

You've learned about partition functions and some uses, now we'll explore them in more depth using ideal monatomic, diatomic and polyatomic gases!

Before we start, remember:

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}$$

What are N, V, and T?

We now apply this to the ideal gas where:

1. The molecules are independent.
2. The number of states greatly exceeds the number of molecules (assumption of low pressure).



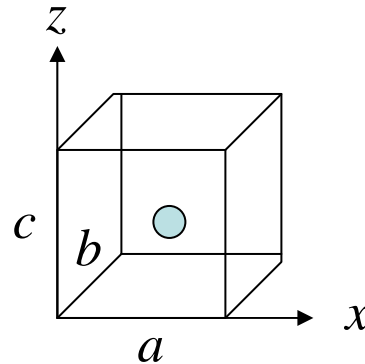


# Translations of Ideal Gas: $q_{trans}(V, T)$

PFIG-3

General form of partition function:  $q_{trans} = \sum_{states} e^{-\beta \epsilon_{trans}}$

Recall from QM slides...



$$\epsilon_{trans} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, \dots, \infty$$

So what is  $q_{trans}$ ?

$$q_{trans} = \sum_{n_x, n_y, n_z=1}^{\infty} e^{-\beta \epsilon_{n_x, n_y, n_z}} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp \left[ -\frac{\beta h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \right]$$



# Let's simplify $q_{trans}$ ...

$$q_{trans} = \sum_{n_x, n_y, n_z=1}^{\infty} e^{-\beta \varepsilon_{n_x, n_y, n_z}} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp \left[ -\frac{\beta h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \right]$$

Recall:  $e^{a+b+c} = e^a e^b e^c$

$$q_{trans} = \sum_{n_x=1}^{\infty} \exp \left( -\frac{\beta h^2 n_x^2}{8ma^2} \right) \sum_{n_y=1}^{\infty} \exp \left( -\frac{\beta h^2 n_y^2}{8ma^2} \right) \sum_{n_z=1}^{\infty} \exp \left( -\frac{\beta h^2 n_z^2}{8ma^2} \right)$$

All three sums are the same because  $n_x, n_y, n_z$  have same form!

We can simplify expression to:

$$q_{trans}(V, T) = \left[ \sum_{n=1}^{\infty} \exp \left( -\frac{\beta h^2 n^2}{8ma^2} \right) \right]^3$$



# $q_{trans}$ is nearly continuous

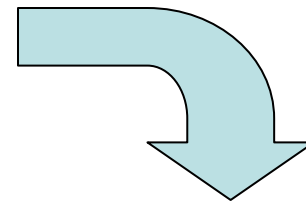
We'd like to solve this expression, but there is no analytical solution for the sum!

$$q_{trans}(V, T) = \left[ \sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right) \right]^3$$

No fears... there is something we can do!

Since translational energy levels are spaced very close together, the sum is nearly continuous function and we can approximate the sum as an integral... which we can solve!

$$q_{trans}(V, T) = \left[ \int_0^{\infty} dn \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right) \right]^3$$



Work the integral

Note limit change ...  
only way to solve but adds very little error to result

$$q_{trans}(V, T) = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

$a^3$



# Translational energy, $\langle \mathcal{E}_{trans} \rangle$

PFIG-6

With  $q$  we can calculate **any** thermodynamic quantity!!

In Ch 17 (BZ notes) we showed this for the average energy ...

$$\langle \mathcal{E}_{trans} \rangle = k_B T^2 \left( \frac{\partial \ln q_{trans}}{\partial T} \right)_V \quad \text{here... } q_{trans}(V, T) = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

$$\langle \mathcal{E}_{trans} \rangle = k_B T^2 \left( \frac{\partial}{\partial T} \ln \left[ T^{3/2} \left( \frac{2\pi m k_B}{h^2} \right)^{3/2} V \right] \right)_V$$

$$\langle \mathcal{E}_{trans} \rangle = k_B T^2 \left( \frac{\partial}{\partial T} \ln T^{3/2} \right)_V = k_B T^2 \left( \frac{\partial}{\partial T} \frac{3}{2} \ln T \right)$$

$$\langle \mathcal{E}_{trans} \rangle = \frac{3}{2} k_B T \quad \text{As we found in BZ notes!}$$

(Recall: this is *per atom*.)





# Can we simplify $q_{elec}$ ?

$$q_{elec}(T) = g_{e1} + g_{e2}e^{-\beta\epsilon_{e2}} + g_{e3}e^{-\beta\epsilon_{e3}} + \dots$$

terms are getting small rapidly...

The electronic energy levels are spaced far apart, and therefore we *typically only need to consider the first term or two in the series...*

General rule of thumb:

At 300 K, you only need to keep terms where  $\epsilon_{ej} < 10^3 \text{ cm}^{-1}$  ( $e^{-\beta\epsilon} > 0.008$ )

TABLE 4.1 (18.1)  
Some atomic energy levels.<sup>a</sup>

Atom	Electron configuration	Degeneracy $g_e = 2J + 1$	Energy/cm <sup>-1</sup>
H	1s	2	0.
	2p	2	82 258.907
	2s	2	82 258.942
	2p	4	82 259.272
He	1s <sup>2</sup>	1	0.
	1s2p	3	159 850.318
		1	166 271.70
Li	1s <sup>2</sup> 2s	2	0.
	1s <sup>2</sup> 2p	2	14 903.66
		4	14 904.00
	1s <sup>2</sup> 3s	2	27 206.12
F	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	4	0.
		2	404.0
	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup> 3s	6	102 406.50
		4	102 681.24
		2	102 841.20
		4	104 731.86
		2	105 057.10

<sup>a</sup>From C.E. Moore, "Atomic Energy Levels" *Natl. Bur. Std. Circ. 1 467*, U.S. Government Printing Office, Washington D.C., 1949



$$q_{elec}(T) = g_{e1} + g_{e2}e^{-\beta\epsilon_{e2}} + g_{e3}e^{-\beta\epsilon_{e3}} + \dots$$

TABLE 4.1 (18.1)  
Some atomic energy levels.<sup>a</sup>

Atom	Electron configuration	Degeneracy $g_e = 2J + 1$	Energy/cm <sup>-1</sup>
H	1s	2	0.
	2p	2	82 258.907
	2s	2	82 258.942
	2p	4	82 259.272
He	1s <sup>2</sup>	1	0.
	1s2p	3	159 850.318
		1	166 271.70
Li	1s <sup>2</sup> 2s	2	0.
	1s <sup>2</sup> 2p	2	14 903.66
		4	14 904.00
F	1s <sup>2</sup> 3s	2	27 206.12
	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	4	0.
		2	404.0
	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup> 3s	6	102 406.50
		4	102 681.24
		2	102 841.20
	4	104 731.86	
	2	105 057.10	

<sup>a</sup>From C.E. Moore, "Atomic Energy Levels" *Natl. Bur. Std. Circ. 1 467*, U.S. Government Printing Office, Washington D.C., 1949

General trends,

1. Noble gas atoms:

$$\epsilon_{e2} = 10^5 \text{ cm}^{-1} \text{ (at 300K, keep \_\_\_ term(s))}$$

2. Alkali metal gas atoms:

$$\epsilon_{e2} = 10^4 \text{ cm}^{-1} \text{ (at 300K, keep \_\_\_ term(s))}$$

3. Halogen gas atoms:

$$\epsilon_{e2} = 10^2 \text{ cm}^{-1} \text{ (at 300K, keep \_\_\_ term(s))}$$



**In general** it is sufficient to keep only the first two terms for  $q_{elec}$

$$q_{elec}(T) \approx g_{e1} + g_{e2} e^{-\beta \varepsilon_{e2}}$$

However, you should always keep in mind that for very high temperatures (like on the sun) or smaller values of  $\varepsilon_{ej}$  (like in F) that additional terms may contribute.

If you find that the second term is of reasonable magnitude (>1% of first term), then you must check to see that the third term can be neglected.



For a *monatomic ideal gas* we have:

$$Q(N, V, T) = \frac{\left( q_{trans}(V, T) q_{elec}(V, T) \right)^N}{N!}$$

with



# Finding thermodynamic parameters... $U$ PFIG-12

We can now calculate the average energy,  $U = \langle E \rangle$

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}$$

$$q(V, T) = q_{trans}(V, T)q_{elec}(V, T)$$

$$U = \langle E \rangle = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V = N k_B T^2 \left( \frac{\partial \ln q}{\partial T} \right)_V = N k_B T^2 \left( \frac{\partial \ln q_{trans} q_{elec}}{\partial T} \right)_V$$

Plug in  $q_{trans}$  and  $q_{elec}$  ...

$$U = N k_B T^2 \left( \frac{\partial}{\partial T} \ln \left( \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V (g_{e1} + g_{e2} e^{-\beta \epsilon_{e2}}) \right) \right)_V$$

$$U = \frac{3}{2} N k_B T + \frac{N g_{e2} \epsilon_{e2} e^{-\beta \epsilon_{e2}}}{q_{elec}}$$

Electronic contribution typically small (i.e., negligible)

So ...  $U \approx \frac{3}{2} N k_B T$  or  $\bar{U} = \frac{3}{2} RT$

↑  
molar energy



Molar heat capacity for a *monatomic ideal gas*:

$$\bar{C}_V = \left( \frac{d\bar{U}}{dT} \right)_{N,V}$$

$$\bar{C}_V = \left( \frac{d\left(\frac{3}{2}RT\right)}{dT} \right)_{N,V} = \frac{3}{2}R$$

Could also find heat capacity:  $C_V = \frac{3}{2}Nk_B$



$$Q(N, V, T) = \frac{q(V, T)^N}{N!}$$

$$q(V, T) = q_{trans}(V, T)q_{elec}(V, T)$$

$$P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N, T} = N k_B T \left( \frac{\partial \ln q}{\partial V} \right)_T = N k_B T \left( \frac{\partial \ln(q_{trans} q_{elec})}{\partial V} \right)_T$$

Plug in  $q_{trans}$  and  $q_{elec}$  ...

$$P = N k_B T \left( \frac{\partial}{\partial V} \ln \left( \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V (g_{e1} + g_{e2} e^{-\beta \epsilon_{e2}}) \right) \right)_T = N k_B T \left( \frac{\partial}{\partial V} \ln V \right)$$

Only function of V

So... 
$$P = \frac{N k_B T}{V}$$

or 
$$\bar{P} = \frac{RT}{V}$$

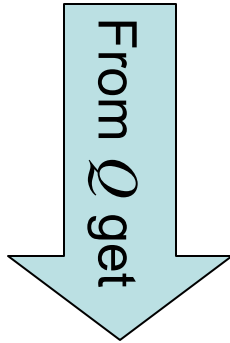
molar pressure

**Look familiar??**



**Partition Function:**

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}$$



$$q_{trans}(V, T) = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V \quad q_{elec}(T) \approx g_{e1} + g_{e2} e^{-\beta \epsilon_{e2}}$$

(molar)

**Energy**

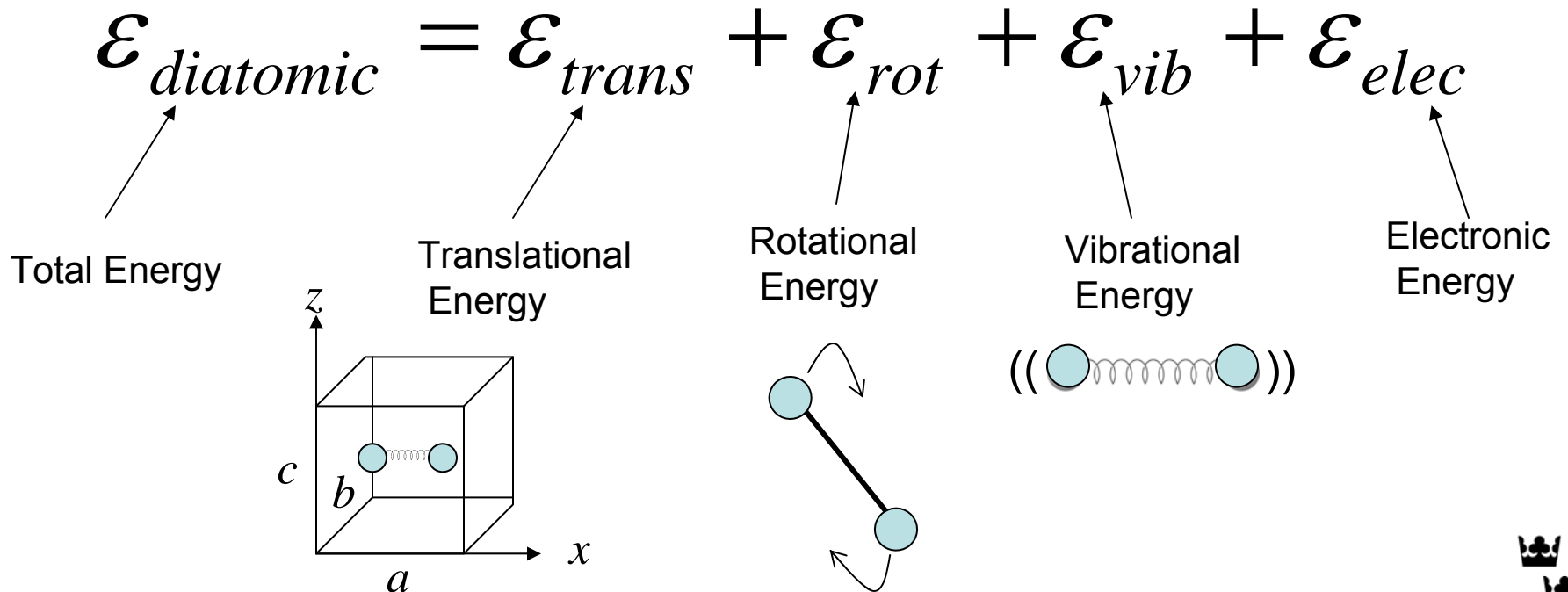
**Heat Capacity**

**Pressure**



In addition to trans. and elec. degrees of freedom, we need to consider:

1. Rotations ← Rigid Rotator Model
2. Vibrations ← Harmonic Oscillator Model



Q. What will the form of the molecular diatomic partition function be given:

$$\mathcal{E}_{diatomic} = \mathcal{E}_{trans} + \mathcal{E}_{rot} + \mathcal{E}_{vib} + \mathcal{E}_{elec} ?$$

Ans.  $q(V, T) = q_{trans} q_{rot} q_{vib} q_{elec}$

Q. How will this give us the diatomic partition function?

Ans.  $Q(N, V, T) = \frac{(q_{trans} q_{rot} q_{vib} q_{elec})^N}{N!}$

Now all we need to know is the form of  $q_{trans}$ ,  $q_{rot}$ ,  $q_{elec}$ , and  $q_{vib}$ .

Start with  $q_{trans}$ : This is the same as in the monatomic case but with  $m = m_1 + m_2$ !

$$q_{trans}(V, T) = \left( \frac{2\pi(m_1 + m_2)k_B T}{h^2} \right)^{3/2} V$$



We define the zero of the electronic energy to be separated atoms at rest in their ground electronic energy states.

With this definition,

$$\varepsilon_{e_1} = -D_e$$

And...

$$q_{elec}(T) \approx g_{e_1} e^{D_e/k_B T} + \left( g_{e_2} e^{-\varepsilon_{e_2}/k_B T} \right)$$

Note the slight difference in  $q_{elec}$  between monatomic and diatomic gases!

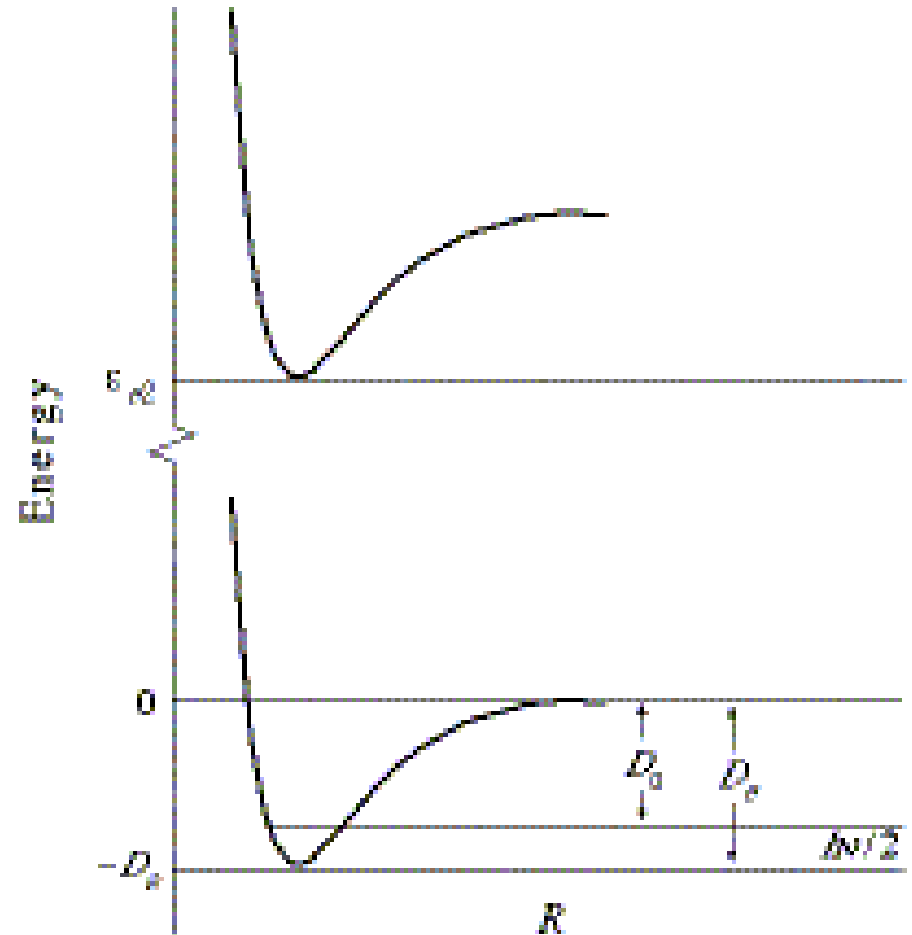


Figure 18.2



The harmonic oscillator approximation is used to describe vibrations.

Recall from QM notes:  $\varepsilon_{vib} = h\nu\left(\nu + \frac{1}{2}\right)$   $\nu = 0, 1, 2, \dots$   
and levels are degenerate...

Plug  $\varepsilon_{vib}$  into  $q_{vib}$ , summed over states...

$$q_{vib}(T) = \sum_{states, \nu} e^{-\beta\varepsilon_{vib}} = \sum_{\nu=0}^{\infty} e^{-\beta\left(\nu + \frac{1}{2}\right)h\nu} = e^{-\beta h\nu/2} \sum_{\nu=0}^{\infty} e^{-\beta(\nu)h\nu}$$

Using relationship:  $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$  For  $x = e^{-\beta h\nu} < 1$

$$q_{vib}(T) = e^{-\beta h\nu/2} \sum_{\nu=0}^{\infty} e^{-\beta(\nu)h\nu} = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

$$q_{vib}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$



It is common to define a **vibrational temperature**,

$$\Theta_{vib} = \frac{h\nu}{k_B}$$

What are the units of  $\theta_{vib}$ ?

We can write  $q_{vib}$  in terms of  $\theta_{vib}$ ...

$$q_{vib}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \xrightarrow{\Theta_{vib} = h\nu/k_B} q_{vib}(T) = \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}}$$



From the partition function, we can calculate the vibrational contribution to the ensemble average energy:

$$\langle \mathcal{E}_{vib} \rangle = Nk_B T^2 \frac{\partial \ln q_{vib}}{\partial T} \quad q_{vib}(T) = \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}}$$

$$\langle \mathcal{E}_{vib} \rangle = Nk_B \left( \frac{\Theta_{vib}}{2} + \frac{\Theta_{vib}}{e^{\Theta_{vib}/T} - 1} \right)$$

And...

$$\bar{C}_{V,vib} = \frac{d\langle \bar{\mathcal{E}}_{vib} \rangle}{dT} = R \left( \frac{\Theta_{vib}}{T} \right)^2 \frac{e^{-\Theta_{vib}/T}}{\left(1 - e^{-\Theta_{vib}/T}\right)^2}$$

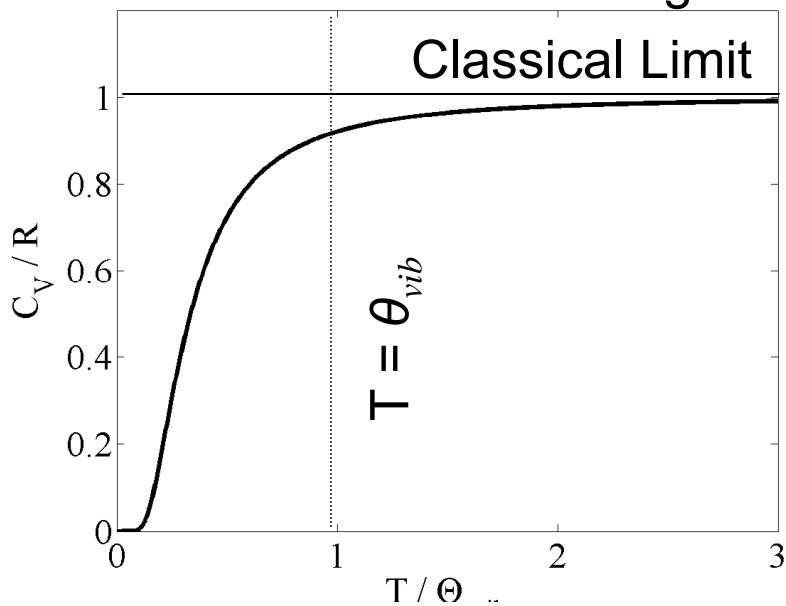
Quotient Rule!



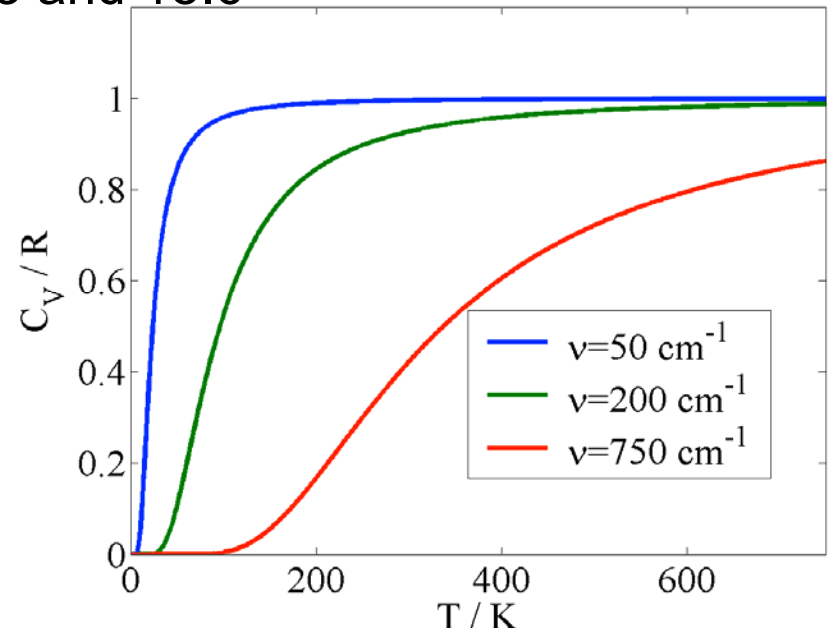
$$\frac{\overline{C}_{V,vib}}{R} = \left( \frac{\Theta_{vib}}{T} \right)^2 \frac{e^{-\Theta_{vib}/T}}{\left( 1 - e^{-\Theta_{vib}/T} \right)^2}$$

Classical limit (at high T),  $C_{V,vib} = R$

Figures 18.3 and 18.6



Classical limit valid at  $T \gg \Theta_{vib}$



What is the difference in these three sets of data?



# Fraction of population in state $v$ , $f_v$

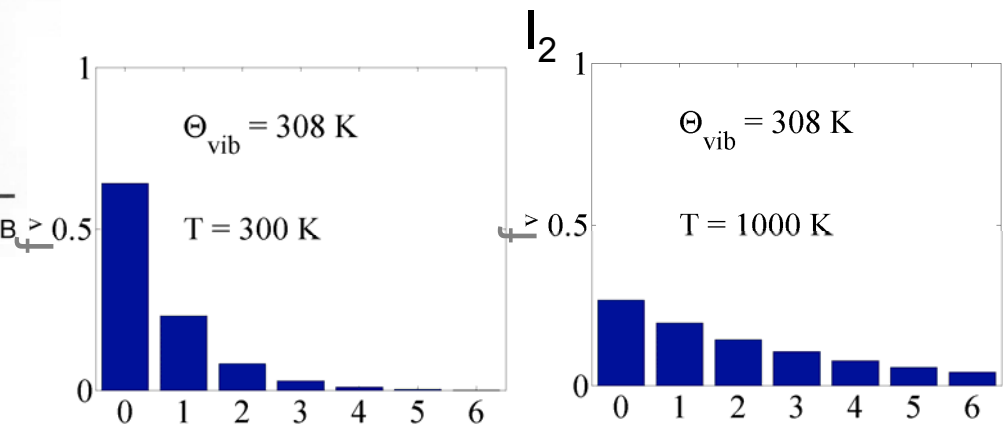
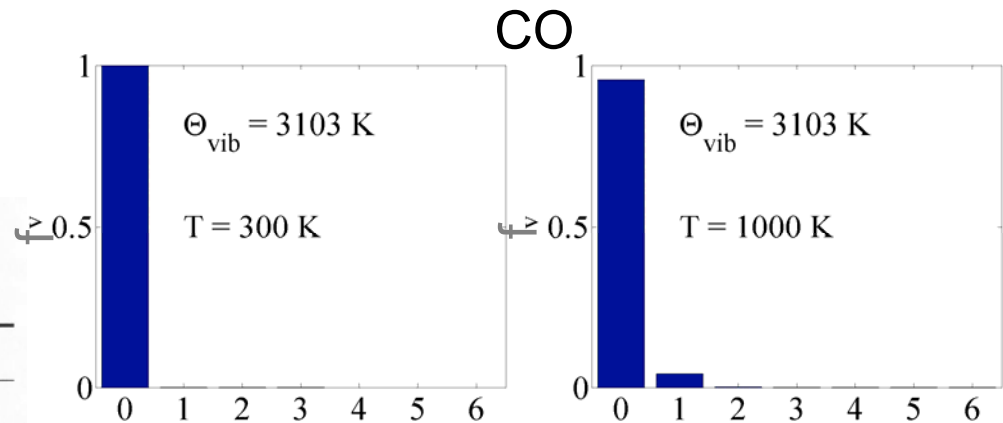
PFIG-23

$$f_v = \frac{e^{-\beta h \nu (v + \frac{1}{2})}}{q_{vib}} = \left(1 - e^{-\Theta_{vib}/T}\right) e^{-v\Theta_{vib}/T}$$

This is also known as...?

TABLE 4.3 (Table 18.3)  
The fraction of molecules in excited vibrational states at 300 K and 1000 K.

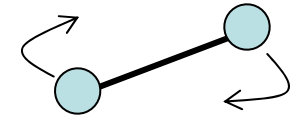
Gas	$\Theta_{vib}/K$	$f_{v>0}$ (T = 300 K)	$f_{v>0}$ (T = 1000 K)
H <sub>2</sub>	6332	$1.01 \times 10^{-9}$	$2.00 \times 10^{-3}$
HCl	4227	$7.59 \times 10^{-7}$	$1.46 \times 10^{-2}$
N <sub>2</sub>	3374	$1.30 \times 10^{-5}$	$3.43 \times 10^{-2}$
CO	3103	$3.22 \times 10^{-5}$	$4.49 \times 10^{-2}$
Cl <sub>2</sub>	805	$6.82 \times 10^{-2}$	$4.47 \times 10^{-1}$
I <sub>2</sub>	308	$3.58 \times 10^{-1}$	$7.35 \times 10^{-1}$



$$f_{v>0} = 1 - f_0 = 1 - (1 - e^{-\Theta_{vib}/T})$$

Copyright 2003 USB

We use the rigid rotator approximation. (Which is...?)



$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2, \dots \quad g_J = 2J + 1$$

Plug into  $q_{rot} \dots$   $q_{rot}(T) = \sum_{\text{levels}, J} g_J e^{-\beta \varepsilon_{rot}}$

$$q_{rot}(T) = \sum_{J=0}^{\infty} (2J + 1) e^{-\beta \hbar^2 J(J+1)/2I}$$

Like the vibrational... we define a **rotational temperature**:

$$\Theta_{rot} = \frac{\hbar^2}{2Ik_B}$$

$q_{rot}$  becomes:

$$q_{rot}(T) = \sum_{J=0}^{\infty} (2J + 1) e^{-\Theta_{rot} J(J+1)/T}$$



This series does not have a simple closed form.

Q. How did we get around this problem for  $\epsilon_{trans}$ ?

A.

Part of Table 18.2

Molecule	$\Theta_{vib}/K$	$\Theta_{rot}/K$
H <sub>2</sub>	6332	85.3
D <sub>2</sub>	4480	42.7
Cl <sub>2</sub>	805	0.351
Br <sub>2</sub>	463	0.116
I <sub>2</sub>	308	0.0537
O <sub>2</sub>	2256	2.07
N <sub>2</sub>	3374	2.88
CO	3103	2.77
NO	2719	2.39
HCl	4227	15.02
HBr	3787	12.02
HI	3266	9.25
Na <sub>2</sub>	229	0.221
K <sub>2</sub>	133	0.081

$$q_{rot} = \frac{T}{\Theta_{rot}} = \frac{2Ik_B T}{h^2} \quad \text{if} \quad \Theta_{rot} \ll T$$



At room temperature (or higher),  $\Theta_{vib} \ll T$  is a good approximation for most molecular rotations... We will assume we are in this high temperature limit to find  $\langle \varepsilon_{rot} \rangle$  and  $C_{V,rot}$ .

**Rotational energy:**

$$\langle \varepsilon_{rot} \rangle = Nk_B T^2 \frac{\partial \ln q_{rot}}{\partial T} = Nk_B T^2 \frac{\partial \ln \frac{T}{\Theta_{rot}}}{\partial T}$$

**Molar heat capacity:**  $\bar{C}_{V,rot} = \frac{d\langle \varepsilon_{rot} \rangle}{dT}$

A diatomic has 2 degrees of rotational freedom, each contributes  $R/2$  to molar heat capacity.

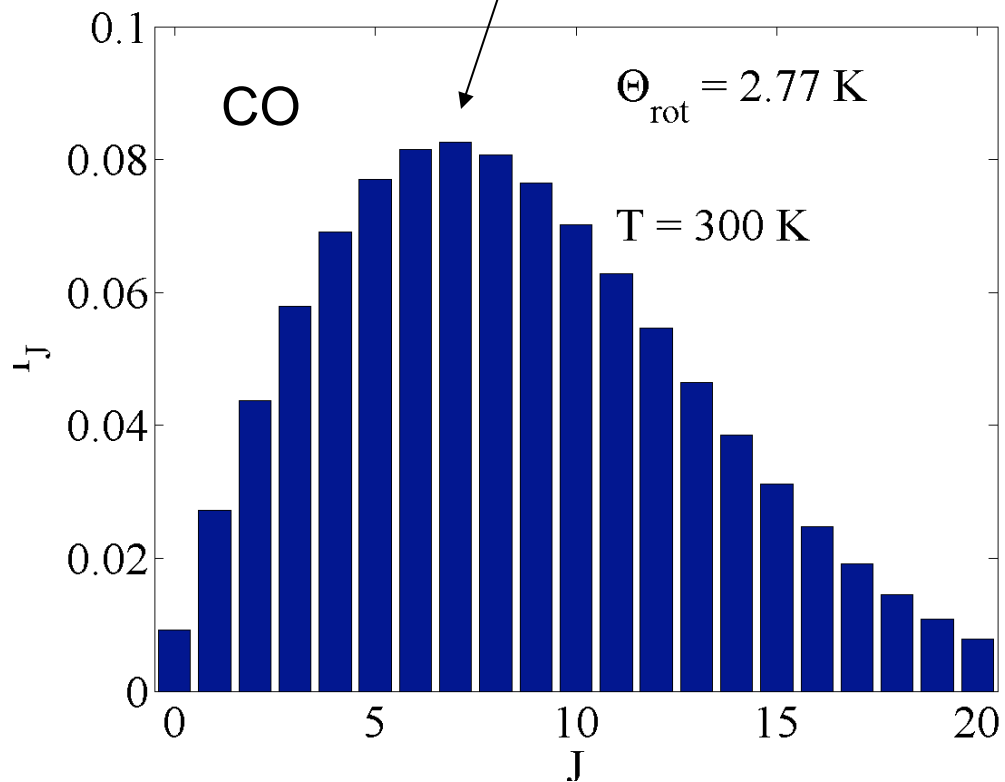


$$f_J = \frac{(2J+1)e^{-\Theta_{rot}J(J+1)/T}}{q_{rot}} = \left( \frac{\Theta_{rot}}{T} \right) (2J+1)e^{-\Theta_{rot}J(J+1)/T}$$

This is also known as...?

Degeneracy moves max away from  $J=0$


Example: CO at 300 K



Due to quantum mechanical considerations beyond the scope of this course, we need to add a **symmetry number** to the rotational partition function,

$$q_{rot} = \frac{T}{\sigma \Theta_{rot}},$$

$\sigma = 1$       Heteronuclear diatomic  
 $\sigma = 2$       Homonuclear diatomic


 Symmetry number

Up to now our derivations were for which case? What would need to change for the other case?



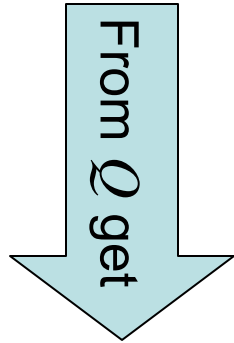
$$q(V, T) = q_{trans} q_{rot} q_{vib} q_{elec}$$

$$q(V, T) = \left( \frac{2\pi(m_1 + m_2)k_B T}{h^2} \right)^{3/2} V \cdot \frac{T}{\sigma \Theta_{rot}} \cdot \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} \cdot g_{e1} e^{D_e/k_B T}$$



**Partition Function:**

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}$$



$$q(V, T) = \left( \frac{2\pi(m_1 + m_2)k_B T}{h^2} \right)^{3/2} V \cdot \frac{T}{\sigma \Theta_{rot}} \cdot \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} \cdot g_{el} e^{D_e/k_B T}$$

**Energy**

$$\bar{U} = \frac{3}{2} RT + RT + R \frac{\Theta_{vib}}{2} + R \frac{\Theta_{vib} e^{-\Theta_{vib}/T}}{1 - e^{-\Theta_{vib}/T}} - N_A D_e$$

**Heat Capacity**

$$\bar{C}_V = \frac{5}{2} R + R \left( \frac{\Theta_{vib}}{T} \right)^2 \frac{e^{-\Theta_{vib}/T}}{\left( 1 - e^{-\Theta_{vib}/T} \right)^2}$$

**Pressure:**

**What would it be?**



Remember... for polyatomic vibrations we divide the motions into normal modes and express the coordinates as independent harmonic oscillators...

$$\mathcal{E}_{vib} = \sum_{j=1}^{\alpha} h\nu_j \left( \nu_j + \frac{1}{2} \right) \quad \nu_j = 0, 1, 2, \dots \quad \text{What is } \alpha \text{ for H}_2\text{O?}$$

**What will the form of the partition function be?**

$$\langle \mathcal{E}_{vib} \rangle = Nk_B \sum_{j=1}^{\alpha} \left( \frac{\Theta_{vib,j}}{2} + \frac{\Theta_{vib,j} e^{-\Theta_{vib,j}/T}}{e^{\Theta_{vib,j}/T} - 1} \right) \quad \text{Polyatomic vibrational energy}$$

Heat capacity

$$C_{V,vib} = Nk_B \sum_{j=1}^{\alpha} \left[ \left( \frac{\Theta_{vib,j}}{T} \right)^2 \frac{e^{-\Theta_{vib,j}/T}}{\left( 1 - e^{-\Theta_{vib,j}/T} \right)^2} \right]$$



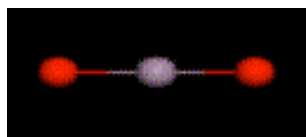
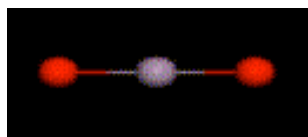
# Example: Contributions to $C_{V,vib}$

PFIG-32

$3n-5 = 4$  normal modes

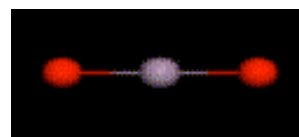
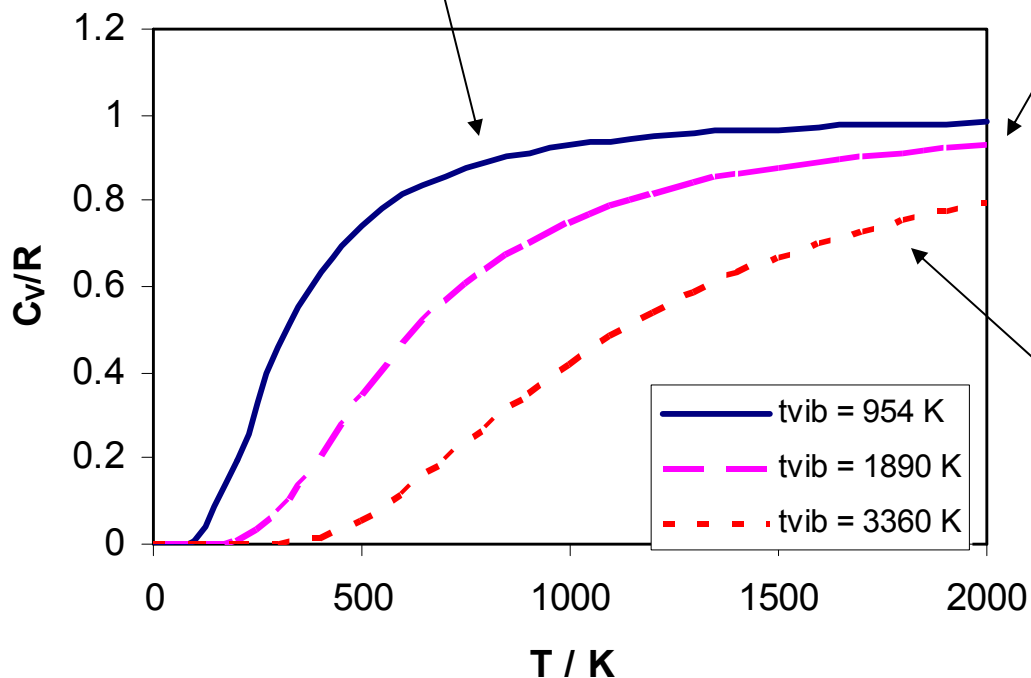
$$C_{V,vib} = Nk_B \sum_{j=1}^4 \left[ \left( \frac{\Theta_{vib,j}}{T} \right)^2 \frac{e^{-\Theta_{vib,j}/T}}{\left(1 - e^{-\Theta_{vib,j}/T}\right)^2} \right]$$

Degenerate,  $\theta_{vib} = 954$  K

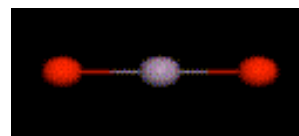


Vertical bend

Horizontal bend



Symmetric stretch,  $\theta_{vib} = 1890$  K



Asymmetric stretch,  $\theta_{vib} = 3360$  K



**Linear polyatomics:** The result is the same as that for a diatomic rigid rotator.

$$q_{rot} = \frac{T}{\sigma \Theta_{rot}}, \quad \begin{array}{ll} \sigma = 1 & \text{COS} \\ \sigma = 2 & \text{CO}_2 \end{array}$$

**Nonlinear polyatomics:** For each of the 3 degrees of rotational freedom (A, B, and C), we have a separate moment of inertia and a separate rotational temperature,

$$I_A = I_B = I_C \quad \text{Spherical top} \quad \Theta_{rot,A} = \Theta_{rot,B} = \Theta_{rot,C}$$

$$I_A = I_B \neq I_C \quad \text{Symmetric top} \quad \Theta_{rot,A} = \Theta_{rot,B} \neq \Theta_{rot,C}$$

$$I_A \neq I_B \neq I_C \quad \text{Asymmetric top} \quad \Theta_{rot,A} \neq \Theta_{rot,B} \neq \Theta_{rot,C}$$



1. From QM, get energy levels (remember, the **equations differ** for each case!);

$$\text{for the spherical top: } \varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2, \dots \quad g_J = 2J + 1$$

2. Plug into:  $q_{rot}(T) = \sum_{\text{levels}, J} g_J e^{-\beta \varepsilon_{rot}}$

3. Assume  $\theta_{rot} \ll T$  & approximate sum as integral:  $q_{rot}(T) = \int_0^{\infty} dJ g_J e^{-\beta \varepsilon_J}$

4. Work the integral...

$$q_{rot}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T}{\Theta_{rot}} \right)^{3/2} \quad \text{Spherical top}$$

$$q_{rot}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T}{\Theta_{rot,A}} \right) \left( \frac{T}{\Theta_{rot,C}} \right)^{1/2} \quad \text{Symmetric top}$$

$$q_{rot}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_{rot,A} \Theta_{rot,B} \Theta_{rot,C}} \right)^{1/2} \quad \text{Asymmetric top}$$



$$q_{rot}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T}{\Theta_{rot}} \right)^{3/2}$$

Spherical top

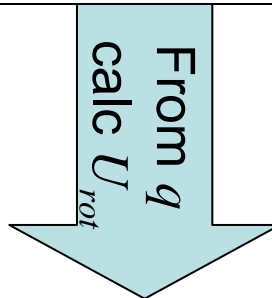
$$q_{rot}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T}{\Theta_{rot,A}} \right) \left( \frac{T}{\Theta_{rot,C}} \right)^{1/2}$$

Symmetric top

$$q_{rot}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_{rot,A} \Theta_{rot,B} \Theta_{rot,C}} \right)^{1/2}$$

Asymmetric top

$$U_{rot} = \langle \epsilon_{rot} \rangle = k_B T^2 \left( \frac{\partial \ln q_{rot}}{\partial T} \right)_V$$



Note: These results are due to our assumption that the distribution of levels is continuous ( $\theta_{rot} \ll T$ ).



**Linear  
Polyatomic**

$$q(V, T) = \left( \frac{2\pi(M)k_B T}{h^2} \right)^{3/2} V \cdot \frac{T}{\sigma \Theta_{rot}} \cdot \prod_{j=1}^{3n-5} \left( \frac{e^{-\Theta_{vib,j}/2T}}{1 - e^{-\Theta_{vib,j}/T}} \right) \cdot g_{el} e^{D_e/k_B T}$$

$$\bar{U} = \frac{5}{2} RT + R \sum_{j=1}^{3n-5} \left( \frac{\Theta_{vib,j}}{2} + \frac{\Theta_{vib,j}}{e^{-\Theta_{vib,j}/T} - 1} \right) - N_A D_e$$

$$\bar{C}_V = \frac{5}{2} R + R \sum_{j=1}^{3n-5} \left[ \left( \frac{\Theta_{vib,j}}{T} \right)^2 \frac{e^{-\Theta_{vib,j}/T}}{\left( 1 - e^{-\Theta_{vib,j}/T} \right)^2} \right]$$

$$q(V, T) = \left( \frac{2\pi(M)k_B T}{h^2} \right)^{3/2} V \cdot \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_{rot,A} \Theta_{rot,B} \Theta_{rot,C}} \right)^{1/2} \cdot \prod_{j=1}^{3n-6} \left( \frac{e^{-\Theta_{vib,j}/2T}}{1 - e^{-\Theta_{vib,j}/T}} \right) \cdot g_{el} e^{D_e/k_B T}$$

**Nonlinear  
Polyatomic**

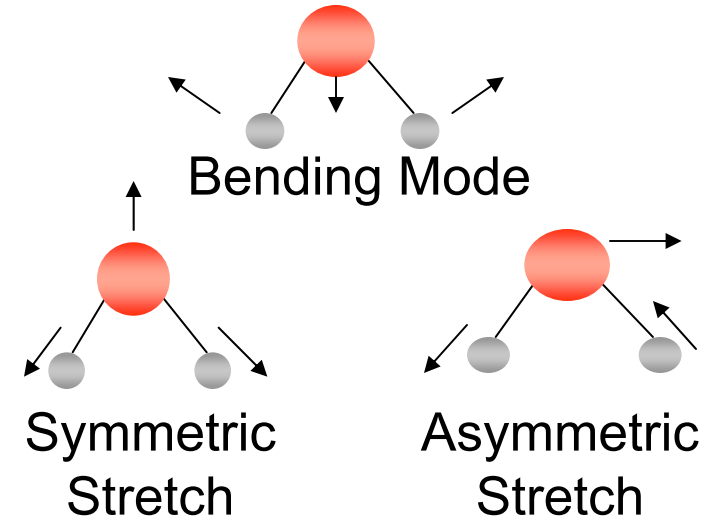
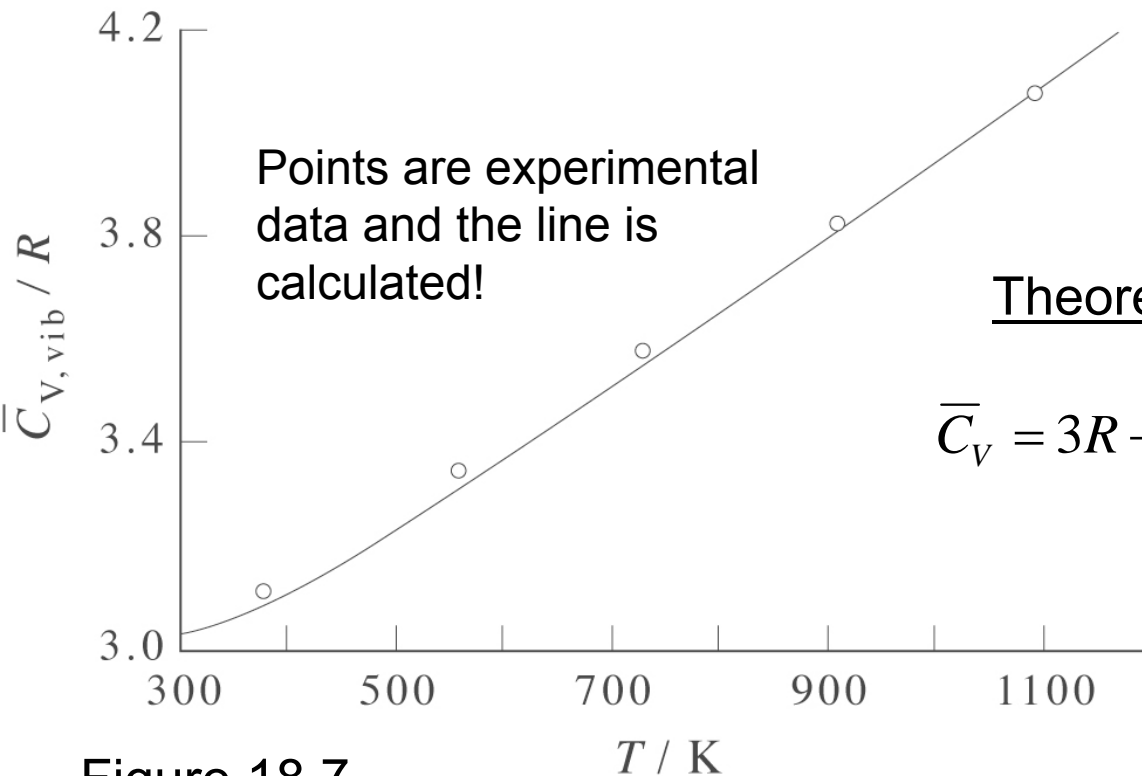
$$\bar{U} = 3RT + R \sum_{j=1}^{3n-6} \left( \frac{\Theta_{vib,j}}{2} + \frac{\Theta_{vib,j}}{e^{-\Theta_{vib,j}/T} - 1} \right) - N_A D_e$$

$$\bar{C}_V = 3R + R \sum_{j=1}^{3n-6} \left[ \left( \frac{\Theta_{vib,j}}{T} \right)^2 \frac{e^{-\Theta_{vib,j}/T}}{\left( 1 - e^{-\Theta_{vib,j}/T} \right)^2} \right]$$



For H<sub>2</sub>O,

$$\Theta_{\text{vib}} = 2290 \text{ K}, 5160 \text{ K}, 5360 \text{ K}$$



Theoretical: Nonlinear polyatomic

$$\bar{C}_V = 3R + R \sum_{j=1}^{3n-6} \left[ \left( \frac{\Theta_{\text{vib},j}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{(1 - e^{-\Theta_{\text{vib},j}/T})^2} \right]$$

Figure 18.7



- From statistical models, we can learn about thermodynamic quantities.
- We can connect the microscopic and the macroscopic through  $Q$ .
- We can find  $Q$  through the molecular partition function,  $q$ , provided our system follows Boltzmann statistics (i.e., # energy levels greater than # of states).
- From  $Q$  we can calculate thermodynamic quantities such as  $U$  or  $C_V$ .
- You have some insight into why different materials have different thermodynamics properties (e.g., think of how quantum mechanical energy levels vary for different materials).

What's next? ... Classical thermodynamics and the laws that govern macroscopic thermodynamic quantities.



## For Boltzmann Statistics

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}$$

## Atoms

$$q_{\text{atomic}}(V, T) = q_{\text{trans}}(V, T)q_{\text{elec}}(V, T)$$

$$q_{\text{trans}}(V, T) = \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2} V$$

$$q_{\text{elec}}(T) = g_{e1} + g_{e2} e^{-\beta \epsilon_{e2}} + g_{e3} e^{-\beta \epsilon_{e3}} + \dots$$

## Physical Properties

$$\langle \epsilon_{\text{trans}} \rangle = k_B T^2 \left( \frac{\partial \ln q_{\text{trans}}}{\partial T} \right)$$

$$P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N, T} = N k_B T \left( \frac{\partial \ln q}{\partial V} \right)_T$$

$$\langle E \rangle = U = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V = N k_B T^2 \left( \frac{\partial \ln q}{\partial T} \right)_V$$

$$C_V = \left( \frac{dU}{dT} \right)_{N, V}$$

## Diatomic Molecules

$$q(V, T) = q_{\text{trans}}(V, T)q_{\text{elec}}(V, T)q_{\text{rot}}(V, T)q_{\text{vib}}(V, T)$$

$$q_{\text{trans}}(V, T) = \left( \frac{2\pi(m_1 + m_2)k_B T}{h^2} \right)^{3/2} V$$

$$q_{\text{elec}}(T) \approx g_{e1} e^{D_e/k_B T} + \left( g_{e2} e^{-\epsilon_{e2}/k_B T} \right)$$

$$q_{\text{vib}}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

$$\Theta_{\text{vib}} = \frac{h\nu}{k_B}$$

$$q_{\text{vib}}(T) = \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}}$$

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1) e^{-\Theta_{\text{rot}} J(J+1)/T} \quad \Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B}$$

$$\text{If } \Theta_{\text{rot}} \ll T, \quad q_{\text{rot}} = \frac{T}{\sigma \Theta_{\text{rot}}}$$

## Probabilities

$$f_v = \left( 1 - e^{-\Theta_{\text{vib}}/T} \right) e^{-v\Theta_{\text{vib}}/T}$$

$$f_J = \frac{(2J+1) e^{-\Theta_{\text{rot}} J(J+1)/T}}{q_{\text{rot}}}$$

