

## Problem 1. Rotational Partition Functions

- (a) Consider HCl gas, which is composed of Hydrogen of mass  $m_H$  and chlorine  $Cl$
- (i) Give a typical distance between the Hydrogen and the Chlorine atoms,  $r_0$  (in meters). We will assume this distance is fixed.
  - (ii) Use classical considerations, to find the center of mass of the two atoms, and compute the moment of inertia of the two atoms around the center of mass exactly. Assume that the HCl is rotating in the  $xy$  plane. Show that

$$I = m_H r_0^2 \left( 1 - \left( \frac{m_H}{m_{Cl}} \right) + \dots \right) \quad (1)$$

up to terms further suppressed by terms of order  $(m_H/m_{Cl})^2$ . We will keep the leading term only  $m_H r_0^2$  in what follows.

- (iii) The rotational energy levels are

$$\epsilon_{\text{rot}} = \left\langle \frac{L^2}{2I} \right\rangle = \frac{\ell(\ell+1)\hbar^2}{2I} = \ell(\ell+1)\Delta \quad (2)$$

where  $\Delta = \hbar^2/2I$ . Estimate  $\Delta$  in eV and in GHz (i.e.  $f = \Delta/h$ ). Estimate  $\Delta/kT$  at room temperature, you should find that  $kT/\Delta$  is around 12.

- (b) (i) Show that for any system that  $C_V$  is directly determined by the variance in the energy

$$C_V = k_B \beta^2 (\langle E^2 \rangle - \langle E \rangle^2) \quad (3)$$

- (ii) Recall that the partition function of  $N$  molecules of H HCl consists of a translational partition function, and a rotational one:

$$Z_{\text{tot}} \simeq \left( \frac{e Z_{\text{trans}}}{N} \right)^N Z_{\text{rot}}^N \quad (4)$$

(Where does the factor  $(e/N)^N$  come from?). Show that

$$C_V = \frac{3}{2} N k_B + N k_B \beta^2 [\langle \epsilon_{\text{rot}}^2 \rangle - \langle \epsilon_{\text{rot}} \rangle^2] \quad (5)$$

where

$$\beta^2 \langle \epsilon_{\text{rot}}^2 \rangle = \frac{1}{Z_{\text{rot}}(\beta\Delta)} \sum_{\ell=0}^{\infty} (2\ell+1) (\ell(\ell+1)\beta\Delta)^2 e^{-\ell(\ell+1)\beta\Delta} \quad (6)$$

$$\beta \langle \epsilon_{\text{rot}} \rangle = \frac{1}{Z_{\text{rot}}(\beta\Delta)} \sum_{\ell=0}^{\infty} (2\ell+1) (\ell(\ell+1)\beta\Delta) e^{-\ell(\ell+1)\beta\Delta} \quad (7)$$

- (c) Write a program to sum from  $\ell = 0$  up to 20 and to compute

$$\beta^2 \langle \epsilon_{\text{rot}}^2 \rangle, \quad \beta \langle \epsilon_{\text{rot}} \rangle, \quad C_V/k_B \quad (8)$$

Make a graph of  $C_v/R$  vs.  $kT/\Delta$  for one mole of substance. You should find something analogous to Figure. 27.

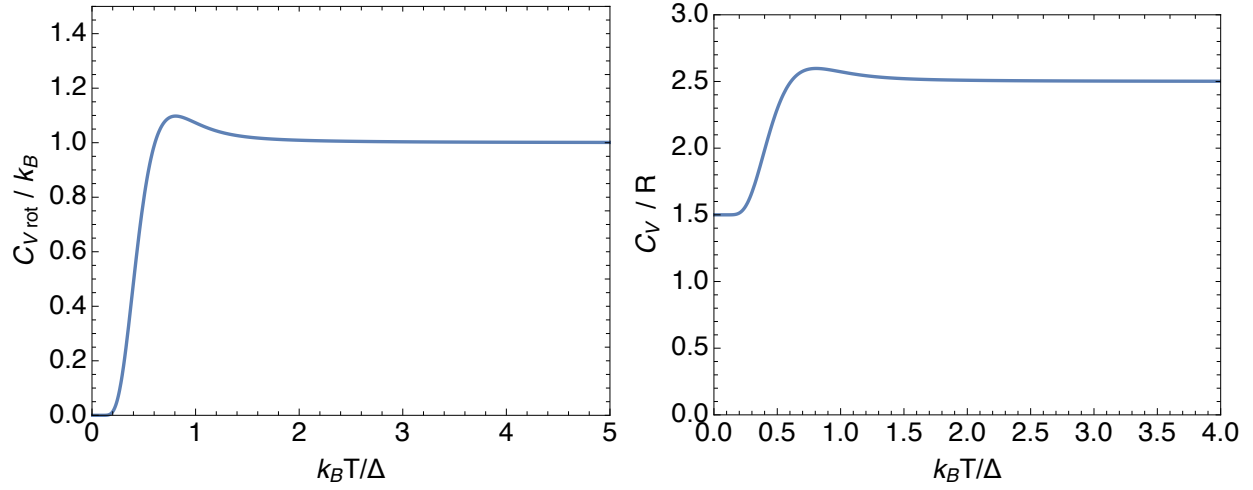
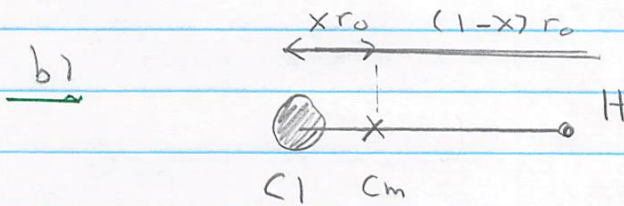


Figure 1: Left: the rotational contribution to the partition function (per particle), i.e.  $\beta^2(\langle \epsilon_{\text{rot}}^2 \rangle - \langle \epsilon_{\text{rot}} \rangle^2)$ . Right: the full partition function for one mole.

- (d) For HCl, use your graph estimate the temperature (in Kelvin) where the classical approximation for the rotational partition function works at the 20% level. What would be the corresponding temperature for diatomic hydrogen  $H_2$ .

HCl

a) Take  $r_0 = 1 \text{ \AA}$



The location of the cm is at  $x r_0$

$$I = m_{Cl} (x r_0)^2 + m_H (1-x)^2 r_0^2$$

Now

$$x r_0 = \frac{m_H r_0}{m_H + m_{Cl}} \quad \text{definition of cm}$$

$$\text{And } x = \frac{m_H}{m_H + m_{Cl}} = \frac{m_H}{m_{\text{Tot}}} \quad (1-x) = \frac{m_{Cl}}{m_{\text{Tot}}}$$

$$I = m_{\text{Tot}} r_0^2 \left[ (1-x) x^2 + x (1-x)^2 \right]$$

$$= m_{\text{Tot}} r_0^2 \left[ x^2 - x^3 + x (1 - 2x + x^2) \right]$$

$$= m_{\text{Tot}} r_0^2 \left[ (1-x)x \right] = \frac{m_H m_{Cl}}{(m_H + m_{Cl})} r_0^2 = \mu r_0^2$$

So since  $m_{Cl} \approx 35 m_H$  we expand

$$\frac{I}{r_0^2} = m_H \frac{1}{(1 + m_H/m_{Cl})} \approx m_H (1 - m_H/m_{Cl} + \dots)$$

So

$$I = m_H r_0^2 \left( 1 - m_H/m_{Cl} + O((m_H/m_{Cl})^2) \right)$$

c) So

$$\Delta = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2m_p r_0^2} = \frac{\hbar^2}{2m_e r_0^2 (m_p/m_e)} \approx \frac{13.6 \text{ eV}}{m_p/m_e} \left( \frac{a_0}{r_0} \right)^2$$

We used knowledge of the Bohr atom

$$\frac{\hbar^2}{2ma_0^2} = 13.6 \text{ eV}$$

where  $a_0 = 0.53 \text{ \AA}$  is the Bohr radius.

Then  $(a/r_0) \approx 1/2$

$$\Delta = \frac{13.6 \text{ eV}}{2000} \frac{1}{2^2} = 0.0017 \text{ eV}$$

$$\frac{\Delta}{kT} = 14.7 \quad \text{for } kT = 1/40 \text{ eV}$$

So

$$\Delta = \hbar \omega$$

$$\omega = \frac{\Delta c}{\hbar c} = \frac{0.0017 \text{ eV} \times 3 \times 10^8 \text{ m/s}}{197 \text{ eV} \times \text{nm}}$$

$$\omega = 400 \text{ GHz}$$



b)

We have

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T} \left( \frac{1}{Z} \frac{-\partial Z}{\partial \beta} \right) = -k_B \beta^2 \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)$$

Note

$$\boxed{\frac{\partial X}{\partial T} = - \frac{\partial X}{\partial \beta} \frac{\partial \beta}{\partial T} = -k \beta^2 \frac{\partial X}{\partial \beta}}$$

see below

this is very useful  
X is anything

$$\frac{\partial X}{\partial T} = -k \beta^2 \frac{\partial X}{\partial \beta}$$

Then differentiating

$$-\frac{\partial}{\partial \beta} \left( \frac{1}{Z} \left( -\frac{\partial Z}{\partial \beta} \right) \right) = \frac{1}{Z} \left( \frac{\partial^2 Z}{\partial \beta^2} \right) - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right) \left( \frac{\partial Z}{\partial \beta} \right)$$

$$= \langle E^2 \rangle - \langle E \rangle^2$$

So

$$\boxed{C_V = -k \beta^2 [\langle E^2 \rangle - \langle E \rangle^2]}$$

Finally

c) Note

$$\boxed{C_V = -k \beta^2 \frac{\partial}{\partial \beta} \frac{1}{Z} \left( -\frac{\partial Z}{\partial \beta} \right) = k \beta^2 \frac{\partial}{\partial \beta} \frac{\partial \ln Z}{\partial \beta} = k \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2}}$$

So

$$Z_{\text{tot}} = \frac{1}{N!} Z_1^N \approx \left( \frac{e Z_1}{N} \right)^N$$

$Z_1$  is always of this form

$$Z_1 = \sum_s \int \frac{d^3r d^3p}{h^3} e^{-(p^2/2m + \epsilon_{\text{int}}^s)/kT}$$

We used that for one particle

$$E = \frac{p^2}{2m} + \epsilon_{\text{int}}$$

$\epsilon_{\text{int}}$  = internal energy levels

$$= \frac{\hbar^2 l(l+1)}{2I} \text{ in this case}$$

$$Z_1 = Z_{\text{trans}} Z_{\text{int}}$$

Where

$$Z_{\text{trans}} = \int \frac{d^3\vec{r} d^3\vec{p}}{h^3} e^{-p^2/2mT} = \frac{V}{\lambda_{\text{th}}^3} = V n_Q$$

$$Z_{\text{int}} = \sum_s e^{-\epsilon_{\text{int}}^s \beta} = \sum_{l,m} e^{-\hbar^2 l(l+1)/2I \beta}$$

$$Z_{\text{int}} = \sum_{l=0}^{\infty} (2l+1) e^{-\hbar^2 l(l+1)/2I \beta}$$

$$= \sum_{l=0}^{\infty} (2l+1) e^{-\beta \epsilon_l} \quad \epsilon_l \equiv \frac{l(l+1)\hbar^2}{2I}$$



So

$$\log Z_{\text{rot}} = N \left[ \log \left( \frac{e Z_{\text{trans}}}{N} \right) + \log Z_{\text{int}} \right]$$

this is a

Now

mono-atomic ideal gas  $\equiv$  MAIG

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \ln Z_{\text{rot}}$$

$$= N \left[ \langle E \rangle_{\text{MAIG}} + \langle E_{\text{rot}} \rangle \right]$$

$$\langle E \rangle = N \left[ \frac{3}{2} k_B T + \langle E_{\text{rot}} \rangle \right]$$

Where  $\langle E_{\text{rot}} \rangle = \frac{1}{Z} \sum_l (2l+1) e^{-\frac{\hbar^2 l(l+1)}{2I} \beta} \left( \frac{\hbar^2 l(l+1)}{2I} \right)$

Differentiating again

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = N \left[ \frac{3}{2} k_B + \frac{\partial \langle E_{\text{rot}} \rangle}{\partial T} \right]$$

Finally since

$$\frac{\partial}{\partial T} = -k_B \beta^2 \frac{\partial}{\partial \beta}$$

We get defining  $\epsilon_l \equiv l(l+1)\hbar^2/2I$

$$\frac{\partial \epsilon_{\text{rot}}}{\partial T} = -k\beta^2 \frac{\partial}{\partial \beta} \left[ \underbrace{\frac{1}{Z} \sum_l (2l+1) e^{-\beta \epsilon_l} \epsilon_l}_{= \frac{1}{Z_{\text{rot}}} \frac{\partial Z_{\text{rot}}}{\partial \beta}} \right]$$

So

$$\frac{\partial \epsilon_{\text{rot}}}{\partial T} = k\beta^2 \left[ \frac{1}{Z} \sum_l (2l+1) e^{-\beta \epsilon_l} \epsilon_l^2 - \left( \frac{-1}{Z} \frac{\partial Z}{\partial \beta} \right) \left( \frac{-1}{Z} \frac{\partial Z}{\partial \beta} \right) \right]$$

$$\boxed{\frac{\partial \epsilon_{\text{rot}}}{\partial T} = k\beta^2 \left[ \langle \epsilon_{\text{rot}}^2 \rangle - \langle \epsilon_{\text{rot}} \rangle^2 \right]}$$

Where

$$\beta^2 \langle \epsilon_{\text{rot}}^2 \rangle \equiv \frac{1}{Z} \sum_{l=0}^{\infty} e^{-\beta \epsilon_l} (\beta \epsilon_l)^2 (2l+1)$$

$$\beta \langle \epsilon \rangle \equiv \frac{1}{Z} \sum_{l=0}^{\infty} e^{-\beta \epsilon_l} \beta \epsilon_l$$

So Finally

$$\boxed{C_V = Nk_B \left[ \frac{3}{2} k_B T + \langle \beta^2 (\langle \epsilon_{\text{rot}}^2 \rangle - \langle \epsilon_{\text{rot}} \rangle^2) \right]}$$

↖ A graph is shown in the problem statement.



d) Looking at the graph, We see a 10% deviation from one when

$$k_B T / \Delta \sim 1$$

Or

$$k_B T \sim \Delta$$

$$T \sim \frac{0.0017 \text{ eV}}{\frac{0.025 \text{ eV}}{300^\circ \text{K}}}$$

$$T \sim 20.4^\circ \text{K}$$

## Problem 2. A solid and a gas with degeneracy

Consider a solid of  $N$  atoms at temperature  $T$ . The atoms are independent of each other and can be in one five states: the first two states have the same energy level, called 0, while the remaining three states have a higher energy level,  $\Delta$ . The level scheme is shown below. To keep the problem general let's denote the degeneracy of the ground state,  $g_0 = 2$ , and the degeneracy of the excited state,  $g_1 = 3$ .



- (a) What is the probability of being in the excited state?
- (b) Determine the entropy of the system, and sketch  $S/Nk_B$  versus  $\Delta/kT$  for  $g_0 = 2$  and  $g_1 = 3$ .
- (c) Explain the value  $S/Nk_B$  physically in the low temperature limit  $k_B T \ll \Delta$ , and the high temperature limit  $k_B T \gg \Delta$ .
- (d) Show that the specific heat of the solid is

$$C_V = Nk_B \frac{g_0 g_1 (\beta \Delta)^2 e^{-\beta \Delta}}{(g_0 + g_1 e^{-\beta \Delta})^2} \quad (9)$$

- (e) Now consider a gas of the same  $N$  atoms. Show that the specific heat at constant pressure per mole is

$$C_p^{\text{1ml}} = R \left[ \frac{5}{2} + \frac{g_0 g_1 (\beta \Delta)^2 e^{-\beta \Delta}}{(g_0 + g_1 e^{-\beta \Delta})^2} \right] \quad (10)$$

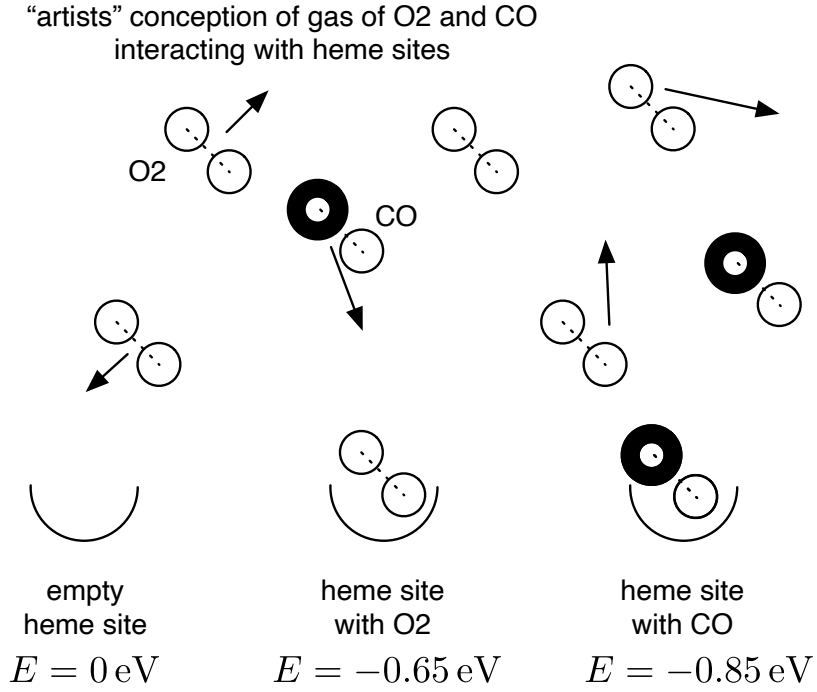


Figure 2: Artists conception of problem 3

### Problem 3. 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.

<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

$$\epsilon_{\text{rot}} = \ell(\ell + 1)\Delta \quad \text{with} \quad \ell = 0, 1, 2, \dots, \infty \quad (11)$$

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

$$Z_{\text{tot}} = \frac{1}{N!} (Z_{\text{trans}} Z_{\text{rot}})^N \quad (12)$$

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

$$\mu = kT \ln(n/n_Q) + kT \ln(\beta\Delta) \quad (13)$$

- (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:  $P = 0.975$

## CO Poisoning

① The quantum concentration is

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

Here  $m = 32 m_p$  so using  $m_p c^2 = 938 \text{ MeV}$   
and  $k_B = \frac{1/40 \text{ eV}}{300^\circ \text{K}}$  we have with  $hc = 1240 \text{ eV nm}$

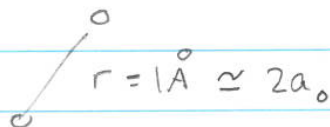
② Then we see since  $m^{\text{CO}} = 28 m_p$  and  $m^{\text{O}_2} = 32 m_p$

$$\frac{n_Q^{\text{CO}}}{n_Q^{\text{O}_2}} = \left( \frac{m^{\text{CO}}}{m^{\text{O}_2}} \right)^{3/2} = \left( \frac{28}{32} \right)^{3/2} = 0.82$$

so,  $n_Q^{\text{CO}}$  is 80% of  $n_Q^{\text{O}_2}$

③ So taking a bond length of  $1 \text{ \AA}$

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



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

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

So

This is a  $\frac{1}{2}$  Rydberg  
 $R = +13.6 \text{ eV}$

$$\Delta = \frac{\hbar^2}{2 \times (16000) m_e (4 a_0^2)} = \frac{1}{4 \times 16000} \left( \frac{\hbar^2}{2 m_e a_0^2} \right)$$

$$= \frac{13.6 \text{ eV}}{4 \times 16000} \approx 0.0002 \text{ eV} \quad \leftarrow \text{this is close}$$

$$\textcircled{4.5} \quad \left\langle \frac{L^2}{2I} \right\rangle = \frac{\langle l(l+1) \hbar^2 \rangle}{2I} = 2 \times \frac{1}{2} kT$$

$\nwarrow$  2 dof in rotation

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

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

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

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

$$\begin{aligned} \textcircled{5.1} \quad Z_{\text{rot}} &= \sum_l \sum_{m=-l}^l e^{-l(l+1) \Delta \beta} \\ &= \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1) \Delta \beta} \approx \int_0^{\infty} dl \, 2l e^{-l^2 \Delta \beta} \\ &= -e^{-l^2 \Delta \beta} \Big|_0^{\infty} = \frac{1}{\Delta \beta} \end{aligned}$$



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

$$\frac{kT}{\Delta_{O_2}} = 139$$

$$\frac{kT}{\Delta_{CO}} = 104$$

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

5.4)  $\mu_{CO} = -0.7173 \text{ eV}$

we used  $n_{CO} = \frac{n}{1000}$

⑥ We have

$$Z_G = 1 + e^{-\beta(\epsilon_1 - \mu_{O_2})} + e^{-\beta(\epsilon_2 - \mu_{CO})}$$

$$Z_G = 1 + c_1 + c_2$$

(for example  $c_1 \equiv e^{-\beta(\epsilon_1 - \mu_{O_2})}$ )

$$c_1 = 41.4, \quad \epsilon_1 = -0.65 \text{ eV}$$

$$c_2 = 201, \quad \epsilon_2 = -0.85 \text{ eV}$$

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

$$P_1 = 0.17$$

⑦ In the limit of low concentration

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

Then  $c_2 \rightarrow 0$  and

$$Z_G \approx 1 + c_1 \quad \text{and}$$

$$P_1 = \frac{c_1}{1 + c_1} \approx 0.975$$