



Figure 1: Artists conception of problem Carbon Monoxide Poisoning. The large Black circles denote Carbon atoms, while the smaller circles denote Oxygen atoms.

## 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 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 K and a pressure of 0.2 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.

<sup>1</sup> $\lambda_{\text{th}}$  is the thermal de Broglie wavelength.  $v_Q \equiv \lambda_{\text{th}}^3$  is the volume of a cube whose side is one thermal de Broglie wavelength. This could be called a “quantum volume” for a particle. The quantum density, or concentration, can be defined (as the book does) as  $n_Q \equiv 1/v_Q$ . If the density  $n$  becomes comparable to the quantum concentration,  $n/n_Q \sim 1$ , then quantum mechanics becomes important.

quantity	value
$T$	290 K
$kT$	0.025 eV
$p$	0.2 bar
$n$	$0.005 \text{ nm}^{-3}$
$(n_Q)_{O_2}$	$1.70 \times 10^5 \text{ nm}^{-3}$
$(n_Q)_{CO}$	$1.39 \times 10^5 \text{ nm}^{-3}$
atomic number $O$	16
atomic number $C$	12

- (a) Without looking up numbers estimate the quantum concentration of  $O_2$  gas, confirming the result in the table.
- (b) Qualitatively explain what determines the ratio of quantum concentrations for the two gasses,  $O_2$  and  $CO$ .
- (c) 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  $\Delta$ .
- (d) 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? Ans:  $\ell \sim 11$ .

- (e) 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) Derive  $Z_{\text{rot}} = kT/\Delta$  using a classical approximation, where the sum is replaced by an integral.
- (ii) Determine the chemical potential of the classical diatomic gas as a function of the concentration  $n$  and the rotational constant  $\Delta$ . Your result should be a function of  $n\lambda_{\text{th}}^3$  and  $\beta\Delta$ , and you can check it by doing the next part.
- (iii) Numerically evaluate the chemical potential  $\mu_{O_2}$  of the  $O_2$  gas. Ans:  $-0.5569 \text{ eV}$

- (iv) Numerically evaluate the chemical potential  $\mu_{CO}$  of the surrounding  $CO$  gas, assuming that the density of  $CO$  is a thousand times smaller than  $O_2$ . Ans:  $-0.7173\text{ eV}$
- (f) Now return to the hemoglobin sites. By considering the grand partition function of the site, determine the probability that the site is occupied by  $O_2$ . Assume that the density of  $CO$  is a thousand times smaller than  $O_2$ . Evaluate this probability numerically, using the numerical results of previous parts. Ans: 0.17
- (g) Determine how the probability of (e) would change if the density of  $CO$  was negligibly small. Ans: 0.976

## Problem 2. Gibbs Free Energy for Several Components

Consider a gas consisting of three types of particles,  $A$ ,  $B$ ,  $C$ . A chemical reaction amongst particles converts an atom of  $A$  plus an atom of  $B$  to a molecule of  $C$



The energy is a function of  $S$ ,  $V$ ,  $N_A$ ,  $N_B$  and  $N_C$ , i.e.  $U(S, V, N_A, N_B, N_C)$ . The change in energy is

$$dU = TdS - pdV + \mu_A dN_A + \mu_B dN_B + \mu_C dN_C \quad (4)$$

This problem will lead you to conclude that equilibrium between  $A$ ,  $B$  and  $C$  is reached when

$$\mu_C = \mu_A + \mu_B \quad (5)$$

- (a) Define the Gibbs Free energy  $G = U - TS + PV$  and compute its differential  $dG$ .
- (b) Generalize the scaling arguments given in the book which led to to Eq. 22.5, to show that

$$G = \mu_A N_A + \mu_B N_B + \mu_C N_C \quad (6)$$

In particular consider how the energy of the system  $U$  changes if all extensive quantities are  $S$ ,  $N_A$ ,  $N_B$ ,  $N_C$  are scaled by a factor  $\lambda$ .

- (c) If a system is held at constant temperature and pressure, it will evolve it will evolve to minimize its Gibbs Free Energy. Equilibrium is reached when  $dG = 0$ . How does the Gibbs Free energy change if the reaction proceeds by one step (i.e. we take one atoms of  $A$  one atom of  $B$  and make a  $C$ ) at constant temperature and pressure. Argue that the system reaches equilibrium when

$$\mu_C - \mu_A - \mu_B = 0 \quad (7)$$

Hint: in one step of the forward reaction  $A + B \rightarrow C$  the change in the number of  $A$  is  $dN_A = -1$ . What are  $dN_B$  and  $dN_C$  for one step? What is  $dG$  then? And what does it need to be in equilibrium?

### 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



Read the setup of problem Blundell 22.5, and recognize that the results of the previous problem apply. The only difference is that in Blundell's part (a), they have approximated  $m_{\text{red}} = m_e m_p / (m_e + m_p) \simeq m_e$ . They (following Saha) also have approximated the internal partition function of the hydrogen atom as a single bound state with binding energy  $\Delta = R = 13.6 \text{ eV}$ . We evaluate the partition function of hydrogen with the same approximation in a previous problem. Answer the following

- (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

$$\frac{y^2}{1-y} = \frac{e^{-\beta R}}{n \lambda_{\text{th}}^3} \quad (16)$$

where  $\lambda_{\text{th}}$  is the thermal wavelength for the electrons. 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  $10000 \text{ }^\circ\text{K}$ .

- (b) Equation 16 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  $10000 \text{ }^\circ\text{K}$ . But, the Boltzmann factor at this temperature is very small

$$e^{-R/k_B T} = e^{-13.6 \text{ eV}/k_B(10^4 \text{ }^\circ\text{K})} \simeq e^{-16} \sim 10^{-7}, \quad (17)$$

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