

# 19 Statistical thermodynamics: the concepts

## Solutions to exercises

### Discussion questions

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- E19.1(b)** Consider the value of the partition function at the extremes of temperature. The limit of  $q$  as  $T$  approaches zero, is simply  $g_0$ , the degeneracy of the ground state. As  $T$  approaches infinity, each term in the sum is simply the degeneracy of the energy level. If the number of levels is infinite, the partition function is infinite as well. In some special cases where we can effectively limit the number of states, the upper limit of the partition function is just the number of states. In general, we see that the molecular partition function gives an indication of the average number of states thermally accessible to a molecule at the temperature of the system.
- E19.2(b)** The statistical entropy may be defined in terms of the Boltzmann formula,  $S = k \ln W$ , where  $W$  is the statistical weight of the most probable configuration of the system. The relation between the entropy and the partition function is developed in two stages. In the first stage, we justify Boltzmann's formula, in the second, we express  $W$  in terms of the partition function. The justification for Boltzmann's formula is presented in *Justification 19.6*. Without repeating the details of this justification, we can see that the entropy defined through the formula has the properties we expect of the entropy.  $W$  can be thought of as a measure of disorder, hence the greater  $W$ , the greater the entropy; and the logarithmic form is consistent with the additive properties of the entropy. We expect the total disorder of a combined system to be the product of the individual disorders and  $S = k \ln W = k \ln W_1 W_2 = k \ln W_1 + k \ln W_2 = S_1 + S_2$ .
- In the second stage the formula relating entropy and the partition function is derived. This derivation is presented in *Justification 19.7*. The expression for  $W$ , eqn 19.1, is recast in terms of probabilities, which in turn are expressed in terms of the partition function through eqn 10. The final expression which is eqn 19.34 then follows immediately.
- E19.3(b)** Since  $\beta$  and temperature are inversely related, strictly speaking one can never replace the other. The concept of temperature is useful in indicating the direction of the spontaneous transfer of energy in the form of heat. It seems natural to us to think of the spontaneous direction for this transfer to be from a body at high  $T$  to one at low  $T$ . In terms of  $\beta$ , the spontaneous direction would be from low to high and this has an unnatural feel.
- On the other hand,  $\beta$  has a direct connection to the energy level pattern of systems of atoms and molecules. It arises in a natural, purely mathematical, manner from our knowledge of how energy is distributed amongst the particles of our atomic/molecular system. We would not have to invoke the abstract laws of thermodynamics, namely the zeroth and second laws in order to define our concept of temperature if we used  $\beta$  as the property to indicate the natural direction of heat flow. We can easily demonstrate that  $\beta$  is directly related to the statistical weight  $W$  through the relation  $\beta = (\partial \ln W / \partial U)_N$ .  $W$ ,  $U$ , and  $N$  are all concrete properties of an atomic/molecular system.
- E19.4(b)** Identical particles can be regarded as distinguishable when they are localized as in a crystal lattice where we can assign a set of coordinates to each particle. Strictly speaking it is the lattice site that carries the set of coordinates, but as long as the particle is fixed to the site, it too can be considered distinguishable.

### Numerical exercises

**E19.5(b)**  $n_i = \frac{N e^{-\beta \varepsilon_i}}{q}$  where  $q = \sum_j e^{-\beta \varepsilon_j}$

Thus

$$\frac{n_2}{n_1} = \frac{e^{-\beta \varepsilon_2}}{e^{-\beta \varepsilon_1}} = e^{-\beta(\varepsilon_2 - \varepsilon_1)} = e^{-\beta \Delta \varepsilon} = e^{-\Delta \varepsilon / kT}$$

Given  $\frac{n_2}{n_1} = \frac{1}{2}$ ,  $\Delta \varepsilon = 300 \text{ cm}^{-1}$

$$k = (1.38066 \times 10^{-23} \text{ J K}^{-1}) \times \left( \frac{1 \text{ cm}^{-1}}{1.9864 \times 10^{-23} \text{ J}} \right) = 0.69506 \text{ cm}^{-1} \text{ K}^{-1}$$

$$\frac{n_2}{n_1} = e^{-\Delta \varepsilon / kT}$$

$$\ln\left(\frac{n_2}{n_1}\right) = -\Delta \varepsilon / kT$$

$$T = \frac{-\Delta \varepsilon}{k \ln(n_2/n_1)} = \frac{\Delta \varepsilon}{k \ln(n_1/n_2)}$$

$$= \frac{300 \text{ cm}^{-1}}{(0.69506 \text{ cm}^{-1} \text{ K}^{-1}) \ln(2)} = 622.7 \text{ K} \approx \boxed{623 \text{ K}}$$

**E19.6(b)** (a)  $\Lambda = h \left( \frac{\beta}{2\pi m} \right)^{1/2}$  [19.22]  $= h \left( \frac{1}{2\pi m k T} \right)^{1/2}$

$$= (6.626 \times 10^{-34} \text{ J s})$$

$$\times \left( \frac{1}{(2\pi) \times (39.95) \times (1.6605 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times T} \right)^{1/2}$$

$$= \frac{276 \text{ pm}}{(T/\text{K})^{1/2}}$$

(b)  $q = \frac{V}{\Lambda^3}$  [22]  $= \frac{(1.00 \times 10^{-6} \text{ m}^3) \times (T/\text{K})^{3/2}}{(2.76 \times 10^{-10} \text{ m})^3} = 4.76 \times 10^{22} (T/\text{K})^{3/2}$

(i)  $T = 300 \text{ K}$ ,  $\Lambda = 1.59 \times 10^{-11} \text{ m} = \boxed{15.9 \text{ pm}}$ ,  $q = \boxed{2.47 \times 10^{26}}$

(ii)  $T = 3000 \text{ K}$ ,  $\Lambda = \boxed{5.04 \text{ pm}}$ ,  $q = \boxed{7.82 \times 10^{27}}$

**Question.** At what temperature does the thermal wavelength of an argon atom become comparable to its diameter?

**E19.7(b)** The translational partition function is

$$q_{\text{tr}} = \frac{V}{h^3} (2kT\pi m)^{3/2}$$

so  $\frac{q_{\text{Xe}}}{q_{\text{He}}} = \left( \frac{m_{\text{Xe}}}{m_{\text{He}}} \right)^{3/2} = \left( \frac{131.3 \text{ u}}{4.003 \text{ u}} \right)^{3/2} = \boxed{187.9}$

$$\mathbf{E19.8(b)} \quad q = \sum_{\text{levels}} g_j e^{-\beta \varepsilon_j} = 2 + 3e^{-\beta \varepsilon_1} + 2e^{-\beta \varepsilon_2}$$

$$\beta \varepsilon = \frac{hc\tilde{\nu}}{kT} = \frac{1.4388(\tilde{\nu}/\text{cm}^{-1})}{T/\text{K}}$$

$$\text{Thus } q = 2 + 3e^{-(1.4388 \times 1250/2000)} + 2e^{-(1.4388 \times 1300/2000)} \\ = 2 + 1.2207 + 0.7850 = \boxed{4.006}$$

$$\mathbf{E19.9(b)} \quad E = U - U(0) = -\frac{N}{q} \frac{dq}{d\beta} = -\frac{N}{q} \frac{d}{d\beta} (2 + 3e^{-\beta \varepsilon_1} + 2e^{-\beta \varepsilon_2}) \\ = -\frac{N}{q} (-3\varepsilon_1 e^{-\beta \varepsilon_1} - 2\varepsilon_2 e^{-\beta \varepsilon_2}) = \frac{Nhc}{q} (3\tilde{\nu}_1 e^{-\beta hc\tilde{\nu}_1} + 2\tilde{\nu}_2 e^{-\beta hc\tilde{\nu}_2}) \\ = \left( \frac{N_A hc}{4.006} \right) \times \left\{ 3(1250 \text{ cm}^{-1}) \times \left( e^{-(1.4388 \times 1250/2000)} \right) \right. \\ \left. + 2(1300 \text{ cm}^{-1}) \times \left( e^{-(1.4388 \times 1300/2000)} \right) \right\}$$

$$= \left( \frac{N_A hc}{4.006} \right) \times (2546 \text{ cm}^{-1})$$

$$= (6.022 \times 10^{23} \text{ mol}^{-1}) \times (6.626 \times 10^{-34} \text{ J s}) \times (2.9979 \times 10^{10} \text{ cm s}^{-1}) \times (2546 \text{ cm}^{-1})$$

$$= \boxed{7.605 \text{ kJ mol}^{-1}}$$

**E19.10(b)** In fact there are two upper states, but one upper level. And of course the answer is different if the question asks when 15 per cent of the molecules are in the upper level, or if it asks when 15 per cent of the molecules are in *each* upper state. The solution below assumes the former.

The relative population of *states* is given by the Boltzmann distribution

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-hc\tilde{\nu}}{kT}\right) \quad \text{so} \quad \ln \frac{n_2}{n_1} = \frac{-hc\tilde{\nu}}{kT}$$

$$\text{Thus } T = \frac{-hc\tilde{\nu}}{k \ln(n_2/n_1)}$$

Having 15 per cent of the molecules in the upper level means

$$\frac{2n_2}{n_1} = \frac{0.15}{1 - 0.15} \quad \text{so} \quad \frac{n_2}{n_1} = 0.088$$

$$\text{and } T = \frac{-(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (360 \text{ cm}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (\ln 0.088)}$$

$$= \boxed{213 \text{ K}}$$

**E19.11(b)** The energies of the states relative to the energy of the state with  $m_l = 0$  are  $-\gamma_N \hbar \mathcal{B}$ ,  $0$ ,  $+\gamma_N \hbar \mathcal{B}$ , where  $\gamma_N \hbar = 2.04 \times 10^{-27} \text{ J T}^{-1}$ . With respect to the lowest level they are  $0$ ,  $\gamma_N \hbar$ ,  $2\gamma_N \hbar$ .

The partition function is

$$q = \sum_{\text{states}} e^{-E_{\text{state}}/kT}$$

where the energies are measured with respect to the lowest energy. So in this case

$$q = 1 + \exp\left(\frac{-\gamma_N \hbar \mathcal{B}}{kT}\right) + \exp\left(\frac{-2\gamma_N \hbar \mathcal{B}}{kT}\right)$$

As  $\mathcal{B}$  is increased at any given  $T$ ,  $q$  decays from  $q = 3$  toward  $q = 1$  as shown in Fig. 19.1(a).

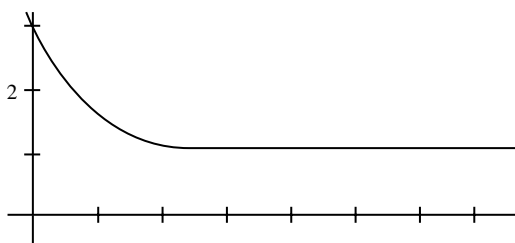


Figure 19.1(a)

The average energy (measured with respect to the lowest state) is

$$\langle E \rangle = \frac{\sum_{\text{states}} E_{\text{state}} e^{-E_{\text{state}}/kT}}{q} = \frac{1 + \gamma_N \hbar \mathcal{B} \exp\left(\frac{-\gamma_N \hbar \mathcal{B}}{kT}\right) + 2\gamma_N \hbar \mathcal{B} \exp\left(\frac{-2\gamma_N \hbar \mathcal{B}}{kT}\right)}{1 + \exp\left(\frac{-\gamma_N \hbar \mathcal{B}}{kT}\right) + \exp\left(\frac{-2\gamma_N \hbar \mathcal{B}}{kT}\right)}$$

The expression for the mean energy measured based on zero spin having zero energy becomes

$$\langle E \rangle = \frac{\gamma_N \hbar \mathcal{B} - \gamma_N \hbar \mathcal{B} \exp\left(\frac{-2\gamma_N \hbar \mathcal{B}}{kT}\right)}{1 + \exp\left(\frac{-\gamma_N \hbar \mathcal{B}}{kT}\right) + \exp\left(\frac{-2\gamma_N \hbar \mathcal{B}}{kT}\right)} = \frac{\gamma_N \hbar \mathcal{B} \left(1 - \exp\left(\frac{-2\gamma_N \hbar \mathcal{B}}{kT}\right)\right)}{1 + \exp\left(\frac{-\gamma_N \hbar \mathcal{B}}{kT}\right) + \exp\left(\frac{-2\gamma_N \hbar \mathcal{B}}{kT}\right)}$$

As  $\mathcal{B}$  is increased at constant  $T$ , the mean energy varies as shown in Fig. 19.1(b).

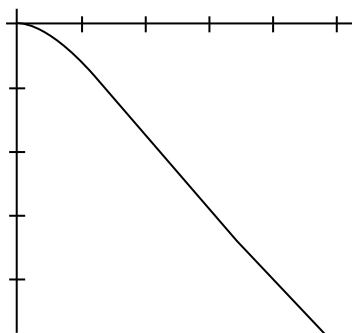


Figure 19.1(b)

The relative populations (with respect to that of the lowest state) are given by the Boltzmann factor

$$\exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-\gamma_N \hbar \mathcal{B}}{kT}\right) \quad \text{or} \quad \exp\left(\frac{-2\gamma_N \hbar \mathcal{B}}{kT}\right)$$

Note that  $\frac{\gamma_N \hbar \mathcal{B}}{k} = \frac{(2.04 \times 10^{-27} \text{ J T}^{-1}) \times (20.0 \text{ T})}{1.381 \times 10^{-23} \text{ J K}^{-1}} = 2.95 \times 10^{-3} \text{ K}$

so the populations are

(a)  $\exp\left(\frac{-2.95 \times 10^{-3} \text{ K}}{1.0 \text{ K}}\right) = \boxed{0.997}$  and  $\exp\left(\frac{2(-2.95 \times 10^{-3} \text{ K})}{1.0 \text{ K}}\right) = \boxed{0.994}$

(b)  $\exp\left(\frac{-2.95 \times 10^{-3} \text{ K}}{298}\right) = \boxed{1 - 1 \times 10^{-5}}$

and  $\exp\left(\frac{2(-2.95 \times 10^{-3} \text{ K})}{298}\right) = \boxed{1 - 2 \times 10^{-5}}$

**E19.12(b)** (a) The ratio of populations is given by the Boltzmann factor

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = e^{-25.0\text{ K}/T} \quad \text{and} \quad \frac{n_3}{n_1} = e^{-50.0\text{ K}/T}$$

(1) At 1.00 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0\text{ K}}{1.00\text{ K}}\right) = \boxed{1.39 \times 10^{-11}}$$

$$\text{and } \frac{n_3}{n_1} = \exp\left(\frac{-50.0\text{ K}}{1.00\text{ K}}\right) = \boxed{1.93 \times 10^{-22}}$$

(2) At 25.0 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0\text{ K}}{25.0\text{ K}}\right) = \boxed{0.368} \quad \text{and} \quad \frac{n_3}{n_1} = \exp\left(\frac{-50.0\text{ K}}{25.0\text{ K}}\right) = \boxed{0.135}$$

(3) At 100 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0\text{ K}}{100\text{ K}}\right) = \boxed{0.779} \quad \text{and} \quad \frac{n_3}{n_1} = \exp\left(\frac{-50.0\text{ K}}{100\text{ K}}\right) = \boxed{0.607}$$

(b) The molecular partition function is

$$q = \sum_{\text{states}} e^{-E_{\text{state}}/kT} = 1 + e^{-25.0\text{ K}/T} + e^{-50.0\text{ K}/T}$$

At 25.0 K, we note that  $e^{-25.0\text{ K}/T} = e^{-1}$  and  $e^{-50.0\text{ K}/T} = e^{-2}$

$$q = 1 + e^{-1} + e^{-2} = \boxed{1.503}$$

(c) The molar internal energy is

$$U_{\text{m}} = U_{\text{m}}(0) - \frac{N_{\text{A}}}{q} \left( \frac{\partial q}{\partial \beta} \right) \quad \text{where } \beta = (kT)^{-1}$$

$$\text{So } U_{\text{m}} = U_{\text{m}}(0) - \frac{N_{\text{A}}}{q} (-25.0\text{ K})k \left( e^{-25.0\text{ K}/T} + 2e^{-50.0\text{ K}/T} \right)$$

At 25.0 K

$$\begin{aligned} U_{\text{m}} - U_{\text{m}}(0) &= - \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (-25.0\text{ K}) \times (1.381 \times 10^{-23} \text{ J K}^{-1})}{1.503} \\ &\quad \times (e^{-1} + 2e^{-2}) \\ &= \boxed{88.3 \text{ J mol}^{-1}} \end{aligned}$$

(d) The molar heat capacity is

$$\begin{aligned} C_{V,\text{m}} &= \left( \frac{\partial U_{\text{m}}}{\partial T} \right)_{\text{V}} = N_{\text{A}}(25.0\text{ K})k \frac{\partial}{\partial T} \frac{1}{q} \left( e^{-25.0\text{ K}/T} + 2e^{-50.0\text{ K}/T} \right) \\ &= N_{\text{A}}(25.0\text{ K})k \times \left( \frac{25.0\text{ K}}{qT^2} \left( e^{-25.0\text{ K}/T} + 4e^{-50.0\text{ K}/T} \right) \right. \\ &\quad \left. - \frac{1}{q^2} \left( e^{-25.0\text{ K}/T} + 2e^{-50.0\text{ K}/T} \right) \frac{\partial q}{\partial T} \right) \end{aligned}$$

$$\text{where } \frac{\partial q}{\partial T} = \frac{25.0\text{ K}}{T^2} \left( e^{-25.0\text{ K}/T} + 2e^{-50.0\text{ K}/T} \right)$$

$$\text{so } C_{V,m} = \frac{N_A(25.0 \text{ K})^2 k}{T^2 q} \left( e^{-25.0 \text{ K}/T} + 4e^{-50.0 \text{ K}/T} - \frac{(e^{-25.0 \text{ K}/T} + 2e^{-50.0 \text{ K}/T})^2}{q} \right)$$

At 25.0 K

$$\begin{aligned} C_{V,m} &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (25.0 \text{ K})^2 \times (1.381 \times 10^{-23} \text{ J K}^{-1})}{(25.0 \text{ K})^2 \times (1.503)} \\ &\quad \times \left( e^{-1} + 4e^{-2} - \frac{(e^{-1} + 2e^{-2})^2}{1.503} \right) \\ &= \boxed{3.53 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

(e) The molar entropy is

$$S_m = \frac{U_m - U_m(0)}{T} + N_A k \ln q$$

At 25.0 K

$$\begin{aligned} S_m &= \frac{88.3 \text{ J mol}^{-1}}{25.0 \text{ K}} + (6.022 \times 10^{23} \text{ mol}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \ln 1.503 \\ &= \boxed{6.92 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\text{E19.13(b)} \quad \frac{n_1}{n_0} = \frac{g_1 e^{-\varepsilon_1/kT}}{g_0 e^{-\varepsilon_0/kT}} = g_1 e^{-\Delta\varepsilon/kT} = 3e^{-hcB/kT}$$

Set  $\frac{n_1}{n_0} = \frac{1}{e}$  and solve for  $T$ .

$$\ln\left(\frac{1}{e}\right) = \ln 3 + \left(\frac{-hcB}{kT}\right)$$

$$\begin{aligned} T &= \frac{hcB}{k(1 + \ln 3)} \\ &= \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 10.593 \text{ cm}^{-1}}{+1.381 \times 10^{-23} \text{ J K}^{-1} \times (1 + 1.0986)} \\ &= \boxed{7.26 \text{ K}} \end{aligned}$$

**E19.14(b)** The Sackur–Tetrode equation gives the entropy of a monoatomic gas as

$$S = nR \ln\left(\frac{e^{5/2} kT}{p \Lambda^3}\right) \quad \text{where } \Lambda = \frac{h}{\sqrt{2kT\pi m}}$$

(a) At 100 K

$$\begin{aligned} \Lambda &= \frac{6.626 \times 10^{-34} \text{ J s}}{\{2(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (100 \text{ K}) \times \pi(131.3 \text{ u}) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1})\}^{1/2}} \\ &= 1.52 \times 10^{-11} \text{ m} \end{aligned}$$

$$\begin{aligned} \text{and } S_m &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{e^{5/2} (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (100 \text{ K})}{(1.013 \times 10^5 \text{ Pa}) \times (1.52 \times 10^{-11} \text{ m})^3} \right) \\ &= \boxed{147 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

(b) At 298.15 K

$$\begin{aligned} \Lambda &= \frac{6.626 \times 10^{-34} \text{ J s}}{\{2(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K}) \times \pi(131.3 \text{ u}) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1})\}^{1/2}} \\ &= 8.822 \times 10^{-12} \text{ m} \end{aligned}$$

$$\begin{aligned} \text{and } S_m &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{e^{5/2} (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})}{(1.013 \times 10^5 \text{ Pa}) \times (8.822 \times 10^{-12} \text{ m})^3} \right) \\ &= \boxed{169.6 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

**E19.15(b)**  $q = \frac{1}{1 - e^{-\beta\varepsilon}} = \frac{1}{1 - e^{-hc\beta\tilde{\nu}}}$

$$hc\beta\tilde{\nu} = \frac{(1.4388 \text{ cm K}) \times (321 \text{ cm}^{-1})}{600 \text{ K}} = 0.7697\bar{6}$$

$$\text{Thus } q = \frac{1}{1 - e^{-0.7697\bar{6}}} = 1.86\bar{3}$$

The internal energy due to vibrational excitation is

$$\begin{aligned} U - U(0) &= \frac{N\varepsilon e^{-\beta\varepsilon}}{1 - e^{-\beta\varepsilon}} \\ &= \frac{Nhc\tilde{\nu} e^{-hc\beta\tilde{\nu}}}{1 - e^{-hc\beta\tilde{\nu}}} = \frac{Nhc\tilde{\nu}}{e^{hc\beta\tilde{\nu}} - 1} = (0.86\bar{3}) \times (Nhc) \times (321 \text{ cm}^{-1}) \end{aligned}$$

$$\begin{aligned} \text{and hence } \frac{S_m}{N_A k} &= \frac{U - U(0)}{N_A k T} + \ln q = (0.86\bar{3}) \times \left( \frac{hc}{kT} \right) \times (321 \text{ cm}^{-1}) + \ln(1.86\bar{3}) \\ &= \frac{(0.86\bar{3}) \times (1.4388 \text{ K cm}) \times (321 \text{ cm}^{-1})}{600 \text{ K}} + \ln(1.86\bar{3}) \\ &= 0.66\bar{4} + 0.6219\bar{9} = 1.28\bar{6} \end{aligned}$$

$$\text{and } S_m = 1.28\bar{6} R = \boxed{10.7 \text{ J K}^{-1} \text{ mol}^{-1}}$$

**E19.16(b)** Inclusion of a factor of  $(N!)^{-1}$  is necessary when considering indistinguishable particles. Because of their translational freedom, gases are collections of indistinguishable particles. The factor, then, must be included in calculations on (a) CO<sub>2</sub> gas.

## Solutions to problems

### Solutions to numerical problems

**P19.4**  $S = k \ln W$  or  $W = e^{S/k}$  [19.30]

$$\left( \frac{\partial W}{\partial V} \right)_{T,N} = \frac{W}{k} \left( \frac{\partial S}{\partial V} \right)_{T,N}$$

$$\begin{aligned}
 S &= nR \ln \frac{e^{5/2} V}{N \Lambda^3} = nR \left[ \ln V + \ln \frac{e^{5/2}}{N \Lambda^3} \right] \\
 \left( \frac{\partial S}{\partial V} \right)_{T,N} &= nR \left( \frac{\partial \ln V}{\partial V} \right)_{T,N} = \frac{nR}{V} = \frac{NR}{N_A V} \\
 \left( \frac{\partial W}{\partial V} \right)_{T,N} &= \frac{NRW}{N_A k V} = \frac{NW}{V} \\
 \frac{\Delta W}{W} &\approx N \frac{\Delta V}{V} = \frac{pV}{kT} \frac{\Delta V}{V} \\
 &\approx \frac{(1 \times 10^5 \text{ Pa}) \times (20 \text{ m}^3) \times (1 \times 10^{-5})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (300 \text{ K})} \\
 &\approx \boxed{4.8 \times 10^{21}}
 \end{aligned}$$

Notice that the value of  $W$  is much larger than that of  $\Delta W/W$ . For example, at the conventional temperature the molar entropy of helium is  $126 \text{ J K}^{-1} \text{ mol}^{-1}$ . Therefore,

$$\begin{aligned}
 S &= nS_m = \left( \frac{pV}{RT} \right) S_m = \frac{(1 \times 10^5 \text{ Pa}) \times (20 \text{ m}^3) \times (126 \text{ J K}^{-1} \text{ mol}^{-1})}{(8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \\
 &= 1.02 \times 10^5 \text{ J K}^{-1} \\
 \frac{S}{k} &= \frac{1.02 \times 10^5 \text{ J K}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1}} = 7.36 \times 10^{27}
 \end{aligned}$$

$$W = e^{S/k} = e^{7.36 \times 10^{27}} = 10^{3.20 \times 10^{27}}$$

**P19.6**

$$\frac{n_1}{n_0} = \frac{g_1 e^{-\varepsilon_1/kT}}{g_0 e^{-\varepsilon_0/kT}} = \frac{4}{2} \times e^{-\Delta\varepsilon/kT} = \frac{4}{2} \times e^{-hc\tilde{\nu}/kT} = 2e^{-\{(1.4388 \times 450)/300\}} = 0.23$$

The observed ratio is  $\frac{0.30}{0.70} = 0.43$ . Hence the populations are **not at equilibrium**.

**P19.8**

First we evaluate the partition function

$$q = \sum_j g_j e^{-\beta\varepsilon_j} [19.12] = \sum_j g_j e^{-hc\beta\tilde{\nu}_j}$$

$$\text{At } 3287^\circ\text{C} = 3560 \text{ K}, \quad hc\beta = \frac{1.43877 \text{ cm K}}{3560 \text{ K}} = 4.041 \times 10^{-4} \text{ cm}$$

$$\begin{aligned}
 q &= 5 + 7e^{-\{(4.041 \times 10^{-4} \text{ cm}) \times (170 \text{ cm}^{-1})\}} + 9e^{-\{(4.041 \times 10^{-4} \text{ cm}) \times (387 \text{ cm}^{-1})\}} \\
 &\quad + 3e^{-\{(4.041 \times 10^{-4} \text{ cm}) \times (6557 \text{ cm}^{-1})\}} \\
 &= (5) + (7) \times (0.934) + (9) \times (0.855) + (3) \times (0.0707) = 19.445
 \end{aligned}$$

The fractions of molecules in the various states are

$$p_j = \frac{g_j e^{-\beta\varepsilon_j}}{q} [19.10] = \frac{g_j e^{-hc\beta\tilde{\nu}_j}}{q}$$

$$\begin{aligned}
 p(^3\text{F}_2) &= \frac{5}{19.445} = \boxed{0.257} & p(^3\text{F}_3) &= \frac{(7) \times (0.934)}{19.445} = \boxed{0.336} \\
 p(^3\text{F}_4) &= \frac{(9) \times (0.855)}{19.445} = \boxed{0.396} & p(^4\text{F}_1) &= \frac{(3) \times (0.0707)}{19.445} = \boxed{0.011}
 \end{aligned}$$



**Comment.**  $\sum_j p_j = 1$ . Note that the most highly populated level is not the ground state.

**P19.10** The partition function is the sum over states of the Boltzmann factor

$$q = \sum_{\text{states}} \exp\left(-\frac{E}{kT}\right) = \sum_{\text{states}} \exp\left(-\frac{hcG}{kT}\right) = \sum_{\text{levels}} g \exp\left(-\frac{hcG}{kT}\right)$$

where  $g$  is the degeneracy. So, at 298 K

$$q = 1 + 3 \exp\left(-\frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (557.1 \text{ cm}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}\right) + \dots$$

$$= \boxed{1.209}$$

At 1000 K

$$q = 1 + 3 \exp\left(-\frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (557.1 \text{ cm}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (1000 \text{ K})}\right) + \dots$$

$$= \boxed{3.004}$$

**P19.11**  $q = \sum_i e^{-\beta \varepsilon_i} = \sum_i e^{-hc\beta \tilde{\nu}_i}$  [19.11]

At 100 K,  $hc\beta = \frac{1}{69.50 \text{ cm}^{-1}}$  and at 298 K,  $hc\beta = \frac{1}{207.22 \text{ cm}^{-1}}$ . Therefore, at 100 K

$$\text{(a)} \quad q = 1 + e^{-213.30/69.50} + e^{-435.39/69.50} + e^{-636.27/69.50} + e^{-845.93/69.50} = \boxed{1.049}$$

and at 298 K

$$\text{(b)} \quad q = 1 + e^{-213.30/207.22} + e^{-425.39/207.22} + e^{-636.27/207.22} + e^{-845.93/207.22} = \boxed{1.55}$$

In each case,  $p_i = \frac{e^{-hc\beta \tilde{\nu}_i}}{q}$  [19.10]

$$p_0 = \frac{1}{q} = \text{(a)} \boxed{0.953}, \quad \text{(b)} \boxed{0.645}$$

$$p_1 = \frac{e^{-hc\beta \tilde{\nu}_1}}{q} = \text{(a)} \boxed{0.044}, \quad \text{(b)} \boxed{0.230}$$

$$p_2 = \frac{e^{-hc\beta \tilde{\nu}_2}}{q} = \text{(a)} \boxed{0.002}, \quad \text{(b)} \boxed{0.083}$$

For the molar entropy we need to form  $U_m - U_m(0)$  by explicit summation

$$U_m - U_m(0) = \frac{N_A}{q} \sum_i \varepsilon_i e^{-\beta \varepsilon_i} = \frac{N_A}{q} \sum_i hc\tilde{\nu}_i e^{-hc\beta \tilde{\nu}_i}$$
 [19.25, 19.26]
 
$$= \boxed{123 \text{ J mol}^{-1} \text{ (at 100 K)}}, \quad \boxed{1348 \text{ J mol}^{-1} \text{ (at 298 K)}}$$

$$S_m = \frac{U_m - U_m(0)}{T} + R \ln q$$
 [19.34]

$$\text{(a)} \quad S_m = \frac{123 \text{ J mol}^{-1}}{100 \text{ K}} + R \ln 1.049 = \boxed{1.63 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\text{(b)} \quad S_m = \frac{1348 \text{ J mol}^{-1}}{298 \text{ K}} + R \ln 1.55 = \boxed{8.17 \text{ J K}^{-1} \text{ mol}^{-1}}$$

### Solutions to theoretical problems

**P19.13**

$$\begin{aligned}
 p &= kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N} \quad [20.4] \\
 &= kT \left( \frac{\partial \ln(q^N/N!)}{\partial V} \right)_{T,N} \quad [19.46] \\
 &= kT \left( \frac{\partial [N \ln q - \ln N!]}{\partial V} \right)_{T,N} = NkT \left( \frac{\partial \ln q}{\partial V} \right)_{T,N} \\
 &= NkT \left( \frac{\partial \ln(V/\Lambda^3)}{\partial V} \right)_{T,N} \\
 &= NkT \left( \frac{\partial [\ln V - \ln \Lambda^3]}{\partial V} \right)_{T,N} = NkT \left( \frac{\partial \ln V}{\partial V} \right)_{T,N} \\
 &= \frac{NkT}{V} \quad \text{or} \quad \boxed{pV = NkT = nRT}
 \end{aligned}$$

**P19.15** We draw up the following table

0	$\varepsilon$	$2\varepsilon$	$3\varepsilon$	$4\varepsilon$	$5\varepsilon$	$6\varepsilon$	$7\varepsilon$	$8\varepsilon$	$9\varepsilon$	$W$
8	0	0	0	0	0	0	0	0	1	9
7	1	0	0	0	0	0	0	1	0	72
7	0	1	0	0	0	0	1	0	0	72
7	0	0	1	0	0	1	0	0	0	72
7	0	0	0	1	1	0	0	0	0	72
6	2	0	0	0	0	0	1	0	0	252
6	0	2	0	0	1	0	0	0	0	252
6	0	0	3	0	0	0	0	0	0	84
6	1	0	0	2	0	0	0	0	0	252
6	1	1	0	0	0	1	0	0	0	504
6	1	0	1	0	1	0	0	0	0	504
6	0	1	1	1	0	0	0	0	0	504
5	3	0	0	0	0	1	0	0	0	504
5	0	3	1	0	0	0	0	0	0	504
5	2	1	0	0	1	0	0	0	0	1512
5	2	0	1	1	0	0	0	0	0	1512
5	1	2	0	1	0	0	0	0	0	1512
5	1	1	2	0	0	0	0	0	0	1512
4	4	0	0	0	1	0	0	0	0	630
4	3	1	0	1	0	0	0	0	0	2520
4	3	0	2	0	0	0	0	0	0	1260
4	2	2	1	0	0	0	0	0	0	3780
3	5	0	0	1	0	0	0	0	0	504
3	4	1	1	0	0	0	0	0	0	2520
2	6	0	1	0	0	0	0	0	0	252
2	5	2	0	0	0	0	0	0	0	756
1	7	1	0	0	0	0	0	0	0	72
0	9	0	0	0	0	0	0	0	0	1

The most probable configuration is the “almost exponential”  $\boxed{\{4, 2, 2, 1, 0, 0, 0, 0, 0, 0\}}$

**P19.16**  $\frac{n_j}{n_0} = e^{-\beta(\varepsilon_j - \varepsilon_0)} = e^{-\beta j \varepsilon}$ , which implies that  $-j\beta\varepsilon = \ln n_j - \ln n_0$

and therefore that  $\boxed{\ln n_j = \ln n_0 - \frac{j\varepsilon}{kT}}$

Therefore, a plot of  $\ln n_j$  against  $j$  should be a straight line with slope  $-\frac{\varepsilon}{kT}$ . Alternatively, plot  $\ln p_j$  against  $j$ , since

$$\boxed{\ln p_j = \text{const} - \frac{j\varepsilon}{kT}}$$

We draw up the following table using the information in Problem 19.8

$j$	0	1	2	3	
$n_j$	4	2	2	1	[most probable configuration]
$\ln n_j$	1.39	0.69	0.69	0	

These are points plotted in Fig. 19.2 (full line). The slope is  $-0.46$ , and since  $\frac{\varepsilon}{hc} = 50 \text{ cm}^{-1}$ , the slope corresponds to a temperature

$$T = \frac{(50 \text{ cm}^{-1}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (6.626 \times 10^{-34} \text{ J s})}{(0.46) \times (1.381 \times 10^{-23} \text{ J K}^{-1})} = \boxed{160 \text{ K}}$$

(A better estimate, 104 K represented by the dashed line in Fig. 19.2, is found in Problem 19.18.)

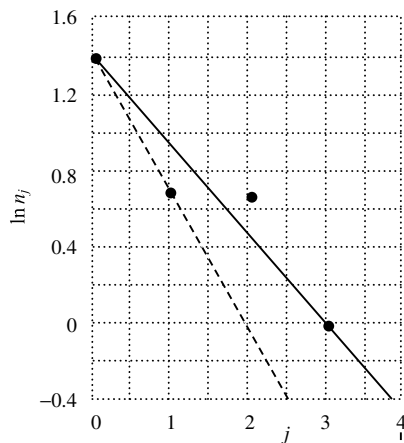


Figure 19.2

(b) Choose one of the weight 2520 configurations and one of the weight 504 configurations, and draw up the following table

	$j$	0	1	2	3	4
$W = 2520$	$n_j$	4	3	1	0	1
	$\ln n_j$	1.39	1.10	0	$-\infty$	0
$W = 504$	$n_j$	6	0	1	1	1
	$\ln n_j$	1.79	$-\infty$	0	0	0

Inspection confirms that these data give very crooked lines.

- P19.19** (a) The form of Stirling's approximation used in the text in the derivation of the Boltzmann distribution is

$$\ln x! = x \ln x - x \quad [19.2] \quad \text{or} \quad \ln N! = N \ln N - N$$

and  $\ln n_i! = n_i \ln n_i - n_i$  which then leads to [ $N$  is cancelled by  $-\sum_i n_i$ ]

$$\ln W = N \ln N - \sum_i n_i \ln n_i \quad [19.3]$$

If  $N! = N^N$ ,  $\ln N! = N \ln N$ , likewise  $\ln n_i! = n_i \ln n_i$  and eqn 3 is again obtained.

- (b) For  $\ln x! = (x + \frac{1}{2}) \ln x - x + \frac{1}{2} \ln 2\pi$  [Marginal note, p. 631],

Since the method of undetermined multipliers requires only (*Justification 19.3*)  $d \ln W$ , only the terms  $d \ln n_i!$  survive. The constant term,  $\frac{1}{2} \ln 2\pi$ , drops out, as do all terms in  $N$ . The difference, then, is in terms arising from  $\ln n_i!$ . We need to compare  $n_i \ln n_i$  to  $\frac{1}{2} \ln n_i$ , as both these terms survive the differentiation. The derivatives are

$$\frac{\partial}{\partial n_i} (n_i \ln n_i) = 1 + \ln n_i \approx \ln n_i \quad [\text{large } n_i]$$

$$\frac{\partial}{\partial n_i} \left( \frac{1}{2} \ln n_i \right) = \frac{1}{2n_i}$$

Whereas  $\ln n_i$  increases as  $n_i$  increases,  $\frac{1}{2n_i}$  decreases and in the limit becomes negligible. For

$n_i = 1 \times 10^6$ ,  $\ln n_i = 13.8$ ,  $\frac{1}{2n_i} = 5 \times 10^{-7}$ ; the ratio is about  $2 \times 10^8$  which could probably not be seen in experiments. However, for experiments on, say, 1000 molecules, such as molecular dynamics simulations, there could be a measurable difference.

### Solutions to applications

**P19.21**

$$\begin{aligned} \frac{p(h)}{p(h_0)} &= \frac{N(h)/V}{N(h_0)/V} = e^{-\{(\varepsilon(h) - \varepsilon(h_0))/kT\}} \quad [19.6] \\ &= e^{-mg(h-h_0)/kT} \end{aligned}$$

For  $p(0) \equiv p_0$ ,

$$\boxed{\frac{p(h)}{p_0} = e^{-mgh/kT}}$$

$$\frac{\mathcal{N}(8.0 \text{ km})}{\mathcal{N}(0)} = \frac{N(8.0 \text{ km})/V}{N(0)/V} = e^{-\frac{M(\text{O}_2)gh}{RT}}$$

$$\frac{\mathcal{N}(8.0 \text{ km})}{\mathcal{N}(0)} [\text{O}_2] = e^{-\left\{ \frac{(0.032 \text{ kg mol}^{-1}) \times (9.81 \text{ m s}^{-2}) \times (8.0 \times 10^3 \text{ m})}{(8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right\}}$$

$$= \boxed{0.36} \quad \text{for O}_2$$

$$\frac{\mathcal{N}(8.0 \text{ km})}{\mathcal{N}(0)} [\text{H}_2\text{O}] = e^{-\left\{ \frac{(0.018 \text{ kg mol}^{-1}) \times (9.81 \text{ m s}^{-2}) \times (8.0 \times 10^3 \text{ m})}{(8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right\}}$$

$$= \boxed{0.57} \quad \text{for H}_2\text{O}$$

- P19.23** (a) The electronic partition function,  $q_E$ , of a perfect, atomic hydrogen gas consists of the electronic energies  $E_n$  that can be written in the form:

$$E_n = \left(1 - \frac{1}{n^2}\right) hcR_H, \quad n = 1, 2, 3, \dots, \infty,$$

where we have used the state  $n = 1$  as the zero of energy (in contrast to the usual zero being at infinite separation of the proton and electron, eqn 13.13). The degeneracy of each level is  $g_n = 2n^2$  where the  $n^2$  factor is the orbital degeneracy of each shell and the factor of 2 accounts for spin degeneracy.

$$q_E = \sum_{n=1}^{\infty} g_n e^{-E_n/kT} = 2 \sum_{n=1}^{\infty} n^2 e^{-\left(1 - \frac{1}{n^2}\right)C},$$

where  $C = hcR_H/kT_{\text{photosphere}} = 27.301$ .  $q_E$ , when written as an infinite sum, is infinitely large because  $\lim_{n \rightarrow \infty} \left\{ n^2 e^{-\left(1 - \frac{1}{n^2}\right)C} \right\} = \lim_{n \rightarrow \infty} \left\{ n^2 e^{-C} \right\} = e^{-C} \lim_{n \rightarrow \infty} (n^2) = \infty$ . The inclusion of partition function terms corresponding to large  $n$  values is clearly an error.

- (b) States corresponding to large  $n$  values have very large average radii and most certainly interact with other atoms, thereby, blurring the distinct energy level of the state. Blurring interaction most likely occurs during the collision between an atom in state  $n$  and an atom in the ground state  $n = 1$ . Collisional lifetime broadening (eqn 16.25) is given by:

$$\delta E_n = \frac{h}{2\pi\tau} = \frac{z_n h}{2\pi},$$

where  $z_n$  = collisional frequency of  $n$ th state of atomic perfect gas

$$= \frac{\sqrt{2}\sigma_n \bar{c} \rho}{kT} = \frac{\sqrt{2}\sigma_n \bar{c} \rho N_A}{M_H} \quad (\text{eqn 24.12})$$

$$\bar{c} = \text{mean speed} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = 1.106 \times 10^4 \text{ m s}^{-1} \quad (\text{eqn 24.7})$$

$\sigma_n$  = collisional cross-section of  $n$ th state (Fig. 24.9)

$$\begin{aligned} &= \pi(\langle r \rangle_n + a_0)^2 \\ &= \pi a_0^2 \left(\frac{3n^2 + 2}{2}\right)^2 \quad (\text{Example 13.2}) \end{aligned}$$

Any quantum state within  $\delta E$  of the continuum of an isolated atom will have its energy blurred by collisions so as to be indistinguishable from the continuum. Only states having energies in the range  $0 \leq E < E_{\infty} - \delta E$  will be a distinct atomic quantum state.

The maximum term,  $n_{\text{max}}$ , that should be retained in the partition function of a hydrogen atom is given by

$$E_{n_{\text{max}}} = E_{\infty} - \delta E_{n_{\text{max}}}$$

$$\left(1 - \frac{1}{n_{\text{max}}^2}\right) hcR_H = hcR_H - \frac{\sqrt{2}\pi a_0^2 \left(\frac{3n_{\text{max}}^2 + 2}{2}\right)^2 \bar{c} \rho N_A h}{2\pi M_H}$$

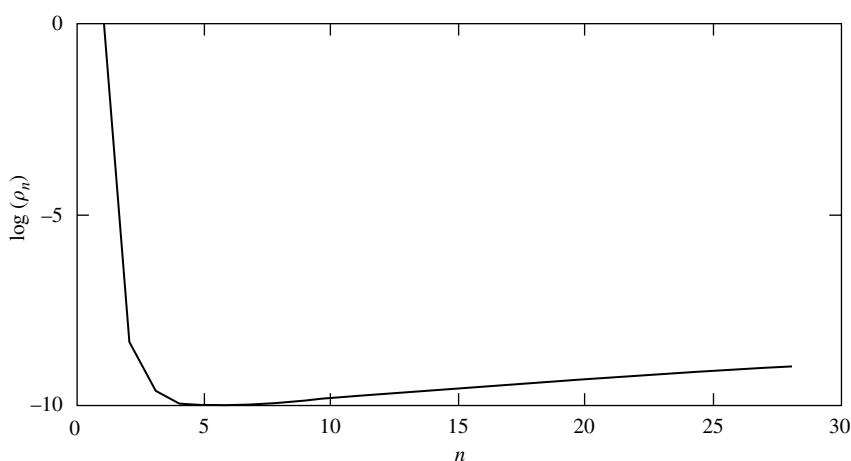
with  $\rho = 1.99 \times 10^{-4} \text{ kg m}^{-3}$  and  $M_H = 0.001 \text{ kg mol}^{-1}$ .

The root function of a calculator or mathematical software may be used to solve this equation for  $n_{\max}$ .

$$n_{\max} = 28 \quad \text{for atomic hydrogen of the photosphere}$$

Furthermore, examination of the partition function terms  $n = 2, 3, \dots, n_{\max}$  indicates that they are negligibly small and may be discarded. The point is that very large  $n$  values should not be included in  $q_E$  because they do not reflect reality.

$$(c) \quad \rho_n = \frac{2n^2 e^{-E_n/kT}}{q_E} \quad \text{where} \quad T = 5780 \text{ K} \quad (\text{eqn 19.6})$$



**Figure 19.3**

Even at the high temperature of the Sun's photosphere only the ground electronic state is significantly populated. This leads us to expect that at more ordinary temperatures only the ground state of atom and molecules are populated at equilibrium. It would be a mistake to thoughtlessly apply equilibrium populations to a study of the Sun's photosphere, however, it is bombarded with extremely high energy radiation from the direction of the Sun's core while radiating at a much low energy. The photosphere may show significant deviations from equilibrium.

See S. J. Strickler, *J. Chem. Ed.*, 43, 364 (1966).