PROBLEM SET 7

1. **Consider a gas in equilibrium with the surface of a solid. Some of the molecules of the gas will be absorbed onto the surface, and the number absorbed will be a function of the pressure of the gas. A simple statistical mechanical model for this system is to picture the solid surface to be a two-dimensional lattice of M sites. Each of these sites can be wither unoccupied, or occupied by at most one molecule of the gas. Let the partition function of an unoccupied site be 1 and of an occupied site be q(T) (we don't need to know q(T) here). Assuming that molecules absorbed onto the lattice sites do not interact with each other, the partition function of N molecules absorbed onto M sites is then**

$$Q(N,M,T) = \frac{M!}{N!(M-N)!}[q(T)]^N$$

The binomial coefficient accounts for the number of ways of distributing the N molecules over the M sites. By using the fact that the absorbed molecules are at equilibrium with the gas phase molecules (considered to be an ideal gas), derive an expression for the fractional coverage, $\theta \equiv N/M$, as a function of the pressure of the gas. Such an expression is called an adsorption isotherm, and this particular model gives the so-called Langmuir adsorption isotherm.

[Mc Quarrie 4-20]

2. **Generalize the calculations of the thermodynamic properties of a pure ideal gas to a binary mixture. In particular, show that**

$$Q = \frac{q_1^{N_1}\, q_2^{N_2}}{N_1!\; N_2!}$$

$$\underline{U} = 3/2\;(N_1 + N_2)kT$$

and

$$\underline{S} = N_1 k \ln\left(\frac{\underline{V}e^{5/2}}{\Lambda_1^3 N_1}\right) + N_2 k \ln\left(\frac{\underline{V}e^{5/2}}{\Lambda_2^3 N_2}\right),$$

if we ignore the electronic contribution to the partition function. Is the result for the entropy consistent with the standard thermodynamic result for the ideal entropy of mixing?

[Mc Quarrie, 5-13]

3. **Starting from the Maxwell-Boltzmann distribution,**
   - (a) **Prove that the most probable molecular speed is $u^* = (2kT/m)^{1/2}$, that the mean speed is $\langle u\rangle = (8kT/\pi m)^{1/2}$, and that the root-mean-square speed is $\langle u^2\rangle^{1/2} = (3kT/m)^{1/2}$.**
   - (b) **Show that the mean-square fluctuation of the velocity of the Maxwell-Boltzmann distribution is**

     $$\langle u^2\rangle - \langle u\rangle^2 = \frac{kT}{m}(3 - 8/\pi)$$

   - (c) **Show that the average velocity in any direction, (say x, y or z) vanishes. What does this mean?**

[McQuarrie, 7-16 to 7-18]

4. The Joule-Thomson coefficient, ζ, is defined by

$$\zeta = (\partial T/\partial P)_H$$

(a) Prove that ζ can be expressed in terms of experimentally measurable quantities as C_P^{-1} [$T(\partial V/\partial T)_P - V$]

(b) Derive a density expansion for ζ. At high temperatures ζ is negative, and for sufficiently low temperatures, it is positive. The temperature at which ζ is zero is called the inversion temperature. Show that for not too dense gases, the inversion temperature is given by $d(B_2/T)/dT = 0$

(c) Calculate the inversion temperature, if any, for a low-pressure fluid obeying the square well potential.

5. For a multicomponent mixture the virial expansion can be written as

$$P/kT = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$$

where ρ is the total density $\rho = N/\underline{V}$. Show that the second virial coefficient for a multicomponent mixture is a quadratic function of composition:

$$B_2(T) = \sum_{i=1}^{n} \sum_{j=1}^{n} B_{ij}(T) x_i x_j$$

where x_i, x_j are the mole fractions of the components and B_{ij} are parameters called *cross second virial coefficients*. How are these coefficients defined, and what is their physical significance?