

Physics 2700H: Assignment IV

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Problem 1. For atomic hydrogen, the allowed energy levels are given by the Bohr equation

$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

which gives energies of -13.6 , -3.4 , and -1.5 eV for the first three energy levels. Rework the example in Section 6.3.2 with atomic hydrogen at 7500 K using these three energy levels.

- (a) Compute the partition function.
- (b) Compute the probabilities of the first three levels.
- (c) Compare your results with the example in the text.

Solution 1.

(a)

$$\begin{aligned} Z &= \sum_i g_i \exp\left\{-\frac{E_i}{k_B T}\right\} \\ &= \exp\left(-\frac{-13.6 \text{ eV}}{k_B \cdot 7500 \text{ K}}\right) + \exp\left(-\frac{-3.4 \text{ eV}}{k_B \cdot 7500 \text{ K}}\right) + \exp\left(-\frac{-1.5 \text{ eV}}{k_B \cdot 7500 \text{ K}}\right) \\ &\approx 1.37 \times 10^9 \end{aligned}$$

(b)

$$\begin{aligned} P(-13.6 \text{ eV}) &= \frac{1}{1.37 \times 10^9} \cdot \exp\left(-\frac{-13.6 \text{ eV}}{k_B \cdot 7500 \text{ K}}\right) \approx 1 \\ P(-3.4 \text{ eV}) &= \frac{1}{1.37 \times 10^9} \cdot \exp\left(-\frac{-3.4 \text{ eV}}{k_B \cdot 7500 \text{ K}}\right) \approx 1.4 \times 10^{-7} \\ P(-1.5 \text{ eV}) &= \frac{1}{1.37 \times 10^9} \cdot \exp\left(-\frac{-1.5 \text{ eV}}{k_B \cdot 7500 \text{ K}}\right) \approx 7.4 \times 10^{-9} \end{aligned}$$

- (c) The numerical results here are different than those in the text however the effective probability remains the same. Only the highest energy state will realistically be occupied in both cases.

Problem 2. Suppose there is a quantized system that can be in one of three energy states, having energies 0, 0.2, and 0.4 eV, respectively. The system is at 5000 K.

- (a) Compute the partition function for this system.
- (b) Find the mean energy.
- (c) Compute the probability that each of the three states will be occupied.

Solution 2.

(a)

$$\begin{aligned}
Z &= \sum_i g_i \exp\left\{-\frac{E_i}{k_B T}\right\} \\
&= \exp\left(-\frac{0 \text{ eV}}{k_B \cdot 5000 \text{ K}}\right) + \exp\left(-\frac{0.2 \text{ eV}}{k_B \cdot 5000 \text{ K}}\right) + \exp\left(-\frac{0.4 \text{ eV}}{k_B \cdot 5000 \text{ K}}\right) \\
&\approx 2.02
\end{aligned}$$

(b)

$$\begin{aligned}
\bar{E} &= \sum_i E_i P(E_i) = 0 \text{ eV} \cdot \exp\left(-\frac{0 \text{ eV}}{k_B \cdot 5000 \text{ K}}\right) \\
&\quad + 0.2 \text{ eV} \cdot \exp\left(-\frac{0.2 \text{ eV}}{k_B \cdot 5000 \text{ K}}\right) \\
&\quad + 0.4 \text{ eV} \cdot \exp\left(-\frac{0.4 \text{ eV}}{k_B \cdot 5000 \text{ K}}\right) \approx 0.284 \times 10^{-20} \text{ eV}
\end{aligned}$$

(c)

$$\begin{aligned}
P(0 \text{ eV}) &= \frac{1}{Z} \approx 0.495 \\
P(0.2 \text{ eV}) &= \frac{1}{Z} \cdot \exp\left(-\frac{0.2 \text{ eV}}{k_B \cdot 5000 \text{ K}}\right) \approx 0.311 \\
P(0.4 \text{ eV}) &= \frac{1}{Z} \cdot \exp\left(-\frac{0.4 \text{ eV}}{k_B \cdot 5000 \text{ K}}\right) \approx 0.196
\end{aligned}$$

Problem 3. It is a result of statistical mechanics that the internal energy of an ideal gas is

$$U = U(S, V) = -Nk_B \left(\frac{N}{V}\right)^{2/3} \exp\left(\frac{2S}{3Nk_B}\right)$$

where α is a constant and the other symbols have their usual meanings. Show that the equation of state $PV = nRT$ follows from this equation.

Solution 3. Where is α here? Anyway, starting with $dU = TdS - PdV$ and the total derivative of U , $dU = \frac{\partial U}{\partial S}dS + \frac{\partial U}{\partial V}dV$ we get

$$TdS - PdV = \frac{\partial U}{\partial S}dS + \frac{\partial U}{\partial V}dV$$

Where

$$\frac{\partial U}{\partial S} = -\frac{2}{3} \left(\frac{N}{V}\right)^{2/3} \exp\left(\frac{2S}{3Nk_B}\right), \quad \frac{\partial U}{\partial V} = \frac{2}{3} k_B \left(\frac{N}{V}\right)^{5/3} \exp\left(\frac{2S}{3Nk_B}\right)$$

From which we get

$$TdS - PdV = -\frac{2}{3} \left(\frac{N}{V}\right)^{2/3} \exp\left(\frac{2S}{3Nk_B}\right) dS + \frac{2}{3} k_B \left(\frac{N}{V}\right)^{5/3} \exp\left(\frac{2S}{3Nk_B}\right) dV$$

Which implies

$$\left[\frac{2}{3} \left(\frac{N}{V}\right)^{2/3} \exp\left(\frac{2S}{3Nk_B}\right) + T \right] dS = \left[\frac{2}{3} k_B \left(\frac{N}{V}\right)^{5/3} \exp\left(\frac{2S}{3Nk_B}\right) + P \right] dV$$

Because this is true everywhere we get

$$\frac{2}{3} \left(\frac{N}{V}\right)^{2/3} \exp\left(\frac{2S}{3Nk_B}\right) = -T, \quad \frac{2}{3} k_B \left(\frac{N}{V}\right)^{5/3} \exp\left(\frac{2S}{3Nk_B}\right) = -P$$

Which means that

$$-P = -\frac{N}{V}k_B T$$

Which can be rearranged to

$$PV = Nk_B T = nRT$$

Problem 4. Water boils at $T = 100^\circ\text{C}$ at one atmosphere of pressure. In the process, the entropy increase is 109 J K^{-1} for each mole of water. Find the molar enthalpy increase.

Solution 4. With $\frac{dQ}{T} = dS$ and $dH = \frac{dQ}{n}$ we get $dH = \frac{TdS}{n} \approx 4.08 \times 10^4\text{ J mol}^{-1}$