Exercise Classes 7 Physical Chemistry 1 2021/2022

Exercise 22

Consider the Boltzmann definition of entropy for n mol of a perfect mono-atomic gas that expands isothermally from a volume V_1 to a volume $V_2 = 2V_1$.

a) First calculate the entropy change ΔS of the perfect gas for this process with the classical definition of entropy $\mathrm{d}S = \frac{\mathrm{d}Q_{rev}}{T}$.

b) Interpret the result from the previous part in terms of the Boltzmann definition of entropy.

Exercise 23

Given is a polypeptide with n amino acids.
We estimate the conformational entropy of a completely unfolded polypeptide compared to that in completely folded state. We assume that the difference is only determined by the difference in torsional degrees of freedom.
In unfolded state the peptide groups can rotate around the N-C$_\alpha$ and the C$_\alpha$-CO bond axes, namely over the two angles ϕ and ψ, respectively. These rotations each have three positions in which the torsion energy is minimal, therefore these three torsion angles occur often. For the conformations of the polypeptide molecule we limit ourselves to those torsion positions (see figure 1).

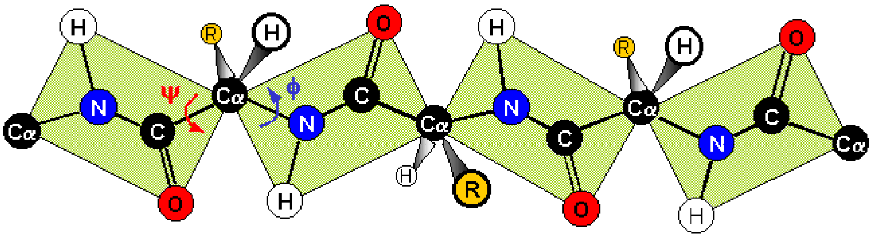

Figure 1: Completely unfolded polypeptide chain. The torsion angles ϕ and ψ each have 3 preferred states.

In the folded state there is one torsion position for both ϕ and ψ.

a) Determine the number of possible conformations N of the polypeptide molecule in the unfolded state.

b) Use the Boltmann definition of the entropy to calculate the molar entropy difference ΔS between all possible unfolded states on one hand and the completely folded state on the other hand for a polypeptide with $n = 100$ amino acids.

c) Make a similar estimation of the entropy as a consequence of the torsion freedom in an ethane molecule, again assuming that three torsion positions can be occupied.

d) How can you reconcile the results of parts b) and c)?

Exercise 24

We determine the occupation of two electron spin states in a magnetic field H using the Boltzmann distribution. In the presence of a magnetic field the otherwise degenerate levels ($\epsilon = 0$) split up into two levels with energies $\epsilon_0 = -\frac{1}{2}\mu_B H$ and $\epsilon_1 = +\frac{1}{2}\mu_B H$, in which $\mu_B = \frac{e\hbar}{2m_e} = 9.27 \cdot 10^{-24}$ J/Tesla is the so-called Bohr magneton. We only take into account the electron spin levels since we can consider them to a good approximation as independent of all other energy states.
We set the lowest level of our energy scale to 0.

a) Determine the partition function q.

b) Determine the distribution of N electrons over the two energy levels as a function of the temperature and make a scetch of that temperature dependent distribution for a magnetic field strength of $H = 10$ Tesla by plotting n_i/N versus T. Also determine the temperature and the occupations in case the thermal energy, kT, is equal to the magnetic energy.

c) Determine the average energy per electron as a function of the temperature and make a scetch of this energy vs. temperature for a magnetic field of $H = 10$ Tesla. Verify for which temperature the influence of the magnetic field on the average energy disappears.

Exercise 25

Consider a system consisting of 1 mol sodium, Na. In the table below a number of thermodynamic parameters is given.

	T_{fus}	$\Delta_{fus}H$	T_{vap}	$\Delta_{vap}H$
Na	371.0 K	2.601 kJ/mol	1156 K	98.01 kJ/mol

The heat capacity for all phases is given by (T is the temperature in K)

$$c_P(\text{J/molK}) = A + BT + CT^2,$$

in which the parameters A, B and C, for temperatures $10\ K \leq T \leq 1500\ K$, in the three phases s(olid), l(iquid) and g(as) are given in the table below

Na	A(J/molK)	B(J/molK^2)	C(J/molK^3)
s	72.6	$-9.49 \cdot 10^{-3}$	$-731 \cdot 10^{-6}$
l	40.3	$-28.2 \cdot 10^{-3}$	$20.7 \cdot 10^{-6}$
g	20.8	$-0.277 \cdot 10^{-3}$	$-0.392 \cdot 10^{-6}$

a) At very high temperature the system behaves like a perfect gas.
What are the values of A, B and C in that case?

b) Which of the following quantities have the same value for both phases (melt and solid) at constant pressure, at $T = T_{fus}$, where the melt and the solid are in equilibrium?

- the entropy,
- the chemical potential,
- the enthalpy,
- the Gibbs free energy,
- the Helmholtz free energy.

c) Calculate the entropy change $\Delta_{vap}S$ at the evaporation temperature T_{vap}.

d) Calculate the entropy of this system at 1000 K; you can neglect the contributions for $T < 10\ K$.