Problem 1. Simple Steps

Each of these consists of small algebra and definitions.

(a) The probability of a system being in the ith microstate is

$$P_i = e^{-\beta E_i}/Z, \tag{1}$$

where E_i is the energy of the ith microstate and β and Z are constants. From the Gibbs expression for the entropy $S = -k_B \sum_m P_m \ln P_m$ show that the entropy is related to Z

$$\frac{S}{k_B} = \ln Z + \beta U \tag{2}$$

where $U = \sum P_i E_i$. Also show that

$$Z = e^{-\beta F} \qquad F = -kT \log Z \tag{3}$$

(b) Starting from the first Law $dE = TdS - pdV$ (i) derive the expression for dF in terms of its natural variables (T, V). (ii) Derive the Maxwell relation stemming from dF.

Simple Steps

a) $$P_i = \frac{e^{-\beta E_i}}{Z}$$

$$\frac{S}{k_B} = -\sum_i P_i \ln P_i$$

$$= -\sum_i \frac{e^{-\beta E_i}}{Z} \ln \frac{e^{-\beta E_i}}{Z}$$

$$= -\sum_i \frac{e^{-\beta E_i}}{Z}(-\beta E_i) + \sum_i \frac{e^{-\beta E_i}}{Z} \ln Z$$

$$= \sum_i -\frac{e^{-\beta E_i}}{Z}(-\beta E_i) + \ln Z \sum_i \frac{e^{-\beta E_i}}{Z}$$

$$\boxed{\frac{S}{k_B} = \beta \bar{E} + \ln Z}$$

So $$\ln Z = \frac{S}{k_B} - \frac{\bar{E}}{k_B T} = -\frac{F}{k_B T}$$

And

$$\boxed{Z = e^{-F/k_B T}}$$

b) $dU = TdS - pdV$

$$d(U - TS) = TdS - pdV - (TdS + SdT)$$

$F \equiv U - TS$ $\quad dF = -SdT - pdV$

$$d(F + pV) = -SdT - pdV + (pdV + Vdp)$$

$G = U - TS + pV$ $\quad \boxed{dG = -SdT + Vdp}$

c) So

$$-T^2 \left(\frac{\partial (F/T)}{\partial T}\right)_V = F - \left(T \frac{\partial F}{\partial T}\right)_V = F + TS$$

we used $dF = -SdT - pdV$. Then since $F = U - TS$, we have

i) $-T^2 \dfrac{\partial F/T}{\partial T} = U$ ✓

ii) $C_V = T\left(\dfrac{\partial S}{\partial T}\right)_V = -T \dfrac{\partial}{\partial T} \left(\dfrac{\partial F}{\partial T}\right)_V = -T\left(\dfrac{\partial^2 F}{\partial T^2}\right)_V$ ✓

iii)
$$-T^2 \left(\frac{\partial (G/T)}{\partial T}\right)_P = G - T\left(\frac{\partial G}{\partial T}\right|_P = G - T(-S) = G + TS$$

But $G = U - TS + pV$ and $H = U + pV$ and so

$$-T^2\left(\frac{\partial (G/T)}{\partial T}\right)_p = H$$

So

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = T\left(\frac{\partial}{\partial T}\right)_p \cdot \left(\frac{\partial G}{\partial T}\right)_p = T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

Problem 2. Ideal gas in two dimensions

- Use methods of partition functions to find the free energy, energy, pressure, and entropy in two dimensions. Compare your result to the 3D case and explain the results for the energy and pressure using previous methods. Express your result for the entropy in terms of the thermal debroglie wavelength.

  Answer: $S = Nk\left[\ln(A/\lambda^2) + 2\right]$

Ideal Gas:

2D

$$Z_1 = \int \frac{d^2r\, d^2p}{h^2} e^{-p^2/2mT}$$

$$\boxed{Z_1 = \frac{A}{\lambda_{th}^2}} \qquad \frac{1}{\lambda_{th}^2} \equiv \frac{2\pi m k_B T}{h^2}$$

1D

$$Z_1 = \int \frac{dr\, dp}{h} e^{-p^2/2mT}$$

$$\boxed{Z_1 = \frac{L}{\lambda_{th}}} \qquad \frac{1}{\lambda_{th}} \equiv \frac{\sqrt{2\pi m k_B T}}{h}$$

So $\quad Z_1 \equiv L^d / \lambda_{th}^d$

$$Z_{TOT} = \frac{1}{N!} Z_1^N \simeq \left(\frac{e Z_1}{N}\right)^N$$

So

$$F = -kT \ln Z_{TOT} = -kTN\left[\ln \frac{Z_1}{N} + 1\right]$$

$$= -kTN\left[-\ln(N/Z_1) + 1\right]$$

So

$$\boxed{F = -kTN\left[-\ln(n\lambda_{th}^{d}) + 1\right]}$$

where $d = 1, 2, 3$ for dimensions $1, 2, 3$

$$S = -\frac{\partial F}{\partial T}$$

Now $\lambda_{th} = \frac{h}{\sqrt{2\pi m k T}} = c\,T^{-1/2}$. Then

$$S = NK\left[-\ln(n\lambda_{th}^{d}) + 1\right] + NKT\frac{\partial}{\partial T}\left(-\ln n\lambda_{th}^{d}\right)$$

Now

$$\ln n\lambda_{th}^{d} = \ln(T^{-d/2}) + \text{const} \qquad \frac{\partial}{\partial T}\ln n\lambda_{th}^{d} = \frac{-d}{2T}$$

So

$$\boxed{S = Nk\left[-\ln(n\lambda_{th}^{d}) + 1\right] + \frac{NkT\,d}{2T}}$$

or

$$S = Nk\left[-\ln(n\lambda_{th}^{d}) + \frac{d+2}{2}\right] \quad \text{with } d = 1, 2, 3$$

The Energy

$F = E - TS \qquad E = F + TS$

So

$$E = -kTN\left[-\ln(n\lambda^d) + 1\right] + TNk\left[-\ln(n\lambda_{th}^d) + \frac{d+2}{2}\right]$$

$$\boxed{E = NkT\,\frac{d}{2}}$$

So finally we need the pressure

$$F = -kTN\left[-\ln\left(\frac{N}{V_d}\lambda_{th}^d\right) + 1\right]$$

Where $V_d = L, A, V = L^d$ in d-dimensions

$$p = -\left(\frac{\partial F}{\partial V_d}\right)_T = kTN\frac{\partial}{\partial V_d}\left(\ln V_d + \text{const}\right)$$

$$\boxed{p = \frac{kTN}{V_d}}$$

Problem 3. 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

$$I = m_H r_0^2 \left(1 - \left(\frac{m_H}{m_{Cl}}\right) + \ldots\right) \tag{4}$$

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

$$\epsilon_{\text{rot}} = \left\langle \frac{L^2}{2I} \right\rangle = \frac{\ell(\ell+1)\hbar^2}{2I} = \ell(\ell+1)\Delta \tag{5}$$

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

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

$$C_V = k_B \beta^2 \left(\langle E^2 \rangle - \langle E \rangle^2\right) \tag{6}$$

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

$$Z_{\text{tot}} \simeq \left(\frac{e Z_{\text{trans}}}{N}\right)^N Z_{\text{rot}}^N \tag{7}$$

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

$$C_V = \frac{3}{2} N k_B + N k_B \, \beta^2 [\langle \epsilon_{\text{rot}}^2 \rangle - \langle \epsilon_{\text{rot}} \rangle^2] \tag{8}$$

where

$$\beta^2 \langle \epsilon_{\text{rot}}^2 \rangle = \frac{1}{Z_{\text{rot}}(\beta\Delta)} \sum_{\ell=0}^{\infty} (2\ell+1) \left(\ell(\ell+1)\beta\Delta\right)^2 e^{-\ell(\ell+1)\beta\Delta} \tag{9}$$

$$\beta \langle \epsilon_{\text{rot}} \rangle = \frac{1}{Z_{\text{rot}}(\beta\Delta)} \sum_{\ell=0}^{\infty} (2\ell+1) \left(\ell(\ell+1)\beta\Delta\right) e^{-\ell(\ell+1)\beta\Delta} \tag{10}$$

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

$$\beta^2 \langle \epsilon_{\text{rot}}^2 \rangle, \qquad \beta^2 \langle \epsilon_{\text{rot}} \rangle^2 \qquad C_V/k_B \tag{11}$$

Make a graph of C_v/R vs. kT/Δ for one mole of substance. You should find something analogous to Figure. 1.

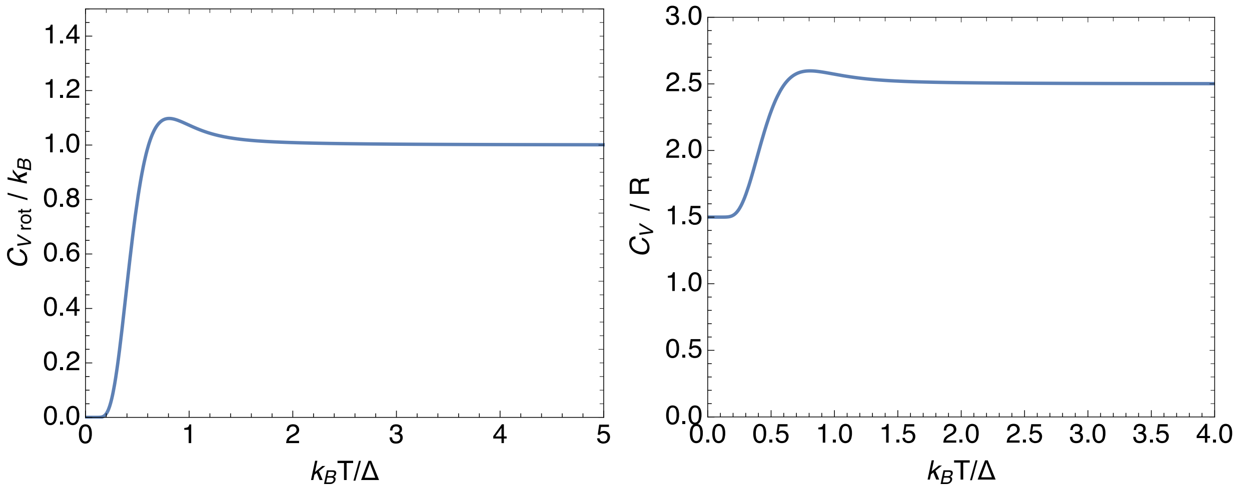


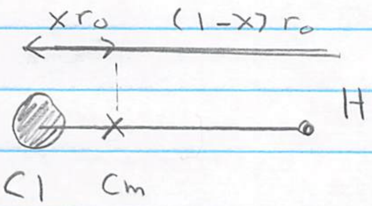
Figure 1: Left: the rotational contribution to the partition function (per particle), i.e. $\beta^2(\langle\epsilon_{\mathrm{rot}}^2\rangle - \langle\epsilon_{\mathrm{rot}}\rangle^2)$. Right: the full partition function for one mole.

(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 $r_0 = 1\ \text{Å}$

b)



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

$$x r_0 = \frac{M_H r_0}{M_H + M_{Cl}} \qquad \text{definition of Cm}$$

And $$x = \frac{M_H}{M_H + M_{Cl}} = \frac{M_H}{M_{TOT}} \qquad (1-x) = \frac{M_{Cl}}{M_{TOT}}$$

$$I = M_{TOT} r_0^2 \left[(1-x) x^2 + x (1-x)^2 \right]$$

$$= M_{TOT} r_0^2 \left[x^2 - x^3 + x(1-2x+x^2) \right]$$

$$= M_{TOT} r_0^2 \left[(1-x) x \right] = \boxed{\frac{M_H M_{Cl}}{(M_H + M_{Cl})} r_0^2 = \mu r_0^2}$$

So since $M_{Cl} \simeq 35 M_H$ we expand

$$\frac{I}{r_0^2} = M_H \frac{1}{(1 + M_H/M_{Cl})} \simeq M_H (1 - M_H/M_{Cl} + \ldots)$$

So

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

c) So

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

We used knowledge of the Bohr atom

$$\frac{\hbar^2}{2ma_0^2} = 13.6\,eV$$ where $a_0 = 0.53\,\text{Å}$ is the Bohr radius.

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

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

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

So

$$\Delta = \hbar\omega \qquad \omega = \frac{\Delta c}{\hbar c} = \frac{0.0017\,eV \times 3\times10^8\,m/s}{197\,eV \times nm}$$

$$\boxed{\omega = 400\,GHz}$$

b)

We have

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

see below

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

this is very useful $\frac{\partial}{\partial T}\left(\frac{1}{kT}\right)$

X is anyting

$\partial X/\partial T = -k\beta^2\,\partial X/\partial \beta$

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

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

Finally

c) Note

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

So

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

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

Z_1 is always of this form

We used that for one particle

$$E = \frac{\vec{p}^{\,2}}{2m} + \varepsilon_{int}$$

ε_{int} = internal energy levels

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

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

Where

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

$$\boxed{Z_{int} = \sum_s e^{-\varepsilon_{int}\beta} = \sum_{\ell, m} e^{-\hbar^2(\ell(\ell+1)/2I)\beta}}$$

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

$$= \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\beta \varepsilon_\ell} \qquad \varepsilon_\ell \equiv \frac{\ell(\ell+1)\hbar^2}{2I}$$

So

$$\log Z_{TOT} = N \Big[\underbrace{\log\left(\frac{e Z_{trans}}{N} \right)}_{\substack{\text{this is a} \\ \text{mono-atomic ideal gas} \equiv MAIG}} + \log Z_{int} \Big]$$

Now

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

$$= N \left[\langle \varepsilon \rangle_{MAIG} + \langle \varepsilon_{rot} \rangle \right]$$

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

Where $\langle \varepsilon_{rot} \rangle = \frac{1}{Z} \sum_{\ell} (2\ell+1) e^{-\hbar^2 \ell(\ell+1)/2I)\beta} \left(\frac{\hbar^2 \ell(\ell+1)}{2I} \right)$

Differentiating again

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

Finally since

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

We get defining $\varepsilon_\ell \equiv \ell(\ell+1)\hbar^2/2I$

$$\frac{\partial \mathcal{E}_{rot}}{\partial T} = -k\beta^2 \frac{\partial}{\partial \beta}\left[\underbrace{\frac{1}{Z}\sum_\ell (2\ell+1)\, e^{-\beta\varepsilon_\ell}\, \varepsilon_\ell}_{=\frac{1}{Z_{rot}}\frac{-\partial Z_{rot}}{\partial \beta}}\right]$$

So

$$\frac{\partial \mathcal{E}_{rot}}{\partial T} = k\beta^2\left[\frac{1}{Z}\sum_\ell (2\ell+1)\, e^{-\beta\varepsilon_\ell}\,\varepsilon_\ell^2 - \left(\frac{-1}{Z}\frac{\partial Z}{\partial \beta}\right)\left(\frac{-1}{Z}\frac{\partial Z}{\partial \beta}\right)\right]$$

$$\boxed{\frac{\partial \mathcal{E}_{rot}}{\partial T} = k\beta^2\left[\langle \varepsilon_{rot}^2\rangle - \langle \varepsilon_{rot}\rangle^2\right]}$$

Where

$$\beta^2\langle \varepsilon_{rot}^2\rangle \equiv \frac{1}{Z}\sum_{\ell=0}^{\infty} e^{-\beta\varepsilon_\ell}\,(\beta\varepsilon_\ell)^2\,(2\ell+1)$$

$$\beta\langle \varepsilon\rangle \equiv \frac{1}{Z}\sum_{\ell=0}^{\infty} e^{-\beta\varepsilon_\ell}\,\beta\varepsilon_\ell$$

So Finally

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

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

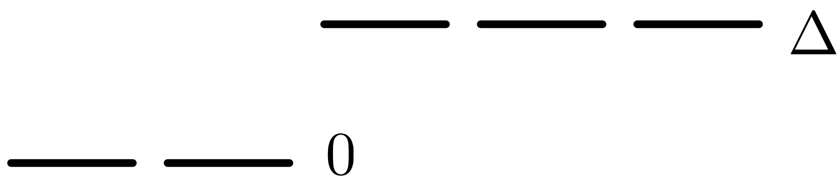
$$k_B T \sim \Delta$$

$$T \sim \frac{0.0017eV}{\frac{0.025eV}{300°K}}$$

$$\boxed{T \sim 20.4\,°K}$$

Problem 4. 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, Δ. The level scheme is shown below. To keep the problem general let's denote the degeracy of the ground state, $g_0 = 2$, and the degernacy 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 $S/N_A k_B$ versus Δ/kT for $g_0 = 2$ and $g_1 = 3$.

(c) Explain the value S/Nk_B physically in the low temperature limit $k_BT \ll \Delta$, and the high temperature limit $k_BT \gg \Delta$.

(d) Show that the specific heat of the solid is

$$C_V = Nk_B \frac{g_0 g_1 (\beta\Delta)^2 e^{-\beta\Delta}}{(g_0 + g_1 e^{-\beta\Delta})^2} \tag{12}$$

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

$$C_p^{1\text{ml}} = R\left[\frac{5}{2} + \frac{g_0 g_1 (\beta\Delta)^2 e^{-\beta\Delta}}{(g_0 + g_1 e^{-\beta\Delta})^2}\right] \tag{13}$$

Solution

(a) The partition function of a single site is

$$Z_1 = \sum_{\text{states}} e^{-\beta\epsilon_s} = g_0 + g_1 e^{-\beta\Delta} \tag{14}$$

So the probability of being in the upper state three states

$$P_{\text{up}} = P_3 + P_4 + P_5 = \frac{g_1 e^{-\beta\Delta}}{Z} \tag{15}$$

(b) So the complete partition function is $Z = Z_1^N$

$$F = -kTN \ln Z_1 = -NkT \ln(g_0 + g_1 e^{-\Delta/kT}) \tag{16}$$

Differentitating with respect to T

$$S = -\left(\frac{\partial F}{\partial T}\right) = Nk \ln(g_0 + g_1 e^{-\Delta/kT}) + \frac{Nk\,(\beta\Delta)\, g_1 e^{-\Delta/kT}}{g_0 + g_1 e^{-\Delta/kT}} \tag{17}$$

Alternatively one computes

$$U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta} = N\frac{g_1 \Delta e^{-\beta\Delta}}{g_0 + g_1 e^{-\beta\Delta}} \tag{18}$$

Then

$$\frac{S}{k} = \ln Z + \beta U = N \ln(g_0 + g_1 e^{-\beta\Delta}) + \frac{N g_1 \beta\Delta e^{-\beta\Delta}}{g_0 + g_1 e^{-\beta\Delta}} \tag{19}$$

This is sketched in Fig. 2.

(c) In the low temperature limit we have $\exp(-\beta\Delta) \to 0$ and $(\beta\Delta)\exp(-\beta\Delta) \to 0$ leading to

$$\frac{S}{k} = \ln(g_0) = \ln(2) \tag{20}$$

This makes sense the subsystem is equally likely to be in any of its two degenerate states.

In the high temperature limit, we have $\exp(-\beta\Delta) \to 1$ and $\beta\Delta \to 0$

$$\frac{S}{k} = \ln(g_0 + g_1) = \ln(5) \tag{21}$$

In this limit the system is equally likely to be in any of its five degenerate states.

(d) The energy is

$$U = N\frac{g_1 \Delta e^{-\beta\Delta}}{g_0 + g_1 e^{-\beta\Delta}} \tag{22}$$

We recall from previous homeworks that

$$C_V = \frac{\partial U}{\partial T} = -k\beta^2 \frac{\partial U}{\partial \beta} \tag{23}$$

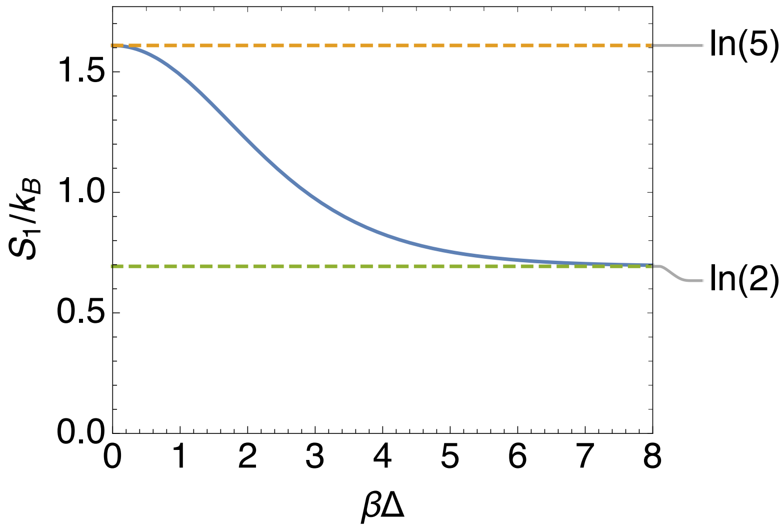


Figure 2: Entropy in the system.

So differentiating straightforwardly gives

$$C_V = Nk\left[\frac{g_1(\beta\Delta)^2e^{-\beta\Delta}}{g_0+g_1e^{-\beta\Delta}} - \frac{g_1(\beta\Delta)^2e^{-2\beta\Delta}}{(g_0+g_1e^{-\beta\Delta})^2}\right] \tag{24}$$

$$= Nk\,\frac{g_0g_1(\beta\Delta)^2e^{-\beta\Delta}}{(g_0+g_1e^{-\beta\Delta})^2} \tag{25}$$

(e) The difference here is that is a gas

$$Z = \frac{1}{N!}Z_1^N \tag{26}$$

Where the single particle partition function is

$$Z_1 = \sum_s \int \frac{d^3r d^3p}{h^3} e^{-(\beta p^2/2m + \beta\epsilon_s)} \tag{27}$$

The energy is a sum of a translation part plus an internal part:

$$\epsilon(p,s) = \underbrace{p^2/2m}\equiv \epsilon_{\rm trans} + +\epsilon_s\,. \tag{28}$$

As is usual this factorizes into a translational part times an intenal part

$$Z_1 = Z_{1\rm trans}Z_{1\rm int} \tag{29}$$

where

$$Z_{1\rm int} = \sum_{\rm states} e^{-\beta\epsilon_s} = g_0 + g_1e^{-\beta\Delta} \tag{30}$$

and

$$U = -\frac{\partial \ln Z}{\partial\beta} = N\left\langle\epsilon_{\rm trans}\right\rangle + N\left\langle\epsilon_s\right\rangle \tag{31}$$

The first term is

$$\langle \epsilon_{\text{trans}} \rangle = \frac{3}{2} kT \tag{32}$$

which can be computed using partition functions (see lecture) or using the equipartition theorem applied to the quadratic form $\langle p^2/2m \rangle$. The second term is what we computed in the previous parts. And so we find

$$U = N \left[\frac{3}{2} kT + \frac{g_1 \Delta e^{-\beta\Delta}}{g_0 + g_1 e^{-\beta\Delta}} \right] \tag{33}$$

The specific heat C_V is simply then additive from our previous results

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = Nk \left[\frac{3}{2} + Nk \, \frac{g_0 g_1 (\beta\Delta)^2 e^{-\beta\Delta}}{(g_0 + g_1 e^{-\beta\Delta})^2} \right] \tag{34}$$

Finally we note that

$$C_p = C_V + Nk \tag{35}$$

for an ideal gas. Using that $N_A k = R$ we find for one mole of atoms the quoted result

$$C_p^{\text{1ml}} = R \left[\frac{5}{2} + \frac{g_0 g_1 (\beta\Delta)^2 e^{-\beta\Delta}}{(g_0 + g_1 e^{-\beta\Delta})^2} \right] \tag{36}$$

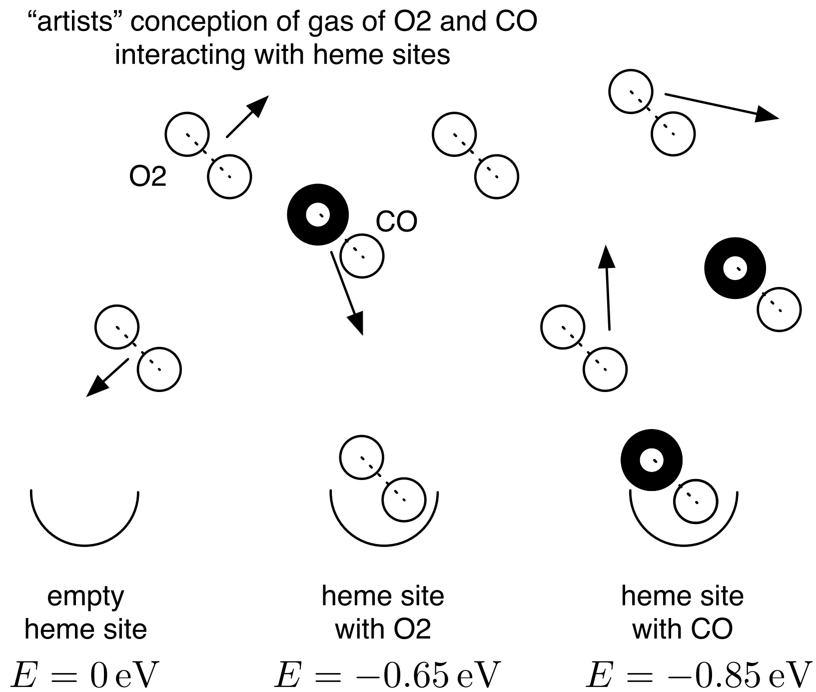


Figure 3: Artists conception of problem 3

Problem 5. 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 $E = -0.65\,\mathrm{eV}$, or occupied by a carbon monoxide molecule with energy $E = -0.85\,\mathrm{eV}$, 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 $295\,\mathrm{K}$ and a pressure of $0.2\,\mathrm{bar}$. 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], $n_Q \equiv \lambda_{\rm th}^{-3}$. 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.

[1] $\lambda_{\rm th}$ is the thermal de Broglie wavelength.

quantity	value
T	295 K
p	0.2 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

$$\epsilon_{\mathrm{rot}} = \ell(\ell+1)\Delta \qquad \text{with} \qquad \ell = 0, 1, 2, \ldots \infty \tag{37}$$

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

$$Z_{\mathrm{tot}} = \frac{1}{N!}(Z_{\mathrm{trans}} Z_{\mathrm{rot}})^N \tag{38}$$

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

$$\mu = kT \ln(n/n_Q) + kT \ln(\beta\Delta) \tag{39}$$

(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: $P = 0.975$

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 $k_B = \frac{1/40\, eV}{300\, °K}$ we have with $hc = 1240\, eV\, nm$

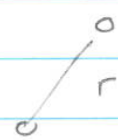
(2) Then we see since $m^{CO} = 28\, m_p$ and $m^{O_2} = 32\, m_p$

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

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

(3) So taking a bond length of 1 Å

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



$r = 1 Å \simeq 2a_0$

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

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

So

This is a $\frac{1}{2}$ Rydberg

$R = +13.6eV$

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

$$= \frac{13.6eV}{4\cdot 16000} \simeq 0.0002eV$$ ← 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 $l(l+1)$

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

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

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

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

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

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

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) $\mu_{CO} = -0.7173\,eV$ 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 $c_1 \equiv e^{-\beta(\varepsilon_1 - \mu_{O_2})}$)

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

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

$$\boxed{P_1 = c_1/(1 + c_1 + c_2) \qquad P_1 = 0.17}$$

(7) In the limit of low concentration

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

Then $c_2 \rightarrow 0$ and

$$Z_G \simeq 1 + c_1 \quad \text{and} \quad \boxed{P_1 = \frac{c_1}{1 + c_1} \simeq 0.975}$$