Physics 112 Fall 2017
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Homework 6 Solutions

Problem 1, Kittel 5.1: Centrifuge

When the gas is in equilibrium, we know that the total chemical potential will be constant throughout. The total chemical potential is $\mu = \mu_{int} + \mu_{ext}$, and we know that the internal chemical potential (of an ideal gas) is related to the number density by $\mu = \tau \ln\left(\frac{n(r)}{n_Q}\right)$, so we see that a spatial variation in the external chemical potential will create a spatially varying number density. A rotating gas feels a centrifugal force $F = Mv^2/r = Mr\omega^2$. We can consider this force to be caused by an effective potential such that $F = -dV/dr$:

$$\mu_{ext}(r) = V(r) = -\int dr F(r) = -\frac{M}{2}r^2\omega^2.$$

The total chemical potential $\mu(r) = \tau \ln\left(\frac{n(r)}{n_Q}\right) - \frac{M}{2}r^2\omega^2$ will be constant throughout the centrifuge in equilibrium, so we can equate the chemical potential at a radius r with the chemical potential at the axis of rotation:

$$\mu(0) = \tau \ln\left(\frac{n(0)}{n_Q}\right) = \tau \ln\left(\frac{n(r)}{n_Q}\right) - \frac{M}{2}r^2\omega^2 = \mu(r)$$

Solving for $n(r)$ we have:

$$n(r) = n(0)\exp\left(\frac{Mr^2\omega^2}{2\tau}\right) \tag{1}$$

So we see that we get an exponentially higher concentration of particles at larger r (as expected).

Problem 2, Kittel 5.4: Active Transport

We know that the ratio of the concentration of K^+ is $n_{sap}/n_{water} = 10^4$, so we can find the difference in the chemical potentials of K^+ of the sap and the water by treating the ions as an ideal gas:

$$
\begin{aligned}
\triangle\mu &= \mu_{sap} - \mu_{water} = \tau \ln\left(\frac{n_{sap}}{n_Q}\right) - \tau \ln\left(\frac{n_{water}}{n_Q}\right) \\
&= \tau \ln\left(\frac{n_{sap}}{n_{water}}\right) = \tau \ln(10^4) \\
&= (300\ K)\,k_b * 4\ln(10) = (1200\ \text{K})\left(1.38 \times 10^{-23}\ \text{J/K}\right)\left(1.60 \times 10^{-19}\ \text{eV/J}\right)\ln(10)\ \text{eV} = 0.24\ \text{eV}.
\end{aligned}
$$

This chemical potential difference is equivalent to an electric potential difference of .24 V.

Problem 3, Kittel 5.8: Carbon Monoxide Poisoning

(a) We want to find an ϵ_A such that 90% of the sites are occupied with 0_2. To find the average occupation in terms of ϵ_a we need to find the Gibbs sum and use the relationship $\langle n \rangle = \frac{1}{\zeta}\sum_{ASN}\lambda^N e^{-\epsilon_a/\tau}$. Because all N sites are identical, we just need to find the average occupation for a single site – the total occupation will just be N times the single site occupation.

$$\zeta_1 = 1 + \lambda_{O_2}e^{-\epsilon_A/\tau}$$

So the average occupation for a single site is:

$$\langle n \rangle = \frac{1}{\zeta} \sum_{ASN} \lambda^N e^{-\epsilon_a/\tau} = \frac{0 + \lambda_{O_2} e^{-\epsilon_A/\tau}}{\zeta} = \frac{\lambda_{O_2} e^{-\epsilon_A/\tau}}{1 + \lambda_{O_2} e^{-\epsilon_A/\tau}}$$

To find the occupation energy such that 90% of the sites are occupied we just need to set $\langle n \rangle = 0.90$ and solve for ϵ_A:

$$
\begin{aligned}
\langle n \rangle &= \frac{\lambda_{O_2} e^{-\epsilon_A/\tau}}{1 + \lambda_{O_2} e^{-\epsilon_A/\tau}} = 0.90 \\
\implies \langle n \rangle &= (\langle n \rangle - 1)\, \lambda_{O_2} e^{-\epsilon_A/\tau} \\
\implies \epsilon_a &= -\tau \ln\left(\frac{\langle n \rangle}{\lambda_{O_2}(\langle n \rangle - 1)}\right) \\
&= \tau\left[\ln\left(\frac{1}{\langle n \rangle} - 1\right) - \ln \lambda_{O_2}\right] \\
&= (310\ \text{K})\, k_b\left[\ln\left(\frac{10}{9} - 1\right) - \ln \lambda_{O_2}\right] \\
&= -(310\ \text{K})\left(1.38 \times 10^{-23}\ \text{J/K}\right)\left(1.60\ \text{eV/J}\right)(\ln 9 + 5\ln 10) \\
&= -0.37\ \text{eV}.
\end{aligned}
$$

(b) Now if we allow CO molecules, the Gibbs sum for a single site is:

$$\zeta_1 = 1 + \lambda_{O_2} e^{-\epsilon_A/\tau} + \lambda_{CO} e^{-\epsilon_B/\tau}.$$

Clearly now the average number of O_2 molecules per site will change depending on ϵ_B:

$$\langle n_{O_2} \rangle = \frac{\lambda_{O_2} e^{-\epsilon_A/\tau}}{1 + \lambda_{O_2} e^{-\epsilon_A/\tau} + \lambda_{CO} e^{-\epsilon_B/\tau}}$$

Solving for ϵ_B we have:

$$\lambda_{CO} e^{-\epsilon_B/\tau} = \left(\frac{1}{\langle n \rangle} - 1\right) \lambda_{O_2} e^{-\epsilon_A/\tau} - 1$$

$$\Rightarrow \epsilon_B = -\tau \ln\left(\frac{\left(\frac{1}{\langle n \rangle} - 1\right) \lambda_{O_2} e^{-\epsilon_A/\tau} - 1}{\lambda_{CO}}\right)$$

Plugging in $\langle n_{O_2} \rangle = 0.10$ and using the value of ϵ_A above, we get:

$$
\begin{aligned}
\epsilon_B &= -(310\ K)\left(1.4 \times 10^{-23}\ \frac{J}{K}\right)\left(1.60\ \frac{eV}{J}\right) \times \\
&\quad \ln\left[9 \times 10^{-5} \exp\left(-\frac{-0.37\ eV}{(310\ K)(1.38 \times 10^{-23}\ J/K)(1.60\ eV/J)}\right) - 1\right] - (-7) \\
&= -0.55\ eV
\end{aligned}
$$

So if the absorption energy of CO is low enough, the CO molecules will be preferentially absorbed and not allow for the absorption of O_2.

Problem 4, Kittel 5.10: Concentration Fluctuations

(a) We can find $\langle N^2 \rangle$ from the weighted sum:

$$
\begin{aligned}
< N^2 > &= \frac{1}{\zeta} \sum_{ASN} N^2 e^{(N\mu - \epsilon_s)/\tau} \\
&= \frac{\tau^2}{\zeta} \sum_{ASN} \frac{\partial^2}{\partial \mu^2} e^{(N\mu - \epsilon_s)/\tau} \\
&= \frac{\tau^2}{\zeta} \frac{\partial^2 \zeta}{\partial \mu^2}
\end{aligned}
$$

(b) Using $\langle N \rangle = \frac{\tau}{\zeta} \left(\frac{\partial \zeta}{\partial \mu} \right)$, we can start from the right side of the equation:

$$
\begin{aligned}
\tau \frac{\partial < N >}{\partial \mu} &= \tau \frac{\partial}{\partial \mu} \left(\frac{\tau}{\zeta} \left(\frac{\partial \zeta}{\partial \mu} \right) \right) \\
&= \tau^2 \left\{ \frac{1}{\zeta} \frac{\partial^2 \zeta}{\partial \mu^2} - \frac{1}{z^2} \left(\frac{\partial \zeta}{\partial \mu} \right)^2 \right\} \\
&= (\triangle N)^2.
\end{aligned}
$$

Problem 5, Kittel 5.12: Ascent of Sap in Trees

To do this problem, we CANNOT just treat the water vapor as an ideal gas in equilibrium and use the barometric pressure equation derived in Kittel, because the water vapor above the pool is diffusing into the rest of the atmosphere and so is NOT in equilibrium.

On the other hand, the column of water in the tree, the pool of water at the bottom and the water vapor just above the pool are in (quasi-static) equilibrium with each other, and so have a constant chemical potential given by

$$
\mu(0) = \tau \ln \left(\frac{n_0}{n_Q} \right)
$$

which is the chemical potential of the vapor. For the water in the tree at some height h, the (constant) total chemical potential is the sum of internal and external contributions, and so

$$
\begin{aligned}
\mu_{\text{int}}(h) + Mgh &= \mu(0) \\
\implies \mu_{\text{int}}(h) &= \tau \ln \left(\frac{n_0}{n_Q} \right) - Mgh.
\end{aligned}
$$

Now, the water in the tree ends up evaporating through the leaves, which will only happen if the internal chemical potential of the water in the tree is greater than that of the water in the surrounding air, i.e.

$$
\begin{aligned}
\mu_{\text{int}}(h) &> \mu_{\text{int}}(\text{air}) \\
\implies \tau \ln \left(\frac{n_0}{n_Q} \right) - Mgh &> \tau \ln \left(\frac{rn_0}{n_Q} \right).
\end{aligned}
$$

Solving this inequality for h and plugging in numbers gives

$$h \quad < \quad -\frac{\tau \ln r}{Mg} \tag{2}$$

$$= \quad -\frac{298 \text{ K} \times \ln(0.9) \times (1.38 \times 10^{-23} \text{ J/K})}{18 \text{ amu} * 9.8 \text{ m/sec}^2}$$

$$= \quad -\frac{298(1.38 \times 10^{-23}) \ln(0.9)}{18(1.7 * 10^{-27})9.8} \text{ m}$$

$$= \quad 1500 \text{ m}.$$

This model predicts that tree should be able to grow no higher than 1.5 km under these conditions. This is about an order of magnitude larger than the tallest trees (giant sequoias can be over 100m), so apparently this isn't the only limiting factor.

Problem 6: Another Derivation of the Chemical Potential of an Ideal Gas

Starting with the Sackur-Tetrode equation for the entropy of an ideal gas

$$\sigma = N \left(\ln \left(\frac{n_Q}{n} \right) + 5/2 \right) \tag{3}$$

we can find the chemical potential using the relation $\mu = -\tau \left(\frac{\partial \sigma}{\partial N} \right)_{U,V}$. We have to be a little careful when taking the derivative with respect to N while holding U and V fixed, though. An expression like $\frac{\partial \sigma}{\partial N}|_{U,V}$ really means to write σ as a function of N, U and V, and then partial differentiate with respect to N. In equation (3) we do NOT have the entropy written this way; remembering that the quantum concentration is usually thought of as a function of temperature

$$n_Q = \left(\frac{M\tau}{2\pi\hbar^2} \right)^{3/2},$$

we see that (3) really gives the entropy as a function of N, V and τ:

$$\sigma(N, \tau, V) = N \left[\frac{3}{2} \ln \left(\frac{M\tau}{2\pi\hbar^2} \right) + \ln V - \ln N + 5/2 \right] \tag{4}$$

To write the entropy in the desired form, we must use the relation $U = \frac{3}{2}N\tau$ to eliminate τ in favor of U. This gives

$$\sigma(N, U, V) = N \left[\frac{3}{2} \ln \left(\frac{MU}{3\pi\hbar^2} \right) + \ln V - \frac{5}{2} \ln N + \frac{5}{2} \right].$$

Note that this changes the N dependence of σ. Finding an expression for the chemical potential is now straightforward: skipping a couple of steps, we have

$$\mu \quad = \quad -\tau \frac{\partial \sigma}{\partial N} \bigg|_{U, V}$$

$$= \quad -\tau \ln \left(V \left(\frac{MU}{3\pi\hbar^2} \right)^{3/2} N^{-5/2} \right) = -\tau \ln \left(\frac{n_Q}{n} \right)$$

$$= \quad \tau \ln \left(\frac{n}{n_Q} \right).$$