

Thermal Physics II – Solutions for Problem Sheet 6

1. Mixture of two Gases

- As all particles in the gases are not interacting with each other, we have $Z_{a+b} = Z_a \times Z_b$ as derived before.
- The partition functions for the two gases are given by

$$Z_a = \frac{1}{N_a!} Z_{1a}^{N_a} \quad \text{and} \quad Z_b = \frac{1}{N_b!} Z_{1b}^{N_b}.$$

as the particles within each species cannot be distinguished. $Z_{1a} = V/\Lambda_a$ and $Z_{1b} = V/\Lambda_b$ are the one particle partition functions for the gases a and b , respectively.

- The total partition functions is thus given by

$$Z_{a+b} = \frac{1}{N_a!} Z_{1a}^{N_a} \times \frac{1}{N_b!} Z_{1b}^{N_b}.$$

- WARNING: a partition function of the form

$$Z_{a+b} = \frac{1}{(N_a + N_b)!} Z_{1a}^{N_a} \times Z_{1b}^{N_b}$$

would be WRONG as it assumes that both species are indistinguishable!

2. Mixing Entropy - Generalised

- If $x = N_b/N$ then we also have $N_a/N = 1 - x$ as $N = N_a + N_b$.
- If two gases mix, they now both occupy the volume V . Before mixing they occupied the volumes V_a and V_b respectively. These volumes must have the similar relation as the particle numbers to have the same pressures: $V_b/V = x$ and $V_a/V = 1 - x$ as $V = V_a + V_b$.
- The entropy change for gas a is related to its volume change as before

$$\begin{aligned}\Delta S_a &= N_a k_B \ln\left(\frac{V}{V_a}\right) = (1 - x)Nk_B \ln\left(\frac{1}{1 - x}\right) \\ &= -(1 - x)Nk_B \ln(1 - x) .\end{aligned}$$

- Similar we find for the entropy change for the particles b

$$\begin{aligned}\Delta S_b &= N_b k_B \ln\left(\frac{V}{V_b}\right) = xNk_B \ln\left(\frac{1}{x}\right) \\ &= -xNk_B \ln x .\end{aligned}$$

- Adding both contribution, we find for the total mixing entropy

$$\Delta S = \Delta S_a + \Delta S_b = -Nk_B \left[(1 - x) \ln(1 - x) + x \ln(x) \right] .$$

- If one uses the same number of particles a and b (same volumes as well, of course), then $x = \frac{1}{2}$. In this case, we find

$$\Delta S = \Delta S_a + \Delta S_b = Nk_B \ln 2$$

as we have $x = 1 - x$ and a negative sign from the logarithm law.

3. Heat capacity due to Rotating Molecules

- If we only consider the two lowest states, the partition function becomes

$$Z_{rot}^1 = 1 + 3 \exp\left(-2 \frac{T_{rot}}{T}\right).$$

- Taking the logarithm and considering that the second term is small, we get

$$\ln Z = \ln\left[1 + 3 \exp\left(-2 \frac{T_{rot}}{T}\right)\right] \approx 3 \exp\left(-2 \frac{T_{rot}}{T}\right).$$

- In the next step, we calculate the internal energy

$$U = Nk_B T^2 \frac{\partial \ln Z}{\partial T} = 6Nk_B T_{rot} \exp\left(-2 \frac{T_{rot}}{T}\right).$$

- The heat capacity follows as the temperature derivative

$$c_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B \left(\frac{2T_{rot}}{T}\right)^2 \exp\left(-2 \frac{T_{rot}}{T}\right)$$

The main functional form is given here by the exponential. Thus, the heat capacity approaches zero for $T \rightarrow 0$.