Dylan Sheehan's second Chem302 Homework. Written in $\LaTeX$

1. Consider a canonical ensemble composed of two different types of systems, which we will label A and B. The partition functions for each component are :

$$Q_A = \sum_{i=0}^{N_A} e^{E_i(N_A,V_A)/k_B T}$$

$$Q_B = \sum_{j=0}^{N_B} e^{E_j(N_B,V_B)/k_B T}$$

Where T must be the same in the two and N_A and N_B are the number of particles of each type of systems. Given that
$Q_{total} = Q_A \cdot Q_B$
a. Derive an equation for U_{total}, the total internal energy, in terms of U_A and U_B

$$U_a = k_B T^2 \frac{1}{Q_A}\left(\frac{\partial Q_A}{\partial T}\right)$$

$$U_b = k_B T^2 \frac{1}{Q_B}\left(\frac{\partial Q_B}{\partial T}\right)$$

$$U_{tot} = k_B T^2 \frac{1}{Q_{tot}}\left(\frac{\partial Q_{tot}}{\partial T}\right)$$

$$U_{tot} = k_B T^2 \frac{1}{Q_A \cdot Q_B}\left(\frac{\partial Q_A \cdot Q_B}{\partial T}\right)$$

$$U_{tot} = k_B T^2 \frac{1}{Q_A \cdot Q_B}\left(\frac{\partial Q_A}{\partial T} Q_B + \frac{\partial Q_B}{\partial T} Q_A\right)$$

$$U_{tot} = k_B T^2 \left(\frac{\frac{\partial Q_A}{\partial T}}{Q_A} + \frac{\frac{\partial Q_A}{\partial T}}{Q_B}\right)$$

$$\boxed{U_{tot} = U_A + U_B}$$

b. Derive an equation for P_{total}, the total pressure, in therms of P_A and P_B. Using the result in b, find the statistical mechanical equivalent of Dalton's law of partial pressure(i.e $P_A = X_A P_{total}$)

$$\text{General Pressure} : k_B T\left(\frac{\partial \ln Q}{\partial V}\right)_T = k_B T\frac{1}{Q}\left(\frac{\partial Q}{\partial V}\right)$$

$$P_A = k_B T\frac{1}{Q_A}\left(\frac{\partial Q_B}{\partial V}\right)$$

$$P_B = k_B T\frac{1}{Q_B}\left(\frac{\partial Q_B}{\partial V}\right)$$

$$P_{tot} = k_B T\frac{1}{Q_{tot}}\left(\frac{\partial Q_{tot}}{\partial V}\right)$$

$$Q_{tot} = Q_A \cdot Q_B$$

So we can rewrite P_{tot} as

$$P_{tot} = k_B T\frac{1}{Q_A \cdot Q_B}\left(\frac{\partial Q_A \cdot Q_B}{\partial V}\right)$$

Now applying chain rule :

$$P_{tot} = k_B T\frac{1}{Q_A \cdot Q_B}\left(\frac{\partial Q_A}{\partial V}Q_B + \frac{\partial Q_B}{\partial V}Q_A\right)$$

This goes to

$$P_{tot} = k_B T\left(\frac{\partial Q_a}{\partial V}\frac{1}{Q_A} + \frac{\partial Q_B}{\partial V}\frac{1}{Q_B}\right)$$

Now when substituting from the pressure definition, you can see :

$$\boxed{P_{tot} = P_A + P_B}$$

This is literally just Dalton's law of partial pressure.
When solving in terms of the mole fraction :

$$X_A = \frac{P_A}{P_{tot}} = \frac{k_BT\left(\frac{\partial}{\partial V}\ln Q_A\right)}{k_BT\left(\frac{\partial}{\partial V}\ln(Q_A\cdot Q_B)\right)} = \frac{k_BT\frac{1}{Q_A}\left(\frac{\partial Q_A}{\partial V}\right)}{k_BT\frac{1}{Q_A\cdot Q_B}\left(\frac{\partial Q_A\cdot Q_B}{\partial V}\right)}$$

$$\frac{\frac{1}{Q_A}\left(\frac{\partial Q_A}{\partial V}\right)}{\frac{1}{Q_A\cdot Q_B}\left(\frac{\partial Q_A\cdot Q_B}{\partial V}\right)}$$

Using the chain rule :

$$\frac{\frac{1}{Q_A}\left(\frac{\partial Q_A}{\partial V}\right)}{\frac{1}{Q_A\cdot Q_B}\left(Q_A\frac{\partial Q_B}{\partial V} + Q_B\frac{\partial Q_A}{\partial V}\right)}$$

Rewriting :

$$\frac{\frac{1}{Q_A}\left(\frac{\partial Q_A}{\partial V}\right)}{\frac{\partial Q_a}{\partial V}\frac{1}{Q_B} + \frac{\partial Q_B}{\partial V}\frac{1}{Q_A}}B$$

Now we have to multiply by a common term for simplification.

$$\frac{\frac{1}{Q_A}\left(\frac{\partial Q_A}{\partial V}\right)}{\frac{\partial Q_a}{\partial V}\frac{1}{Q_B} + \frac{\partial Q_B}{\partial V}\frac{1}{Q_A}}\frac{Q_AQ_B}{Q_AQ_B}$$

$$\frac{Q_B\left(\frac{\partial Q_A}{\partial V}\right)}{Q_A\frac{\partial Q_A}{\partial V} + Q_B\frac{\partial Q_B}{\partial V}}$$

Now for a very unique trick with the derivative we will multiply both the numerator and denominator by $\frac{\partial V}{\partial Q_A}$

$$\frac{Q_B\left(\frac{\partial Q_A}{\partial V}\right)}{Q_A\frac{\partial Q_A}{\partial V} + Q_B\frac{\partial Q_B}{\partial V}}\frac{\frac{\partial V}{\partial Q_A}}{\frac{\partial V}{\partial Q_A}}$$

This simplifies down to

$$\boxed{\frac{Q_B}{Q_A + Q_B \frac{\partial Q_B}{\partial Q_A}}}$$

2. Fluorine Atoms have an electron configuration$1s^2 2s^2 2p^5$ This gives two possible spin-orbit states represented by ${}^2P_{3/2}$ and ${}^2P_{1/2}$ states that differ by only 0.05 eV in energy. The important thing is that the degeneracy of each state is related to the subscript, J, and equals (2J+1).

   a. Write the electronic partition function for the F atoms (take the energy of the ${}^2P_{3/2}$ to be zero and that of the ${}^2P_{1/2}$ to be 0.05eV and ignore all other states.)

$$Q = \sum_{j=1} g_n e^{-E_j/k_B T}$$

$$Q = 4 + 2e^{-0.05/k_B T}$$

   b. Using $<E> = k_B T^2 (\frac{\partial \ln Q}{\partial T})$, derive an expression for the average electronic energy $<E>$ of N gaseous F atoms.

$$<E> = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} = k_B T^2 \frac{1}{Q}\left(\frac{\partial Q}{\partial T}\right)_v$$

$$<E> = k_B T^2 \frac{1}{4 + 2e^{-0.05/k_B T}} \left(\frac{\partial \left[4 + 2e^{-0.05/k_B T}\right]}{\partial T}\right)_V$$

$$\frac{\partial \left[4 + 2e^{-0.05/k_B T}\right]}{\partial T} = \frac{e^{-0.05/k_B T}}{10 k_B T^2}$$

$$<E> = \cancel{k_B T^2} \frac{1}{4 + 2e^{-0.05/k_B T}} \frac{e^{-0.05/k_B T}}{10\ \cancel{k_B T^2}}$$

$$\boxed{<E> = \frac{e^{-0.05/k_B T}}{40 + 20e^{-0.05/k_B T}}}$$

   c. Using the fact that $k_B T = 0.025eV$ at $T = 300K$, find the relative population of ${}^2P_{1/2}$ of ${}^2P_{3/2}$ atoms at $300K$

$$P_n = \frac{q_n e^{-E_n/k_BT}}{Q}$$

$$P_{\frac{1}{2}} = \frac{2e^{-0.05/0.025}}{4+2e^{-0.05/0.025}}$$

$$P_{\frac{3}{2}} = \frac{4e^{-0}}{4+2e^{-0.05/0.025}}$$

$$\boxed{P_{\frac{1}{2}} = 0.063}$$

$$P_{\frac{3}{2}} = 1 - P_{\frac{1}{2}}$$

$$\boxed{P_{\frac{3}{2}} = 0.94}$$

d. Make a (qualitative) graph of $<\!E\!>$ vs. T for the temperature ranging from $10K$ to $3000K$
By looking at the function

$$<\!E\!> = \frac{e^{-0.05/k_BT}}{40+20e^{-0.05/k_BT}}$$

You can see that as T increases, the behavior of the function tends towards $\frac{1}{60}$ or 0.0166.
Based on the other point at 300K, we can evaluate that point at 0.00317
Based on these values, we can determine that as heat increases the $<\!E\!>$ increases. This is quite intuitive. However, as larger values are substituted into T, one can determine that the maximum value of $<\!E\!>$ caps out at the $\frac{1}{60}$ proportion. This essentially points to an asymptotic function that caps out at $\frac{1}{60}$ while increasing at a rather rapid rate initially.
(values in the y axis are wrong due to issues getting the scale to

work, but the shape should be accurate.)