"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 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[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]$\lambda_{\text{th}}$ 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 |
|---|---|
| $T$ | $290\,\mathrm{K}$ |
| $kT$ | $0.025\,\mathrm{eV}$ |
| $p$ | $0.2\,\mathrm{bar}$ |
| $n$ | $0.005\,\mathrm{nm}^{-3}$ |
| $(n_Q)_{O_2}$ | $1.70 \times 10^5\,\mathrm{nm}^{-3}$ |
| $(n_Q)_{CO}$ | $1.39 \times 10^5\,\mathrm{nm}^{-3}$ |
| 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 $\Delta_{CO} = 0.00024\,\mathrm{eV}$ 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 $\Delta$.

(d) 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 $\ell$ 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

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

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

   (i) Derive $Z_{\mathrm{rot}} = kT/\Delta$ 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 $n\lambda_{\mathrm{th}}^3$ 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: $-0.5569\,\mathrm{eV}$

(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: $-0.7173\,\mathrm{eV}$

(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 $C$

$$A + B \leftrightarrow C \tag{3}$$

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

$$dU = TdS - pdV + \mu_A dN_A + \mu_B dN_B + \mu_C dN_C \tag{4}$$

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

$$\mu_C = \mu_A + \mu_B \tag{5}$$

(a) Define the Gibbs Free energy $G = U - TS + PV$ and compute its differential $dG$.

(b) Generalize the scaling arguements given in the book which led to to Eq. 22.5, to show that

$$G = \mu_A N_A + \mu_B N_B + \mu_C N_C \tag{6}$$

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 procedes 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

$$\mu_C - \mu_A - \mu_B = 0 \tag{7}$$

Hint: in one step of the forward reaction $A + B \to C$ 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

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

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 $Z_{\text{tot}}$ 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

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

(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 $\lambda_A$ 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

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

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

## Problem 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

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

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

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

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 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 $10000\,°\text{K}$.

(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 $10000\,°\text{K}$. But, the Boltzmann factor at this temperature is very small

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

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