

## Chem 534: Problem Set #4

Due in class: Tues, Oct. 6th

Useful websites for

atoms: [http://physics.nist.gov/PhysRefData/Handbook/element\\_name.htm](http://physics.nist.gov/PhysRefData/Handbook/element_name.htm)

diatomic molecules: <http://webbook.nist.gov/chemistry/>

- (1) Molecular nitrogen is heated in an electric arc and it is found spectroscopically that the relative populations of excited vibrational levels are

$n$	0	1	2	3	4
$\frac{f_n}{f_0}$	1.000	0.200	0.040	0.008	0.002

Is the nitrogen in thermodynamic equilibrium with respect to vibrational energy? What is the vibrational temperature of the gas? Is this necessarily the same as the translational temperature?

- (2) The harmonic oscillator-rigid rotor approximation can be corrected using expressions from vibrational perturbation theory:

$$\varepsilon_{vib} = \omega_e \left(n + \frac{1}{2}\right) - \omega_e x_e \left(n + \frac{1}{2}\right)^2 + \dots$$

$$\varepsilon_{rot} = \tilde{B}_e J(J+1) - \tilde{D}_e [J(J+1)]^2 + \dots \quad (\text{all in cm}^{-1} \text{ units})$$

$$\varepsilon_{vib,rot} = -\alpha_e \left(n + \frac{1}{2}\right) J(J+1) + \dots$$

where the anharmonicity constant ( $\omega_e x_e$ ) accounts for vibrational anharmonicity, the centrifugal distortion constant,  $\tilde{D}_e$ , not to be confused with the dissociation energy, accounts for centrifugal stretching, and the vibration-rotation interaction constant  $\alpha_e$  corrects for the fact that  $\langle r \rangle$  is not the same in each vibrational state due to the asymmetry of the potential function (compared to the HO). Hence the total vibration+rotation energy can be written as:

$$\varepsilon_{vib+rot} = \omega_e \left(n + \frac{1}{2}\right) - \omega_e x_e \left(n + \frac{1}{2}\right)^2 + \tilde{B}_e J(J+1) - \tilde{D}_e [J(J+1)]^2 - \alpha_e \left(n + \frac{1}{2}\right) J(J+1)$$

With this more rigorous expression, that the molecular partition function can be written in the form

$$q(V, T) = q'_{HO-RR} q_{anharm}$$

where

$$q'_{HO-RR} = \frac{kT}{\sigma hc(\tilde{B}_e - \alpha_e/2)} \frac{e^{(-\omega_e/2 + \omega_e x_e/4)hc/kT}}{1 - e^{-hc\omega_e/kT}}$$

$$q_{anharm} = 1 + \frac{2\tilde{D}_e kT}{hc(\tilde{B}_e - \alpha_e/2)^2} + \frac{\alpha_e}{(\tilde{B}_e - \alpha_e/2)(e^{hc\omega_e/kT} - 1)} + \frac{2hc\omega_e x_e}{kT(e^{hc\omega_e/kT} - 1)^2}$$

Calculate the values of  $q'_{HO-RR}$ ,  $q_{anharm}$  and  $q(V,T)$  for CO at 300 K.

- (3) For the CO molecule, calculate the value of  $q_{rot}$  and plot the distribution of rotational energy levels at  $T = 200$  K and 2000 K.
- (4) Consider the gas phase  $N_2$  molecule at a temperature of 300 K.
- (a) What is the most probable value of the rotational quantum number  $J$  if one ignores the fact that  $N_2$  is homonuclear?
- (b) Determine the possible nuclear spin states of  $N_2$  and discuss their effects on the rotational partition function, i.e., give the form of  $q_{rot,nuc}$ .
- (c) Determine the fraction of molecules in each  $J$  state from 0 to 9 at  $T=300$  K (just use the high temperature limit for  $q_{rot}$  in these calculations). Compare your results with what you determined in part (a).
- (d) What is the most probable vibrational quantum number  $n$  for this same temperature?
- (5) Calculate the rotational contribution to the entropy of HD at 20 K, 100 K, and 300 K using the formulas appropriate for each particular temperature (justify your choice via the values of  $\frac{\theta_r}{T}$ ). Note that the equilibrium bond length of HD is identical to that of  $H_2$ .
- (6) What is the thermal correction ( $T$ -dependent contribution) to the total energy at 300 K for one mole of CO?