Solutions to home work week 2

1. Because S is a state function, we can choose always the reversible path for computing the entropy difference. For a reversible heating from 300 K to 320 K at constant pressure we have that

$$dS = \frac{dQ}{T} = \frac{mC_p dT}{T} \tag{1}$$

with m the mass of water (1 kg in our example). Integrating both sides

$$\Delta S = mC_p \int_{T_1}^{T_2} \frac{1}{T} dT = mC_p \ln \frac{T_2}{T_1} \tag{2}$$

The heat capacity is so large because of the hydrogen bonding in water.

2. Use that for an ideal gas at constant temperature $dU = 0$. Thus, upon reversible expansion

$$dQ = dU - dW = pdV \tag{3}$$

For the entropy change we have

$$dS = dQ/T = \frac{p}{T} dV = R \frac{1}{V} dV \tag{4}$$

Integrating both sides gives the entropy difference in going from V_1 to V_2:

$$\Delta S = R \ln \frac{V_2}{V_1} \tag{5}$$

   - no, because entropy is state funtion
   - For reversible expansion, the entropy of the environment changes by

the oposite amount

$$\Delta S_0 = -\Delta S = -R \ln \frac{V_2}{V_1} \tag{6}$$

In this case the entropy change of the total system is zero:

$$\Delta S^{\text{tot}} = \Delta S + \Delta S_0 = 0 \tag{7}$$

- For irreversible work against the constant external pressure at constant temperature we have $dW = -p_0 dV$, while $dU = 0$. Thus,

  $$\Delta Q = p_0 \Delta V \tag{8}$$

  so that for the entropy change of the environment

  $$\Delta S_0 = -\frac{Q}{T} = -\frac{p_o \Delta V}{T_0} \tag{9}$$

  because S is a state function, ΔS is the same as for the reversible process. Thus for the entropy change in the total system we haev that

  $$\Delta S^{\text{tot}} = R \ln \frac{V_2}{V_1} - \frac{p_o \Delta V}{T_0} > 0 \tag{10}$$

  The inequality follows from fact that the expansion work is maximal when done reversibly.

3. During the adiabatic expansion ($dQ = 0$), not only work is done, but also the temperature changes. Thus, we go from (p_1, V_1, T_1) to (p_2, V_2, T_2) . We choose again the reversible path. For a reversible process we have that

   $$dU = TdS - pdV \tag{11}$$

and for the ideal gas we have that.

$$dU = C_V dT \tag{12}$$

Isolating dS in equation 11 and using the expression for dU from equation 12 we get:

$$dS = \frac{C_V}{T} dT + \frac{p}{T} dV \tag{13}$$

From the equation of state we have that $\frac{p}{T} = \frac{R}{V}$. Inserting and integrating on both sides

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \tag{14}$$

Thus, to get the entropy change, we need to know both the volume and the temperature at the end states. We only know the volumes: V_1 and V_2. However, in exercise 3 of the previous homework set we derived that for *reversible* adiabatic expansion pV^γ is a constant. Because we choose the reversible pathway also now to do the expansion, we may use *irreversible* adiabatic expansion!):

$$p_1 V_1^\gamma = p_2 V_2^\gamma \tag{15}$$

which we can re-write to

$$p_1 V_1 V_1^{(\gamma-1)} = p_2 V_2 V_2^{(\gamma-1)} \tag{16}$$

Using the equation of state for the ideal gas ($pV = RT$, assuming one mole throughout):

$$\begin{aligned} RT_1 V_1^{(\gamma-1)} &= RT_2 V_2^{(\gamma-1)} \\ \tfrac{T_1}{T_2} &= (\tfrac{V_2}{V_1})^{(\gamma-1)} \end{aligned} \tag{17}$$

For the ideal gas we also have that

$$\gamma - 1 = \frac{C_p}{C_V} - 1 = \frac{R}{C_v} \tag{18}$$

Therefore,

$$\begin{aligned} \Delta S &= C_V \ln \left(\tfrac{V_1}{V_2}\right)^{\frac{R}{C_V}} + R \ln \tfrac{V_2}{V_1} \\ &= -R \ln \tfrac{V_2}{V_1} + R \ln \tfrac{V_2}{V_1} \\ &= 0 \end{aligned} \tag{19}$$

Thus, the *reversible* adiabatic expansion is *isentropic*, $\Delta S = 0$. The reason is that although we increase volume and do work, we also lower the temperature. This is an example of turning all heat into work!

If not reversible, the final temperature will be higher, and hence entropy increased.

4. At equilibrium, we have that

$$\left(\frac{\partial S_{AB}}{\partial V_A}\right)_{N_A,N_B,E_A,E_B} = \left(\frac{\partial S_A}{\partial V_A}\right)_{N_A,E_A} + \left(\frac{\partial S_B}{\partial V_B}\right)_{N_B,E_B} \frac{dV_B}{dV_A} = 0 \tag{20}$$

From the fact that the total volume is conserved $V_A + V_B = V_{AB}$, we have that $dV_A + dV_B = 0$ and therefore

$$\frac{dV_B}{dV_A} = -1 \tag{21}$$

Thus, at equilibrium, we have that

$$\left(\frac{\partial S_A}{\partial V_A}\right)_{N_A,E_A} = \left(\frac{\partial S_B}{\partial V_B}\right)_{N_B,E_B} \tag{22}$$

We know (intuitively) that the pressures are the same in equilibrium. Furthermore, the units of these derivatives are are JK^{-1}m^{-3}, while pressure has Jm^{-3}, we apparently need to multiply by temperature:

$$P_A = T_A \left(\frac{\partial S_A}{\partial V_A}\right)_{N_A,E_A} \tag{23}$$

5. There are two energy levels per nucleus. If we set (arbitrary, but convenient) the lower level to 0 ($E_0 = 0$ J), the probability for a single nucleus to be in the higher energy level ($E_1 = 3\ 10^{-20}$ J) is given by the Boltzmann factor:

   $$p_1 = \frac{\exp[-\beta E_1]}{1 + \exp[-\beta E_1]} \tag{24}$$

   where we used that $\exp[0] = 1$. Thus, of the N nuclei, there will be $p_1 N$ in the higher energy state with energy E_1,

   $$N_1 = N p_1 = \frac{N \exp[-\beta E_1]}{1 + \exp[-\beta E_1]} \tag{25}$$

   and $p_0 N$ in the lower energy state with energy $E_0 = 0$:

   $$N_0 = N p_0 = \frac{N}{1 + \exp[-\beta E_1]} \tag{26}$$

   With N = 1,000,000 and k = 1.3806 10^{-23} JK^{-1}, we have at

   - 0 K: $N_0 = 1000000$ and $N_1 = 0$
   - 10 K: $N_0 = 1000000$ and $N_1 = 0$
   - 100 K: $N_0 = 1000000$ and $N_1 = 0$
   - 300 K: $N_0 = 999286$ and $N_1 = 714$.
   - 1000 K: $N_0 = 897796$ and $N_1 = 102204$
   - 10,000 K: $N_0 = 554111$ and $N_1 = 445889$

In Figure 1 the number of particles in energy level E_1 is plotted as a function of temperature.

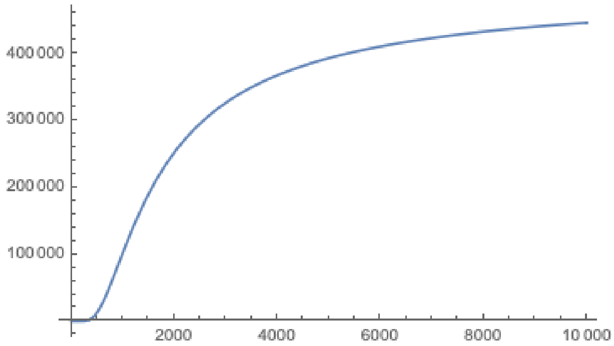

Figure 1: number of particles with energy level E_1 as a function of temperature (x-axis, K)

6. For the quantum harmonic oscillator, the partition function:

$$\begin{aligned} Z &= \textstyle\sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \textstyle\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \qquad (27) \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \textstyle\sum_{n=0}^{\infty} (e^{-\beta\hbar\omega})^n \end{aligned}$$

Since $\exp[-\beta\hbar\omega] \leq 1$, we can use $\sum_i x^n = \frac{1}{1-x}$:

$$Z = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \tag{28}$$

To calculate the ratio between the occupancies (*i. e.*, probabilities) of energy levels 0 and 1, we use the Boltzmann factors:

$$p_n = \frac{e^{-(n+\frac{1}{2})\beta\hbar\omega}}{Z} \tag{29}$$

with Z in equation 28. However, we only need the ratio here, *i. e.*,:

$$\begin{aligned}
\frac{p_1}{p_0} &= \frac{e^{-1\frac{1}{2}\beta\hbar\omega}}{e^{-\frac{1}{2}\beta\hbar\omega}} \\
&= e^{-\beta\hbar\omega}
\end{aligned} \tag{30}$$

Thus the ratios are at

- 1 K: 0
- 10 K: 0
- 100 K: 0
- 1,000 K: 0.38
- 10,000 K: 0.91

The average energy is obtained as the derivative of the logarithm of the partition function (equation 28) with respect to β;

$$\begin{aligned}
\langle E \rangle &= -\frac{\partial}{\partial\beta} \ln Z \\
&= -\frac{\partial}{\partial\beta} \ln\left[\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right] \\
&= -\frac{\partial}{\partial\beta}\left(\ln\left[e^{-\frac{1}{2}\beta\hbar\omega}\right] - \ln\left[1-e^{-\beta\hbar\omega}\right]\right) \\
&= \frac{\partial}{\partial\beta}\frac{1}{2}\beta\hbar\omega + \frac{\partial}{\partial\beta}\ln\left[1-e^{-\beta\hbar\omega}\right] \\
&= \frac{1}{2}\hbar\omega + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}
\end{aligned} \tag{31}$$

Thus, irrespective of temperature, the energy always contains the zero-point energy ($\frac{1}{2}\hbar\omega$), and higher levels contribute to the energy only if the temperature is sufficiently high, as shown in figure 2.

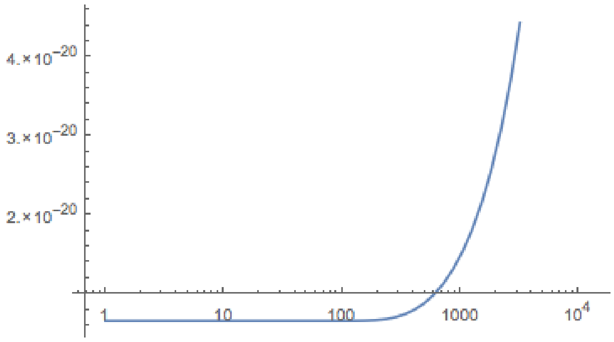

Figure 2: Average energy (y-axis, J) of a single harmonic oscillator as a function of temperature (x-axis, K)