

Chemistry 1480, Hour Exam 2, March 14, 2007.

This exam consists of four (4) problems. Please work them all, and provide brief descriptions of your reasoning as appropriate. GOOD LUCK! [Note the designation $\beta \equiv (k_B T)^{-1}$, where k_B is Boltzmann's constant and T is the absolute temperature in degrees K.]

1) [30%] Consider a noninteracting lattice gas, in which N particles (“molecules”) occupy M sites. See Fig. 1 for a 2D illustration. In 3D the volume of each site (“cell”) is equated with the volume taken up by one molecule.

For such a system in thermal equilibrium at temperature T , the entropy can be shown to be given by the formula:

$$S = k_B \ln \frac{M!}{N!(M-N)!} \quad [1]$$

[Note: You do not have to prove this here!]

a) Use Stirling's approximation to show that Eq. 1 implies:

$$S \cong -Mk_B [\theta \ln \theta + (1-\theta) \ln(1-\theta)] ; \theta \equiv N/M \quad [2]$$

b) Under normal (“ideal”) gas phase conditions the particle density is low, i.e., $N/M \ll 1$. If so, then the 2nd term in Eq. 2 can be neglected, and $S \cong -Mk_B \theta \ln \theta = -Nk_B \ln(N/M)$. Using this formula for the entropy of the lattice gas, consider a transition in which the gas is transferred from a container consisting of M_1 sites to a container consisting of M_2 sites at the same temperature. Calculate $\Delta S \equiv S_2 - S_1$ for this process. Show that your results are consistent with the predictions of classical thermodynamics, namely, $\Delta S = Nk_B \ln(V_2/V_1)$, where V_1 is the volume of container 1, and analogously for V_2 .

x			
		x	
	x		

Fig. 1: Lattice gas model with $N=3$ and $M=16$.

2) [20%] Benzene, C_6H_6 , is a planar molecule with hexagonal symmetry. Consider an idealized version of this molecule, “Benzane”, indicated in Fig. 2. Benzane is also a planar molecule with hexagonal symmetry: essentially, we have fused each $C-H$ group into an effective “atom” of mass m for the sake of geometric simplicity. Calculate the three principal moments of inertia for Benzane (cf. Fig. 2 for axis labels). In particular, show that: i) $I_x = I_y$, and ii) $I_z = 2I_x$.

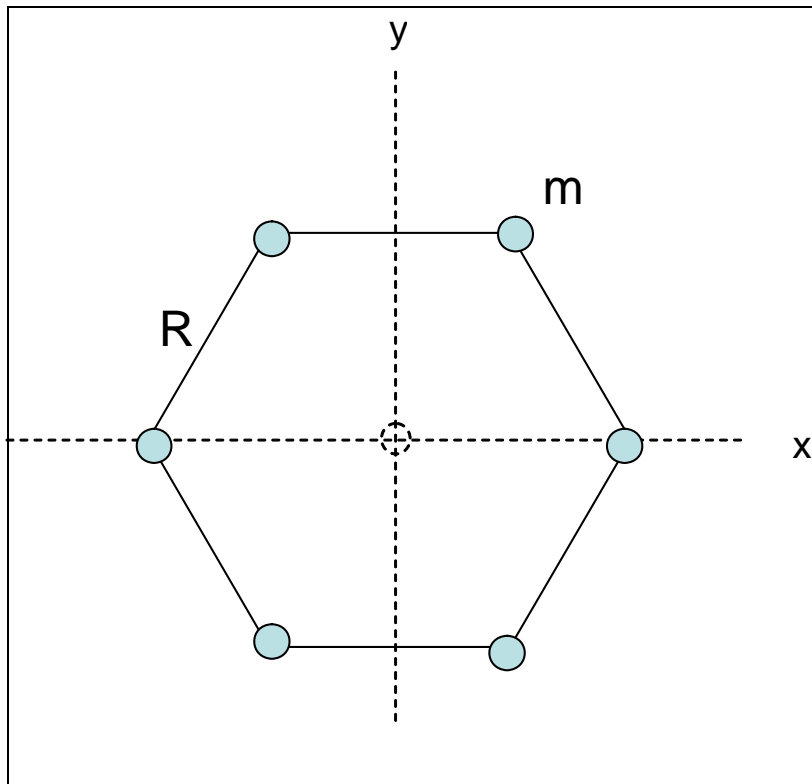
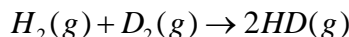


Fig. 2. Benzane: a perfect hexagon. All “atoms” have mass m ; all bond lengths are R . Dashed circle indicates z axis pointing out of the plane.

(3) [25%] Consider the isotopic exchange reaction:



(a) The equilibrium constant K_c for this reaction (in the direction indicated) can be written in terms of the molecular partition function q_{H_2} , q_{D_2} , and q_{HD} , describing H_2 , D_2 , and HD , respectively, as

$$K_c = \frac{(q_{HD}/V)^2}{(q_{H_2}/V)(q_{D_2}/V)}$$

(V being the volume of the container). Show how this constant is related to the concentrations of the three gases at equilibrium, *i.e.*, write the law of mass action for this reaction.

(b) For each gas species involved, the molecular partition function is a product of factors for translational, rotational, vibrational, and electronic motion. For example, $q_{H_2} = q_{H_2}^{elect} q_{H_2}^{trans} g_{H_2}^{rot} q_{H_2}^{vib}$. Furthermore, since D is an isotope of H (they have the same number of protons and electrons), the chemical bonding characteristics of a molecule is unaltered if D is substituted for H , or vice versa. This means that the electronic factors cancel out the equilibrium constant expression, and K_c can be written as

$$K_c = K^{trans} K^{rot} K^{vib}$$

with

$$K^{trans} = \frac{(q_{HD}^{trans}/V)^2}{(q_{H_2}^{trans}/V)(q_{D_2}^{trans}/V)}; K^{rot} = \frac{(q_{HD}^{rot})^2}{q_{H_2}^{rot} q_{D_2}^{rot}}; K^{vib} = \frac{(q_{HD}^{vib})^2}{q_{H_2}^{vib} q_{D_2}^{vib}}$$

(i) Show that:

$$K^{trans} = \frac{m_{HD}^3}{(m_{H_2} m_{D_2})^{3/2}}$$

where m_{HD} is the mass of HD , etc.

(ii) Because the chemical bonding properties of all three species are the same, their equilibrium bond lengths are the same. Show that this implies:

$$K^{rot} = \frac{4\mu_{HD}^2}{\mu_{H_2} \mu_{D_2}}$$

where μ_{HD} is the reduced mass of HD , etc.

- (4) [25%] Calculate the molar heat capacity of gaseous O=C=O (carbon dioxide, a linear molecule) at 300° K. Assume the total heat capacity can be broken into translational, rotational, and vibrational contributions using the formulas developed in class for each type of motion. The only molecular data needed are the four vibrational frequencies of carbon dioxide, namely 1337 cm⁻¹ (symmetric stretch), 2349 cm⁻¹ (asymmetric stretch), and two degenerate bend modes each with vibrational frequency 667 cm⁻¹.

Note: (i) The following conversion factor may be of use: At 300K, $k_B T \cong 207 \text{ cm}^{-1}$.

(ii) To compute the vibrational contributions you will need to evaluate the function $f(y) = y^2 / \sinh^2(y)$ at certain values of y . A tabulation of this function is given in Table 1.

y	$f(y)$
0.2	0.987
0.4	0.948
0.6	0.888
0.8	0.811
1	0.724
1.2	0.632
1.4	0.54
1.6	0.454
1.8	0.374
2	0.304
2.2	0.244
2.4	0.193
2.6	0.151
2.8	0.117
3	0.09
3.2	0.068
3.4	0.052
3.6	0.039

Table 1.