Solutions Exercise Classes 7 Physical Chemistry 1 2021/2022

Exercise 22

a) Since S is a state function we can choose a reversible process, so $\mathrm{d}W = -P_{ext}\mathrm{d}V = -P\mathrm{d}V$. For an isothermal process and a perfect gas it holds that $\Delta U = 0$ such that $Q = -W$, so $\mathrm{d}Q_{rev} = P\mathrm{d}V$. The result for the entropy change is $\Delta S = \int_{V_1}^{V_2} \frac{\mathrm{d}Q_{rev}}{T} = \int_{V_1}^{V_2} \frac{P\mathrm{d}V}{T} = \int_{V_1}^{V_2} \frac{nRT\mathrm{d}V}{VT} = nR\ln\frac{V_2}{V_1} = nR\ln 2$.

b) The Boltzmann definition of entropy is $S = k\ln W$ in which W is the number of realization possibilities of the system, that is, the number of micro states. Even though we expand isothermally, the distribution of the molecules over the energy levels changes. This is because the energy levels of the particles depend on the volume.
Since $nR = Nk$, in which N is the number of particles, we can write the result of part a) as $\Delta S = Nk\ln 2 = k\ln 2^N$. In terms of the Boltzmann definition this implies that $\Delta S = k\ln W_2 - k\ln W_1 = k\ln\frac{W_2}{W_1}$, so $k\ln\frac{W_2}{W_1} = k\ln 2^N$, or $\frac{W_2}{W_1} = 2^N$.
We can interpret this result as twice the amount of realization possibilities per particle in the system; it is tempting to argue that twice the number of positions can be occupied per particle due to the volume of the final state being twice as large. For N particles there are thus 2^N as many position possibilities. In other words, in this reasoning for the term ‘number of realization possibilities’ we have to account for not only the number of possibilities to realize the distribution of particles over the energy states, but also the position possibilities. From a quantum mechanical point of view, this is already covered by the volume dependence of the energy levels (see Study Guide, p.26, eq (130)).

Exercise 23

a) There are n amino acids and thus $(n-1)$ peptide bonds in the polypeptide chain. Every peptide bond has two rotational degrees of freedom, the torsion angles ϕ and ψ, which each have three positions so there are $3^2 = 9$ torsional states per peptide bond (see figure 1).

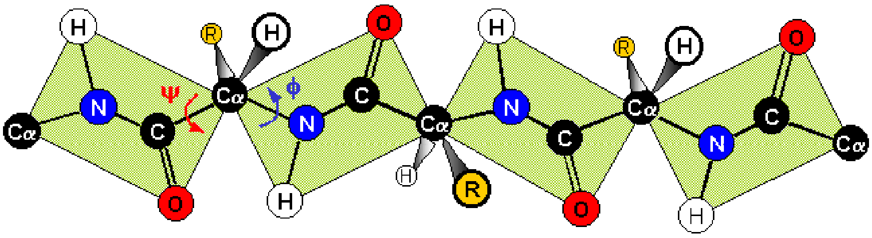

Figure 1: Completely unfolded polypeptide chain; ϕ and ψ each have 3 preferred states.

Thus for the n peptides of the entire molecule there are $N_c = 3^{2(n-1)} = 9^{(n-1)}$ conformations.

b) $\Delta S = k\ln W_u - k\ln W_n$, in which the number of conformations is $W_n = 1$ for the folded (native) state, whereas part a) shows that $W_u = N_c = 3^{2(n-1)}$ for all unfolded states. With this we find $\Delta S = k\ln 3^{2(n-1)} - k\ln 1 = k\ln 3^{2\cdot 99} - 0 = 2\cdot 99k\ln 3 = 218k = 3.0\cdot 10^{-21}$ J/K. This is the entropy per molecule. The molar entropy thus becomes $\Delta S_m = N_A\Delta S = 1.8$ kJ/mol K.

c) The torsional degrees of freedom in an ethane molecule result in an entropy gain per mol ethane of $\Delta S = N_A k\ln 3 = R\ln 3 = 9.1$ J/mol K.

d) The conformational torsional entropy per group in the molecule for the polypeptide molecule is $\frac{\Delta S}{100} = 18$ J/mol K, which is twice as much as for the ethane molecule. The factor two is a consequence of the number of torsion angles (ϕ and ψ). The huge difference between the two cases of part b) and c) is the result of the large difference in possible molecular conformations.

Exercise 24

a) Since we set the lowest energy level to 0, all energy levels shift up with $\frac{1}{2}\mu_B H$, such that $\epsilon_0 = 0$ and $\epsilon_1 = \mu_B H$.

$$q = \sum_i \exp\left(-\frac{\epsilon_i}{kT}\right) = 1 + \exp\left(-\frac{\mu_B H}{kT}\right)$$

b) The Boltzmann distribution results in

$$n_i = N\frac{\exp\left(-\frac{\epsilon_i}{kT}\right)}{q} \quad (i = 0, 1),$$

such that

$$n_0 = N\frac{1}{1 + \exp\left(-\frac{\mu_B H}{kT}\right)} \quad \text{and} \quad n_1 = N\frac{\exp\left(-\frac{\mu_B H}{kT}\right)}{1 + \exp\left(-\frac{\mu_B H}{kT}\right)}.$$

In the figure below $\frac{n_0}{N}$ and $\frac{n_1}{N}$ are plotted for a magnetic field of 10 Tesla, for which $\mu_B H = 9.27 \cdot 10^{-23}$ J. We see that for $T \to \infty$ the distribution of both levels becomes equal to 0.5, whereas for $T \to 0$ all spins are in the ground state ($n_0(T = 0) = N$ and $n_1(T = 0) = 0$). We also see that if the thermal energy is equal to the magnetic energy ($kT = \mu_B H$), the distributions become equal to $\frac{n_0}{N} = 0.731$ and $\frac{n_1}{N} = 0.269$. The corresponding temperature is $T = \frac{\mu_B H}{k} = \frac{9.27 \cdot 10^{-23}}{1.38 \cdot 10^{-23}} = 6.7$ K.

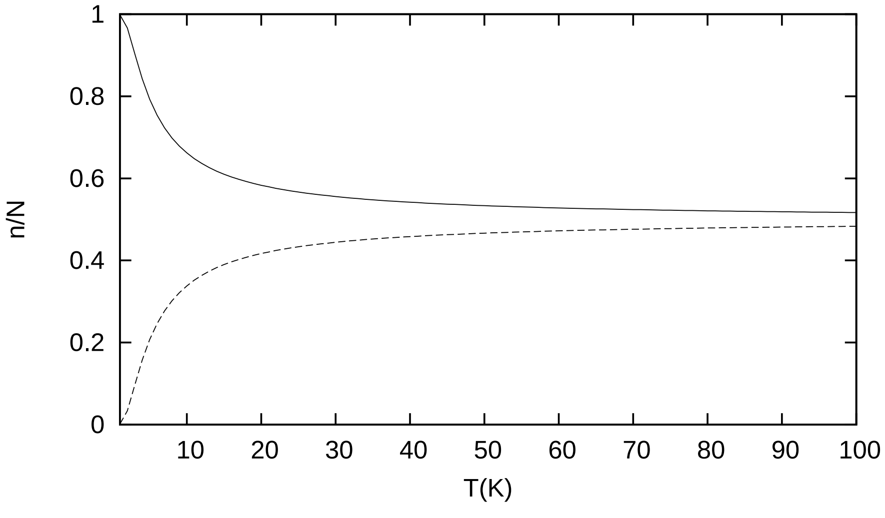

Figure 2: $\frac{n_0}{N}$ and $\frac{n_1}{N}$ for $H = 10$ Tesla

c) The average energy per electron as a consequence of the spins in the magnetic field is

$$< \epsilon >= \frac{1}{N}\sum_i \epsilon_i n_i = \frac{1}{N}\left(\epsilon_0 n_0 + \epsilon_1 n_1\right) = \frac{1}{N}\left(0 \cdot n_0 + \mu_B H N\frac{\exp\left(-\frac{\mu_B H}{kT}\right)}{1 + \exp\left(-\frac{\mu_B H}{kT}\right)}\right)$$

Actually we have to shift this result over $-\frac{1}{2}\mu_B H$ to go back to the original energy scale, so we find

$$< \epsilon > -\frac{1}{2}\mu_B H = \mu_B H \frac{\exp\left(-\frac{\mu_B H}{kT}\right)}{1+\exp\left(-\frac{\mu_B H}{kT}\right)} - \frac{1}{2}\mu_B H.$$

The plot of $< \epsilon > (T)$ is the same as the lowest line in figure 2, even though the vertical axis is

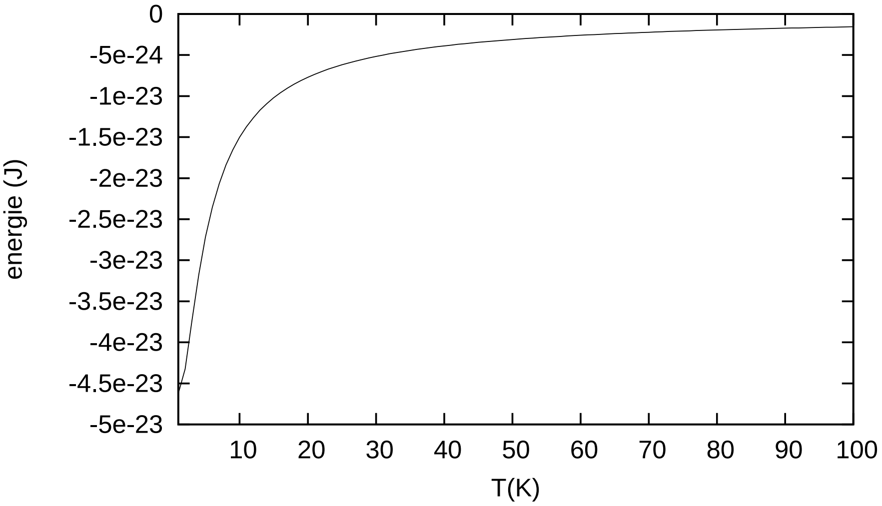

Figure 3: The average energy $\epsilon(T)$ per electron for $H = 10$ Tesla

multiplied by $\mu_B H$ and shifted over $-\frac{1}{2}\mu_B H$. The effect of the magnetic field is no longer noticeable for $T \to \infty$, since then $< \epsilon > \to 0$

Exercise 25

a) For a perfect atomic gas

$$H = \frac{5}{2}nRT, \quad \text{so} \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{5}{2}nR, \quad \text{so} \quad c_P = \frac{5}{2}R = 20.79 \text{ J/molK}.$$

Therefore $A = 20.79$ J/molK and $B = C = 0$.

b) At $T = T_{fus}$ the melt and the solid phase are in equilibrium and thus, at constant T and P, $\Delta_{fus}G = G_l - G_s = 0$, or $\Delta_{fus}H - T_{fus}\Delta_{fus}S = 0$, whereas $\Delta_{fus}H \neq 0$ and $\Delta_{fus}S \neq 0$.
For a pure substance the chemical potential is equal to the molar Gibbs free energy, so $\Delta_{fus}\mu = \Delta_{fus}G_m = \Delta_{fus}G/n = 0$.
The Helmholtz free energy, $A \equiv U - TS$, is in equilibrium only constant during the transition if T and V are constant (see Study Guide p.11). Moreover, there is also a chemical potential belonging to the Helmholtz free energy, namely $\mu = \left(\frac{\partial A}{\partial n}\right)_{V,T}$, which of course has a different value than the chemical potential $\mu = \left(\frac{\partial G}{\partial n}\right)_{P,T}$, that belongs to G.
The answers are therefore

- the entropy: no,
- the chemical potential (at constant T and P): yes,
- the enthalpy: no,

  - the Gibbs free energy: yes,
  - the Helmholtz free energy: no.

c) At $T = T_{vap}$ the melt and the vapour phase are in equilibrium and therefore

$$\Delta_{vap}G = G_g - G_l = 0, \quad \text{or} \quad \Delta_{vap}H - T_{vap}\Delta_{vap}S = 0,$$

such that

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T_{vap}} = \frac{98.01 \cdot 10^3}{1156} = 84.78 \text{ J/molK}.$$

d) The general expression for the temperature dependence of C_p is

$$S(T) = S(0) + \int_0^{T_{fus}} \frac{C_P(s)}{T}\mathrm{d}T + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_P(l)}{T}\mathrm{d}T + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_{vap}}^{T} \frac{C_P(g)}{T}\mathrm{d}T.$$

At the lowest temperatures the temperature dependence given in the exercise no longer holds, so we integrate from $T = 10\ K$ and neglect the small contribution at the lowest temperatures. For the molar heat capacity at 1000 K, which is below the boiling point, this results in ($S(0) = 0$)

$$S(T) = 0 + \int_{10}^{T_{fus}} \frac{c_P(s)}{T}\mathrm{d}T + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{1000} \frac{c_P(l)}{T}\mathrm{d}T.$$

Substituting the temperature dependence of the heat capacity results in

$$S(T) = \int_{10}^{T_{fus}} \left(\frac{A_s}{T} + B_s + C_sT\right)\mathrm{d}T + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{1000} \left(\frac{A_l}{T} + B_l + C_lT\right)\mathrm{d}T,$$

or

$$S(T) = \left[A_s \ln T + B_sT + \frac{1}{2}C_sT^2\right]_{10}^{T_{fus}} + \frac{\Delta_{fus}H}{T_{fus}} + \left[A_l \ln T + B_lT + \frac{1}{2}C_lT^2\right]_{T_{fus}}^{1000}.$$

Finally, filling in all values from the tables of the exercise results in

$$S(T = 1000 \text{ K}) = 208.65 + 7.0108 + 31.147 = 246.8 \text{ J/molK}.$$