10.40 Thermodynamics **Fall 2003**
Problem Set 7

Problem 1

Sketch how C_v of xenon, carbon monoxide, and water behave as a function of temperature at low densities. Carefully note the limits as *T* goes to 0 K and as *T* gets large (but less than the first electronic excited state).

Solution:

Over the problem conditions, the three gases can be modeled as ideal gases since the density is low.

Over the range of *T* from 0 K to as *T* gets large (but less than the first electronic excited state), three parts of the partition function will contribute to the constant volume heat capacity: translational, rotational, and vibrational. The electronic partition function will not contribute since *T* will be less than the first electronic excited state.

Translational Contribution

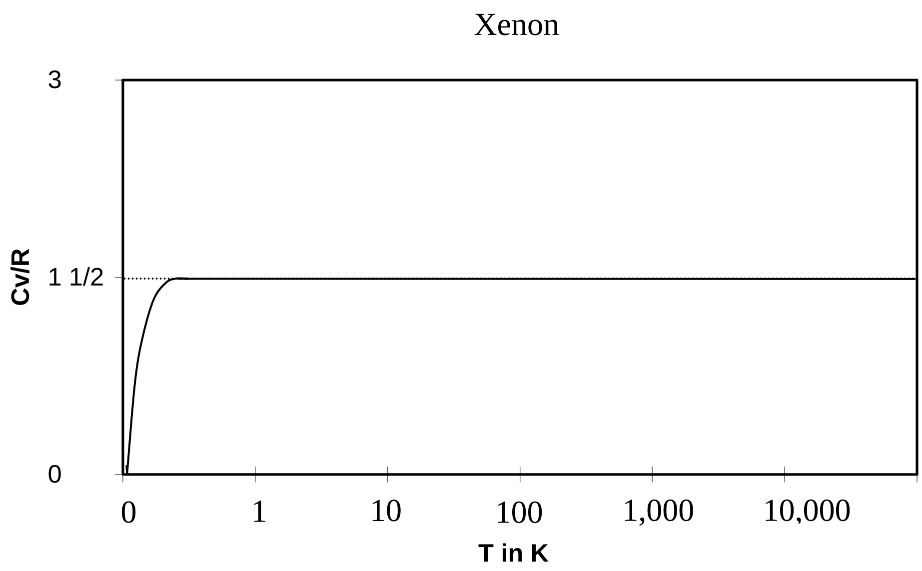
All substances at absolute zero can only occupy one energy state, so the partition function is equal to a constant. A differential change in temperature will not be enough to allow the system to occupy higher energy levels, so its total energy will not change. Therefore:

$$U\big|_{T=0} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} = 0 \text{ since } Q = \text{constant}$$

$$C_V\big|_{T=0} = \left(\frac{\partial U}{\partial T}\right)_{V,N} = 0$$

As the temperature increases, C_v quickly increases to the full translational contribution of 3/2 *R* since each translational degree of freedom contributes ½ *R* for an ideal gas.

Since xenon is monatomic, it has no rotational or vibrational contributions. As *T* gets large, C_v goes to 3/2 *R* as shown in the figure below.



Rotational Contribution

When the temperature is less than θ_r, the rotational levels are not appreciably populated. The rotational contribution to the partition functions becomes significant when $T \approx \theta_r \quad \left(\theta_r \;\; \mathrm{O}(1\,\mathrm{K})\right)$ and the rotational levels do not approach an equal population distribution until T is at least an order of magnitude larger than θ_r. As T gets large, the rotational contribution for C_v goes to ½ R for each rotational degree of freedom for an ideal gas. Thus, carbon monoxide, which is diatomic, has 1 R rotational contribution, and water, which is polyatomic, has a 3/2 R rotational contribution.

Vibrational Contribution

Similar to the rotational contribution, the vibrational energy levels are not appreciably populated until $T \approx \theta_v \quad \left(\theta_v = \mathrm{O}(1000 \text{ to } 10000\text{ K})\right)$ and the full vibrational contribution to C_v does not occur until T is at least an order of magnitude larger than θ_v. Since the vibrational energy levels are usually close to each other, the C_v versus T curve often only shows one jump for the total vibrational contribution. Before we can draw our C_v versus T curves for carbon monoxide and oxygen, we must determine the high temperature limit of the vibrational contribution.

$$\frac{C_v\big|_{vibrational_i}}{R} = \sum_{i=q}^{3N_{atoms}-x}\left[\left(\frac{\theta_{i,v}}{T}\right)^2 \frac{e^{\left(\theta_{i,v}/T\right)}}{\left(e^{\left(\theta_{i,v}/T\right)}-1\right)^2}\right]$$

where $x = 5$ for diatomic and linear molecules

$x = 6$ for polyatomic molecules

for $T \to \infty, C_v\big|_{vibrational} \to \frac{0}{0}$

Changing variable from T to $\left(\theta_{i,v}/T\right)$, applying L'Hôpital's rule twice, and canceling out an e^x factor yields,

$$\lim_{T\to\infty}\frac{C_v\big|_{vibrational_i}}{R} = \lim_{z\to 0}\left[\frac{z^2 e^{(z)}}{\left(e^{(z)}-1\right)^2}\right] \text{ where z=} \theta_{i,v}\big/T\sum_{i=1}^{n} X_i$$

As $T \to \infty$, $z \to 0$

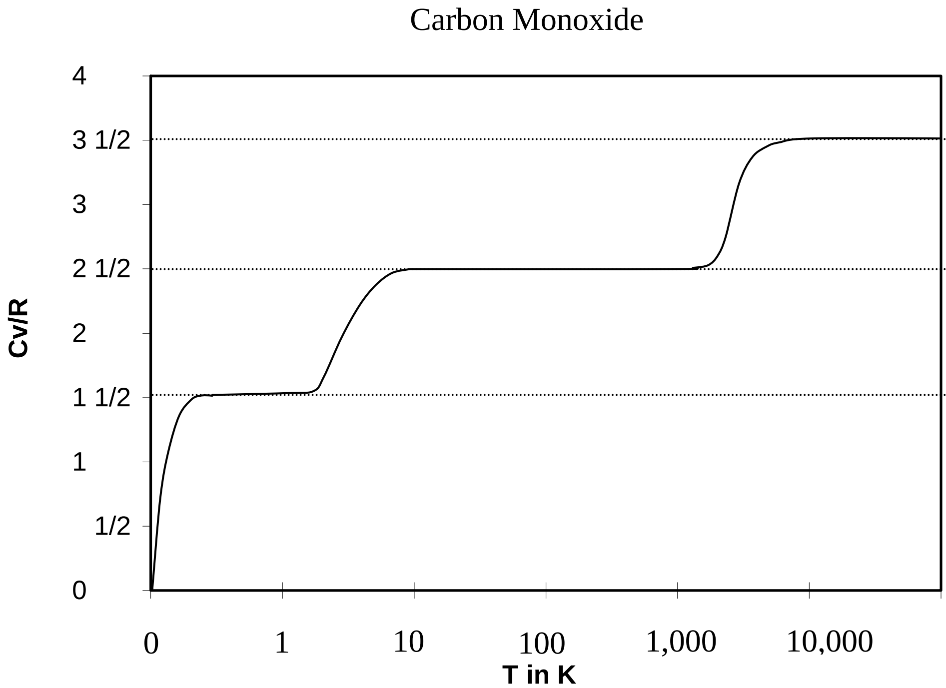
$$\lim_{T\to\infty}\frac{C_v\big|_{vibrational_i}}{R} = \lim_{z\to 0}\frac{\frac{\partial}{\partial z}\left[z^2 e^{(z)}\right]}{\frac{\partial}{\partial z}\left[\left(e^{(z)}-1\right)^2\right]} = \frac{2ze^z + z^2 e^z}{2e^{2z}-2e^z} = \frac{2z+z^2}{2e^z-2}$$

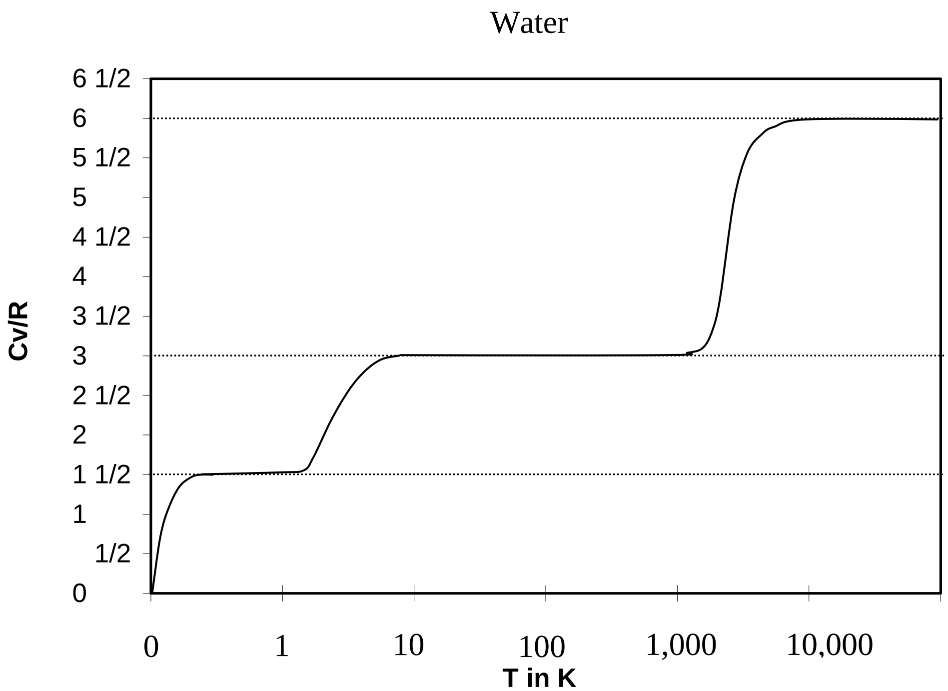
$$\lim_{T\to\infty}\frac{C_v\big|_{vibrational_i}}{R} = \lim_{z\to 0}\frac{\frac{\partial}{\partial z}\left[2z+z^2\right]}{\frac{\partial}{\partial z}\left[2e^z-2\right]} = \frac{2+2z}{2e^z} = \frac{2}{2} = 1$$

Thus, the vibrational contribution for $C_v = R$ times the rotational degrees of freedom. For carbon monoxide, C_v *(vib)*= R in the high temperature limit, and for water, C_v *(vib)*= $3R$ in the high temperature limit.

C_v/R High Temperature Limit

	Xe	CO	H_2O
q_t	3/2	3/2	3/2
q_r	0	2/2	3/2
q_v	0	1	3
total	3/2	7/2	6


Carbon Monoxide
Cv/R
0
1/2
1
1 1/2
2
2 1/2
3
3 1/2
4
0
1
10
100
1,000
10,000
T in K


Water
Cv/R
0
1/2
1
1 1/2
2
2 1/2
3
3 1/2
4
4 1/2
5
5 1/2
6
6 1/2
0
1
10
100
1,000
10,000
T in K