactions, as you change the collision partner. Data of Westley[1980].

reaction	$k_0$ when X = Argon	$k_0$ when X = Water	$k_0$ when X = N <sub>2</sub>
NO <sub>2</sub> + X → OH + H + X	$1.7 \times 10^{14}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$6.7 \times 10^{15}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$1.57 \times 10^{15}$ cm <sup>6</sup> /mole <sup>2</sup> sec
H <sub>2</sub> O + X → OH + H + X	$2.1 \times 10^{15}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$3.5 \times 10^{17}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$5.1 \times 10^{16}$ cm <sup>6</sup> /mole <sup>2</sup> sec
HO <sub>2</sub> + X → O <sub>2</sub> + H + X	$1.5 \times 10^{15}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$3.2 \times 10^{16}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$2 \times 10^{15}$ cm <sup>6</sup> /mole <sup>2</sup> sec
H <sub>2</sub> + X → H + H + X	$6.4 \times 10^{17}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$2.6 \times 10^{15}$ cm <sup>6</sup> /mole <sup>2</sup> sec	
O <sub>2</sub> + X → 2O + X	$1.9 \times 10^{13}$ cm <sup>6</sup> /mole <sup>2</sup> sec		$1.0 \times 10^{14}$



**Figure 9.13** An Arrhenius plot for the reaction  $\text{H}+\text{H}_2\rightarrow\text{H}_2+\text{H}$ .



Modern versions of transition state theory:

Variational transition state theory

Key idea: TST is saddle point in the free energy plot, not the energy plot

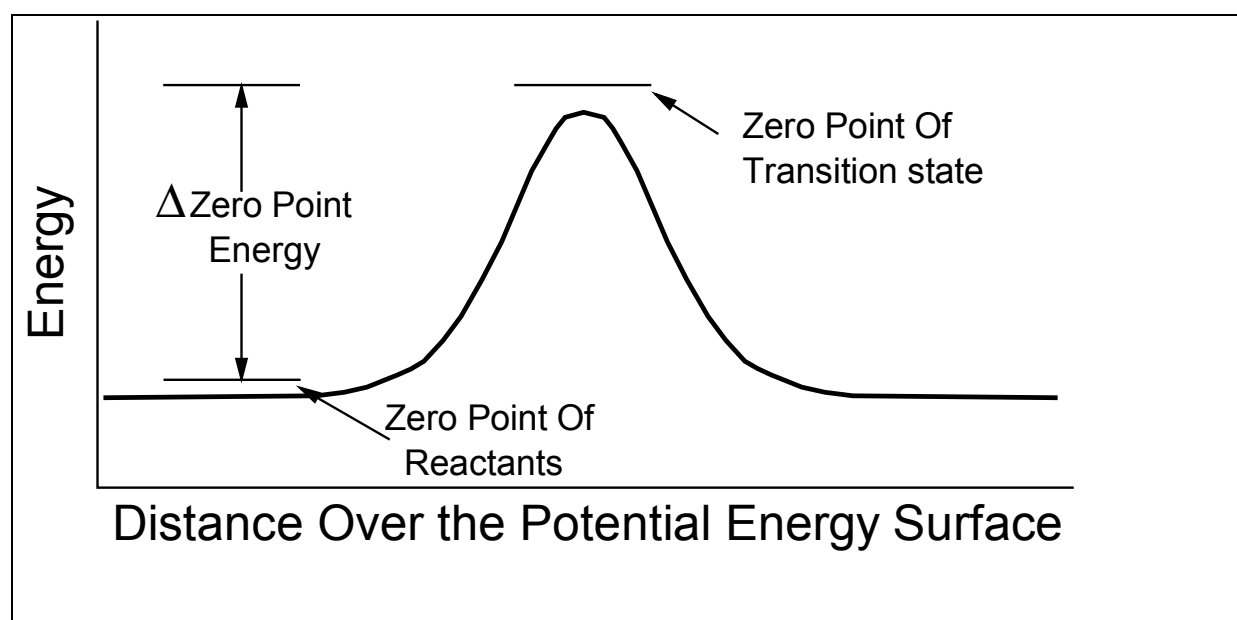
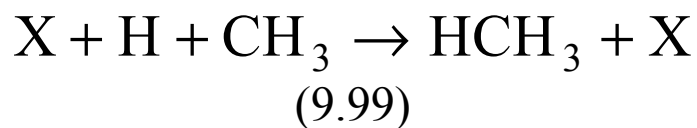
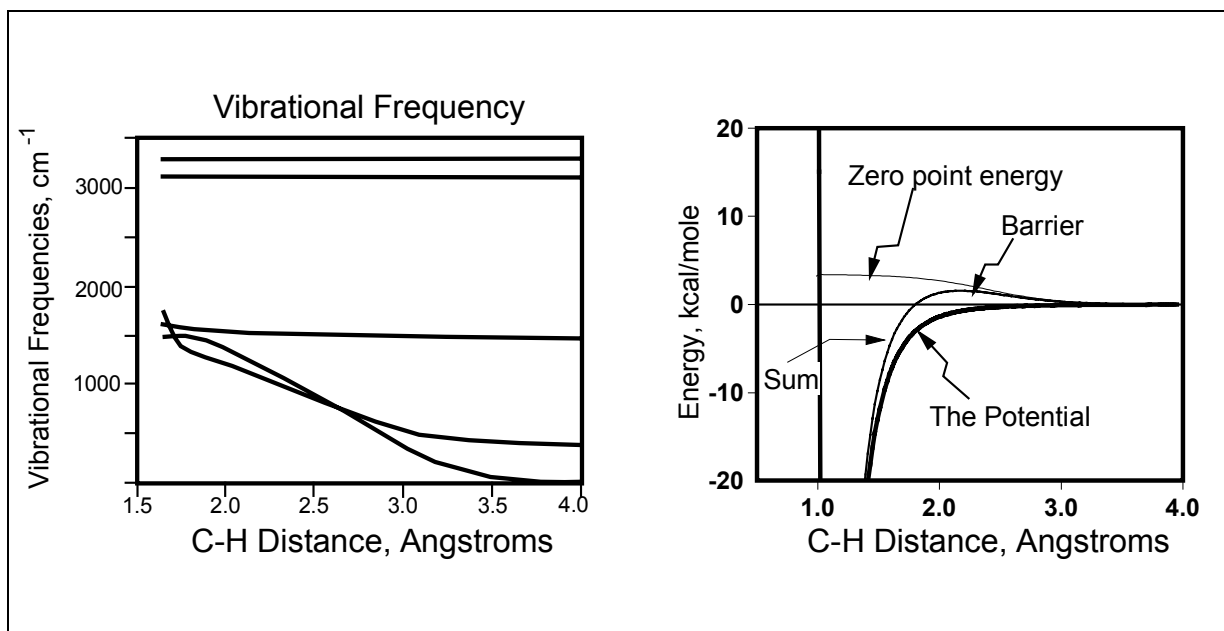


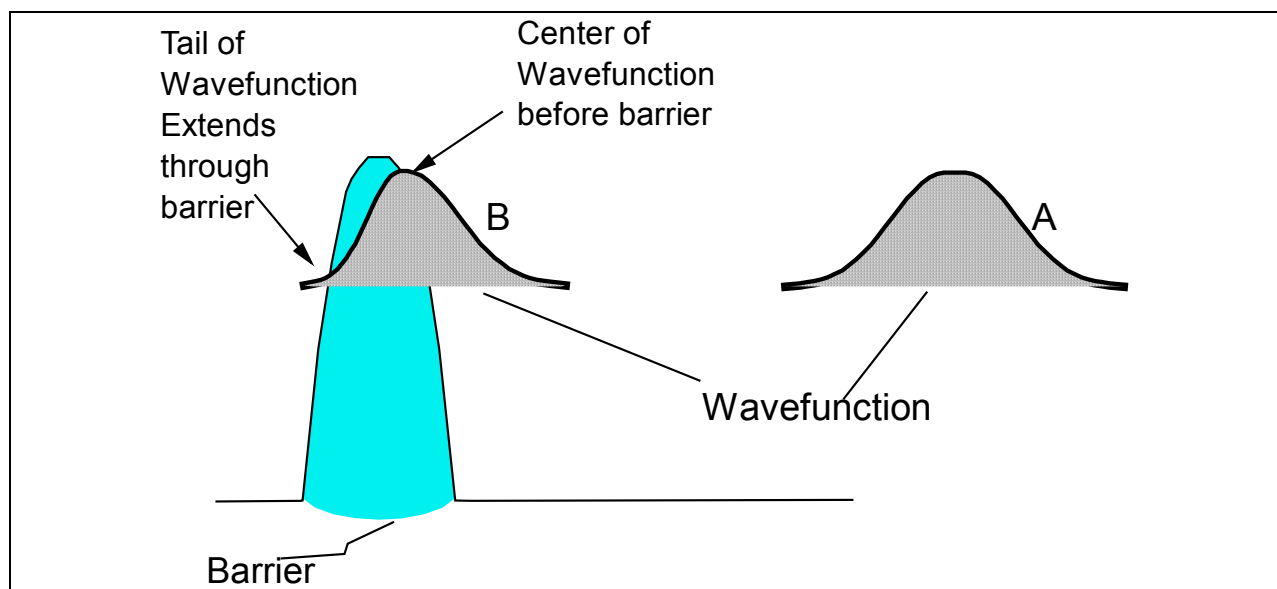
Figure 9.4 The activation barriers for the reactions in Table 9.6.



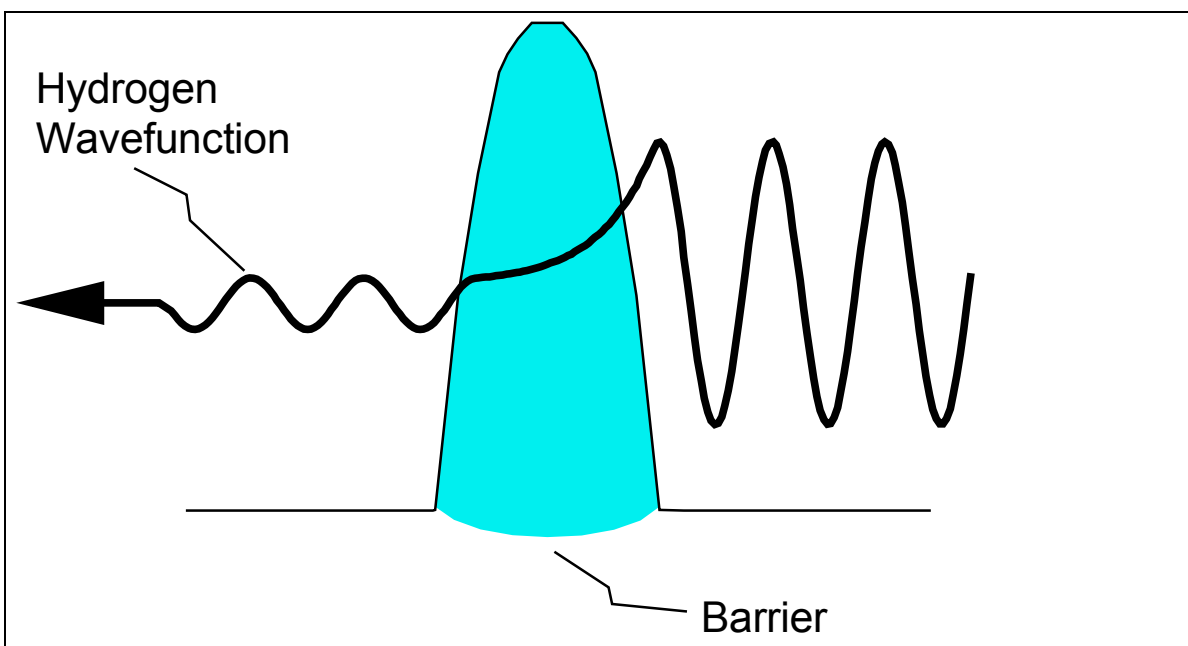


**Figure 9.17** The vibrational frequency, zero point energy potential energy and the sum of potential and zero point energy for reaction (9.51) as a function of the C-H bond length. After Hase [1997].

## Tunnelling corrections:

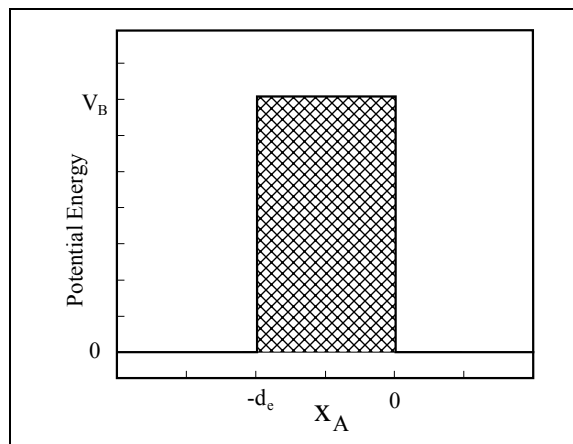


**Figure 9.9** A diagram showing the extent of the wavefunction for a molecule. In A the molecule is by itself. In B the molecule is near a barrier. Notice that the wavefunction has a finite size (i.e. there is some uncertainty in the position of the molecule.) As a result, when a molecule approaches a barrier, there is a component of the molecule on the other side of the barrier.



**Figure 9.8** Tunneling through a barrier.

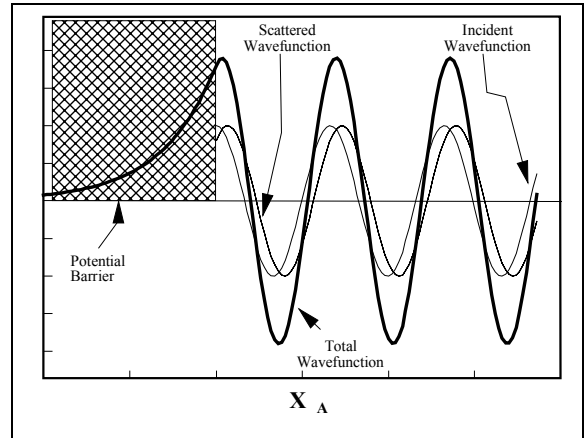
## An equation for tunnelling"



**Figure 9.11** A plot of the square-well barrier.

$$\left( \frac{\hbar^2}{2m_i} \frac{d^2}{dX_A^2} + V_B \right) \psi_i = E\psi_i$$

(9.73)



**Figure 9.12** The real part of the incident ( $\psi_i$ ) scattered ( $\psi_r$ ) and total wavefunction ( $\psi_T$ ) for the square-well barrier.

$$P(-d_e) = \left| \left( \frac{2K_i}{K_i + p_i} \right) \exp \left( -2d_e \sqrt{\frac{2m_i (V_B - E_i)}{\hbar^2}} \right) \right|$$

(9.81)

Square wells are not good assumptions:

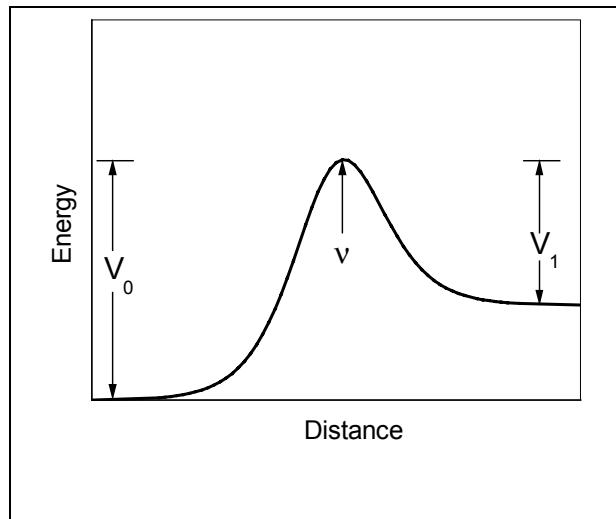


Figure 9.14 The Eckart potential.

$$k_{A \rightarrow BC} = \left( \frac{kT}{h} \right) \kappa_T \frac{q^\ddagger}{q_A q_{BC}} \exp\left(-E^\ddagger / k_B T\right)$$

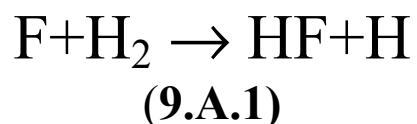
(9.63)

$$\kappa(T) = 1 + \frac{1}{24} \left( \frac{h_P v_i}{k_B T} \right)^2 \left( 1 + \frac{k_B T}{E^\ddagger} \right)$$

(9.89)

## Example 9.A Tunneling Corrections Using the Eckart Barrier.

In problem 7.C we calculated the preexponential for the reaction:



How much will the pre-exponential change at 300 K if we consider tunneling?

### **Solution**

From Equation 9.69

$$k_{\text{A} \rightarrow \text{BC}} = \kappa(T) \left[ \left( \frac{k_{\text{B}} T}{h_{\text{p}}} \right) \frac{q^{\ddagger}}{q_{\text{A}} q_{\text{BC}}} \exp(-E^{\ddagger} / k_{\text{B}} T) \right]$$

(9.A.2)

We already evaluated the term in brackets in Equation (9.A.1) in Example 7.C. Substituting that result:

$$k_{A \rightarrow BC} = \kappa(T) \left[ 2 \times 10^{14} \text{ \AA}^3 / \text{molecule-sec} \right]$$

**(9.A.3)**

According to Equation (9.101)

$$\kappa(T) = 1 + \frac{1}{24} \left( \frac{h_p \nu_i}{k_B T} \right)^2 \left( 1 + \frac{k_B T}{E^\ddagger} \right)$$

**(9.A.4)**

Where according to Table 7.C.1  $\nu_i = 310 \text{ cm}^{-1}$ .  
Equation (7.C.17) says:

$$\frac{h_p \nu_i}{k_B T} = \nu \left( 4.784 \times 10^{-3} \text{ cm} \right) \left( \frac{300\text{K}}{T} \right)$$

**(9.A.5)**

Substituting  $\nu_i = 310 \text{ cm}^{-1}$  at  $T=300\text{K}$  into Equation (9.A.5) yields

$$\frac{h_p \nu_i}{k_B T} = (310 \text{ cm}^{-1}) (4.784 \times 10^{-3} \text{ cm}) \left( \frac{300\text{K}}{300\text{K}} \right) = 1.48.$$

**(9.A.6)**



Substituting into Equation (9.A.4) yields

$$\kappa(T) = 1 + \frac{1}{24} (1.48)^2 \left( 1 + \frac{.00198 \text{ kcal / mole } ^\circ\text{K} (300\text{K})}{5.6 \text{ kcal / mole}} \right) = 1.10 .$$

**(9.A.7)**

Therefore the rate will only go up by 10% at 300K.  
At 100K

$$\frac{h_p v_i}{\kappa T} = (310 \text{ cm}^{-1}) (4.784 \times 10^{-3} \text{ cm}) \left( \frac{300\text{K}}{100\text{K}} \right) = 4.45 .$$

**(9.A.8)**

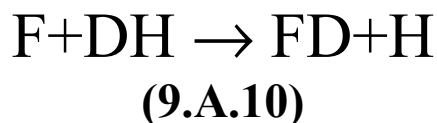
Substituting into Equation (9.A.4) yields

$$\kappa(T) = 1 + \frac{1}{24} (4.45)^2 \left( 1 + \frac{.00198 \times 100}{5.6} \right) = 1.85 .$$

**(9.A.9)**

The tunneling correction in this example is smaller than normal, because the barrier has such a small curvature. A typical number would be  $1000 \text{ cm}^{-1}$ . Still it illustrates the point that tunneling becomes more important as the temperature drops.

Finally, it is interesting to note that if we replace the hydrogen with a deuterium in the reaction



the curvature drops to  $215 \text{ cm}^{-1}$ . In that case

$$\frac{h_p \nu_i}{k_B T} = (215 \text{ cm}^{-1}) (4.784 \times 10^{-3} \text{ cm}) \left( \frac{300 \text{ K}}{100 \text{ K}} \right) = 3.08$$

**(9.A.11)**

$$\kappa(T) = 1 + \frac{1}{24} \left( \frac{h_p \nu_i}{k_B T} \right)^2 \left( 1 + \frac{k_B T}{E^\ddagger} \right) = 1.41$$

**(9.A.12)**

so the tunneling correction for deuterium is half that of hydrogen.

## Key assumptions in TST

1) no recrossing trajectories

2)  $q_{\text{hot}} = q_{\text{tst}}$

3) no tunnelling

OK to factor of 20 for bimolecular reactions - usually low because of missed tunneling, improper dynamics

Fails miserably for unimolecular reactions:

<b>Table 9.8</b> The preexponential for a series of unimolecular reactions, as you change the collision partner. Data of Westley[1980].			
reaction	$k_0$ when X = Argon	$k_0$ when X = Water	$k_0$ when X = N <sub>2</sub>
NO <sub>2</sub> + X → OH + H + X	$1.7 \times 10^{14}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$6.7 \times 10^{15}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$1.57 \times 10^{15}$ cm <sup>6</sup> /mole <sup>2</sup> sec
H <sub>2</sub> O + X → OH + H + X	$2.1 \times 10^{15}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$3.5 \times 10^{17}$ cm <sup>6</sup> /mole <sup>2</sup> sec	$5.1 \times 10^{16}$ cm <sup>6</sup> /mole <sup>2</sup> sec
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O <sub>2</sub> + X → 2O + X	$1.9 \times 10^{13}$ cm <sup>6</sup> /mole <sup>2</sup> sec		$1.0 \times 10^{14}$

## RRKM model

Try to fix unimolecular reactions:

Why does transition state theory fail?

$$q_{\text{hot}} \gg q_{\text{TST}}$$

Recall Transition state theory assumes  $q_{\text{hot}} = q_{\text{TST}}$

$q_{\text{hot}}$  = partition function for molecules poised to react

$q_{\text{TST}}$  = partition function for TST

TST has energy localized in the bond which breaks.

Unimolecular reactions, energy does not have to be localized.

Physically - bimolecular reactions last  $10^{-13}$  seconds. Reaction occurs only if energy localized in the correct bonds.

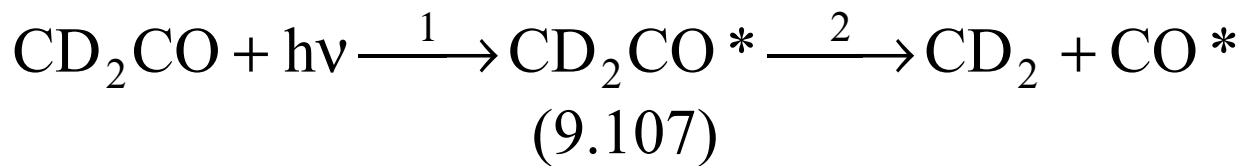
Unimolecular reactions different.

- First form a hot complex
- hot complex reacts

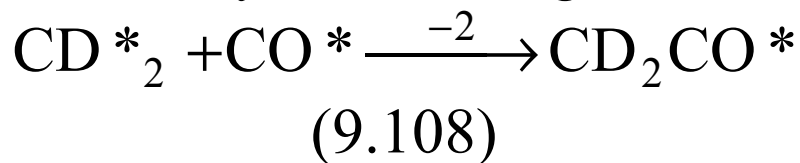
Hot complex lasts for  $10^{-8}$  seconds. As a result, there is time for energy to get localized in a key bond.

Tolman's equation still works for unimolecular reactions - the big change is that the partition function is different than the TST partition function.

Next derive an equation for the rate of a unimolecular reaction initiated with a laser



Derive expression by considering reverse reaction:



$$\frac{k_2}{k_{-2}} = K_2^{\text{eq}} = \frac{q_{\text{CD}_2} q_{\text{CO}}}{q^*} \quad (9.109)$$

From before

$$k_{-2} = \frac{1}{2d_{\text{ABC}}} \bar{v}_{\text{ABC}} (d_{\text{ABC}} q_{\text{A} \rightarrow \text{BC}}) \frac{q^\ddagger}{q_{\text{CD}_2} q_{\text{CO}}} \quad (9.110)$$

Lots of algebra:

$$k_{-2} = \frac{1}{h_P} \frac{q^\ddagger}{q_{\text{CD}_2} q_{\text{CO}}}$$

(9.117)

$$k_2 = \frac{1}{h_P} \frac{q^\ddagger}{q_{\text{A}^*}}$$

(9.118)

Change notation:

$$q_{A^*} = \sum_n g_n$$

(9.122)

$$N(E^*) = q^*$$

(9.123)

$N(E^*)$ =number of states with energy E

$$q^\ddagger = G(E^*)$$

$G(E^*)$ = number of states with vibrational/rotational energy between TST and  $E^*$

$$k_2(E^*) = \frac{1}{h_p} \frac{G^T(E^*)}{N(E^*)}$$

(9.127)



## RRKM model

- $N(E^*) \delta E^*$  is the number of vibrational modes of the reactants with an vibrational energy between  $E^*$  and  $E^* + \delta E^*$
- $G^\ddagger(E^*)$  is the number of vibrational modes of the transition state with a vibrational energy between  $E^\ddagger$  and  $E^*$  independent of whether the mode directly couples to bond scission.

$$k_2(E^*) = \frac{1}{h_P} \left( \frac{q_R^\ddagger}{q_{A^*}} \right) \frac{G_V^T(E^*)}{N_V(E^*)}$$

(9.128)

where  $G_V^T(E^*)$  is the number of vibrational states at the transition state, with an energy between  $E^\ddagger$  and  $E^*$ .  $N_V(E^*) \delta E^*$  is the number of vibrational states of the reactants with an energy between  $E^*$  and  $(E^* + \delta E^*)$ ;  $q_R^\ddagger$  is the rotational partition function for the transition state and  $q_{A^*}$  is the rotational partition function for the excited products.

Note

$$G^T(E^*) = \int_{E^\ddagger}^{E^*} N^T(E^*) dE^*$$

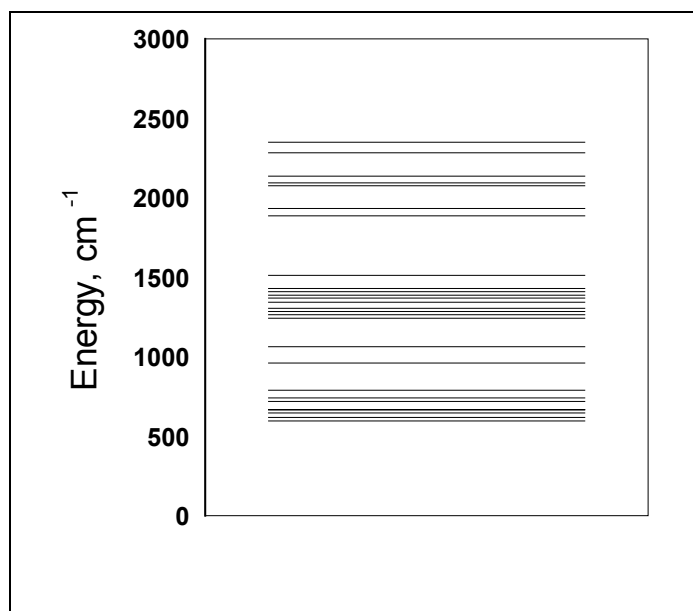
(9.129)

Qualitative results:

$$G^0(E^*) = \sum_n g_n$$

(9.130)

$G^0(E)$  is the number of states, not just number with enough energy to get over TST



**Figure 9.19** The vibrational levels of methyl chloride. From Pearson, Rabonowitz and Whitten, *J.Phys Chem* 42 2470 (1965).

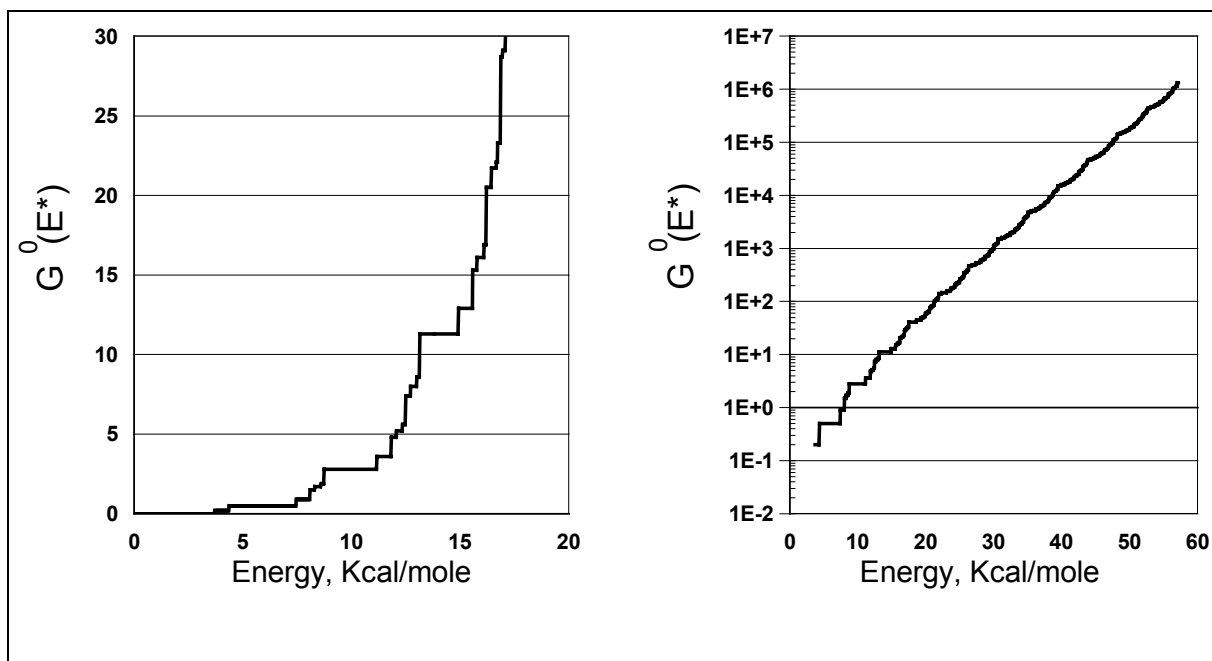


Figure 9.20  $G^0(E^*)$  for the vibrations of methane.

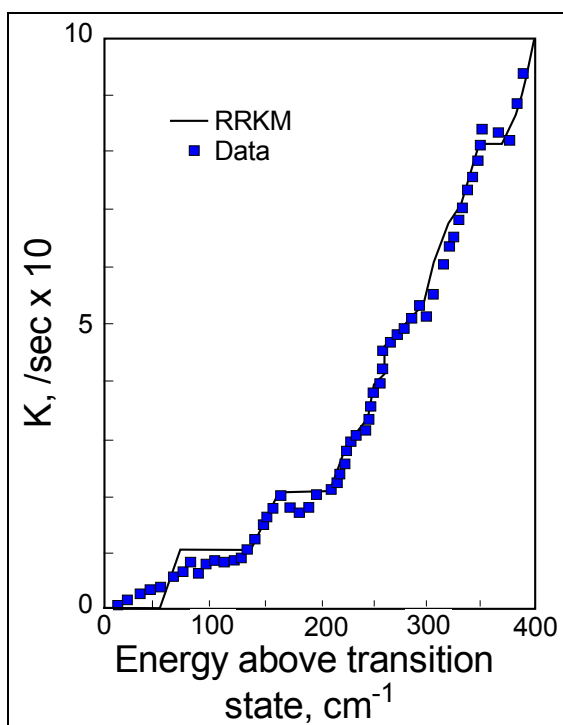
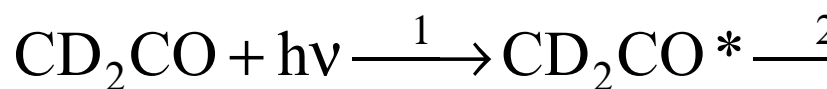
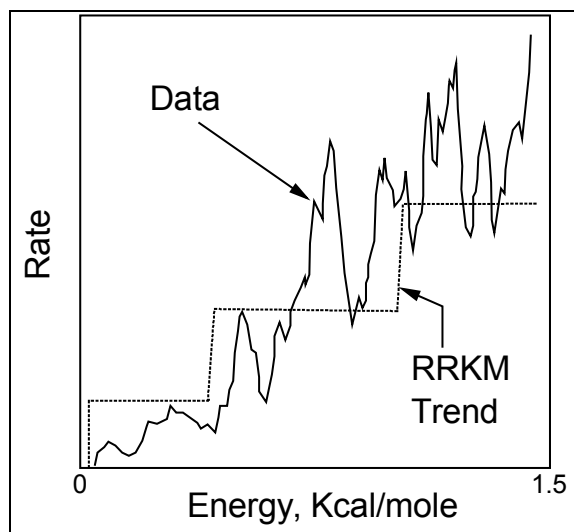


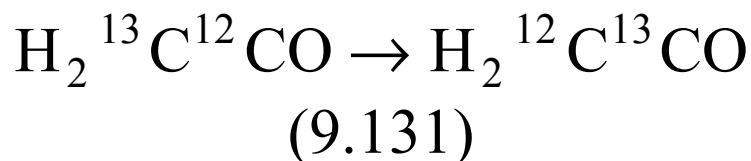
Figure 9.21 A plot of  $G^{\ddagger}(E^*)$  and  $K_2(E^*)$  for reaction (9.107).



(9.107)

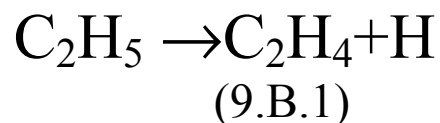


**Figure 9.22** A plot of  $K_2(E^*)$  for reaction (9.131).



### Example 9.B. AN RRKM CALCULATION

In Section 8.9 we noted that RRKM calculations are often used to model photolysis reactions. In this example we will calculate  $k_{A \rightarrow BC}$  for the reaction



for  $E^*$  between  $13046 \text{ cm}^{-1}$  (37.3 kcal/mole) and  $15046 \text{ cm}^{-1}$  (43 kcal/mole).

**Table 9.B.1** Data for the reaction  $\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$  from Gilbert and Smith [1990]

	<b>Reactants</b>	<b>Transition State</b>
<b>Vibrational Frequencies</b> $\text{cm}^{-1}$	111 409 851 1007 1099 1295 1527 1589 1618 1625 3123 3193 3229 3268 3373	409 432 863 895 996 1026 1305 1328 1583 1682 3278 3365 3302 3392
<b>Rotational Modes</b> $\text{cm}^{-1}$	0.713 (1,2) 3.44 (1,1)	0.769 (1,2) 2.68 (1,1)
<b><math>E^\ddagger</math></b>		$13046 \text{ cm}^{-1}$ (37.3 kcal/mole)

Note: The notation 0.769 (1,2) means that the rotational mode has a degeneracy of 2 and a  $\sigma$  of 1 and a frequency of  $0.769 \text{ cm}^{-1}$ .

## Solution:

According to Equation 9.129

$$k_{A \rightarrow BC} = \frac{1}{h_p} \frac{G_V^\ddagger(E^*)}{N_V(E^*)} \frac{q_r^\ddagger}{q_{rA}^\ddagger} \quad (9.B.2)$$

There are two common ways to calculate  $G_V^\ddagger(E^*)$  and  $N_V(E^*)$ : the Beyer-Swinehart direct count algorithm, and the semi-classical approximation of Marcus-Rice and Whitten-Rabinovich. The following is a computer program to do the direct count.

Computer Program for Problem 9.B
----------------------------------

```

Program Beyer_Swinehart
C! density of vibrational states by
C! Beyer-Swinehart algorithm
implicit none
integer(2), parameter ::
MODES=15
integer(2), parameter ::
points=5000
integer(2):: vibr_freq(MODES)
integer(2)::
vibr_degen(MODES)
integer i, j
integer(2):: start_frequency=0
real(8) n(0:points)
real(8) g(0:points), x, y
real :: energy_scale=2.
c!energy_scale equals spacing for
energy bins IN cm-1
data vibr_freq
/111,409,851,1067,1099,
1
1295,1527,1589,1618,1625,3123,
2 3193,3229,3268,3373/
data vibr_degen/ 15*1/
do 5 i=1,MODES
vibr_freq(i)=vibr_freq(i)/energy
_scale
5 enddo
start_frequency=start_frequenc
y/
energy_scale
C! next initialize arrays
do 2 i=1,points
n(i)=0
g(i)=1
2 enddo
n(0)=1
g(0)=1

```

```

c! count the number of modes
do 10 j=1,MODES
do 9 i=vibr_freq(j),points
n(i)=n(i)+n(i-
vibr_freq(j))*vibr_degen(j)
g(i)=g(i)+g(i-
vibr_freq(j))*vibr_degen(j)
if(mod(i,500).eq.0)write(*,*)i,n(i)
9 enddo
10 enddo
n(0)=0.
c! next write data in format for
microsoft Excel, lotus
open(unit=8,file="statedens.csv
",status=
"replace",action="write")
write(8,101)
write(8,102)
101 format("'E', 'E','N(E)','G(E)'"')
102 format("'cm-
1/molecule','kcal/mole','/cm-
1','dimensionless'")
do 20
I=start_frequency,points,100
x=I*energy_scale
y=x*2.859e-3
n(i)=n(I)/energy_scale
g(i)=g(I)-1.0
write(8,100)x,y,n(i),g(i)
20 enddo
100 format(f9.1,', ',f9.3,', ',e15.7,',
',e15.7)
40 stop
end

```



The program calculates  $n(E^*)$  by dividing the energy scale into a series of cells and counting how many vibrational bands are in each cell. The algorithm goes through with the lowest frequency and puts a 1 in each cell where the frequency or its overtone arise. It then goes through with the second frequency and adds one to the cell if the cell is an overtone, or if some combination of the previous frequencies are in the cell. The effect is a complete count of the number of frequencies contributing to the cell. The algorithm only takes 15 seconds on a Pentium PC, so it is quite robust. I recommend that you use the direct count method for RRKM calculations.

Still, I want to note that there are several analytical approximation for  $n(E^*)$  and  $G(E^*)$ . There are several in the literature. The simplest approximation comes from classical mechanics

$$G(E^*) = \frac{(E^*)^S}{(S)! \prod h_p \nu_i}$$

(9.B.3)

$$N(E^*) = \frac{dG(E^*)}{dE^*} = \frac{(E^*)^{S-1}}{(S-1)! \prod h_p \nu_i}$$

(9.B.4)

Marcus and Rice showed that a better approximation is

$$G(E^*) \frac{(E^* + \alpha E_Z)^S}{S! \prod h_p \nu_i}$$

(9.B.5)

Where  $\alpha$  is a constant between 0 and 1, and  $E_Z$  is the zero point energy

$$E_Z = \frac{h_p}{2} \sum \nu_i$$

(9.B.6)

Marcus and Rice assume that  $\alpha$  is a constant: typically 1.0. Whitten and Rabinovich proposed different approximations where it is assumed that  $\alpha$  varies via the following formula:

$$\alpha = 1 - \beta W\left(\frac{E^*}{E_Z}\right)$$

$$\beta = (S-1) \frac{\sum_i v_i^2}{\left(\sum_i v_i\right)^2}$$

(9.B.7)

$$W\left(\frac{E^*}{E_Z}\right) = 1 / \left( 5\left(\frac{E^*}{E_Z}\right) + 2.73\left(\frac{E^*}{E_Z}\right)^{0.75} + 3.51 \right) \text{ for } \frac{E^*}{E_Z} \leq 1$$

$$\exp\left(-2.4191\left(\frac{E^*}{E_Z}\right)\right) \text{ for } \frac{E^*}{E_Z} > 1$$

(9.B.8)

I do not like any of these approximations so I always use the direct count method. Getting back to problem 9.B, first I ran the program and picked out the values of  $n(E^*)$  for energies between  $13046 \text{ cm}^{-1}$  and  $15046 \text{ cm}^{-1}$ . Then I re-ran the program, put in the vibrational modes of the transition state and looked at the region between 0 and  $2000 \text{ cm}^{-1}$ . (Note: the barrier is  $13046 \text{ cm}^{-1}$ , so if the total energy is  $14046 \text{ cm}^{-1}$ , the transition state will only have  $1000 \text{ cm}^{-1}$  of vibrational energy. Table 9.B.2 shows some of these results.

**Table 9.B.2 – Calculated Values of  $n(E^*)$  and  $G(E^*)$** 

$E^*, \text{cm}^{-1}$	$N_v(E), \text{cm}^{-1}$	$E^* - E_1^\ddagger, \text{cm}^{-1}$	$G_v^T(E^*-E_1^\ddagger)$	$K, \text{sec}^{-1}$
13046	3818	0	0	0
13246	4286	200	0	0
13446	4807	400	0	0
13646	5388	600	2	$1.17 \times 10^7$
13846	6044	800	2	$1.04 \times 10^7$
14046	6758	1000	8	$3.73 \times 10^7$
14246	7485	1200	9	$3.79 \times 10^7$
14476	8443	1400	19	$7.10 \times 10^7$
14696	9439	1600	24	$8.02 \times 10^7$
14846	10513	1800	43	$1.29 \times 10^8$
15046	11715	2000	55	$1.48 \times 10^8$

Next, let's calculate  $k$ . First let's calculate

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma_A \sigma_B \sigma_C} \left( \frac{8\pi I_A k_B}{h_p^2} \right)^{1/2} \left( \frac{8\pi I_B k_B}{h_p^2} \right)^{1/2} \left( \frac{8\pi I_C k_B T}{h_p^2} \right)^{1/2}$$

(9.B.9)

Where  $I_A$ ,  $I_B$  and  $I_C$  are the three moments of inertia,  $\sigma_A$ ,  $\sigma_B$  and  $\sigma_C$  are the symmetry factors,  $h_p$  is Plank's Constant,  $k_B$  is Boltzman's constant and  $T$  is temperature.

The rotational frequency  $\omega_r$  satisfies

$$\omega_r = \frac{h_p}{8\pi I_A}$$

(9.B.10)

SO

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma_A \sigma_B \sigma_C} \left( \frac{(k_B T)^3}{\omega_r^A \omega_r^B \omega_r^C} \right)^{1/2}$$

(9.B.11)

Where  $\omega_r^A$ ,  $\omega_r^B$  and  $\omega_r^C$  are the rotational frequencies of the reactants. Plugging equation (9.B.11) and an equivalent equation for  $q_{\ddagger}$  into equation (9.B.3) yields

$$k_2 = \frac{G_v^T(E^* - E_{\ddagger}^{\ddagger})}{h_p N_v(E^*)} \left( \frac{\sigma_A \sigma_B \sigma_C}{\sigma_{\ddagger}^A \sigma_{\ddagger}^B \sigma_{\ddagger}^C} \right) \left( \frac{\omega_A \omega_B \omega_C}{\omega_{\ddagger}^A \omega_{\ddagger}^B \omega_{\ddagger}^C} \right)^{1/2}$$

(9.B.12)

Next, let's substitute numbers in the equation (9.B.12) for  $E^* = 15046 \text{ cm}^{-1}$ . Taking numbers from Table 9.B.2 and noting  $h_p = 3.33 \times 10^{-11} \text{ (cm}^{-1}\text{)-sec.}$  yields

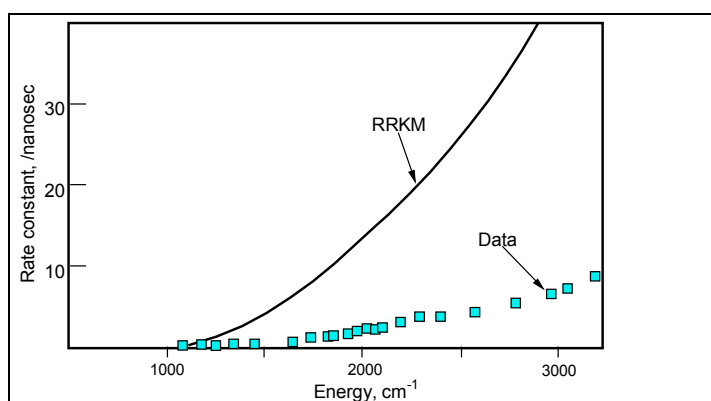
$$k_2 = \frac{55}{\left(\frac{(1175)}{\text{cm}^{-1}}\right) \left(3.33 \times 10^{-11} (\text{cm}^{-1})\text{-sec}\right)} \left( \frac{(344)(0.713)(0.713)}{(268)(0.769)(0.769)} \right)^{1/2}$$

**(9.B.13)**

doing the arithmetic shows,  $k_2 = 1.48 \times 10^8 / \text{sec}$ .

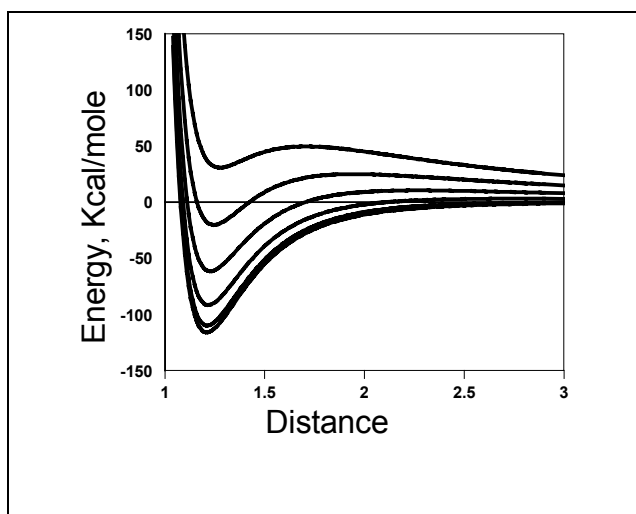
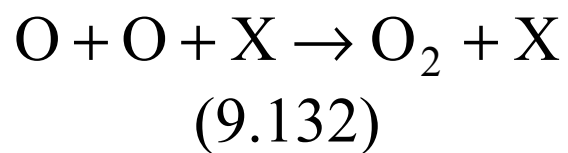
Does RRKM always work?

No - it assumes all states with enough energy to cross barrier contribute with unity reaction probability - actually some states have higher probability than others



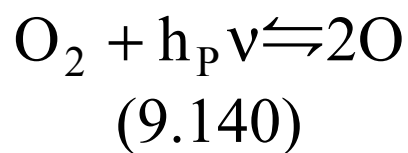
**Figure 9.23** A comparison of the experimental rate of isomerization of stilbene to the predictions of the RRKM model.

Also fails for barrierless reactions:



**Figure 9.25** A plot of  $V_{\text{eff}}$  as a function of  $b_{\text{A} \rightarrow \text{BC}}$ , for  $E_{\text{KE}} = 1 \text{ kcal/mole}$ .

$$k_{\text{A} \rightarrow \text{BC}} = \bar{v}_{\text{ABC}} \left( 2\pi (b_{\text{crit}})^2 \right) \quad (9.137)$$



$$k_{136} = 2\pi (b_{\text{crit}})^2$$



(9.141)

Quantum effects also matter (rotations quantized)