Thermodynamics HW #7

<center>Due October 16</center>

1. Schroeder 3.38

   Solution: I think the answer in the solution manual for the question is pretty miserable. Here is what I hope you'll agree is a more methodical solution.

   First let's be clear about what we are being asked to prove. If we have an ideal gas with N different species (e.g. O_2, He, N_2) with partial pressure P_i for the ith species, prove that for $j \neq i$ we have that

   $$\left(\frac{\partial \mu_i}{\partial P_j}\right)_{T, P_{k \neq j}} = 0$$

   so that the chemical potential of the ith species is independent of the partial pressures of the other species. Since $P_i V = n_i k T$ we find then at fixed V this is equivalent to the statement

   $$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T, n_{k \neq j}} = 0$$

   As a first step we note the *definition* of the chemical potential of the ith species of a multi-component system:

   $$\mu_i \equiv -T \left(\frac{\partial S}{\partial U}\right)_{n_1, \ldots, n_N}$$

   (In this problem we are always at fixed volume V so we omit its mention for convenience.) Since by assumption none of the particles interact, we can certainly assert that particles of different species don't interact. This means we can construct an expression for the entropy $S(U, n_1, \ldots, n_N)$ of the whole system by treating each component as separate sub-systems in thermal contact with each other. We have a lot of experience with such systems by now. Suppose that the entropy for the ith component is given by $S_i(U_i, n_i)$. The total entropy is $S(\hat{U}, n_1, \ldots, n_N)$ of such a system with total energy $\hat{U}$ is given by the sum $\sum_{i=1}^{N} S_i(\hat{U}_i, n_i)$ where

   $$\sum_{i=1}^{N} \hat{U}_i = \hat{U}$$

   and the unconstrained heat flow between the different components implies that the total energy $\hat{U}$ is partitioned into the different $\hat{U}_i$ in such a way that equalizes their temperatures, i.e. so that there is some T such that

   $$\left(\frac{\partial S_i}{\partial U_i}\right)_{n_i} (\hat{U}_i, n_i) = \frac{1}{T}$$

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for all i. We have then that

$$\mu_i = -T \left(\frac{\partial S}{\partial n_i} \right)_{U, n_{j \neq i}}$$

$$= -T \sum_{j=1}^{N} \left(\frac{\partial S_j}{\partial n_i} \right)_{U, n_{k \neq i}}$$

$$= -T \sum_{j=1}^{N} \left(\left(\frac{\partial S_j}{\partial n_j} \right)_{U_j} \left(\frac{\partial n_j}{\partial n_i} \right)_{U, n_{k \neq i}} + \left(\frac{\partial S_j}{\partial U_j} \right)_{n_j} \left(\frac{\partial U_j}{\partial n_i} \right)_{U, n_{k \neq i}} \right)$$

where in the last line we apply the chain rule for partial derivatives. Make sure you completely understand the previous step before continuing. For the first term in the outer parentheses we have

$$\left(\frac{\partial S_j}{\partial n_j} \right)_{U_j} \left(\frac{\partial n_j}{\partial n_i} \right)_{U, n_{k \neq i}} = -\frac{\tilde{\mu}_j}{T} \delta_{ij}$$

where $\tilde{\mu}_j$ is the chemical potential at a temperature T of a system containing n_j particles of the jth species and nothing else. Make sure the part about the temperature is clear to you.

The second term in the outer parentheses gives

$$\left(\frac{\partial S_j}{\partial U_j} \right)_{n_j} \left(\frac{\partial U_j}{\partial n_i} \right)_{U, n_{k \neq i}} = \frac{1}{T} \left(\frac{\partial U_j}{\partial n_i} \right)_{U, n_{k \neq i}}$$

so that returning to the evaluation of μ_i we find

$$\mu_i = -T \sum_{j=1}^{N} \left(-\frac{\tilde{\mu}_j}{T} \delta_{ij} + \frac{1}{T} \left(\frac{\partial U_j}{\partial n_i} \right)_{U, n_{k \neq i}} \right)$$

$$= \tilde{\mu}_i - \sum_{j=1}^{N} \left(\frac{\partial U_j}{\partial n_i} \right)_{U, n_{k \neq i}}$$

$$= \tilde{\mu}_i - \left(\frac{\partial \sum_{j=1}^{N} U_j}{\partial n_i} \right)_{U, n_{k \neq i}}$$

$$= \tilde{\mu}_i - \left(\frac{\partial U}{\partial n_i} \right)_{U, n_{k \neq i}}$$

$$= \tilde{\mu}_i$$

So I have appeared to have derived the result $\mu_i = \tilde{\mu}_i$, which asserts the equality of

- μ_i, which is a *function* of the thermodynamic variables $U, n_1, \ldots, n_N$, and

- $\tilde{\mu}_i$, which we defined to be a *number* equal to the chemical potential potential of a ith species-only gas of n_i particles at a temperature T.

As it stands the statement is nonsense since it equates objects not even of the same type. I leave it to you to go back through the derivation, instead deriving an expression

for the *value* of the *function* μ_i *evaluated* at a temperature T and particle numbers $n_1, \ldots, n_N$. You should find that you get

$$\mu_i(T, n_1, \ldots, n_N) = \tilde{\mu}_i$$

so that we find that the chemical potential μ_i of the multi-component system at a temperature T and partial pressure P_i is equal to the chemical potential $\tilde{\mu}_i$ of a single component system with a pressure $P = P_i$ (i.e. particle number $n = n_i$) at the same temperature. μ_i is thus clearly independent of the partial pressures $P_{j \neq i}$, thus completing the proof.

I think this is a really good exercise that covers a lot of the tricky conceptual subtleties of thermodynamic calculations. If there are steps in the derivation that aren't totally clear to you I strongly encourage you to work through it again slowly, filling in for yourself any steps that I might have skipped over.

2. Schroeder 4.1

   Solution: Using the ideal gas law, equipartition function, and first law of thermodynamics we find that

   - **A:**
       - $\Delta U = \frac{f}{2} n k \Delta T = \frac{f}{2} V \Delta P = \frac{f}{2} V_1 (P_2 - P_1)$
       - $W = -P \Delta V = 0$
       - $Q = \Delta U - W = \frac{f}{2} V_1 (P_2 - P_1)$
   - **B:**
       - $\Delta U = \frac{f}{2} n k \Delta T = \frac{f}{2} P \Delta V = \frac{f}{2} P_2 (V_2 - V_1)$
       - $W = -P \Delta V = -P_2 (V_2 - V_1)$
       - $Q = \Delta U - W = \left(\frac{f}{2} + 1 \right) P_2 (V_2 - V_1)$
   - **C:**
       - $\Delta U = \frac{f}{2} V_2 (P_1 - P_2)$
       - $W = 0$
       - $Q = \frac{f}{2} V_2 (P_1 - P_2)$
   - **D:**
       - $\Delta U = \frac{f}{2} P_1 (V_1 - V_2)$
       - $W = -P_1 (V_1 - V_2)$
       - $Q = \Delta U - W = \left(\frac{f}{2} + 1 \right) P_1 (V_1 - V_2)$

   So that the work done *on* the system, i.e. the *negative* of the work produced *by* the system, is

   $$W = W_A + W_B + W_C + W_D = -(P_2 - P_1)(V_2 - V_1) = -2P_1 V_1$$

   and the heat *absorbed* by the system, i.e. the heat transferred to the system when in

contact with the higher temperature reservoir, is

$$Q_h = Q_A + Q_B$$
$$= \frac{f}{2}V_1(P_2 - P_1) + \left(\frac{f}{2}+1\right)P_2(V_2 - V_1)$$
$$= \frac{f}{2}V_1 P_1 + 4\left(\frac{f}{2}+1\right)P_1 V_1$$
$$= \left(5\frac{f}{2}+4\right)P_1 V_1$$
$$= \frac{33}{2}P_1 V_1$$

So that the efficiency e, which is the ratio of the work produced divided by the heat absorbed, is

$$e = \frac{-W}{Q_h} = \frac{2}{33}$$

while the ideal engine has an efficiency e_i

$$e_i = 1 - \frac{T_c}{T_h}$$

where in our case we have a minimum temperature

$$T_c \propto P_1 V_1$$

and a maximum temperature

$$T_h \propto \frac{P_2 V_2}{=} 6 P_1 V_1$$

giving

$$e_i = 1 - \frac{1}{6} = \frac{5}{6}$$

giving an efficiency ratio of

$$\frac{e_i}{e} = \frac{5}{6} \cdot \frac{33}{2} = \frac{165}{12} = 1375\%$$

so our engine is quite a ways off from ideal.

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:

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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

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- 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.
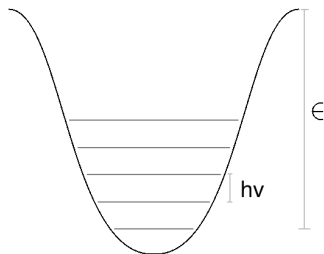

Figure 1: Oscillator with energy quanta $h\nu$ and binding energy ϵ.

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.

$$N_A = n$$

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 $\frac{h\nu}{kT} \to \infty$ so that the oscillator degrees of freedom are "frozen out". Use the fact that $\frac{q}{n} = \frac{1}{e^{\frac{h\nu}{kT}} - 1}$.

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[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.

Answer: $\mu_A = kT \ln \frac{x}{1-x} - \epsilon$

Solution:

We start with the definition of the chemical potential

$$\mu_A \equiv -T \left(\frac{\partial S}{\partial N_A} \right)_U$$

note that the derivative is with respect to N_A, not N, since we are considering addition and removal not of absorption sites (of which there are a fixed number N of) but rather of argon atoms (of which there are N_A of).

We then expand S into $S_1 + S_2$. Since S_1 and S_2 are expressed in terms of variables x, n, q that are themselves *functions* of the variables N_A and U, we must use the chain rule so that

$$\left(\frac{\partial S}{\partial N_A} \right)_U = \frac{dS_1}{dx} \frac{dx}{dN_A} + \left(\frac{\partial S_2}{\partial n} \right)_q \left(\frac{\partial n}{\partial N_A} \right)_U + \left(\frac{\partial S_2}{\partial q} \right)_n \left(\frac{\partial q}{\partial N_A} \right)_U$$

looking at the expressions one by one we find

$$\frac{dS_1}{dx} = -kN \ln \frac{x}{1-x}$$

$$\frac{dx}{dN_A} = \frac{1}{N}$$

$$\left(\frac{\partial S_2}{\partial n} \right)_q = k \ln \left(1 + \frac{q}{n} \right)$$

$$\left(\frac{\partial n}{\partial N_A} \right)_U = 1$$

$$\left(\frac{\partial S_2}{\partial q} \right)_n = k \ln \left(1 + \frac{n}{q} \right)$$

$$\left(\frac{\partial q}{\partial N_A} \right)_U = \frac{\epsilon}{h\nu}$$

for any temperature T we have

$$1 + \frac{n}{q} = 1 + e^{\frac{h\nu}{kT}} - 1 = e^{\frac{h\nu}{kT}}$$

so that

$$\ln \left(1 + \frac{n}{q} \right) = \frac{h\nu}{kT}$$

while in the low temperature limit we have

$$1 + \frac{q}{n} \approx 1$$

so that

$$\ln \left(1 + \frac{q}{n} \right) \approx 0$$

putting this all together we arrive at the desired expression for μ_A.

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

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

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

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

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?

Solution:

In equilibrium two systems in thermal contact that are free to exchange particles will do so until they reach an equal temperature and chemical potential.

Setting $\mu_A = \mu_G$ and $T_A = T_G = T$ and solving for x we arrive at the desired expression.

(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.

Solution:

The concentration x at very low pressures $P \ll P_o$ increases as $\frac{P}{P_o}$ while at very high pressures $p \gg P_o$ the concentration saturates to $\frac{P}{P} = 1$.

Microscopically we can rationalize this as follows:

- At fixed temperature the average impulse each atom delivers to the container walls per collision is fixed, so that if the pressure increases it follows that the *rate* of collisions must too increase. So too then we have that the in-flux of atoms into the absorbent increases.

- The concentration of atoms in the absorbent must adjust so that the out-flux balances this increased in-flux. Qualitative the out-flux can be understood as the concentration of atoms divided by the average amount of time τ any given atom spends in the absorbent before being ejected by thermal agitation. At fixed temperature τ is fixed, so therefore the concentration of atoms must increase to increase the out-flux.

Since both factors in the expression for $\mathcal{P}(T)$ are *decreasing* function of T, we conclude that the concentration decreases with increasing T, since $\mathcal{P}$ appears in the denominator.

Microscopically we reason that the in-flux is now decreased since we have equal force on the walls by higher impulse per collision. This is borne out in the thermodynamics by the factor $(T/T_o)^{5/2}$ in $\mathcal{P}(T)$.

In addition, the increased temperature will decrease τ since the increased thermal agitation increases the likelihood that an atom is dislodged from its binding site. This is borne out in the thermodynamics by the factor $e^{-\frac{\epsilon}{kT}}$ in $\mathcal{P}(T)$. Therefore the concentration must decrease to balance the decreased in-flux.