5 Advanced Physical Chemistry – Exercizes

5.1 How does a Boltzmann distribution behave in the limit of T = 0 K and of infinite temperature? Derive the Taylor series of the Boltzmann distribution at high temperatures.

5.2 The energies of the ground state and of the first excited state of a system differ by 300 cm^{-1}. What is the temperature, if the population of the excited state amounts to a) 50%, b) 1% of the population of the ground state?

5.3 The four lowermost electronic energy levels of titanium atoms are: $^3F_2$ (0 cm^{-1}), $^3F_3$ (170 cm^{-1}), $^3F_4$ (387 cm^{-1}) und $^5F_1$ (6557 cm^{-1}). They are $(2J+1)$-fold degenerate.

a) Calculate the population probabilities of these levels at the boiling point of titanium, 3287 °C.
b) By irradiation with a tuned laser, the niveau $^5F_1$ is filled up until it has the same population as the $^3F_2$ niveau. To which temperature does this state correspond?

5.4 Langmuir's equation describes the adsorption of a gas on a solid surface, making the following assumptions:

- The surface has a fixed number of adsorption sites. Only there molecules can be adsorbed (1 per site). Only monolayer adsorption is allowed.
- The zero of the energy scale is the ground state of the not adsorbed molecules.
- The ground state of the adsorbed molecules has the same energy $-u_0$ for all adsorption sites.
- The adsorbed molecules can vibrate in all three spatial directions; the associated molecular partition funtions are q_x, q_y, and q_z.
- There is no lateral interaction between adsorbed molecules.

a) Derive the partition function of an adsorption layer consisting of N molecules on N adsorption sites.
b) Derive the partition function of an adsorption layer consisting of N molecules on M adsorption sites ($M \geq N$).
c) Calculate the chemical potential of the adsorbed molecules.
d) Assume that the adsorption layer is in equilibrium with an ideal gas, and derive Langmuir's equation. What do you obtain for the adsorption constant?

5.5 Apply the Boltzmann distribution to the energies of gas molecules in a gravitational field.

a) Derive the so-called barometric law for the case of a gravitation field of constant strength.
b) Calculate the relative particle densities, $N(h)/N(0)$, for N_2 and O_2 at an altitude above sea level of h = 8 km. How does the N_2/O_2 ratio vary in comparison with the situation at ground level? Does the result agree with reality?
c) Calculate the gravitation potential at 8 km, using the real gravitation law $V(r) = -GMm/r$ (G: gravitation constant). Discuss the resulting Boltzmann distribution in the limit $r \to \infty$.