Chapter 7 Summary
Reaction Rate Theory

- Collision theory - simple model for preexponential
- Transition state theory - better model for preexponential - bimolecular
- RRKM - better model for preexponential - unimolecular

All models based on Arrhenius Model

$$A \rightarrow B \tag{7.1}$$

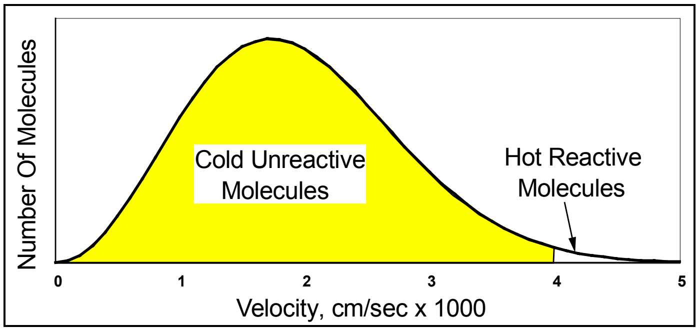


Figure 7.1 The Boltzmann distribution of molecular velocities**.**

Cold unreactive molecules
Hot reactive molecules
Assume equilibrium between cold and hot molecules

Collision theory: Molecules react whenever molecules collide with enough total energy

Next derive equation for rate. Consider

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

(7.9)

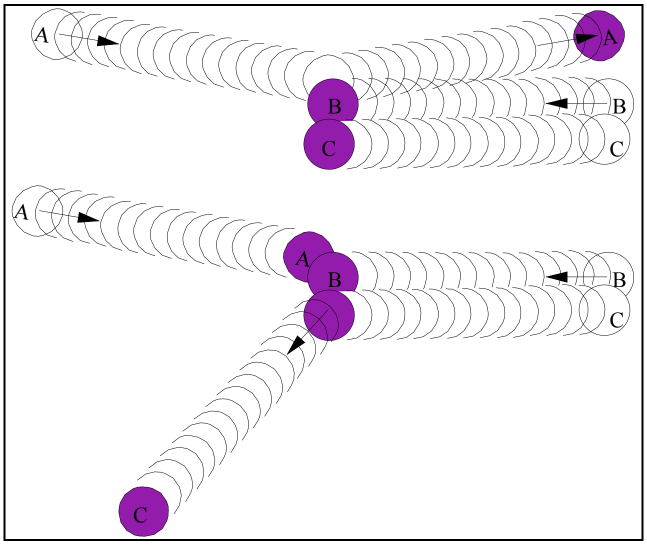


Figure 7.2 A collision between an A molecule and BC molecules.

Equilibrium between hot and cold molecules

$$C_A^{\dagger} = C_A^{u}\, e^{-\left(\frac{\Delta G^{\dagger}}{k_B T}\right)}$$

(7.2)

Derivation shows

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

(7.10)

$$P_{reaction} = e^{-\Delta G^{\dagger}/k_B T}$$

(7.11)

$$\boxed{r_{A\to BC} = Z_{ABC} e^{-\Delta G^{\dagger}/k_B T}}$$

(7.12)

$$Z_{ABC} = \overline{v}_{A\to BC} C_A C_{BC} \sigma^{c}_{A\to BC}$$

(7.22)

where $\overline{v}_{A\to BC}$ is the average velocity of A toward BC. Equation (7.22) gives the total rate of collisions between hot A molecules and hot BC molecules.

Substituting equations (7.5) and (7.19) into equation into equation (7.12) yields:

$$r_{A\rightarrow BC} = \left(\bar{v}_{A\rightarrow BC}\sigma^{c}_{A\rightarrow BC}e^{\Delta S^{\dagger}/k_B}\right)\left(e^{-\Delta H^{\dagger}/k_B T}\right)C_A C_{BC}$$

(7.23)

where $\bar{v}_{A\rightarrow BC}$ is the average velocity of A moving toward BC.

$$k_0 = \bar{v}_{A\rightarrow BC}\sigma^{c}_{A\rightarrow BC}e^{\Delta S^{\dagger}/k_B}$$

(7.25)

Equation 7.25 is the a classical version of Tolman's equation. It is an excellent approximation.

Collision theory and collision theory approximate $\Delta S^\dagger$ and $\Delta H^\dagger$

	Collision Theory	Transition state theory
Approximation to $\Delta S^\dagger$	0	Transition state entropy
Approximation to $\Delta H^\dagger$	???	Transition state energy
Approximation to $\bar{v}_{A\to BC}$	$\left(\frac{8kT}{\pi\mu_{ABC}}\right)^{1/2}$	$\left(\frac{8kT}{\pi\mu_{ABC}}\right)^{1/2}$

Note:

$$\frac{1}{\mu_{ABC}}=\frac{1}{m_A}+\frac{1}{m_B+m_C}$$

(7.28)

and m_A, m_B and m_C are the masses of A, B and C in atomic mass units (1 AMU = 1.66×10^{-24}g).

I find it convenient to rewrite equation (7.27) as:

$$\bar{v}_{ABC} = 2.52 \times 10^{13}\,\frac{\text{Å}}{\sec}\left(\frac{T}{300K}\right)^{1/2}\left(\frac{1\text{AMU}}{\mu_{ABC}}\right)^{1/2}$$

(7.29)

Example 7.A A Collision Theory Calculation

Use collision theory to calculate the preexponential for the reaction:

$$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$$

(7.A.1)

at 500K.

Solution: According to collision theory:

$$k_0 = \pi d_{coll}^2 \, \bar{v}_{ABC}$$

(7.A.2)

First let us calculate $\bar{v}_{ABC}$

According to equation (7.26):

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

(7.A.3)

with

$$\mu_{ABC} = \frac{1}{\frac{1}{M_A} + \frac{1}{M_{BC}}}$$

(7.A.4)

For reaction (7.A.1):

$$\mu_{A\text{-}BC} = \frac{1}{\frac{1}{1\text{AMU}} + \frac{1}{30\text{AMU}}} = 0.968\text{AMU}$$

(7.A.5)

Plugging in the numbers shows that at 500K:

$$\bar{v}_{ABC} = 2.4 \times 10^{13} \left(\frac{500\text{K}}{300\text{K}}\right)^{1/2} \left(\frac{1\text{AMU}}{.968\text{AMU}}\right) = 3.15 \times 10^{13}\,\text{Å} / \sec$$

(7.A.6)

There is some question about what values of d_{coll} to use in the calculation. Hydrogen has a Van der Waals diameter of 1.5Å, while ethane has a Van der Waals diameter of 3.5 Å. One approximation to d_{coll} is:

$$d_{coll} = \frac{1.5\text{Å} + 3.5\text{Å}}{2} = 2.5\text{Å}$$

(7.A.7)

Substituting (7.A.5) and (7.A.6) into equation (7.A.2) yields:

$$k_0 = \pi \frac{(2.5\text{Å})^2}{\text{molecule}}\left(3.15 \times 10^3 \text{Å} / \text{sec}\right) = 6.18 \times 10^{14} \frac{\text{Å}^3}{\text{molecule - sec}}$$

(7.A.8)

Predictions of collision theory

Table 7.1 Molecular Velocities and Collision Diameters for a Number of Molecules at 273 K.

Molecule	Molecule Velocity Å/sec	Collision Diameter Å
He	1.2×10^{13}	2.2
N_2	4.5×10^{12}	3.5
O_2	4.2×10^{12}	3.1
H_2O	5.6×10^{12}	3.7
C_2H_6	4.37×10^{12}	3.5
C_6H_6	2.7×10^{12}	5.3

$$k_o = (4\times10^{12}\text{Å/sec}) \times (\pi(3\text{Å})^2) = 1.1 \times 10^{14}\ \text{Å}^3\text{/sec}$$

Table 7.2 A selection of the preexponentials reported by Wesley[1980].

Reaction	Preexponential Å^3/molecule Sec	Reaction	Preexponential Å^3/molecule Sec
$H+C_2H_6 \rightarrow C_2H_5+H_2$	1.6×10^{14}	$O+C_2H_6 \rightarrow OH+C_2H_5$	2.5×10^{13}
$H+CH \rightarrow H_2+C$	1.1×10^{12}	$O+C_3H_8 \rightarrow (CH_3)_2CH+OH$	1.4×10^{10}
$H+CH_4 \rightarrow H_2+CH_3$	1×10^{14}	$O_2+H \rightarrow OH+O$	1.5×10^{14}
$O+H_2 \rightarrow OH+H$	1.8×10^{13}	$OH+OH \rightarrow H_2O+O$	1×10^{13}
$O+OH \rightarrow O_2+H$	2.3×10^{13}	$OH+CH_4 \rightarrow H_2O+CH_3$	5×10^{13}
$O+CH_4 \rightarrow CH_3+OH$	2.1×10^{13}	$OH+H_2CO \rightarrow H_2O+HCO$	5×10^{13}
$O+CH_3 \rightarrow H+CH_3O$	5×10^{13}	$OH+CH_3 \rightarrow H+CH_3O$	1×10^{13}
$O+HCO \rightarrow H+CO_2$	5×10^{12}	$OH+CH_3 \rightarrow H_2O+CH_2$	1×10^{13}

Table 7.3 Preexponentials calculated from equation (7.30) for a number of reactions compared to experimental data.

Reaction	Calculated Preexponential assuming b_{coll}=van Der Waals radius Å^3/molec sec	Calculated Preexponential assuming b_{coll}=covalent radius Å^3/molec sec	Experimental Preexponential
$H+C_2H_6 \rightarrow C_2H_5H_2$	6.2×10^{14}	2.0×10^{14}	1.6×10^{14}
$H+CH \rightarrow H_2+C$	4×10^{14}	2.0×10^{14}	1.1×10^{12}
$O+C_2H_6 \rightarrow OH+C_2H_5$	1.9×10^{14}	7.6×10^{13}	2.5×10^{13}
$OH+OH \rightarrow H_2O+O$	1.25×10^{14}	5.8×10^{13}	1×10^{13}
$H+O_2 \rightarrow OH+O$	4.0×10^{14}	2×10^{14}	1.5×10^{14}

$$\mathrm{CH_3CH_2CH_3 + O\!:\rightarrow CH_3\overset{\bullet}{C}HCH_3 + \bullet OH}$$

(7.30)

$k_o = 1.4\times10^{10}$ Å^3/molecule-sec

$$\mathrm{2O_2 \rightarrow 2O\bullet + O_2}$$

(7.31)

$k_o = 5.8\times10^{15}$ Å^3/molecule-sec

Reaction 7.30 requires a special collision geometry:

$$\begin{aligned} \mathrm{CH_3CH_2CH_3 + O\!:} \quad & \mathrm{\rightarrow CH_3\overset{\bullet}{C}HCH_3 + \bullet OH} && \text{(a)} \\ & \mathrm{\rightarrow \bullet CH_2CH\ CH_3 + \bullet OH} && \text{(b)} \end{aligned}$$

(7.32)

$$\text{configurations} = \exp\left(S / k_B\right)$$

(7.33)

$$\exp\left(\Delta S^{\dagger} / k_B\right) = \frac{\text{configurations which lead to reaction}}{\text{average number of configurations of the reactants}}$$

(7.34)

Summary:

Collision theory: reaction occurs whenever reactants collide.

Gives correct order of magnitude or slightly high pre-exponential

Some spectacular failures

Next Transition state theory Next Transition state theory - also called
conventional transition state theory (CTST)

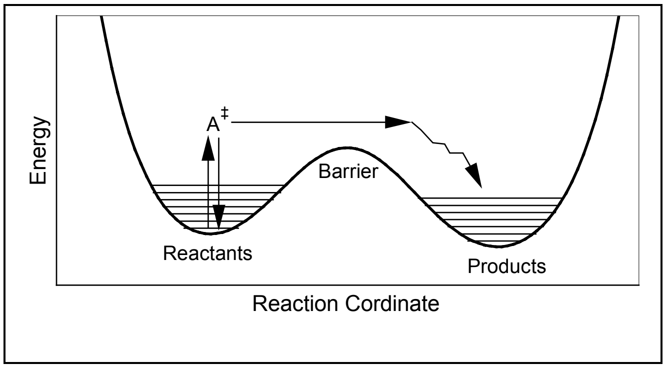


Figure 7.5 Polanyi's picture of excited molecules.

	Collision Theory	Transition state theory
Approximation to $\Delta S^{\dagger}$	0	Transition state entropy
Approximation to $\Delta H^{\dagger}$	???	Transition state energy
Approximation to $\overline{v}_{A\to BC}$	$\left(\frac{8kT}{\pi\mu_{ABC}}\right)^{1/2}$	$\left(\frac{8kT}{\pi\mu_{ABC}}\right)^{1/2}$

Again this is an approximation:

Activation energy not exactly TST energy:
Recall: activation energy = the average energy of the molecules which react.

- Hot molecules have higher reaction probability - this raises the average energy of the molecules which react to something above the top of the barrier
- Cold molecules have some probability of reacting due to a quantum mechanical effect called tunneling. This lowers the average energy of the molecules which react.

TST assumes that these two effects exactly cancel.

Entropy of activation = the average entropy of the species which react relative to the reactants - this is not exactly the transition state entropy.

Again there are two effects:

- In the reaction A +BC → AB + C TST assumes that only collisions where the incoming A molecule collides C lead to reaction. In fact the A molecule can collide with B, push B out of the way and then get C to leave. This effect raises the rate of reaction
- Conversely, when A - BC collide, you might not deposit enough momentum into the BC bond to carry C away. This effect leads to a lowering of the rate of reaction.

Again TST assumes that these two effects exactly cancel.

In reality, the two effects rarely exactly cancel so TST is an approximation.

$$\boxed{k_{A \to BC} = \left(\frac{k_B T}{h_P} \right) \frac{q_T^{\ddagger}}{q_A q_B} \exp\left(- E_T^{\ddagger} / k_B T \right)}$$

(7.43)

Example 7.C A True Transition State Theory Calculation

Use TST to calculate the rate of the reaction.

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

(7.C.1)

Table 7.C.1 Parameters used to calculate the transition state theory rate constant for $F + H_2 \rightarrow HF + H$. The exact parameters are also shown for comparison.

	Transition State		Reactants	
	Exact	Used for transition state calculations	F	H_2
r_{HF}	1.34Å	1.602Å		
r_{HH}	0.801Å	0.756Å		0.7417Å
υH-H stretch	about 3750cm^{-1}	4007cm^{-1}		4395.2cm^{-1}
υFH_2 Bend	?	397.9 cm^{-1}		
υFH_2 Bend	?	397.9 cm^{-1}		
Curvature barrier	?	310 cm^{-1}		
$E^{\ddagger}$	5.6 kcal/mole	1.7 kcal/mole		
M	21 AMU	21 AMU	19 AMU	2 AMU
I	5.48AMU-Å^2	7.09AMU-Å^2		0.275AMU-Å^2
g_e	4	4	4	1

According to transition state theory:

$$k_{F\rightarrow H_2}=\left(\frac{k_B T}{h_P}\right)\frac{q^{\ddagger T}_{F-H_2}}{q_{H_2}q_F}e^{-E_T^{\ddagger}/k_B T}$$

(7.C.2)

It is useful to divide up the partition functions in equation (7.C.2) into the contributions from the translation, vibration, rotation and electronic modes, i.e.,:

$$k_{F\rightarrow H_2}=\frac{k_B T}{h_P}1^{\ddagger}\left(\frac{q^{\ddagger}}{q_{H_2}q_F}\right)_{\text{trans}}\left(\frac{q^{\ddagger}}{q_{H_2}q_F}\right)_{\text{vibration}}\left(\frac{q^{\ddagger}}{q_{H_2}q_F}\right)_{\text{rotation}}\left(\frac{q^{\ddagger}}{q_{H_2}q_F}\right)_{\text{elect}}e^{-E_T^{\ddagger}/k_B T}$$

(7.C.3)

where $1^{\ddagger}$ is an extra factor of 2 that arises because there are two equivalent transition states, one with the fluorine attacking one hydrogen, and the other with one fluorine attaching the other hydrogen.

Now it is useful to use the results in Chapter 6 to calculate the various terms in equation (7.C.3). According to Table 6.5:

$$q_t = \left(\frac{2\pi m ķ_B T}{h_P^2} \right)^{1/2}$$

(7.C.4)

where q_t is the translational partition function for a single translational mode of a molecule, m is the mass of the molecule, $ķ_B$ is Boltzman's constant, T is temperature, and h_P is Plank's constant. For our particular reaction, the fluorine can translate in three directions; the H_2 can translate in three directions; the transition state can translate in three directions.

Consequently,:

$$\left(\frac{q^{\ddagger}}{q_{H_2} q_F}\right)_{\text{trans}} = \frac{\left(\frac{2\pi m_{\ddagger} k_B T}{h_P^2}\right)^{3/2}}{\left(\frac{2\pi m_F k_B T}{h_P^2}\right)^{3/2}\left(\frac{2\pi m_{H_2} k_B T}{h_P^2}\right)^{3/2}}$$

(7.C.5)

where m_F, m_{H_2} and $m_{\ddagger}$ are the masses of fluorine, H_2 and the transition state.

Performing the algebra:

$$\left(\frac{q^{\ddagger}}{q_F q_{H_2}}\right)_{\text{trans}} = \left(\frac{m_{\ddagger}}{m_F m_{H_2}}\right)^{3/2} \left(\frac{h_P^2}{2\pi k_B T}\right)^{3/2}$$

(7.C.6)

Let’s calculate the last term in equation (7.C.6). Rearranging the last term shows

$$\left(\frac{h_P^2}{2\pi k_B T}\right)^{3/2} = \left(\frac{300\text{K}}{T}\right)^{3/2} \left(\frac{h_P^2}{2\pi k_B (300^\circ \text{K})}\right)^{3/2}$$

(7.C.7)

Plugging in the numbers yields:

$$\left(\frac{h_P^2}{2\pi k_B T}\right)^{3/2} = \left(\frac{300\text{K}}{T}\right)^{3/2} \left(\frac{\left(6.626\times 10^{-34}(\text{kg})\text{m}^2 / \text{sec}\right)^2 \left(\frac{10^{10}\,\text{Å}}{\text{m}}\right)^2 \left(\frac{\text{AMU}}{1.66\times 10^{-27}\,\text{kg}}\right)}{2\pi\left(1.381\times 10^{-23}(\text{kg})\text{m}^2 / \text{sec}^2 \text{-}^\circ\,\text{K}\right)\left(300^\circ\,\text{K}\right)}\right)^{3/2}$$

(7.C.8)

Doing the arithmetic yields:

$$\left(\frac{h_P^2}{2\pi k_B T}\right)^{3/2} = \left(\frac{300\text{K}}{T}\right)^{3/2} 1.024\text{Å}^3\text{AMU}^{3/2}$$

(7.C.9)

Combining equations (7.C.6) and (7.C.9) yields:

$$\left(\frac{q^{\ddagger}}{q_F q_{H_2}}\right)_{\text{trans}} = \left(\frac{M_{\ddagger}}{(M_F)M_{H_2}}\right)^{3/2} \left(\frac{300\text{K}}{T}\right)^{3/2} \left(1.024\text{Å}^3\text{AMU}^{3/2}\right)$$

(7.C.10)

Setting T = 300K $M_{\ddagger}$ = 21AMU, M_F = 19$_{\text{AMU}}$, M_{H_2} = 2AMU yields:

$$\left(\frac{q^{\ddagger}}{q_F q_{H_2}}\right)_{\text{trans}} = \left(\frac{21\text{AMU}}{(19\text{AMU})2\text{AMU}}\right)^{3/2} 1.024\text{Å}^3\text{AMU}^{3/2} = 0.42\text{Å}^3$$

(7.C.11)

Next, let's calculate the ratio of the rotational partition functions. The fluorine atom does not rotate so:

$$\left(\frac{q^{\ddagger}}{q_{H_2}q_{F_2}}\right)_{rot} = \left(\frac{q^{\ddagger}}{q_{H_2}}\right)_{rot}$$

(7.C.12)

According to equation (6.5)

$$q_r = \frac{8K\,ķ_B\,T\,I}{h_P^3}$$

(7.C.13)

where $ķ_B$ is Boltzmann's constant, T is temperature, hp is Plank's constant and I is the moment of inertia of the molecule. Combining (7.C.12) and (7.C.13) yields

$$\left(\frac{q^{\ddagger}}{q_{H_2}}\right)_{rot} = \left(\frac{8\pi\,ķ_B\,T\,I^{\ddagger}/h_P^2}{8\pi\,ķ_B\,T\,I_{H_2}/h_P^2}\right) = \frac{I^{\ddagger}}{I_{H_2}}$$

(7.C.14)

Substituting in the adjusted value of $I^{\ddagger}$ and I_{H_2} from Table 7.C.1 yields:

$$\left(\frac{q^{\ddagger}}{q_{H_2}}\right)_{rot} = \frac{I^{\ddagger}}{I_{H_2}} = \frac{7.011\text{AMU} - \text{Å}^2}{0.275\text{AMU} - \text{Å}^2} = 25.8$$

(7.C.15)

Next, let's calculate the vibrational partition functions. According to Table 6.5:

$$q_v = \frac{1}{1 - \exp\left(-\frac{h_p \upsilon}{k_B\, T}\right)}$$

(7.C.16)

Let's first get an expression for the term in exponential in equation (7.C.16):

It is easy to show

$$\frac{h_p U}{\text{ķ}_B\ T} = \left(\frac{h_p(1CM^{-1})}{(\text{ķ}_B)(300^\circ K)}\right)\left(\frac{300^\circ K}{T}\right)\left(\frac{U}{1CM^{-1}}\right)$$

(7.C.17)

Plugging in values at h_p and ķ_B from the appendix yields.

$$\frac{h_P \upsilon}{\text{ķ}_B\ T} = \frac{\left(2.85\times10^{-3}\,\text{kcal / mole - cm}^{-1}\right)\left(1\text{cm}^{-1}\right)}{\left(1.980\times10^{-3}\,\text{kcal / mole}^\circ\text{K}\right)\left(300^\circ K\right)}\left(\frac{300^\circ K}{T}\right)\left(\frac{\upsilon}{1\text{cm}^{-1}}\right)$$

(7.C.18)

Note we actually used $h_P\mathbb{C}/\mathbf{N}_a$ and $\text{ķ}_B/N_a$ in equation (7.C.16), and not h_P where $\mathbf{N}_a$ is Avargado’s number and $\mathbb{C}$ is the speed of light, to get the units right. Doing the arithmetic in equation 7.C.18 yields:

$$\frac{h_P \upsilon}{\text{ķ}_B\ T} = \left(4.784\times10^{-3}\right)\left(\frac{300K}{T}\right)\left(\frac{U}{1CM^{-1}}\right)$$

(7.C.19)

Table 7.C.2 The vibrational partition function.			
Mode	υ	$h_P\upsilon/k_BT$	q_v
$q^{\ddagger}_{HH}$	4395.2 cm^{-1}	21.	1.0
$(q_{HH})_{H_2}$	4007 cm^{-1}	19.2	1.0
$q^{\ddagger}_{Bend}$	379.9 cm^{-1}	1.82	1.19

Table 7.C.2 shows numerical values for various values of υ. The vibrational partition function ratio equals:

$$\left(\frac{q^{\ddagger}}{q_{H_2}}\right)_{vib} = \frac{q^{\ddagger}_{HH}q^{\ddagger}_{Bend}q^{\ddagger}_{Bend}}{(q_{H-H})_{H_2}} = \frac{(1)(1.19)(1.19)}{1} = 1.42$$

(7.C.20)

Next, let's calculate the ratio of the partition functions for the electronic state. Let's only consider the ground electronic state:

$$\left(\frac{q^{\ddagger}}{q_{H_2}q_F}\right)_{elec} = \frac{g^{\ddagger}_e}{(g_e)_{H_2}(g_e)_F} = \frac{4}{1\times4} = 1$$

(7.C.21)

Finally, let’s calculate $k_B T/h_P$:

$$\frac{k_B\,T}{h_P} = \frac{\left(1.381\times 10^{-23}\,\mathrm{Kg}-\mathrm{M}^2\ /\ \mathrm{sec\text{-}mole}^\circ\mathrm{K}\right)\left(300^\circ\,\mathrm{K}\right)}{\left(6.626\times 10^{-30}\,\mathrm{Kg}-\mathrm{M}^2\ /\ \mathrm{sec}\right)}\left(\frac{\mathrm{I}}{300^\circ\,\mathrm{K}}\right) = 6.05\times 10^{12}\ /\ \mathrm{sec}\left(\frac{T}{300\mathrm{K}}\right)$$

(7.C.22)

Putting this all together, allows one to calculate a preexponential:

$$k_o = 1^{\ddagger}\left(\frac{k_B\,T}{h_P}\right)\left(\frac{q^{\ddagger}}{q_{H_2}q_F}\right)_{\text{trans}}\left(\frac{q^{\ddagger}}{q_{H_2}q_F}\right)_{\text{rot}}\left(\frac{q^{\ddagger}}{q_{H_2}q_F}\right)_{\text{vib}}\left(\frac{q^{\ddagger}}{q_{H_2}q_F}\right)_{\text{elec}}$$

(7.C.23)

Plugging in the numbers:

$$k_o = 2\left(6.65\times 10^{12}\ /\ \mathrm{molecule}-\mathrm{sec}\right)\left(0.42\text{Å}^3\right)(25.8)(1.42)(1) = 2.05\times 10^{14}\ \text{Å}^3\ /\ \mathrm{molecule}-\mathrm{sec}$$

(7.C.24)

If one uses the actual transition state geometry, the only thing that changes significantly is the rotational term. One obtains:

$$\left(\frac{q^{\ddagger}}{q_{H_2}}\right)_{rot} = \left(\frac{I^{\ddagger}}{I_{H_2}}\right)_{rot} = \frac{5.48\left(\mathrm{AMU} - \text{Å}^2\right)}{0.275\left(\mathrm{AMU} - \text{Å}^2\right)} = 19.9$$

(7.C.25)

k_o becomes:

$$k_o = 2\left(6.65 \times 10^{12}\ /\ \mathrm{molecule} - \mathrm{sec}\right)\left(0.42\text{Å}^3\right)(18.9)(1.4)(1) = 1.56 \times 10^{14}\ \text{Å}^3\ /\ \mathrm{molecule} - \mathrm{sec}$$

(7.C.26)

One can also calculate the pre-exponential via old collision theory. In collision theory, one considers the translations and rotations, but not the vibrations., i.e.,:

$$k_0 = 1^{\ddagger}\left(\frac{k_B\,T}{h_p}\right)\left(\frac{q^{\ddagger}}{q_{H_2} q_F}\right)_{trans}\left(\frac{q^{\ddagger}}{q_{H_2} q_F}\right)_{rot}$$

(7.C.27)

in equation (7.C.26), the rotational partition function should be calculated at the collision diameter and not the transition state geometry.

If we assume a collision diameter of 2.3 Å (i.e., the sum of the Van der Wall radii) we obtain:

$$I^{\ddagger} = \left(r_{F-H_2}\right)^2 \left(\mu_{FH_2}\right) = \left(2.31\text{Å}\right)^2 \left(\frac{(2\text{AMU})(19\text{AMU})}{21\ \text{AMU}}\right) = 9.57\text{Å}^2\text{AMU}$$

(7.C.28)

Plugging into equation 7.C.25 using the results above:

$$k_o = 2\left(6.65\times10^{12}\ /\ \text{mole}-\text{sec}\right)\left(0.42\text{Å}^3\right)\left(\frac{9.57\text{Å}^2\text{AMU}}{0.275\text{Å}^2\text{AMU}}\right) = 1.9\times10^{14}\ \text{Å}^3\ /\ \text{mole}-\text{sec}$$

(7.C.29)

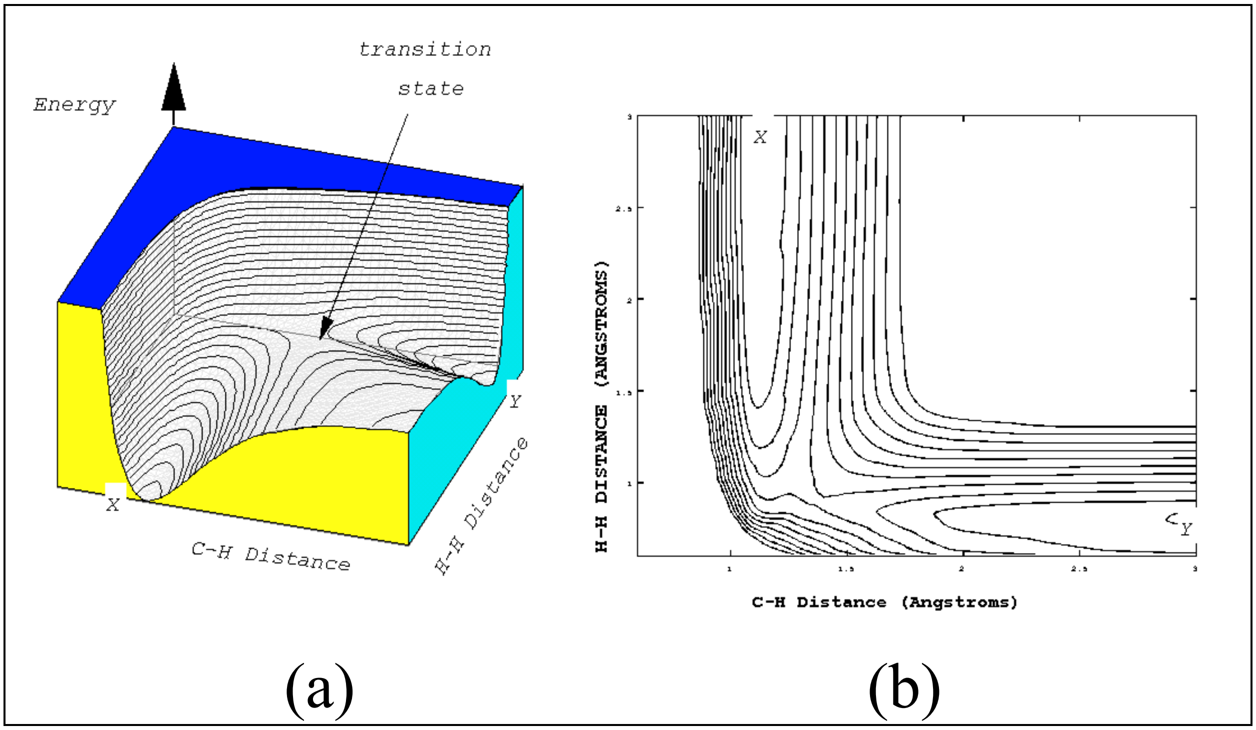
Table 7.C.3 A comparison of the preexponential calculated by transition state theory and collision theory to the experimental value.

k_o Transition state theory with adjusted transition state geometry	2.05×10^{14} Å^3/mole-sec
k_o Transition state theory with exact transition state geometry	1.65×10^{14} Å^3/mole-sec
k_o Collision theory	1.9×10^{14} Å^3/mole-sec
k_o Experiment	2.3×10^{14} Å^3/mole-sec

Transition state theory makes two corrections to collision theory:

1. Transition state theory uses the transition state diameter rather than the collision diameter in the calculation.
2. Transition state theory multiplies by two extra terms: the ratio of the vibrational partition function, and the electronic partition function for the transition state, and the reactants.

Review of PE surfaces



(a)

(b)

Figure 7.6 A potential energy surface for the reaction H + $CH_3OH \rightarrow H_2 + CH_2OH$ from the calculations of Blowers and Masel. The lines in the figure are contours of constant energy. The lines are spaced 5 kcal/mole apart.

Example 7.G Understanding contour plots

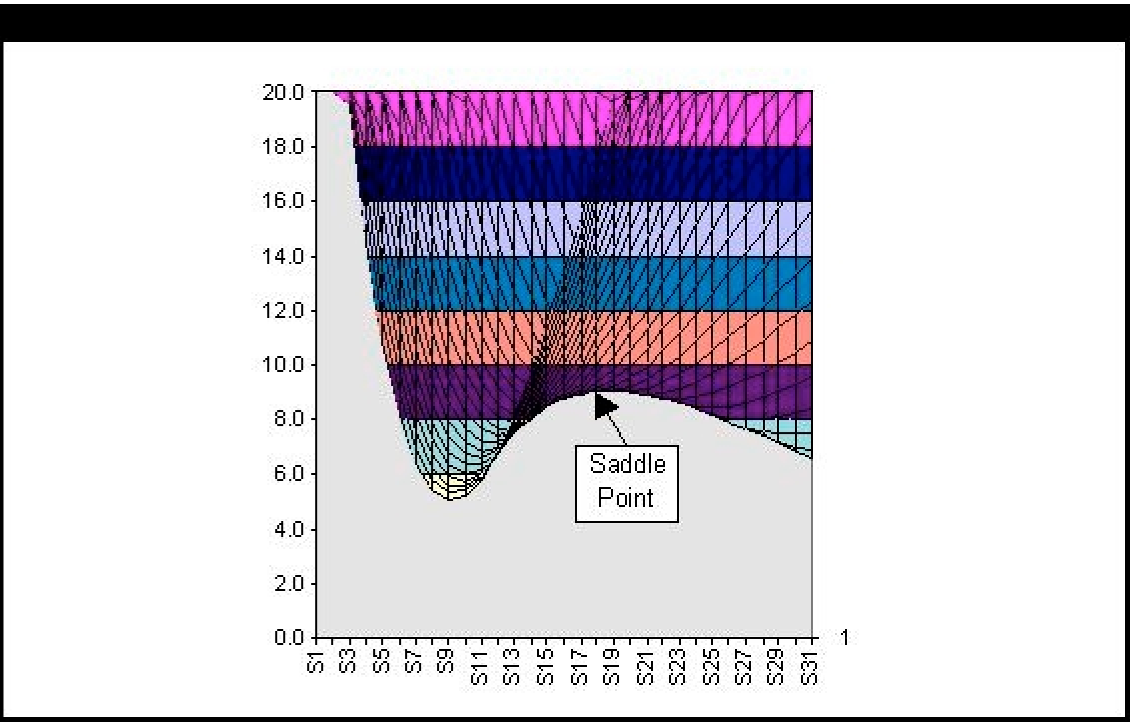
Consider a potential v defined by:

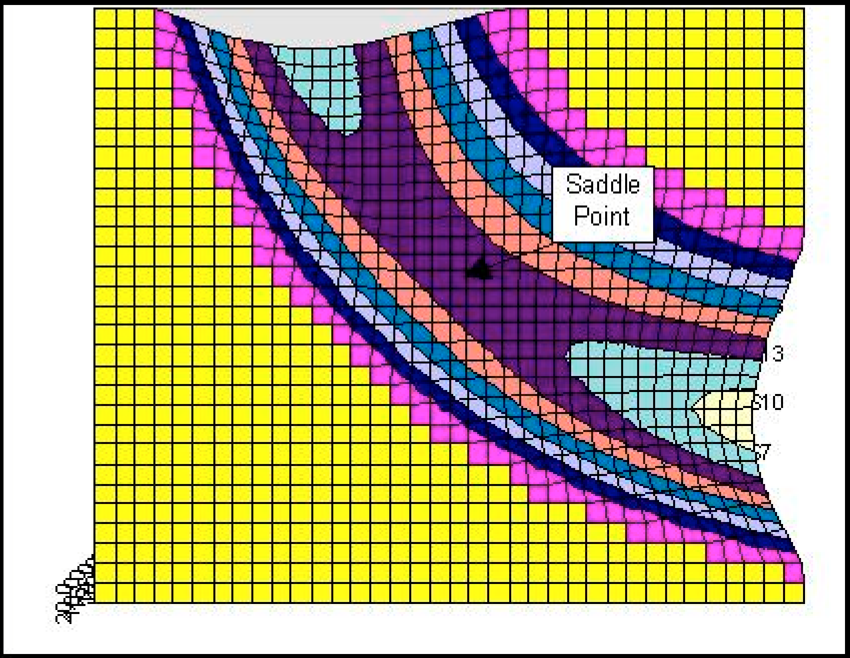
```
v(r1, r2, r0, a, w, vp, wa, hr)= w * (Exp(-2 * a * (r1 - r0)) - 2 * Exp(-a * (r1 - r0)))+
    (w+hr) * (Exp(-2 * a * (r2 - r0)) - 2 * Exp(-a * (r2 - r0)))+ vp * Exp(-a * (r1 + r2 - 2 * r0))+
        w + wa * Exp(-4*a * a * ((r1 - r0) ^ 2 + (r2 - 3 * r0) ^ 2)) +
        wa * Exp(-4*a * a * (((r1 - 3 * r0) ^ 2) + ((r2 - r0) ^ 2)))
                    If (v > 20+abs(hr)) Then
                         v = 20+abs(hr)
```

(7.G.1)

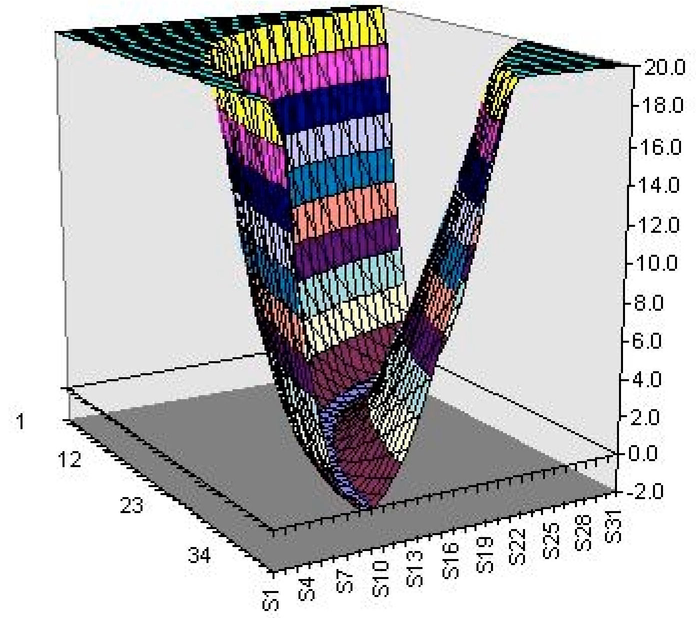
Make contour plots for the following function of r1 and r2 with parmeters r0,a,w, hr, vp,wa given by:

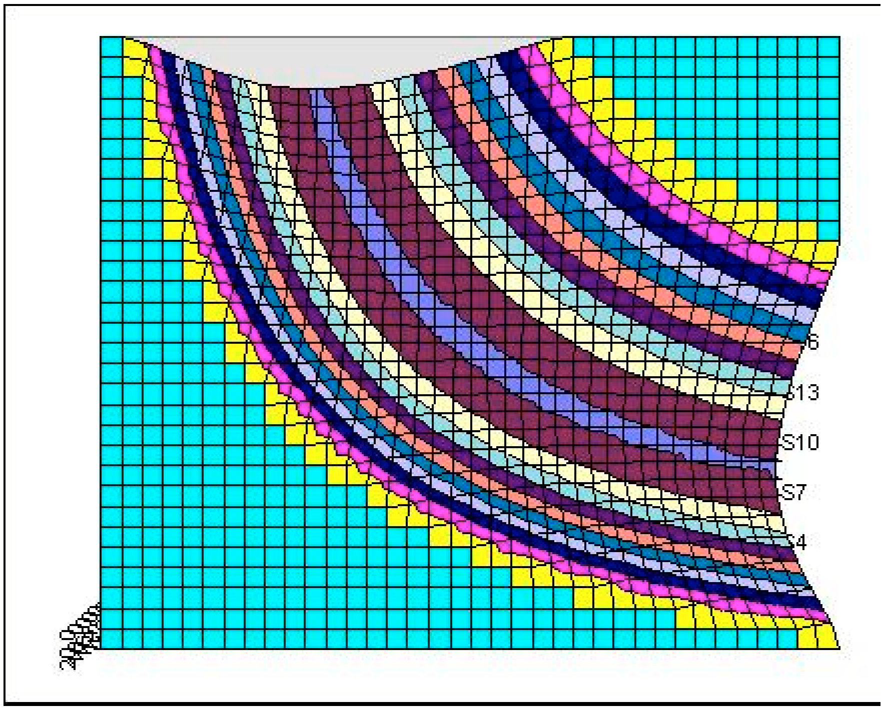
PE surface with a saddle point



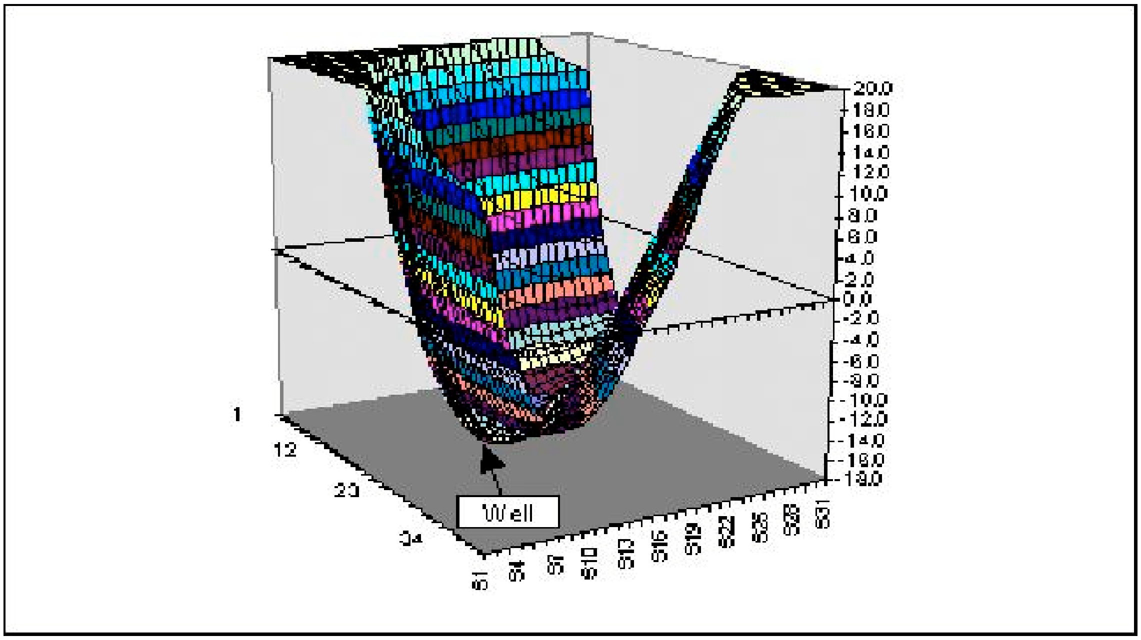


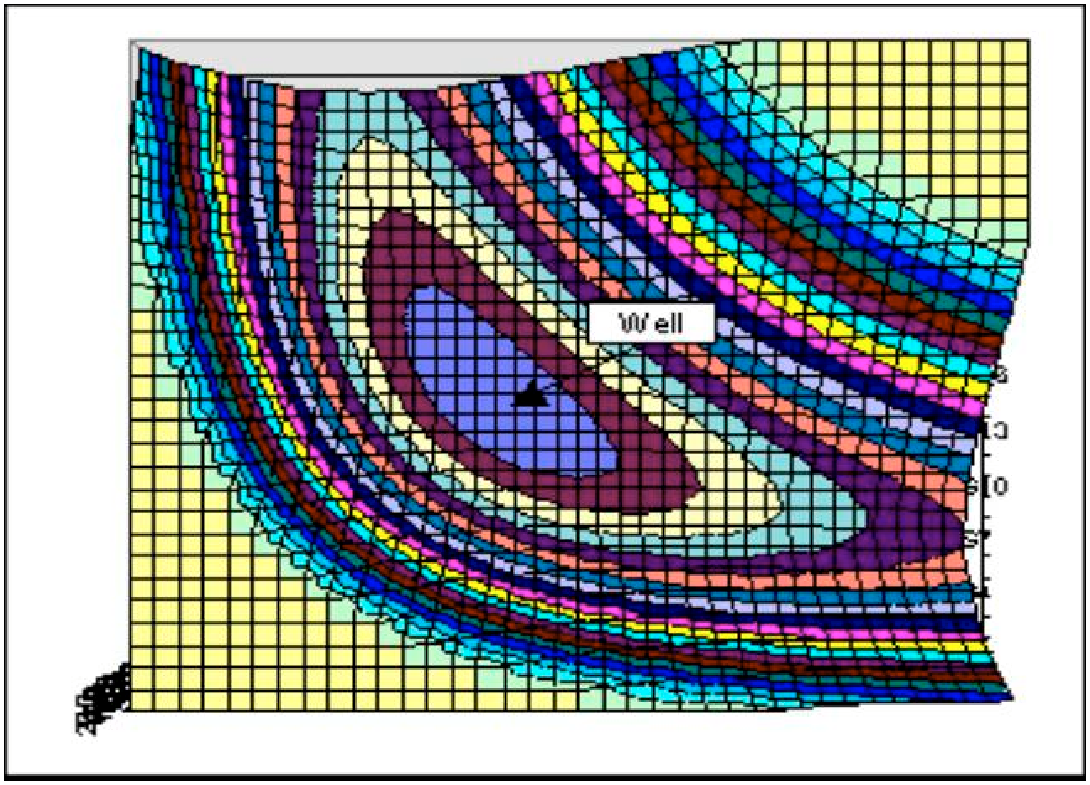
PE surface with no saddle point




6
S13
S10
S7
4

Potential with a well




Well

A more complex case