Tutorials 7 Thermodynamics 2, 2023/2024

Exercise 26

Calculate the ionic strength of a solution which consists of 0.20 mol/kg KCl and 0.10 mol/kg $FeCl_3$.

Exercise 27

We determine the change in solubility of the poorly soluble salt AgCl in water at 298.15 K ($s = 1.274 \cdot 10^{-5}$ mol/kg) when we increase the ionic strength by adding 0.00200 mol/kg K_2SO_4.

a) Calculate the equilibrium constant for dissolving AgCl in a saturated solustion in the absence of K_2SO_4 using the Debye-Hückel limiting law.

b) Calculate the ionic strength of the solution with K_2SO_4 but without AgCl.

c) Calculate the mean activity coefficient of the Ag^+ and Cl^- ions in the K_2SO_4-solution using the Debye-Hückel limiting law and the result of b), i.e. by neglecting the ionic strength of the AgCl in the solution.

d) Calculate the solubility of AgCl in the K_2SO_4-solution with the result of c) and a).

e) In part b) the ionic strength calculation only included the ions of K_2SO_4. This is a reasonable aproximation since AgCl is poorly soluble compared to K_2SO_4. Determine the solubility of AgCl in the solution with K_2SO_4 if we include the result of d) in the calculation of the ionic strength of the (whole) solution (i.e. use the solubility found in d) to recalculate the ionic strength and with that result the solubility).

Exercise 28

Show that the solubility s of a poorly soluble monovalent (1:1) salt (in water at 298.15 K) in terms of the solubility constant K_s equals

$$s = \sqrt{K_s} \exp\left(1.172\sqrt{\frac{s}{b^{\ominus}}}\right) b^{\ominus}.$$

Hint: translate the poor solubility into a mean activity coefficient which can be approximated by the Debye-Hückel limiting law.

Exercise 29

A certain molecule has two energy states, the ground state and an excited state at 540 cm^{-1}.
At what temperature will 10 % of the molecules be in the excited state?

Exercise 30

We will use the Boltzmann distribution to determine the occupancy of two spin states of electrons in a magnetic field B. In zero magnetic field the spin states are degenerate and have therefore equal energy. When a magnetic field is applied the degenerate spin states, with energy ϵ, split up into two states with energies $\epsilon_0 = -\frac{1}{2}\mu_B B$ and $\epsilon_1 = +\frac{1}{2}\mu_B B$, 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 states of the electrons since we can consider them to be independent of the other energy states. We furthermore set our state with the lowest energy to 0.

a) Determine the partition function q.

b) Determine the distribution of N electrons over the two energy states as a function of the temperature. Plot this distribution for a magnetic field of $B = 10$ Tesla and determine the occupancy if the thermal energy (kT) is equal to the magnetic energy.

c) Determine the average energy per electron as a function of temperature and plot this for a magnetic field of $B = 10$ Tesla. At what temperature does the influence of the magnetic field on the average energy disappear?

d) The system is placed in an Electron Spin Resonance (ESR) machine at a temperature of $\beta = 1/kT$. The distribution over the two energy states is inverted by applying a so-called $180°$ pulse. Determine the temperature of the system and interpret the result.