"artists" conception of gas of O2 and CO
interacting with heme sites

O2

CO

empty heme site	heme site with O2	heme site with CO
$E = 0\,\text{eV}$	$E = -0.65\,\text{eV}$	$E = -0.85\,\text{eV}$

Figure 1: Artists conception of problem 3

Problem 1.   Carbon Monoxide Poisoning

A model for carbon monoxide poisoning is the following. Consider a gas which is mixture of diatomic oxygen O_2 and carbon monoxide CO. The hemoglobin molecule contained in red blood cells are responsible for capturing O_2 from the air and delivering the oxygen to the tissues. The sites on the hemoglobin molecule can either be unoccupied, with energy $E = 0$, occupied by an O_2 molecule with energy $E = -0.65\,\text{eV}$, or occupied by a carbon monoxide molecule with energy $E = -0.85\,\text{eV}$, see figure. In this problem you will calculate the probability that the hemoglobin site will be occupied by an O_2 (what we want!). This depends on the concentration of O_2 and sensitively on the concentration of carbon monoxide.

The questions below refer to the surrounding O_2 gas at a temperature of $295\,\text{K}$ and a pressure of $0.2\,\text{bar}$. From the temperature and pressure of O_2, the corresponding concentration $n = N/V$ of the gas can be found, as can its quantum concentration[1], $n_Q \equiv \lambda_{\text{th}}^{-3}$. The quantum concentration of CO can be found similarly. These values and the atomic numbers of the two atoms are given in the table below.

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[1] λ_{th} is the thermal de Broglie wavelength.

quantity	value
T	$295\,\mathrm{K}$
p	$0.2\,\mathrm{bar}$
n	$0.005\,\mathrm{nm}^{-3}$
$(n_Q)_{O_2}$	$1.68 \times 10^5\,\mathrm{nm}^{-3}$
$(n_Q)_{CO}$	$1.37 \times 10^5\,\mathrm{nm}^{-3}$
atomic number O	16
atomic number C	12

(a) Explain the ratio of quantum concentrations for the two gasses, O_2 and CO.

(b) The CO and O_2 molecules in the surrounding gas rotate with moment of inertia I. Their rotational constants, i.e. $\Delta \equiv \hbar^2/2I$, are $\Delta_{CO} = 0.00024\,\mathrm{eV}$ and $\Delta_{O_2} = 0.00018\,\mathrm{eV}$ respectively. Show that the rotational constant of O_2 is roughly consistent with an order of magnitude estimate for Δ.

(c) Recall that the rotational energy levels are

$$\epsilon_{\mathrm{rot}} = \ell(\ell+1)\Delta \qquad \text{with} \qquad \ell = 0, 1, 2, \ldots \infty \tag{1}$$

and that the rotational partition function (i.e. an appropriate sum over these levels) is $Z_{\mathrm{rot}} \simeq kT/\Delta$ in a classical approximation. Estimate the typical value of ℓ for the CO gas. Based on this estimate how accurate is the classical approximation?

(d) Recall that the partition function of the classical diatomic gas is

$$Z_{\mathrm{tot}} = \frac{1}{N!}(Z_{\mathrm{trans}}Z_{\mathrm{rot}})^N \tag{2}$$

where $Z_{\mathrm{rot}} \equiv kT/\Delta$ with $\Delta = \hbar^2/2I$, and Z_{trans} describes the translational motion.

  (i) Show the chemical potential of the classical diatomic gas as a function of the concentration n and the rotational constant Δ is

$$\mu = kT \ln(n/n_Q) + kT \ln(\beta\Delta) \tag{3}$$

  (ii) Numerically evaluate the chemical potential μ_{O_2} of the O_2 gas. Ans: $-0.5569\,\mathrm{eV}$
  Note: The numbers need to be evaluted with a lot of precision here, use $k_B = 0.02542\,\mathrm{eV}/(295\,\mathrm{Kelvin})$.

  (iii) Numerically evaluate the chemical potential μ_{CO} of the surrounding CO gas, assuming that the concentration of CO is a thousand times smaller than O_2. Ans: $-0.7173\,\mathrm{eV}$

(e) Now return to the hemoglobin sites. By considering the grand partition function of the site, determine the probability that the site is occupied by O_2. Evaluate this probability numerically, using the numerical results of previous parts. Ans: $P = 0.17$

(f) Determine how the probability of (e) would change if the concentration of CO was negligibly small. Ans: $P = 0.975$

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CO Poisoning

(1) The quantum concentration is

$$n_Q = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} = 1.65 \times 10^5 \; \frac{1}{nm^3}$$

Here $m = 32 m_p$ so using $m_p c^2 = 938 \, MeV$

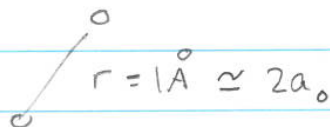and $k_B = \dfrac{1/40 \, eV}{300 \, {}^\circ K}$ we have with $hc = 1240 \, eV \, nm$

(2) Then we see since $m^{CO} = 28 m_p$ and $m^{O_2} = 32 m_p$

$$\frac{n_Q^{CO}}{n_Q^{O_2}} = \left(\frac{m^{CO}}{m^{O_2}}\right)^{3/2} = \left(\frac{28}{32}\right)^{3/2} = 0.82$$

So, n_Q^{CO} is 80% of $n_Q^{O_2}$

(3) So taking a bond length of $1 \, \mathring{A}$

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2$$

$$r = 1 \mathring{A} \simeq 2 a_0$$

$$I = \frac{m^O}{2} r^2 = \mu r^2$$

$$\Delta = \frac{\hbar^2}{2\mu r^2} \qquad \text{Now} \quad \mu = 8 m_p = 16,000 \, m_e$$

So

$$\Delta = \frac{\hbar^2}{2 \times (16000) \, m_e \, (4a_o^2)} = \frac{1}{4 \times 16000} \left(\frac{\hbar^2}{2 m_e a_o^2} \right)$$

$$= \frac{13.6 \, eV}{4 \cdot 16000} \sim 0.0002 \, eV \quad \leftarrow \text{this is close}$$

④ $$\left\langle \frac{L^2}{2I} \right\rangle = \left\langle \frac{l(l+1) \hbar^2}{2I} \right\rangle = 2 \times \frac{1}{2} kT$$

↖ 2 dof in rotation

So neglecting one in $l(l+1)$

$$l^2 = \frac{kT}{\Delta} \qquad \Delta \equiv \frac{\hbar^2}{2I}$$

$$l = \sqrt{\frac{kT}{\Delta}} = \left(\frac{1/40 \, eV}{0.0002 \, eV} \right)^{1/2} \simeq 12$$

So l is pretty large and a classical approximation is good.

⑤,① $$Z_{rot} = \sum_l \sum_{m=-l}^{l} e^{-l(l+1)\Delta\beta}$$

$$= \sum_{l=0}^{\infty} (2l+1) \, e^{-l(l+1)\Delta\beta} \simeq \int_0^{\infty} dl \, 2l \, e^{-l^2\Delta\beta}$$

$$= \left. -\frac{e^{-l^2\Delta\beta}}{\Delta\beta} \right|_0^{\infty} = \frac{1}{\Delta\beta}$$

Now substitute #'s using the #'s in the table and

$$\frac{kT}{\Delta_{O_2}} = 139 \qquad \frac{kT}{\Delta_{CO}} = 104$$

5.3) $\mu_{O_2} = -0.5569 \, eV$

5.4) $\mu_{CO} = -0.7173 \, eV$ $\qquad$ we used $n_{CO} = \frac{n}{1000}$

⑥ We have

$$z_G = 1 + e^{-\beta(\varepsilon_1 - \mu_{O_2})} + e^{-\beta(\varepsilon_2 - \mu_{CO})}$$

$$z_G = 1 + c_1 + c_2$$

(for example $c_1 \equiv e^{-\beta(\varepsilon_1 - \mu_{O_2})}$)

$c_1 = 41.4$, $\varepsilon_1 = -0.65 \, eV$

$c_2 = 201$, $\varepsilon_2 = -0.85 \, eV$

$$P_1 = c_1 / (1 + c_1 + c_2)$$

$$P_1 = 0.17$$

⑦ In the limit of low concentration

$$\mu_{CO} \longrightarrow -\infty \qquad \text{and} \quad e^{\beta \mu_{CO}} \longrightarrow 0$$

Then $c_2 \longrightarrow 0$ and

$$z_G \cong 1 + c_1 \qquad \text{and} \qquad P_1 = \frac{c_1}{1 + c_1} \approx 0.975$$

Problem 2. Charge Neutrality

Consider a lattice of protons consisting of a total of N sites. The protons (located at the sites) share the available electrons which can hop from site to site. The total system is neutral so that the number of electrons is equal to the number of protons (or lattice sites). Electrons can hop from site to site, so each site does not need to be neutral. Suppose that each atom can exist in four states which are listed and illustrated schematically below.

state	$N_{\text{electrons}}$	Energy
ground state	1	$-\frac{1}{2}\Delta$
positive ion	0	$-\frac{1}{2}\delta$
negative ion	2	$\frac{1}{2}\delta$
excited hydrogen	1	$\frac{1}{2}\Delta$

H   H+   H−   H⋆

H−   H−   H+   H+

H   H⋆   H⋆   H⋆

H−   H   H+   H

(a) Compute the grand potential $\Phi_G = -kT \log \mathcal{Z}_G$ of a single site by evaluating the grand partition function, $\mathcal{Z}_G$. After some algebra you should find

$$Z_G = 2e^{\beta\mu}\cosh(\beta\Delta/2) + 2e^{\beta\mu}\cosh(\beta(\delta/2 - \mu)) \tag{4}$$

(b) Determine the mean number of electrons per site as a function of the electron chemical potential and temperature.

(c) Show that the electron chemical potential is $\delta/2$ and that probability of having neutral hydrogen is

$$\frac{e^{\beta(\Delta+\delta)/2}}{4e^{\beta\delta/2}\cosh^2(\beta\Delta/4)} \tag{5}$$

and that grand partition function evaluated at this chemical potential is

$$\mathcal{Z}_G|_{\mu=\delta/2} = 4e^{\beta\delta/2}\cosh^2(\beta\Delta/4) \tag{6}$$

Hint: The indentity $(\cosh(x)+1)/2 = \cosh^2(x/2)$, is the hyperbolic analog of the cosine identity $(\cos(\theta)+1)/2 = \cos^2\theta$.

(d) (Optional) Determine the the entropy per site at $\mu = \delta/2$. You should find

$$\frac{S}{k_B} = \log\left[4\cosh^2\left(\frac{\beta\Delta}{4}\right)\right] - \frac{\beta\Delta}{2}\tanh\left(\frac{\beta\Delta}{4}\right) \tag{7}$$

Make a sketch of this function as function of $\beta\Delta$. What is the limit of this function as $\beta\Delta \to 0$? Give a physical interpretation of this limit.

Neutrality

a) $$\mathcal{Z} = \sum_s e^{-\beta(\varepsilon_s - \mu N_s)}$$

$$= e^{-\beta(-\Delta/2 - \mu)} + e^{-\beta(\Delta/2 - \mu)}$$

$$+ e^{+\beta\delta/2} + e^{-\beta(\delta/2 - 2\mu)}$$

$$= e^{\beta\mu}\left(e^{\beta\Delta/2} + e^{-\beta\Delta/2}\right) + e^{\beta\delta/2} + e^{2\beta\mu}e^{-\beta\delta/2}$$

$$\boxed{\begin{aligned}\mathcal{Z} &= 2e^{\beta\mu}\cosh(\beta\Delta/2) + e^{\beta\delta/2} + e^{2\beta\mu}e^{-\beta\delta/2} \\ \mathcal{Z} &= 2e^{\beta\mu}\left(\operatorname{ch}(\beta\Delta/2) + \operatorname{ch}(\beta(\delta/2 - \mu))\right)\end{aligned}}$$

b)
$$\bar{N} = \Big[1\cdot e^{-\beta(-\Delta/2 - \mu)} + 1\cdot e^{-\beta(\Delta/2 - \mu)}$$

$$+ 2e^{2\beta\mu}e^{-\beta\delta/2}\Big]/\mathcal{Z}$$

So

this can be simplified see
last page

$$\boxed{\bar{N} = \frac{2e^{\beta\mu}\cosh(\beta\Delta/2) + 2e^{2\beta\mu}e^{-\beta\delta/2}}{\mathcal{Z}}}$$

c) Skipped -- included below if really interested.

d) We require $\bar{N} = 1$, or writing $\bar{N} = \text{numerator}/\text{den}$

$$2e^{\beta\mu}\cosh(\beta\Delta/2) + 2e^{2\beta\mu}e^{-\beta\delta/2} = 2e^{\beta\mu}\cosh(\beta\Delta/2) + e^{\beta\delta/2}$$

$$+ e^{2\beta\mu}e^{-\beta\delta/2}$$

So we have

$$2 e^{2\beta\mu} e^{-\beta\delta/2} = e^{\beta\delta/2} + e^{2\beta\mu} e^{-\beta\delta/2}$$

$$e^{2\beta\mu} e^{-\beta\delta/2} = e^{\beta\delta/2}$$

So $\mu = \delta/2$

e) Lets Find The entropy at the neutrality point

First note that for $\frac{\delta}{2} = \mu$ we have

$$\mathcal{Q} = 2 e^{\beta \delta/2} \cosh(\beta \Delta/2) + 2 e^{\beta \delta/2}$$

$$= 2 e^{\beta \delta/2} (\cosh(\beta \Delta/2) + 1) = 4 e^{\beta \delta/2} \cosh^2(\beta \Delta/4)$$

Now

$$\overline{\Phi}_G = -k_B T \ln \mathcal{Q} \quad \text{and} \quad S = -\left(\frac{\partial \overline{\Phi}_G}{\partial T}\right)_\mu$$

$$\frac{S}{k_B} = \ln \mathcal{Q} + T \frac{\partial \ln \mathcal{Q}}{\partial T}$$

$$= \ln \mathcal{Q} - \beta \frac{\partial \ln \mathcal{Q}}{\partial \beta}$$

$$= \ln(4 \cosh^2(\beta \Delta/4)) + \frac{\beta \delta}{2} - \beta \frac{\partial}{\partial \beta}\left(\frac{\beta \delta}{2} + \ln(4 \cosh^2(\beta \Delta/4))\right)$$

$$\boxed{\frac{S}{k_B} = \ln(4 \cosh^2(\beta \Delta/4)) - \frac{\beta \Delta}{2} \tanh\left(\frac{\beta \Delta}{4}\right)}$$

Sketch
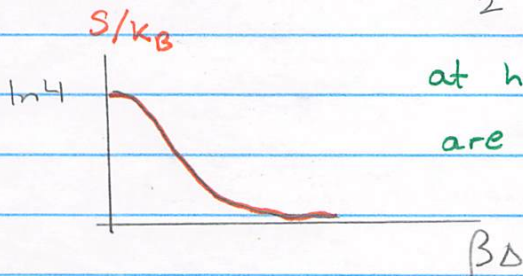
at high T, $\beta \Delta \simeq 0$, and all four states are equally likely and thus the entropy is $\ln 4$. At low T only one state is possible and $\ln(1) = 0 = S$

c) This was a bit more algebra than I intended. You can skip this it won't be graded. A rewrite is given below.

From a) $\quad \mathcal{Z} = 2e^{\beta\mu}\left(\text{ch}\,\beta\Delta/2 + \text{ch}(\beta(\delta/2-\mu))\right)$

Then

$$\overline{\Phi}_G = -k_B T \ln \mathcal{Z} = U - TS - \mu N$$

So

$$\frac{S}{k_B} = \ln \mathcal{Z} + \beta(U - \mu N)$$

Now

$$\beta(U-\mu N) = -\beta\frac{\partial}{\partial\beta}\ln\mathcal{Z} = -\beta\frac{\partial}{\partial\beta}\left[\beta\mu + \ln\left(\text{ch}(\beta\Delta/2) + \text{ch}(\beta\tfrac{\delta}{2}-\mu)\right)\right]$$

$$\beta(U-\mu N) = -\beta\mu - \frac{\beta\Delta/2\,\text{sh}(\beta\Delta/2) - \beta\delta/2\,\text{sh}(\beta(\delta/2-\mu))}{\text{ch}(\beta\Delta/2) + \text{ch}(\beta(\delta/2-\mu))}$$

So

$$\frac{S}{k_B} = \ln\left[2\left(\text{ch}\,\beta\Delta/2 + \text{ch}(\beta(\delta/2-\mu))\right)\right] - \frac{\beta\Delta/2\,\text{sh}(\beta\Delta/2) - \beta\delta/2\,\text{sh}(\beta(\delta/2-\mu))}{\text{ch}(\beta\Delta/2) + \text{ch}(\beta(\delta/2-\mu))}$$

finally from b

$$\overline{N} = \frac{ch(\beta\Delta/2) + e^{-\beta(\delta/2 - \mu)}}{ch(\beta\Delta/2) + ch(\beta(\delta/2 - \mu))}$$

putting $\mu = \delta/2$ as a sanity check we get

$$\overline{N} = 1$$

and

$$S = \ln\left[2(ch\,\beta\Delta/2 + 1)\right] - \frac{\beta\Delta/2\,sh\,\beta\Delta/2}{ch(\beta\Delta/2) + 1}$$

$$= \ln\left[4\,ch^2(\beta\Delta/4)\right] - \frac{\beta\Delta}{2}\,th(\beta\Delta/4)$$

Problem 3.   Yields of three species

Consider three ideal gasses in equilibrium. They participate in the following chemical reaction

$$A + B \leftrightarrow C. \tag{8}$$

It is energetically favorable to form atom C, so that the energy of one molecule of C is

$$\epsilon_C = \frac{p^2}{2m_C} - \Delta, \tag{9}$$

where $\Delta > 0$ is the binding energy of C. The molecule C has only one internal state. The other two atoms have energies $\epsilon_A = p^2/2m_A$ and $\epsilon_B = p^2/2m_B$ and form simple ideal gasses

(a) If the partition function Z_{tot} of a gas of N indistinguishable particles is given by $Z_{\text{tot}} = Z_1^N/N!$, where Z_1 is the single–particle partition function, show that the chemical potential is given by

$$\mu = -kT \log \left(\frac{Z_1}{N} \right) \tag{10}$$

(b) Assume that at one moment there are N_A, N_B, and N_C particles of type A, B, and C, respectively. Determine the partition function of each species, and find the corresponding chemical potentials.

(c) Show that

$$n_A = \frac{e^{\mu_A/kT}}{\lambda_A^3} \tag{11}$$

$$n_B = \frac{e^{\mu_B/kT}}{\lambda_B^3} \tag{12}$$

$$n_C = \frac{e^{\mu_C/kT} e^{\beta\Delta}}{\lambda_C^3} \tag{13}$$

Here $n_A = N_A/V$ is the density of species A, and λ_A is the thermal wavelength of A, with an analogous notation for B and C.

(d) Show that in equilibrium the densities of A, B and C satisfy

$$\frac{n_A n_B}{n_C} = \frac{(2\pi m_{\text{red}} kT)^{3/2}}{h^3} e^{-\beta\Delta} \tag{14}$$

where $m_{\text{red}} = m_A m_B/(m_A + m_B)$ is the reduced mass. Note $m_C = m_A + m_B$.

Problem: Yields

a)   So

$$Z_{tot} = \frac{Z_1^N}{N!} \cong \left(\frac{e Z_1}{N}\right)^N$$

Then

$$F = -kT \ln Z_{tot} = -kT \, N \, \ln\left(\frac{e Z_1}{N}\right) = -kTN\left[\ln \frac{Z_1}{N} + 1\right]$$

So

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{+} = -kT\left[\ln\left(\frac{Z_1}{N}\right) + 1\right] + kTN \frac{\partial}{\partial N}\left(\ln N + const\right)$$

$$\boxed{\mu = -kT \ln Z_1 / N}$$

Now

b) $\quad Z_1 = Z_1^{trans} \, Z_{int}$

$\quad\quad Z_1^A = V n_Q^A \cdot 1 \qquad\qquad$ with $\quad n_Q^A = \frac{(2\pi m^A k_B T)^{3/2}}{h^3}$

$\quad\quad Z_1^B = V n_Q^B \cdot 1$

$\quad\quad Z_1^C = V n_Q^C \cdot \sum_s e^{-\beta \varepsilon_s}$

$\quad\quad Z_1^C = V n_Q^C \, e^{\beta \Delta}$

Then

$$e^{\mu_A/kT} = \frac{N}{z_1}$$

Now this yields:

$$e^{\mu_A/kT} = \frac{N}{V n_Q^A} = \frac{n^A}{n_Q^A}$$

Similarly

$$e^{\mu_B/kT} = \frac{n}{n_Q^B}$$

$$e^{\mu_C/kT} = \frac{n}{n_Q^C} e^{-\beta\Delta}$$

Finally sine

$$e^{+(\mu_A + \mu_B - \mu_C)/kT} = 1 \qquad \text{we have:}$$

$$\left(\frac{n^A}{n_Q^A}\right)\left(\frac{n^B}{n_Q^B}\right)\left(\frac{n_Q^C e^{\beta\Delta}}{n_C}\right) = 1$$

Or

$$\frac{n^A n^B}{n_C} = \left(\frac{n_Q^A n_Q^B}{n_Q^C}\right) e^{-\beta\Delta}$$

So

$$n_c \propto n^A n^B e^{\beta \Delta}$$

if the Binding energy is strong we get lots of particle C. But the yield of C is limitted by the availability of A and B.

We note $n_Q = C_o m^{3/2}$ or $n_Q = (2\pi m kT)^{3/2}/h^3$

$$\frac{n_Q^A n_Q^B}{n_Q^C} = C_o \left(\frac{m_A m_B}{m_A + m_B}\right)^{3/2} \qquad \hookrightarrow C_o = (2\pi kT)^{3/2}/h^3$$

$$= C_o m_{red}^{3/2} \qquad \text{with} \quad m_{red} = \frac{m_A m_B}{m_A + m_B}$$

So finally we have

$$\boxed{\frac{n_A n_B}{n_C} = \frac{(2\pi m_{red} kT)^{3/2}}{h^3} e^{-\beta \Delta}}$$

Problem 4.   The Saha Equation

The Saha equation describes the relative abundance of neutral hydrogen to ionized hydrogen at a given temperature. The reaction here is

$$p + e \leftrightarrow H \tag{15}$$

The bound states of the hydrogen atom have internal energies

$$\epsilon_n = -\frac{R}{n^2} \qquad n = 1, 2, 3, \ldots. \tag{16}$$

where $R = -13.6\,\mathrm{eV}$ as well as translational kinetic energy

$$\epsilon(\boldsymbol{p}, n) = \frac{p^2}{2m} + \epsilon_n \tag{17}$$

Following Saha approximate the internal partition function of hydrodygen by just including the lowest energy state (the $n{=}1$ state) with energy $-R$. This amounts to treating the hydrogen atom as a single bound state with binding energy $\Delta = R = 13.6\,\mathrm{eV}$ and then evaluate the partition function of hydrogen with the same approximation in a previous problem. You can also approximate the reduced mass of the electron and proton as $m_{\mathrm{red}} = m_e m_p/(m_e + m_p) \simeq m_e\left(1 + \mathcal{O}(m_e/m_p)\right)$.

(a) Explain why charge neutrality implies that $n_e = n_p$ and conservation of nucleons implies $n_H + n_p = n$, where n is the total number density of hydrogen (neutral and ionized). Writing $y = n_p/n$ as the degree of ionization, show that

$$\frac{y^2}{1-y} = x(T) \qquad x(T) \equiv \frac{e^{-\beta R}}{n\lambda_{\mathrm{th}}^3} \tag{18}$$

where λ_{th} is the thermal wavelength for the electrons. This equation determines the degree of ionization $y(T) = n_p/n$ as a function of temperature. The ionization fraction is plotted below
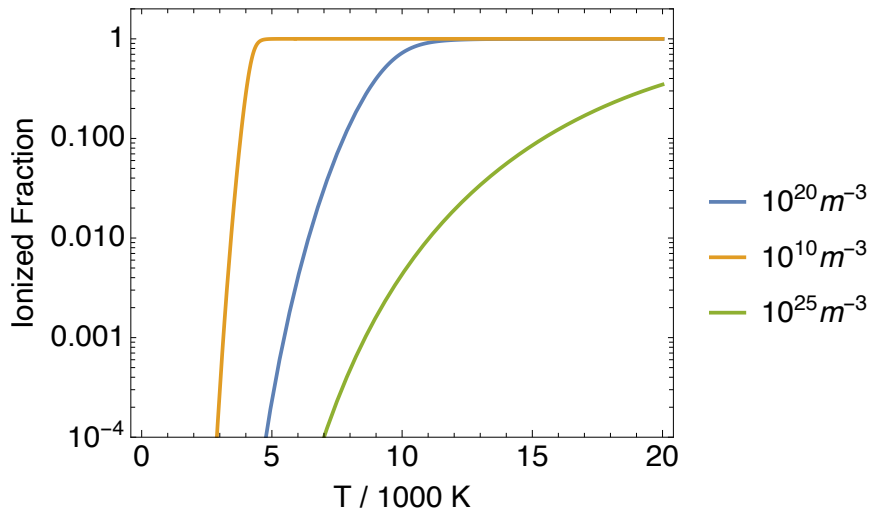
(b) (Optional) Solve for y in terms of $x(T) = e^{-\beta R}/n\lambda_{\text{th}}{}^3$ and graph the degree of of ionization as a function of temperature in kelvin for a density of $10^{20}\,\text{m}^{-3}$. You should find that the temperature where the system becomes fully ionizied is approximately $10000\,°\text{K}$.

(c) (Optional) Equation 18 shows that the degree of ionization goes up when the density n goes down. Why is that? Answer the following closely related question: The temperature where the hydrogen becomes fully ionized is approximately $10000\,°\text{K}$. But, the Boltzmann factor at this temperature is very small

$$e^{-R/k_B T} = e^{-13.6\,\text{eV}/k_B(10^4\,°\text{K})} \simeq e^{-16.} \sim 10^{-7}, \tag{19}$$

Qualitatively explain why the ionized fraction at this temperature is of order unity in spite of this penalizing factor.

b)

- We charge neutrality implies

☆ $n_e = n_p$

- And we must have

☆☆ $n_p + n_H = n$ constant

free + bound

- Since the total number of protons^ is constant, We have from ☆

$$\frac{n_e n_p}{n_H} = \frac{1}{\lambda_{th}^3} e^{-\beta R} \quad \text{where} \quad \lambda_{th} = \frac{(2\pi m_e k_B T)^{3/2}}{h^3}$$

$$\frac{n_p^2}{n_H} = \frac{1}{\lambda_{th}^3} e^{-\beta R}$$

- So the ionization fraction $y = n_p/n$ satifies

$$n \frac{y^2}{n_H/n} = \frac{1}{\lambda_{th}^3} e^{-\beta R}$$ note

Now note $n_H/n = 1 - y$ from ☆☆
So

$$\boxed{\frac{y^2}{1-y} = \frac{1}{n\lambda_{th}^3} e^{-\beta R}}$$

- So Lets substitute #'s

$m_e c^2 = 0.511 \text{ MeV} = 0.5 \times 10^6 \text{ eV}$

$hc = 1240 \text{ eV nm}$

$n = 10^{-7} \text{ nm}^3$

$$\lambda_{th} = \frac{h}{(2\pi m_e k_B T)^{1/2}} = 2.40 \text{ nm}$$

$1/n\lambda_{th}^3 = 7.25 \times 10^5$

$\log(1/n\lambda_{th}^3) = 13.4951$ $\qquad$ $\beta = \frac{1}{kT}$ $\qquad$ $kT = 0.0833 \text{ eV}$

$$\beta R = \frac{13.6 \text{ eV}}{\underset{300°k}{0.025 \text{ eV}}} \quad_{1000k} = 163.2$$

So

$$x \equiv \frac{1}{n\lambda_{th}^3} \, e^{-\beta R} = e^{13.5 - 163.2} = e^{-150}$$

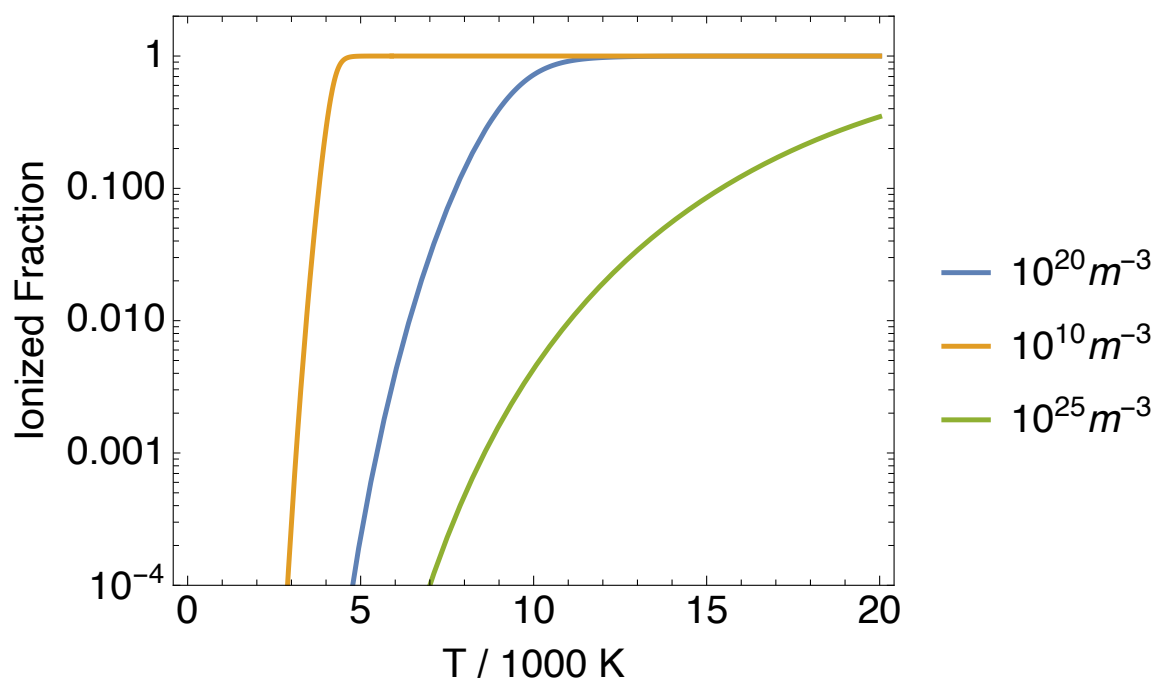- This is very small which means, that y will be
  small.

$$\frac{y^2}{1-y} = x$$
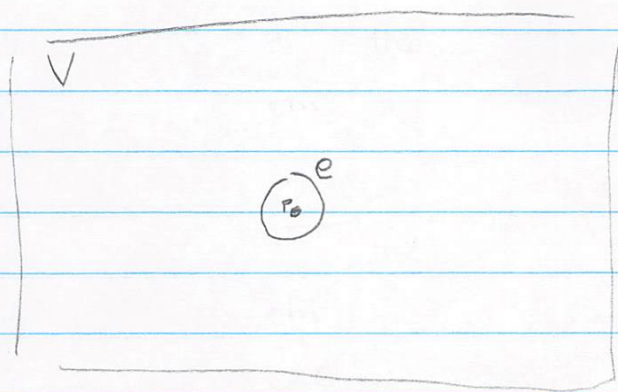
$$y \simeq \sqrt{x} = e^{-75} \simeq 10^{-32.5}$$

Once can just solve the Saha equation. It is a quadratic equation for y

$$y^2 = x(\beta, n)(1 - y)$$

Where $x(\beta, n) = e^{-\ln(n\lambda_{\mathrm{th}}^3) - \beta R}$. I did this and made a graph of the ionization fraction versus temperature. Notice that at low density, the system very rapidly transitions from bound to unbound.

c) To understand the phenomena consider one hydrogen atom in a big box

$\dfrac{N}{V} = \dfrac{1}{V}$

There is a small amount of phase space of order $\underline{1}$ where the electron is bound, and a $\overset{\text{large}}{\wedge}$ phase-space $(V p_e^3/h^3)$ of order $V p_e^3/h^3$, where the electron is unbound.

The entropy associated with the unbound states is of order $S/k \sim k \ln \Omega \sim k \ln (V/\lambda_{th}^3)$ So, this grows with the accessible volume when the density is low. Indeed the formula is roughly

$$y^2 \propto e^{(TS_{uubnd} - u)/kT}$$

any y becomes appreciable for $\dfrac{S}{k_B} \sim \dfrac{u}{k_B T}$.

So in short the unbound states are penalized energetically, but there are a lot of them, i.e. they are favored entropically.

Problem 5.   Absorption and Oscillations

Consider an ideal mono-atomic gas at temperature T and pressure P in contact with a surface. The atoms of the gas can be absorbed on specific sites on the surface, which are sparsely enough distributed over the surface that they do not interact. There are N_0 such sites and each site can absorb zero, one, or two atoms. If a site is empty, we can take that energy as zero. If the site is singly occupied the energy is ϵ_1. If it is doubly occupied, the two absorbed atoms interact and vibrate with frequency ω_0, so that the corresponding energy levels are $\epsilon_2 + n'\hbar\omega_0$. Here ϵ_2 is the energy for absorbing a pair and $n' = 0, 1, \ldots$ is the vibrational quantum number, parametrizing the additional energy associated with the vibrations.

(a) The temperature and chemical potential that the absorption site experiences is determined by the properties of the surrounding gas. The chemical potential of this gas is determined by its temperature and pressure, in much the same way that the temperature is determined by the energy per particle of the gas $kT = 2/3(E/N)$.

Recall that the single particle partition function of the gas (mono-atomic or even poly-atomic) is

$$Z_1 = \sum_s \int \frac{d^3r\,d^3p}{h^2} e^{-\beta p^2/2m} e^{-\beta \epsilon_s} \tag{20}$$

Let's strip off the overall dependence on volume and define:

$$Z_1 \equiv V\zeta_1(T) \tag{21}$$

Show that the so-called *fugacity* $z \equiv e^{\beta\mu}$ of the gas is proportional to the pressure, with proportionality constant determined by $\zeta_1(T)$:

$$z \equiv \frac{P}{kT\zeta_1(T)} \tag{22}$$

Show that for a mono-atomic gas

$$z = \frac{P}{kTn_Q(T)} \tag{23}$$

(b) Compute the grand partition function for an absorption site.

(c) Compute the grand potential Φ_G for an absorption site.

(d) Compute the mean number of atoms absorbed by a site by finding the probabilities for each state and then using these probabilities to find the average number of atoms absorbed by a site.

(e) Compute the mean number of atoms absorbed by a site by differentiating (c).

(f) What is the probability that a site will absorb two atoms? And what is the probability that the site will absorb two atoms and that the pair will vibrate with three vibrational quanta?

Answers:

(b) See (c).

(c)
$$\Phi_G = -kT \ln[1 + z\,e^{-\beta\epsilon_1} + z^2\,e^{-\beta\epsilon_2} Z_{HO}(\beta)] \tag{24}$$

where z is the fugacity of the surrounding gas, and $Z_{HO}(\beta) = 1/(1 - e^{-\beta\hbar\omega_0})$ is the partition function of the Harmonic Oscillator (HO).

(d)
$$\bar{n} = \frac{ze^{-\beta\epsilon_1} + 2z^2 e^{-\beta\epsilon_2} Z_{HO}}{1 + ze^{-\beta\epsilon_1} + z^2 e^{-\beta\epsilon_2} Z_{HO}} \tag{25}$$

(e) Same as (d).

(f)
$$\mathscr{P}_2 = \frac{z^2 e^{-\beta\epsilon_2} Z_{HO}}{1 + ze^{-\beta\epsilon_1} + z^2 e^{-\beta\epsilon_2} Z_{HO}}, \qquad \mathscr{P}_{2,3} = \mathscr{P}_2 \cdot \left(\frac{e^{-3\beta\hbar\omega_0}}{Z_{HO}}\right). \tag{26}$$

Solution

(a) We have

$$Z_N = \frac{V^N}{N!}\zeta_1^N = (eV\zeta_1/N)^N \tag{27}$$

and

$$F = -NkT\ln(eV\zeta_1/N) \tag{28}$$

We note

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ln(eV\zeta_1/N) + kT = -kT\ln(V\zeta_1/N) \tag{29}$$

So

$$z = e^{\beta\mu} = \frac{N\zeta_1}{V} = \frac{P}{kT\zeta_1} \tag{30}$$

Now in the mono-atomic case

$$\zeta_1(T) = n_Q(T) = \int \frac{d^3p}{h} e^{-\beta p^2/2m} \tag{31}$$

So for a mono-atomic gas

$$z = e^{\beta\mu} = \frac{N\zeta_1}{V} = \frac{P}{kTn_Q(T)} \tag{32}$$

(b) The states are listed below

- ground state $E = 0$, $N = 0$
- first state $E = \epsilon_1$, $N = 1$
- second and higher states $E = \epsilon_2 + n_{\text{vib}}\hbar\omega_0$, $N = 2$, with $n_{\text{vib}} = 0, 1, 2, \dots$.

So

$$Z_G = 1 + e^{-\beta(\epsilon_1-\mu)} + \sum_{n_{\text{vib}}} e^{-\beta(\epsilon_2+n_{\text{vib}}\hbar\omega_0-2\mu)} \tag{33}$$

$$Z_G = 1 + e^{-\beta(\epsilon_1-\mu)} + e^{-\beta(\epsilon_2-2\mu)} Z_{HO}(\beta) \tag{34}$$

$$= 1 + ze^{-\beta\epsilon_1} + z^2 e^{-\beta\epsilon_2} Z_{HO} \tag{35}$$

with $Z_{HO} = 1/(1 - e^{-\beta\hbar\omega_0})$.

(c) So

$$\Phi_G = -kT\ln\left(1 + ze^{-\beta\epsilon_1} + z^2 e^{-\beta\epsilon_2} Z_{HO}\right) \tag{36}$$

(d) The probability of being in a state is

$$P_s = e^{-\beta(\epsilon_s-\mu N_s)} \mathcal{Z}_G \tag{37}$$

The probability of being in a state with $N = 1$ is given by the probability of being in just one state:

$$P_{N=1} = e^{-\beta(\epsilon_1-\mu)} \mathcal{Z}_G = ze^{-\beta\epsilon_1} \mathcal{Z}_G \tag{38}$$

The probability of being in *any* state with $N = 2$ is found by summing up the harmonic oscillator states:

$$P_{N=2} = \sum_{n_{\text{vib}}} P_s|_{N=2} = \frac{1}{Z_G} \sum_{n_{\text{vib}}} e^{-\beta(\epsilon_2 + n_{\text{vib}}\hbar\omega_0 - 2\mu)} = \frac{e^{-\beta(\epsilon_2 - 2\mu)} Z_{HO}(\beta)}{\mathcal{Z}_G} = z^2 \frac{e^{-\beta\epsilon_2} Z_{HO}(\beta)}{\mathcal{Z}_G} \quad (39)$$

So the mean N is

$$\langle N \rangle = P_{N=1} \cdot 1 + P_{N=2} \cdot 2 \quad (40)$$

$$= \frac{z e^{-\beta\epsilon_1} + 2z^2 e^{-\beta\epsilon_2}}{\mathcal{Z}_G} \quad (41)$$

(e) Alternatively we may differentiate the partition function

$$\langle N \rangle = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_T \quad (42)$$

Using

$$\partial_\mu z = \partial_\mu e^{\beta\mu} = \beta z \quad (43)$$

we find after differentiation of Eq. (36)

$$\langle N \rangle = \frac{kT}{\mathcal{Z}_G} \times (z\beta e^{-\beta\epsilon_1} + 2z^2 \beta e^{-\beta\epsilon_2}) \quad (44)$$

$$= \frac{z e^{-\beta\epsilon_1} + 2z^2 e^{-\eta\epsilon_2}}{\mathcal{Z}_G} \quad (45)$$

in agreement with part (d)

(f) We already worked this out in Eq. (39). If we ask to be in one specific state with $N_S = 2$ and $\epsilon_S = \epsilon_2 + 3\hbar\omega_0$

$$P_s = \frac{e^{-\beta(\epsilon_S - \mu N_S)}}{Z_G} = z^2 e^{-\beta\epsilon_2} \frac{e^{-3\hbar\omega_0}}{\mathcal{Z}_G} \quad (46)$$