

Probability II

Partition functions and wavefunctions

31

Answers to additional problems

31.1 Using eqn. (31.1), $W = \frac{N!}{N_0!N_1!N_2! \dots} = \frac{35!}{15!0!8!5!0!3!2!0!2!} = 6.80 \times 10^{19}$

31.2 Rearranging the Boltzmann distribution given in eqn. (31.2), $\frac{N_i}{N} = \frac{\exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{\sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right)}$
we see that $N_i = \frac{N}{q} \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$

For degenerate energy states, we need to include the degeneracy g_i in the calculation of N_i ,

as we did for eqn. (31.5), $N_i = g_i \frac{N}{q} \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$

Therefore the ratio $\frac{N_2}{N_1} = \frac{g_2 \left(\frac{N}{q}\right) \exp\left(-\frac{\varepsilon_2}{k_B T}\right)}{g_1 \left(\frac{N}{q}\right) \exp\left(-\frac{\varepsilon_1}{k_B T}\right)} = \frac{g_2}{g_1} \exp\left(-\frac{(\varepsilon_2 - \varepsilon_1)}{k_B T}\right)$

We can write this as $\frac{N_2}{N_1} = \frac{p_2}{p_1} = \frac{g_2}{g_1} \exp\left(-\frac{\Delta E}{k_B T}\right)$ where $\Delta E = \varepsilon_2 - \varepsilon_1$.

31.3 The most accessible, highest-energy electron to be removed during ionization is that in a non-degenerate 3s orbital. We assume both states have a degeneracy of 1. Using the equation derived in Additional Problem 31.2,

$$\frac{N_2}{N_1} = \exp\left(-\frac{\Delta E}{RT}\right) = \exp\left(-\frac{495.85 \times 10^3}{8.314 \times (7500 + 273)}\right) = 4.65 \times 10^{-4}$$

We have used RT here instead of $k_B T$ since the energy is given in molar units (J mol^{-1}).

31.4 As for the similar halogen molecule in the Worked Example 31.8, we assume that the degeneracy of the ground state for a chlorine molecule is 1 and for a chlorine atom is 4. The energy difference between the states $\Delta E = 242 \text{ kJ mol}^{-1}$.

Using the equation from Additional Problem 31.2

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \exp\left(-\frac{\Delta E}{RT}\right) = \frac{4}{1} \exp\left(-\frac{242 \times 10^3}{8.314 \times (1800 + 273)}\right) = 3.19 \times 10^{-6}$$

Note how the magnitude of this proportion is of parts per million even at this very high temperature.

31.5 The relative populations of the two states can be given as $N_1 = n$ for the lower state and $N_2 = n/4$ for the upper state. Both levels are non-degenerate so $g_1 = g_2 = 1$. The energy

difference between the states is 500 cm^{-1} . This value can be converted to Joules by multiplying by hc . In units of cm^{-1} the value of c is $2.998 \times 10^{10} \text{ cm s}^{-1}$.

Starting from the expression derived in Additional Problem 31.2,

$$\frac{N_2}{N_1} = \exp\left(-\frac{\Delta E}{k_B T}\right) = \exp\left(-\frac{hc\tilde{\nu}}{k_B T}\right)$$

we can rearrange to make T the subject,

$$\ln\left(\frac{N_2}{N_1}\right) = -\frac{hc\tilde{\nu}}{k_B T}$$

$$\text{and then } T = -\frac{hc\tilde{\nu}}{k_B \ln\left(\frac{N_2}{N_1}\right)}$$

Substituting into this equation

$$T = -\frac{hc\tilde{\nu}}{k_B \ln\left(\frac{N_2}{N_1}\right)} = \frac{-6.626 \times 10^{-34} \times 2.998 \times 10^{10} \times 500}{1.38065 \times 10^{-23} \times \ln\left(\frac{n/4}{n}\right)} = \frac{-9.93 \times 10^{-21}}{1.38065 \times 10^{-23} \times \ln\left(\frac{1}{4}\right)} = 519 \text{ K}$$

The temperature is 519 K.

- 31.6** The relative populations of the two states can be given as $N_2 = 0.3$ for the excited state and $N_1 = (1-0.3) = 0.7$ for the ground state. The degeneracy of the ground state $g_1 = 1$ but the excited state is triply degenerate and so $g_2 = 3$. The energy difference between the states is 200 cm^{-1} which can be converted to Joules by multiplying by hc , where $c = 2.998 \times 10^{10} \text{ cm s}^{-1}$.

Starting from the expression derived in Additional Problem 31.2,

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \exp\left(-\frac{\Delta E}{k_B T}\right) = \frac{g_2}{g_1} \exp\left(-\frac{hc\tilde{\nu}}{k_B T}\right)$$

we can rearrange to make T the subject,

$$\ln\left(\frac{N_2 g_1}{N_1 g_2}\right) = -\frac{hc\tilde{\nu}}{k_B T}$$

$$\text{and then } T = -\frac{hc\tilde{\nu}}{k_B \ln\left(\frac{N_2 g_1}{N_1 g_2}\right)}$$

Substituting into this equation,

$$T = -\frac{hc\tilde{\nu}}{k_B \ln\left(\frac{N_2 g_1}{N_1 g_2}\right)} = \frac{-6.626 \times 10^{-34} \times 2.998 \times 10^{10} \times 200}{1.38065 \times 10^{-23} \times \ln\left(\frac{0.3 \times 1}{0.7 \times 3}\right)} = 147.9 \text{ K}$$

The temperature will be 148 K.

- 31.7** At 0 K, water is arranged in a diamond-like tetrahedral structure, with the oxygen in the central position with short σ bonds to two hydrogens and longer hydrogen bonds to another 2 hydrogen atoms. For every N molecules of H_2O , there are $2N$ atoms of hydrogen, which can be arranged in one of 2 positions (attached to the oxygen by a short or long bond). Four hydrogens can be arranged around an oxygen atom in $2^4 (= 16)$ ways. Only 6 out of 16 of these arrangements have 2 short and 2 long bonds, and are thus permissible arrangements at 0 K. Therefore only a fraction $(6/16)^N$ of the 2^{2N} orientations of the hydrogens are possible.

$$W = 2^{2N} (6/16)^N = 2^{2N} (3/8)^N = ((2^2 \times 3)/8)^N = (3/2)^N$$

To calculate the molar residual entropy $N = N_A$ and substituting into eqn. (31.14),

$$S = k_B \ln(3/2)^{N_A}$$

Using the third laws of logarithms, we can rearrange as $N_A k_B \ln(3/2)$

$$S = R \ln(3/2) = 3.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

This value is in good agreement with the experimentally measured value.

- 31.8** In order to calculate the equilibrium constant for the dissociation of Cl_2 , we need to use eqn. (31.3)

$$K = \frac{\left(\frac{q_{\text{Cl},m}^{\ominus}}{N_A}\right)^2}{\left(\frac{q_{\text{Cl}_2,m}^{\ominus}}{N_A}\right)} \exp\left(\frac{-\Delta E_0}{RT}\right) = \frac{\left(q_{\text{Cl},m}^{\ominus}\right)^2}{q_{\text{Cl}_2,m}^{\ominus} N_A} \exp\left(\frac{-\Delta E_0}{RT}\right)$$

The energy difference between the ground states is equal to the bond dissociation energy

$$\Delta E_0 = 2U_m^{\ominus}(\text{Cl}) - U_m^{\ominus}(\text{Cl}_2) = D_0(\text{Cl}-\text{Cl}) = 242 \times 10^3 \text{ J mol}^{-1}$$

We also need to calculate the molar partition functions for Cl and Cl_2 .

Molar partition function of Cl

For an individual atom of chlorine, there are only two contributions to the molar partition function: the translational and electronic partition functions.

The mass of a single chlorine atom is $35.5 \times 1.66054 \times 10^{-27} = 5.89 \times 10^{-26} \text{ kg}$ and the molar volume can be calculated using the ideal-gas law $V_m = RT/p^{\ominus} = 8.314 \times 2500/10^5 = 0.208 \text{ m}^3$. We can calculate $\Lambda = 5.86 \times 10^{-12}$ and the translation partition function using eqn. (31.6),

$$q_{\text{Cl},m}^{\text{T}} = \frac{0.208}{(5.86 \times 10^{-12})^3} = 1.03 \times 10^{33}$$

The electronic partition function $q^{\text{E}} = g^{\text{E}} = \text{degeneracy of the ground state} = 4$. We calculate the overall molar partition function for a chlorine atom as,

$$q_{\text{Cl},m}^{\text{o}} = q_{\text{Cl},m}^{\text{T}} q_{\text{Cl}}^{\text{E}} = 1.03 \times 10^{33} \times 4 = 4.13 \times 10^{33}$$

Molar partition function of Cl_2

In effect, we want the product of the translational, vibrational, rotational, and electronic partition functions for Cl_2 .

Translational partition function of Cl_2

The mass of $\text{Cl}_2 = 2 \times 35.5 \times 1.66054 \times 10^{-27} = 1.18 \times 10^{-25} \text{ kg}$, $T = 2500 \text{ K}$, and $V_m = 0.208 \text{ m}^3$.

Using eqn. (31.6), we say

$$\Lambda = \frac{6.626 \times 10^{-34}}{(2\pi \times 1.18 \times 10^{-25} \times 1.38065 \times 10^{-23} \times 2500)^{1/2}} = 4.14 \times 10^{-12} \text{ m}$$

$$q^{\text{T}} = \frac{0.208}{(4.14 \times 10^{-12})^3} = 2.92 \times 10^{33}$$

Vibrational partition function of Cl_2

The speed of light $c = 2.998 \times 10^{10} \text{ cm s}^{-1}$, $T = 2500 \text{ K}$, and $\tilde{\nu} = 559.7 \text{ cm}^{-1}$.

Substituting into eqn. (31.7), we say

$$q^V = \frac{1}{1 - \exp(-6.626 \times 10^{-34} \times 2.998 \times 10^{10} \times 559.7 / (1.38065 \times 10^{-23} \times 2500))} = 3.63$$

Rotational partition function of Cl₂

$\tilde{B} = 0.2439 \text{ cm}^{-1}$ and the symmetry number $\sigma = 2$, for this homonuclear diatomic molecule. Using eqn. (31.9) for high temperatures

$$q^R = \frac{1.38065 \times 10^{-23} \times 2500}{2 \times 6.626 \times 10^{-34} \times 2.998 \times 10^{10} \times 0.2439} = 3562.0$$

Electronic partition function of Cl₂

The ground state of Cl₂(g) is nondegenerate and there is a large energy gap to the 1st excited state. Therefore $g^E = 1$ and $q^E = 1$.

The overall molecular partition function is,

$$q = q^T q^V q^R q^E = 2.92 \times 10^{33} \times 3.63 \times 3562 \times 1 = 3.77 \times 10^{37}.$$

Equilibrium constant

We can calculate the equilibrium constant using eqn. (31.13), as

$$K = \frac{(q_{\text{Cl},m}^{\ominus})^2}{q_{\text{Cl}_2,m}^{\ominus} N_A} \exp\left(\frac{-\Delta E_0}{RT}\right) = \frac{(4.13 \times 10^{33})^2}{3.77 \times 10^{37} \times 6.023 \times 10^{23}} \exp\left(\frac{-242 \times 10^3}{8.314 \times 2500}\right) = 6.58$$

The equilibrium constant K is calculated to be > 1 , which tells us the dissociated monomer form will predominate at 2500 K.

- 31.9** The tunnelling probability P is the ratio of the probability that the particle is in region 3 (after the barrier) to the probability it is in region 1 (before the barrier). Increasing P will lead to a higher probability that the particle tunnels through the barrier.

The expression says that larger particles of mass m are associated with more negative terms inside the bracket. The tunnelling probability is therefore smaller. Similarly, the tunnelling probability decreases with increased barrier height V_0 and width L .

Tunnelling is most likely when the energetic barrier height is relatively low and light particles move a short distance.

In scanning tunnelling microscopy, the tunnelling current is proportional to the tunnelling probability. The proportionality does not follow a linear relationship, though, because the tunnelling current increases by approximately a factor of ten for every 0.1 nm increment that the tip is brought closer to the surface.

- 31.10** We call the time required for half of the nuclei to decay the **half-life**, $t_{1/2}$.

We can rearrange the equation for nuclear decay to make t the subject,

$$t = -\frac{1}{\lambda} \ln\left(\frac{n_t}{n_0}\right)$$

$$\text{At } t_{1/2}, n_t = \frac{1}{2} n_0, \text{ so } t_{1/2} = -\frac{1}{\lambda} \ln\left(\frac{\frac{1}{2} n_0}{n_0}\right) = -\frac{1}{\lambda} \ln(2^{-1}) = \frac{\ln(2)}{\lambda}.$$

The probability of a radioactive atom decaying within its half-life is 50%.