Summary Chapter 6
Review of some thermo and statistical mechanics

Key issues in chapter:

- Bond additivity as a way of estimating thermodynamic properties
    - Simple way to get approximate thermodynamic properties
- Statistical Mechanics
    - More exact, but computationally expensive way to get approximate thermodynamic properties
    - Needed for next few chapters

Bond additivity to estimate thermodynamic properties

- old fashioned idea
- 2-3 kcal/mole of well studied systems
- Good enough for mechanisms
- Not good enough for equilibrium const

The idea is to construct thermodynamic properties for a molecule as a sum of bond energies/bond contributions

Total energy= Σ atomic energies + Σ bond energies

Good to 0.1%. Ethane

- total energy is 42000 kcal/mole
- accurate to 42 kcal/mole

People actually use it by calculating relative properties. e.g heat of formation is total energy of molecule-total energy of elements. (small difference of big numbers). errors 1-5 kcal/mole

General there are a series of methods:

1) Method based on adding up effects of all bonds (CH, CC)
2) Method based on adding effects of all bonds accounting for the effects of local ligands
3) Method based on adding effects of all bonds accounting for the effects of groups

In practice these are the only ways to get accurate thermo for larger molecules (i.e. cases where QM takes too much computer time).

Simple bond additivity - only consider which bonds form

Table 6.1 The contribution of various bonds to key thermodynamic properties. Data of Benson[1976].

Bond	C_p, cal/mole°K	S cal/mole°K	ΔH_f, kcal/mole	Bond	C_p, cal/mole°K	S cal/mole°K	ΔH_f, kcal/mole
C—H	1.74	12.90	-3.83	C_D—C	2.6	-14.3	6.7
C—C	1.98	-16.40	2.63	C_D—H	2.6	13.8	3.2
C—F	3.34	16.9	-52.5	C_D—F	4.6	18.6	-3.9
C—O	2.7	-4.0	-12.0	C_D—C_D	—	—	7.5
O—H	2.7	24.0	-27.0	CO—H	4.2	26.8	-13.9
C—N	2.1	-12.8	9.3	CO—N	3.7	-0.6	-14.4
N—H	2.3	17.7	-2.6	C_B—H	3.0	11.7	3.25
C_B—C_B	—	—	10.0	C_B—C	4.5	-17.4	7.25

For CH_4 (4 C-H bonds)

$$\Delta H_f = 4 \times H(C-H)$$
$$= 4 \times (-3.83) = -15.3\text{kcal / mole}$$

(6.1)

experiment -17.9 kcal/mole

For CH_3CH_3

$$\Delta H_f = 6 \times H(C-H) + H(C-C)$$
$$= 6 \times (-3.83) + 2.73 = -20.3\text{kcal / mole}$$

(6.2)

experiment -20.2 kcal/mole

Gives us OK estimates (almost as good as QM)

Ligand methods - add up all carbons n a hydrocarbon

Table 6.2 The contribution of various functional to key thermodynamic properties in the gas. Data of Benson Thermochemical Kinetics [1976], with revision due to Cohen, J. Phys. Chem. Ref. Data, 25 (1998) 1411.

Ligand	C_p, cal/mole°K	S cal/mole°K	ΔH_f, kcal/mole	Ligand	C_p, cal/mole°K	S cal/mole°K	ΔH_f, kcal/mole
$C-(H)_3C$	6.19	30.41	-10.00	$O-(H)_2$	8.0	45.1	-57.8
$C-(H)_2(C)_2$	5.50	9.42	-5.00	$O-(H)(C)$	4.3	29.07	-37.9
$C-(H)(C)_3$	4.54	-12.07	-2.4	$O-(H)(C_B)$	4.3	29.1	-37.9
$C-(C)_4$	4.37	-35.10	-0.1	$O-(H)(C_D)$	3.8	24.5	-58.1
$C_D-(H)_2$	5.10	27.61	6.26	$O-(C)_2$	-3.4	8.68	-23.2
$C_D-(H)(C)$	4.16	7.97	8.6	$CO-(H)_2$	8.5	52.3	26.0
$C_D-(C)_2$	4.10	-12.70	10.34	$CO-(H)(C)$	7.0	34.9	29.1
$C_D-(C_D)(H)$	4.46	6.38	6.8	$CO-(H)(C_B)$	7.0	—	29.1
$C_D-(C_D)(C)$	4.40	-14.6	8.8	$CO-(C)_2$	5.6	15.0	-31.4
$C_D-(C_B)(H)$	4.46	6.38	6.8	$CO-(C)(O)$	6.0	14.8	-35.1
$C_D-(C_B)C$	4.40	-14.6	8.64	$C-(H)_3(O)$	6.19	30.41	-10.8
$C_D-(C_T)(H)$	4.46	6.38	6.78	$C-(H)_2(O)(C)$	4.99	9.8	.-8.1
$C-(C_D)(C)(H)_2$	5.2	9.80	-4.76	$C-(H)_3(CO)$	6.19	30.41	-10.08
$C-(C_D)(H)_2$	4.7	10.2	-4.29	$C-(H)_2(CO)(C)$	6.2	9.6	-5.2
$C-(C_D)(C_B)(H)_2$	4.7	10.2	-4.29	C_B-O	3.9	-10.2	-0.9
$C-(C_T)(C)(H)_2$	4.95	10.3	-4.73	$C-(N)(H)_3$	6.19	30.41	-10.08
$C_T-(H)$	5.27	24.7	26.93	$C-(N)(C)(H)_2$	5.25	9.8	-6.6
$C_T-(C)$	3.13	6.35	27.55	$N-(C)(H)_2$	5.72	29.71	4.8
$C_T-(C_D)$	2.57	6.43	29.20	$N-(C)_2(H)$	4.20	8.94	15.4
$C_T-(C_B)$	2.57	6.43	29.20	$C-(H)_3(C)$	12.7	42.5	-161
$C_B-(H)$	3.25	11.53	3.30	$C-(F)_2(H)(C)$	9.9	39.1	-102.3
C_B-C	2.07	-7.69	5.51	$C-(F)(H)_2(C)$	8.1	35.4	-51.5
C_B-C_D	3.59	-7.80	5.68	$C-(F)_2(C)_2$	9.9	17.4	-99

$C-(C)(H)_3$ carbon bound to one carbon and three hydrogens

Example CH_3CH_3

$$\Delta H_f = 2 \times H\left(C-(C)(H)_3\right) = 2 \times (-10.0) = -20.0 \text{kcal / mole} \tag{6.3}$$

experiment = -20.2 kcal/mole

Ethylene CH_2CH_2

$$\Delta H_f = 2 \times H\left(C_D-(H)_2\right) = 2 \times (+6.26) = +12.52 \text{kcal / mole} \tag{6.4}$$

experiment 12.50

Table 6.3 The contribution of various functional to key thermodynamic properties of Radicals. Data of Benson [1976].

Ligand	C_p, cal/mole°K	ΔS cal/mole°K	ΔH_f, kcal/mole	Ligand	C_p, cal/mole°K	ΔS cal/mole°K	ΔH_f, kcal/mole
$\bullet C-(C)(H)_2$	5.99	30.7	35.82	$C-(O\bullet)(C)_2(H)$	7.7	14.7	7.8
$\bullet C-(C)_2(H)$	5.16	10.74	37.45	$C-(O\bullet)(C)_3$	7.2	-7.5	8.6
$\bullet C-(C)_3$	4.06	-10.77	38.00	$\bullet C-(H)_2(C_D)$	5.39	27.65	23.2
$C-(C\bullet)(H)_3$	6.19	30.41	-10.08	$\bullet C-(H)(C)(C_D)$	4.58	7.02	25.2
$C-(C\bullet)(C)(H)_2$	5.50	9.42	-4.95	$\bullet C-(C)_2(C_D)$	4.00	-15.0	24.8
$C-(C\bullet)(C)_2(H)$	4.54	-12.07	-1.90	$\bullet C-(C_B)(H)_2$	4.10	26.85	23.0
$C-(C\bullet)(C)_3$	4.37	-35.10	1.50	$\bullet C-(C_B)(C)(H)$	5.30	6.38	24.7
$C-(O\bullet)(C)(H)_2$	7.9	36.4	6.1	$\bullet C-(C_B)(C)_2$	4.72	-15.46	25.5
$H\bullet$	3		52.1	$O\bullet$	3		59.5

For $CH_3CH_2\bullet$

Experiment 26.5 kcal/mole.

(Note benson's rules were 1970 - before accurate QM).

This produces energies good enough to predict mechanisms.

Method does not work for ions

Table 6.4 The heat of reaction of $H^+ + NH_2R \Rightarrow [NH_3R]^+$ as a function of the R group. Data of Bowers [1977].

R	ΔH kcal/mole	R	ΔH kcal/mole	R	ΔH kcal/mole
H	-205	CH_3	-214.1	C_2H_5	-217.1
n-C_3H_7	-218.5	n-C_4H_9	-219.0	n-C_6H_{13}	-220.1
n-C_8H_{17}	-220.4	n-$C_{10}H_{17}$	-220.7	iC_4H_9	-219.5
s-C_4H_9	-220.5	t-C_4H_9	-221.3		

Works for surfaces (dissociative adsorption only)

Table 6.5 Approximate contributions of metal surface bond to ΔH_f kcal/mole . The data in the table is calculated from results in Benziger [1991] and results in Masel [1996]. Most of the numbers are ±5−10 kcal/mole. The numbers in brackets are based on extrapolations. Consequently, those numbers may have larger errors.

	Group							
	IVA	VA	VIA	VIIA	VIII	VIII	VIII	IB
Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
H(M-C)	[-62]	[-56]	-53	-50	-49	-48	-50	-41
H(M-N)	[-77]	[-61]	[-44]	[-36]	-14	[-1]	-10	-3
H(M-O)	-68	-55	-58	-44	-45	-40	-38	-30
H(M-H)	-19	-15	-14	-12	-11	-12	-12	-5
Element	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
H(M-C)	-62	-59	-53.1	-49	-43	-40	-40	-25
H(M-N)	-34	-23	-19	[-12]	[-10]	[-9]	[-7]	+10
H(M-O)	-78	-58	[-41]	-[37]	[-36]	-28	-24	-22
H(M-H)	-20	-13	-13	-12	-11	-10	-10	0
Element	Hf	Ta	W	Re	Os	Ir	Pt	Au
H(M-C)	-65	-81	-72.5	-52.5	-43	-40	-40	-20
H(M-N)	-34	-26	-13	-15	[-11]	[-8]	[-5]	+10
H(M-O)	-80	-61	-47	-33	-24	-29	-24.5	-19.5
H(M-H)	?	-19	-16	-12	-11	-8	-6	+10

Example $CH_3CH_{2(ad)}$

$$\begin{aligned}\Delta H_f &= H\big(C-(C)(H_3)\big) + H(\bullet C-(C)(H_2)) + H(Pt-C)\\ &= (-10.2) + 35.82 + (-40)\\ &= -14.3\,\mathrm{kcal/mole}\end{aligned}$$

(6.6)

Discussion problem:

Consider:

$$CH_3CH_3 + X \xrightarrow{1} 2CH_3$$

$$CH_3 + CH_3CH_3 \xrightarrow{2} CH_4 + CH_2CH_3$$

$$CH_2CH_3 + X \xrightarrow{3} CH_2CH_2 + H + X$$

$$H + CH_3CH_3 \xrightarrow{4} H_2 + CH_2CH_3$$

$$2\ CH_2CH_3 + X \xrightarrow{5} CH_3\ CH_2CH_2CH_3 + X$$

a) Estimate the heat of reaction of each step.
Hint: first estimate the heat of formation of all of the species
b) Estimate activation barriers for each step

note CH_3 left out of table $H_f = 34.82$

My solution

ethane

$$\Delta H_f = 2 \times H(C-(C)(H)_3) = 2 \times (-10.0) = \text{-20.0kcal / mole}$$

(6.3)

ethyl radical

$$\Delta H_f = H(C-(C\bullet)(H_3)) + H(\bullet C-(C)(H_2)) = (-10.08) + 35.82 = 25.7\text{kcal / mole}$$

(6.5)

$CH_3CH_2CH_2CH_3$
$H_f = 2\ [C\text{-}(C)(H)_3] + 2\ [C\text{-}(C)_2(H)_2]$
= 2*(-10.00)+ 2(-5)= -30.0 kcal/mole

H radical - +52.1 given in table
CH_3 - +34.82 (above)
methane - not in table -17.9 (above)

Reaction 1

$\Delta H_r = 2H_f(CH_3)-H_f(CH_3CH_3)$

$= 2*(+34.82)-(-20.0)= +89.64$

Reaction 2

$$CH_3 + CH_3CH_3 \xrightarrow{2} CH_4 + CH_2CH_3$$

$\Delta H_r = H_f(CH_4)+H_f(CH_2CH_3) -H_f(CH_3CH_3)$
$\quad -H_f(CH_3)$
$= (-17.9) + (+25.7) - (-20.0)-(+34.8)$
$= -7$ kcal/mole

Statistical Mechanics

- The key concept in statistical mechanics is that one can calculate all thermodynamic properties as an average. For example, the internal energy of molecules in a box is an average of the internal energies of each molecule, which is then also averaged over time. The entropy is an average of all of the entropies of the molecules averaged over time.

- There are alternative ways to compute the averages. For example instead of computing a time average, one can compute an ensemble average, where the ensemble average will be defined later in this chapter. If you do everything right, all of the averages should come out to be the same value, which is why statistical mechanics is so valuable.

- When you do statistical mechanics, you use all of the normal state variables that you learned about in thermodynamics: pressure, temperature, volume, free energy, enthalpy … In addition there are some special state variables called partition functions.

- The partition functions are like any other state variable. The partition functions are completely defined if you know the state of the system. You can also work backwards, so if you know the partition functions, you can calculate any other state variable of the system.

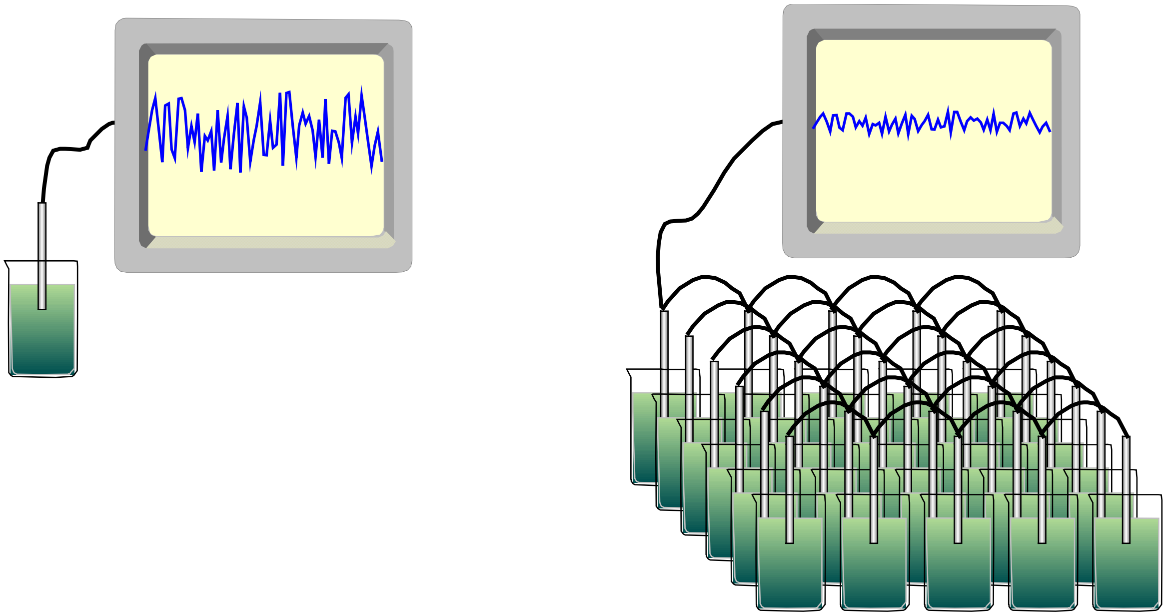
- The partition functions are defined via equations (6.15) and (6.16). These equations allow the partition functions to be calculated from the properties of the molecules in the system (i.e. energy levels, atomic masses etc). The fact that the partition functions can be calculated easily makes them particularly convenient thermodynamic variables. If you know the properties of all of the molecules, you can calculate the partition functions. You can then work backwards and calculate any thermodynamic property of the system.

- The key variable for the work later in this book is the equilibrium constant for a reaction. K, the equilibrium constant for the reaction A+B ⇆ C+D is given by

$$\boxed{K = \frac{q_C q_D}{q_A q_B}} \tag{6.7}$$

Important concept due to Gibbs:

Can replace time average with ensemble average:



Replace system with a set of systems "identical" to the first and average over all of the systems.

Identical - same thermodynamic state

Canonical ensemble
grand canonical ensemble
microcanonical ensemble

Key idea in statistical mechanics: can define a new state variable called a partition function

$$Q_{canon}^{N} = \sum_{n} g_n e^{-\beta U_n} \tag{6.15}$$

- Partition function is easy to calculate if energy levels are known.
- Partition function just like any other state variable -
  - state known if V, T and composition known
  - state known if Q, T and composition known
  - Q is like a volume (actually the volume of states)

- Partition function related to other state variables via Maxwell relationships

$$S = -k_B \sum_n p_n \mathrm{Ln}\left[\frac{p_n}{g_n}\right]$$

(6.40)

$$A = -k_B T\mathrm{Ln}(Q^N_{canon})$$

(6.59)

$$\frac{\partial(\mathrm{Ln}Q^N_{canon})}{\partial\beta} = \langle U \rangle$$

(6.60)

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = k_B T\left(\frac{\partial \mathrm{Ln}Q^N_{canon}}{\partial T}\right)_{V,N} + k_B \mathrm{Ln}Q^N_{canon}$$

(6.61)

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = k_B T\left(\frac{\partial \mathrm{Ln}Q^N_{canon}}{\partial V}\right)_{T,N}$$

(6.62)

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = k_B T\left(\frac{\partial \mathrm{Ln} Q^{N}_{\mathrm{canon}}}{\partial N}\right)_{T,V}$$

(6.63)

$$S = \left(\frac{\partial PV}{\partial T}\right)_{V,\mu} = k_B T\left(\frac{\partial \mathrm{Ln} Q_{\mathrm{grand}}}{dT}\right)_{V,\mu} + k_B \mathrm{Ln}(Q_{\mathrm{grand}})$$

(6.64)

$$N = \left(\frac{\partial PV}{\partial \mu}\right)_{T,V} = k_B T\left(\frac{\partial \mathrm{Ln} Q_{\mathrm{grand}}}{\partial \mu}\right)_{V,T}$$

(6.65)

Key equation for the molecular partition function:

$$q = (q_t)^3 (q_r)^3 (q_V)^{3n_a - 6} g_e e^{-\beta U_O}$$

(6.77)

Lets us calculate properties:

Table 6.6 Equations for the partition function for translational, rotational, vibrational modes and electronic levels.

Type of Mode	**Partition Function**	**Approximate Value of the Partition Function for Simple Molecules**
Translation of a molecule of an ideal gas in a one dimensional box of length a_x	$q_t = \frac{(2\pi m_g k_B T)^{\frac{1}{2}} a_x}{h_p}$	$q_t \approx 1 - 10/Å\ a_x$
Translation of a molecule of an ideal gas at a pressure P_A and a temperature T	$\frac{q_t^{\ 3}}{N} = \frac{(2\pi m_g k_B T)^{\frac{3}{2}}}{h_p^{\ 3}} \left(\frac{k_B T}{P_A} \right)$	$q_t^3 \approx 10^6 - 10^7$
Rotation of a linear molecule with moment of inertia I	$q_r^{\ 2} = \frac{8\pi^2 I k_B T}{S_n h_p^{\ 2}}$ where S_n is the symmetry number	$q_r^2 \approx 10^2 - 10^4$
Rotation of a nonlinear molecule with a moment of inertia of I_a, I_b, I_c, about three orthogonal axes	$q_r^{\ 3} = \frac{I_a I_b I_c)^{1/2} (8\pi k_B T)^{3/2}}{S_n h_p^{\ 3}}$	$q_r^3 \approx 10^4 - 10^5$
Vibration of a harmonic oscillator when energy levels are measured relative to the harmonic oscillator's zero point energy	$q_V = \frac{1}{1 - \exp(-h_p \upsilon / k_B T)}$ where υ = the vibrational frequency	$q_v \approx 1 - 3$
Electronic Level (Assuming That the Levels Are Widely Spaced)	$q_e = \exp\left(- \frac{\Delta E}{k_B T} \right)$	$q_e = \exp(-\beta \Delta E)$

Table 6.7 **Simplified expressions for the average velocity and the translational, rotational, vibrational partition function. Derivations are given in example 6.B and 6.C.**

Type of Mode	**Partition Function**	**Partition function after substituting in values of k_B, h_p**
Average velocity of a molecule	$\bar{v}=\left(\frac{8\pi k_B T}{m_g}\right)^{1/2}$	$\bar{v}=2.52\times10^{13}\frac{Å}{sec}\left(\frac{T}{300K}\right)^{1/2}\left(\frac{1AMU}{m_g}\right)^{1/2}$
Translation of a molecule in three dimensions, (partition function per unit volume)	$q_t^3=\frac{\left(2\pi m_g k_B T\right)^{3/2}}{\left(h_p\right)^3}$	$q_t^3=\frac{1.16}{Å^3}\left(\frac{T}{300K}\right)^{3/2}\left(\frac{m_g}{1AMU}\right)^{3/2}$
Rotation of a linear molecule	$q_r^2=\frac{8\pi I k_B T}{S_n\left(h_p\right)^2}$	$q_r^2=\left(\frac{12.4}{S_n}\right)\left(\frac{T}{300K}\right)\left(\frac{I}{1Å\text{-}AMU}\right)$
Rotation of a nonlinear molecule	$q_r^2=\frac{\left(8\pi k_B T\right)^{\frac{3}{2}}\left(I_aI_bI_c\right)^{\frac{1}{2}}}{S_n\left(h_p\right)^3}$	$q_r^3=\left(\frac{43.7}{S_n}\right)\left(\frac{T}{300K}\right)^{\frac{3}{2}}\left(\frac{I_aI_bI_c}{1Å^3\text{-}AMU^3}\right)^{\frac{3}{2}}$
Vibration of a harmonic oscillator	$q_V=\frac{1}{1-\exp(-h_p\upsilon/k_B T)}$	$q_V=\frac{1}{1-\exp\left(-\left(\frac{\upsilon}{209.2cm^{-1}}\right)\left(\frac{300K}{T}\right)\right)}$

Example 6.C Calculate the partition function for HBr at 300°K

Data for Example 6.C	
υ	2650 cm^{-1}
bond length	1.414Å
m_H	1 AMU
m_{Br}	80AMU

Calculate the a) translational, b) rotational, c) vibrational partition function for HBr. Data is given above.

Solution:

Total Modes = 3n
Translations = 3
Rotations = 2 (linear molecule)
Rotations = 3 (non linear molecule)
Whatever left is vibrations

a) The translational partition function.

From Table 6.6:

$$q_t^3 = \frac{\left(2\pi m_g\, ķ_B\, T\right)^{3/2}}{h_p^3}$$

(6.3.1)

where q_t is the translational partition function per unit volume, m_g is the mass of the gas atom in AMU, $ķ_B$ is Boltzmann’s constant, T is temperature and h_p is Plank’s constant.

Equation 6.3.1 is not that convenient so first I was to derive a simple. One can rewrite equation (6.32) as

$$q_t^3 = \left(\frac{m_g}{1\text{AMU}}\right)^{3/2}\left(\frac{T}{300^\circ\text{K}}\right)^{3/2}\left(\frac{2\pi \times 1\text{AMU} \times ķ_B \times 300^\circ\text{K}}{h_p^3}\right)^{3/2}$$

(6.3.2)

Next let us evaluate the third term on the right of equation (6.3.2)

$$\frac{\left(2\pi\times 1\text{AMU}\times k_B\times 300\text{K}\right)^{3/2}}{h^3}=$$

$$\frac{\left(2\pi(1\text{AMU})\left(\frac{1.66\times 10^{-27}\,\text{kg}}{1\text{AMU}}\right)\left(1.381\times 10^{23}\,\frac{\text{kgM}^2}{\sec^{2\circ}\text{K}}\right)\left(300^\circ\text{K}\right)\right)^{3/2}}{\left(6.626\times 10^{-34}\,\frac{\text{kgM}^2}{\sec}\right)^3\left(\frac{10^{10}\,\text{Å}}{\text{M}}\right)^3}=\frac{1.16}{\text{Å}^3}$$

(6.3.3)

Combining 6.3.2 and 6.3.3 yields

$$\boxed{q_t^3=\left(\frac{m_g}{1\text{AMU}}\right)^{3/2}\left(\frac{T}{300^\circ\text{K}}\right)^{3/2}\frac{1.16}{\text{Å}^3}}$$

(6.3.4)

Equation 6.3.4 is the equation we will actually use to evaluate the translational partition function. For our case m_g = 81 AMU, T = 300°K. Plugging in the numbers:

$$q_T = \left(\frac{81\text{AMU}}{1\text{AMU}}\right)^{3/2} \left(\frac{300^\circ\text{K}}{300^\circ\text{K}}\right)^{3/2} \frac{1.16}{\text{Å}^3} = 843/\text{Å}^3$$

(6.3.5)

b) **The rotational partition function.**
similar to above

c) **The vibrational partition function.**
similar to above

EXAMPLE 6.B The calculation of molecular velocities.

Derive an expression for the a) average velocity of a ideal gas molecule, b) the average internal energy, c) plug in numbers into your expression at temperature T = 273 K.

Solution

a) Molecular velocities can be calculated using the classical partition function, equation (6.78). According to equation (6.80), one can calculate the expectation value of the molecular velocity, $\langle v \rangle$, from:

$$\langle v \rangle = \frac{1}{Q_{classical}} \frac{1}{h^{3m}} \iiint \ldots \int v e^{-\beta U} d\vec{r}_1 d\vec{r}_2 \ldots d\vec{r}_m d\vec{p}_1 d\vec{p}_2 \ldots d\vec{p}_m \tag{6.103}$$

Therefore:

$$\overline{V}=2.52\times10^{13}\,\frac{\text{Å}}{\sec}\left(\frac{T}{300\text{K}}\right)^{1/2}\left(\frac{1\text{AMU}}{m_g}\right)^{1/2}$$

b) A similar derivation shows that the average translational energy, $\langle U_T \rangle$ is:

$$\boxed{\langle U_T \rangle = \frac{\iiint \frac{1}{2} m_g v^2 e^{-\beta U}\, d\vec{v}}{\iiint e^{-\beta U}\, d\vec{v}} = \frac{3}{2} k_B T \qquad (6.111)}$$

c) Plugging Numbers into equation (6.110) allows one to calculate the following table of molecular velocities:

Some properties of gases at 0◦C		
Molecule	Average Velocity, <v> m/sec	Molecular Diameter
Hydrogen	1687	2.74
Helium	1197	2.18
Carbon Monoxide	453	3.12
Nitrogen	453	2.74
Krypton	262	4.16
Xenon	209	4.85

The numbers in this table are calculated in J.F. O'Hanlon, A User's Guide To Vacuum Technology, Wiley (1980).

Example:

Calculate the equilibrium constant for the reaction

$F + H_2 \leftrightarrows \text{complex}$

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

$$k_{F\to H_2} = \left(\frac{k_B T}{h_P}\right)\frac{q_{F-H_2}^{\ddagger T}}{q_{H_2} q_r} e^{-E_T^{\ddagger}/k_B T}$$

(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.,:

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

(7.C.3)

where $l^{\ddagger}$ 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:

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

(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, k_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:

$$\left(\frac{h_P^2}{2\pi\, k_B\, T}\right)^{3/2} = \left(\frac{300\text{K}}{T}\right)^{3/2} \left(\frac{\left(6.626\times10^{-34}(\text{kg})\text{m}^2\ /\ \text{sec}\right)^2 \left(\frac{10^{10}\,\text{Å}}{\text{m}}\right)^2 \left(\frac{\text{AMU}}{1.66\times10^{-27}\,\text{kg}}\right)}{2\pi\left(1.381\times10^{-23}(\text{kg})\text{m}^2\ /\ \text{sec}^2\ \text{-}^\circ\,\text{K}\right)(300^\circ\,\text{K})}\right)^{3/2}$$

(7.C.8)

Doing the arithmetic yields:

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

(7.C.9)

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

$$\left(\frac{q^{\ddagger}}{q_F q_{H_2}}\right)_{\text{trans}} = \left(\frac{M_{\ddagger}}{(M_{\ddagger})MH_2}\right)^{3/2} \left(\frac{300\text{K}}{\text{T}}\right)^{3/2} \left(1.024\text{Å}^3\text{AMU}^{3/2}\right)$$

(7.C.10)

Setting T = 300K $M_{\ddagger}$ = 21AMU, M_F = 19_{AMU}, M_{H2} = 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:

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

(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

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

(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

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

(7.C.17)

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

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

(7.C.18)

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

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

(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:

$$\left(\frac{q^{\ddagger}}{q_{H_2}}\right)_{vib} = \frac{q^{\ddagger}_{HH}q^{\ddagger}_{Bend}q^{\ddagger}_{Bend}}{(q_{H-H})_{H_2}} = \frac{(1)(1.19)(1.19)}{1} = 1.42 \tag{7.C.20}$$

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

$$\left(\frac{q^{\ddagger}}{q_{H_2}q_F}\right)_{elec} = \frac{g^{\ddagger}_e}{(g_e)_{H_2}(g_e)_F} = \frac{4}{1\times 4} = 1 \tag{7.C.21}$$

Finally, let’s calculate $ķ_B T/h_P$:

$$\frac{ķ_B\,T}{h_P}=\frac{\left(1.381\times10^{-23}\,\mathrm{Kg}-\mathrm{M}^2\ /\ \mathrm{sec}\text{-}\mathrm{molecule}^\circ\mathrm{K}\right)\left(300^\circ\,\mathrm{K}\right)}{\left(6.626\times10^{-30}\,\mathrm{Kg}-\mathrm{M}^2\ /\ \mathrm{sec}\right)}\left(\frac{\mathrm{I}}{300^\circ\,\mathrm{K}}\right)$$

$$=6.65\times10^{12}\ /\ \mathrm{molecule\ \ sec}\left(\frac{\mathrm{T}}{300\mathrm{K}}\right)$$

(7.C.22)

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

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

(7.C.23)

Plugging in the numbers:

$$k_o=2\left(6.65\times10^{12}\ /\ \mathrm{molecule}-\mathrm{sec}\right)\left(0.42\text{Å}^3\right)(25.8)(1.42)(1)=2.05\times10^{14}\,\text{Å}^3\ /\ \mathrm{molecule}-\mathrm{sec}$$

(7.C.24)

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

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

(7.C.25)

k_o becomes:

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

(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.,:

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

(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)