Thermodynamics HW #7

Due October 16

1. Schroeder 3.38
2. Schroeder 4.1
3. **Gas Absorption** In this problem we investigate the role of the chemical potential in the absorption of argon atoms by an absorbent[1]. You will get practice calculating the chemical potential from the entropy[2], and then using the chemical potential to determine how the concentration of absorbed gas depends on the temperature and pressure of the surrounding gas.

   To get started we must first decide how to model the absorbed argon atoms. In general this is complicated chemistry problem, but let's try to simplify the situation as much as possible while still capturing the essence of the siutation. Consider the following hypothesis:

   - The absorbent contains N sites where atoms can attach. Each site can accomodate at most one argon atom.
   - An argon atom bound to an absorption site can oscillate in one direction about its equilibrium[3] position, and that the oscillatory energy in quantized so that it can take only integer multiples of some energy quantum $h\nu$.
   - The energy of an atom at the equilibrium position in the absorption site is $-\epsilon$, i.e. the sites have a *binding energy* ϵ. See figure 1 for an illustration of the energy level structure of the absorption sites.

   From the above assumptions we find the total energy U is given by

   $$U = qh\nu - n\epsilon$$

   [4]where q is the total number of vibrational quanta and n is the number of oscillators which is equal to the number N_A of absorbed argon atoms, i.e.

   $$N_A = n$$

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[1] graphite, for example, is a good absorbent on account of its high surface area to volume ratio

[2] In particular you will get practice negotiating the fussy partial derivatives commonly encountered in thermodynamics

[3] Equilibrium here is meant as the position in the absorption site where the atom experiences zero forces, not to be confused with thermodynamic equilibrium :)

[4] This was incorrectly written as $U = qh\nu + n\epsilon$ in an earlier version.

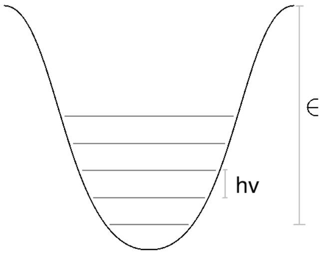

Figure 1: Oscillator with energy quanta $h\nu$ and binding energy ϵ.

The entropy $S(U, N_A)$ of the absorbed argon atoms can then be written as

$$S(U, N_A) = S_1\left(x(N_A)\right) + S_2\left(n(U, N_A), q(U, N_A)\right)$$

where

- $S_1(x) = -Nk\left(x \ln x + (1-x)\ln(1-x)\right)$ is the entropy associated with the $\binom{N}{N_A}$ ways of distributing the N_A atoms among the N absorption sites, with $x \equiv \frac{N_A}{N}$ representing the concentration of absorbed argon atoms, and
- $S_2(n, q) = k\left((n+q)\ln(n+q) - n\ln n - q\ln q\right)$ is the entropy of an Einstein solid with n oscillators and q quanta.

(a) Find an expression for the chemical potential μ_A of the absorbed atoms in terms of x, T, ϵ, and $\frac{q}{n}$.
Take the limit where $\frac{hv}{kT} \to \infty$ so that the oscillator degrees of freedom are "frozen out". Use the fact that $\frac{q}{n} = \frac{1}{e^{\frac{h\nu}{kT}}-1}$.
Answer: $\mu_A = kT \ln \frac{x}{1-x} - \epsilon$

(b) In certain units T_o, P_o the chemical potential μ_G of the argon gas has the form

$$\mu_G(T, P) = kT \ln \frac{P/P_o}{\left(T/T_o\right)^{5/2}}$$

Show that when the absorbent is in equilibrium with the gas the absorbent concentration $x \equiv \frac{N_A}{N}$ takes the following form, known as the *Langmuir absorption isotherm.*

$$x = \frac{P}{\mathcal{P}(T) + P}$$

where

$$\mathcal{P}(T) = P_o e^{-\frac{\epsilon}{kT}} \left(T/T_o\right)^{5/2}$$

is the pressure at which the absorbent is half full.
Hint: What is true about the temperature and chemical potential of the two systems (A and G) in equilibrium?

(c) What happens to the concentration x with increased P at constant T? Sketch a plot.
How about when T is increased at constant P?

For both questions give a *qualitative* explanation in terms of the microscopic behavior of the system. In particular try to account for the $e^{-\frac{\epsilon}{kT}}$ and $\left(\frac{T}{T_o}\right)^{5/2}$ factors in $\mathcal{P}(T)$.

Hint: microscopically we can think of equilbrium as the condition where the rate of atoms leaving the absorbent equals the rate of atoms exiting.