Physics 112 Problem Set 6 Holzapfel, Section 102

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1. The centrifugal force on an atom of the gas is $F_c(r) = M\omega^2 r$, so the potential energy due to the rotation is $U_c(r) = -M\omega^2 r^2/2$. Let $\mu_{ext}(r) = U_c$, and note that $\mu_{int}(r) = \tau \log(n(r)/n_Q)$ for an ideal gas. Then, $\mu(r) = \mu_{ext} + \mu_{int}$ needs to be constant in the cylinder, so

$$\begin{split} \mu(0) &= \mu(r) \\ \tau \log \left(\frac{n(0)}{n_Q}\right) &= -\frac{M\omega^2 r^2}{2} + \tau \log \left(\frac{n(r)}{n_Q}\right) \\ \log \left(\frac{n(r)}{n(0)}\right) &= \frac{M\omega^2 r^2}{2\tau} \\ n(r) &= n(0) \exp \left(\frac{M\omega^2 r^2}{2\tau}\right). \end{split}$$

2. The potential difference is given by

$$\begin{split} \mu_{inside} &= \mu_{outside} \\ \tau \log \left(\frac{n_{inside}}{n_Q} \right) &= \tau \log \left(\frac{n_{outside}}{n_Q} \right) \\ &= \tau \log \left(\frac{n_{inside}}{n_{outside}} \right). \end{split}$$

At 300 K, this is approximately

$$k \times (300 \text{ K}) \times \log(10^4) = 3.8 \times 10^{-20} \text{ J} = 0.24 \text{ eV}$$

and since each K^+ atom has charge e, this corresponds to an energy difference of 0.24 V.

3. (a) If 90% of the sites are occupied by oxygen, then the probability of a single Hb site being occupied by oxygen is 0.9, so

$$\begin{aligned} 0.9 &= \frac{\lambda(\mathrm{O}_2) \exp(-\epsilon_A/\tau)}{1 + \lambda(\mathrm{O}_2) \exp(-\epsilon_A/\tau)} \\ 0.9 &= 0.1 \lambda(\mathrm{O}_2) \exp(-\epsilon_A/\tau) \\ \epsilon_A &= \tau \log\left(\frac{\lambda(\mathrm{O}_2)}{9}\right) \end{aligned}$$

which, for T = 37 + 273 = 310 K and $\lambda(O_2) = 10^{-5}$, evaluates to $\epsilon_A = -5.87 \times 10^{-20}$ J = -0.366 eV.

(b) Now, we admit carbon monoxide, and if 10% of the sites are occupied by oxygen, then

$$0.1 = \frac{\lambda(O_2) \exp(-\epsilon_A/\tau)}{1 + \lambda(O_2) \exp(-\epsilon_A/\tau) + \lambda(CO) \exp(-\epsilon_B/\tau)}$$
$$0.1 + 0.1\lambda(CO) \exp(-\epsilon_B/\tau) = 0.9\lambda(O_2) \exp(-\epsilon_A/\tau)$$
$$\exp(-\epsilon_B/\tau) = \frac{9\lambda(O_2) \exp(-\epsilon_A/\tau) - 1}{\lambda(CO)}$$
$$\epsilon_B = \tau \log\left(\frac{\lambda(CO)}{9\lambda(O_2) \exp(-\epsilon_A/\tau) - 1}\right)$$

which, for T = 310 K, $\lambda(CO) = 10^{-7}$ and $\lambda(O_2)$ and ϵ_A as previously, evaluates to $\epsilon_B = -8.78 \times 10^{-20}$ J = -0.548 eV.

4. (a) If

$$\mathcal{Z} = \sum_{ASN} \exp\left(\frac{N\mu - \epsilon}{\tau}\right)$$

then

$$\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} = \sum_{ASN} \frac{N^2}{\tau^2} \exp\left(\frac{N\mu - \epsilon}{\tau}\right).$$

So

$$\frac{\tau^2}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} = \frac{\sum_{ASN} N^2 \exp((N\mu - \epsilon)/\tau)}{\mathcal{Z}} = \langle N^2 \rangle.$$

(b) If

$$\langle N \rangle = \frac{\tau}{\mathcal{Z}} \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)_{\tau V}$$

then

$$\tau \frac{\partial \langle N \rangle}{\partial \mu} = \tau^2 \left(-\frac{1}{\mathcal{Z}^2} \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)_{\tau, V}^2 + \frac{1}{\mathcal{Z}} \left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \right)_{\tau, V} \right) = \langle (\Delta N)^2 \rangle.$$

5. The water vapor at the roots must be in diffusive equilibrium with the water vapor at the uppermost leaves. Note that $\mu_{ext} = Mgh$ and $\mu_{int} = \tau \log(n/n_Q)$. So

$$\mu(0) = \mu(h)$$

$$\tau \log(n(0)/n_Q) = \tau \log(n(h)/n_Q) + Mgh$$

$$\tau \log(n_0/rn_0) = Mgh$$

$$h = -\frac{kT}{Mg} \log r.$$

For T = 298 K, r = 0.9, M = 18 amu $= 2.99 \times 10^{-26}$ kg, this evaluates to h = 1480 m.

6. Starting from the Sackur-Tetrode equation

$$\sigma = N \log \left(\frac{V}{N^{5/2}} \left(\frac{4\pi mU}{3\hbar^2} \right)^{3/2} \right) + \frac{5}{2} N$$

and differentiating with respect to N,

$$\begin{split} \left(\frac{\partial\sigma}{\partial N}\right)_{U,V} &= \log\left(\frac{V}{N^{5/2}}\left(\frac{4\pi mU}{3\hbar^2}\right)^{3/2}\right) + N\frac{N^{5/2}}{V}\left(\frac{3\hbar^2}{4\pi mU}\right)^{3/2}V\left(\frac{4\pi mU}{3\hbar^2}\right)^{3/2}\left(\frac{-5}{2}\right)^{-7/2} + \frac{5}{2} \\ &\left(\frac{\partial\sigma}{\partial N}\right)_{U,V} = \log\left(\frac{1}{n}\left(\frac{4\pi mU}{3\hbar^2N}\right)^{3/2}\right) - \frac{5}{2} + \frac{5}{2}. \end{split}$$

For an ideal gas, $U = 3N\tau/2$, so

$$\left(\frac{\partial \sigma}{\partial N}\right)_{U,V} = \log\left(\frac{1}{n}\left(\frac{2\pi m\tau}{\hbar^2}\right)^{3/2}\right) = \log\left(\frac{n_Q}{n}\right)$$

and

$$\mu = -\tau \left(\frac{\partial \sigma}{\partial N}\right)_{UV} = \tau \log \left(\frac{n}{n_Q}\right).$$