

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<sup>1</sup>,  $n_Q \equiv \lambda_{\text{th}}^{-3}$ . 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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<sup>1</sup> $\lambda_{\text{th}}$  is the thermal de Broglie wavelength.

| quantity          | value                              |
|-------------------|------------------------------------|
| $T$               | 295 K                              |
| $p$               | 0.2 bar                            |
| $n$               | $0.005 \text{ nm}^{-3}$            |
| $(n_Q)_{O_2}$     | $1.68 \times 10^5 \text{ nm}^{-3}$ |
| $(n_Q)_{CO}$      | $1.37 \times 10^5 \text{ nm}^{-3}$ |
| 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  $\Delta_{CO} = 0.00024 \text{ eV}$  and  $\Delta_{O_2} = 0.00018 \text{ eV}$  respectively. Show that the rotational constant of  $O_2$  is roughly consistent with an order of magnitude estimate for  $\Delta$ .

- (c) Recall that the rotational energy levels are

$$\epsilon_{\text{rot}} = \ell(\ell + 1)\Delta \quad \text{with} \quad \ell = 0, 1, 2, \dots, \infty \quad (1)$$

and that the rotational partition function (i.e. an appropriate sum over these levels) is  $Z_{\text{rot}} \simeq kT/\Delta$  in a classical approximation. Estimate the typical value of  $\ell$  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

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

where  $Z_{\text{rot}} \equiv kT/\Delta$  with  $\Delta = \hbar^2/2I$ , and  $Z_{\text{trans}}$  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  $\Delta$  is

$$\mu = kT \ln(n/n_Q) + kT \ln(\beta\Delta) \quad (3)$$

- (ii) Numerically evaluate the chemical potential  $\mu_{O_2}$  of the  $O_2$  gas. Ans:  $-0.5569 \text{ eV}$   
*Note:* The numbers need to be evaluated with a lot of precision here, use  $k_B = 0.02542 \text{ eV}/(295 \text{ Kelvin})$ .
- (iii) Numerically evaluate the chemical potential  $\mu_{CO}$  of the surrounding  $CO$  gas, assuming that the concentration of  $CO$  is a thousand times smaller than  $O_2$ .  
 Ans:  $-0.7173 \text{ eV}$

- (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:  $P = 0.975$

## 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               | H  | H+ | H− | H* |
|------------------|------------------------|----------------------|----|----|----|----|
| ground state     | 1                      | $-\frac{1}{2}\Delta$ | H− | H− | H+ | H+ |
| positive ion     | 0                      | $-\frac{1}{2}\delta$ | H  | H* | H* | H* |
| negative ion     | 2                      | $\frac{1}{2}\delta$  | H− | H  | H+ | H  |
| excited hydrogen | 1                      | $\frac{1}{2}\Delta$  |    |    |    |    |

- (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

$$\mathcal{Z}_G = 2e^{\beta\mu} \cosh(\beta\Delta/2) + 2e^{\beta\mu} \cosh(\beta(\delta/2 - \mu)) \quad (4)$$

- (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

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

and that grand partition function evaluated at this chemical potential is

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

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

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

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

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

## Problem 3. Yields of three species

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



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

$$\epsilon_C = \frac{p^2}{2m_C} - \Delta, \quad (9)$$

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  $Z_{\text{tot}}$  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

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

- (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

$$n_A = \frac{e^{\mu_A/kT}}{\lambda_A^3} \quad (11)$$

$$n_B = \frac{e^{\mu_B/kT}}{\lambda_B^3} \quad (12)$$

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

Here  $n_A = N_A/V$  is the density of species  $A$ , and  $\lambda_A$  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

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

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

## Problem 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



The bound states of the hydrogen atom have internal energies

$$\epsilon_n = -\frac{R}{n^2} \quad n = 1, 2, 3, \dots \quad (16)$$

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

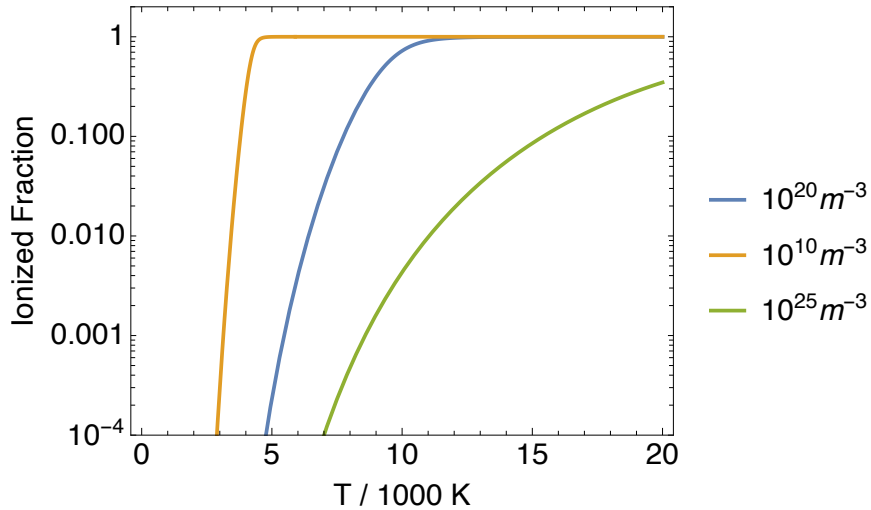
$$\epsilon(\mathbf{p}, n) = \frac{p^2}{2m} + \epsilon_n \quad (17)$$

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  $\Delta = R = 13.6 \text{ eV}$  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  $m_{\text{red}} = m_e m_p / (m_e + m_p) \simeq m_e (1 + \mathcal{O}(m_e/m_p))$ .

- (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

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

where  $\lambda_{\text{th}}$  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 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 ionized is approximately  $10000^\circ \text{K}$ .
- (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  $10000^\circ \text{K}$ . But, the Boltzmann factor at this temperature is very small

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

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

### 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 one one 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  $\epsilon_1$ . If it is doubly occupied, the two absorbed atoms interact in a vibrational mode of frequency  $\omega_0$ , so that the corresponding energy levels are  $\epsilon_2 + n'\hbar\omega_0$ . Here  $\epsilon_2$  is the energy for absorbing a pair and  $n' = 0, 1, \dots$  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

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

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

$$Z_1 \equiv V \zeta_1(T) \quad (21)$$

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

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

Show that for a mono-atomic gas

$$z = \frac{P}{T n_Q(T)} \quad (23)$$

- (b) Compute the grand partition function for an absorption site.  
(c) Compute the grand potential  $\Phi_G$  for an absorption site.  
(d) Compute the mean number of atoms absorbed by a site directly from (b)  
(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)

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

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)

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

- (e) Same as (d).

- (f)

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