TKJ4215 Statistisk termodynamikk i kjemi og biologi
Eksamen 26.05.2012, 09.00-13.00

Norges Teknisk-Naturvitenskapelige Universitet
Hjelpemiddelkode A. (Alle trykte og håndskrevne hjelpemidler tillatt. Alle kalkulatorer tillatt.)
Kontaktperson under eksamen: Prof. Per-Olof Åstrand, Institutt for Kjemi, mobil: 9346 3033
NB: Oppgavene teller ikke like mye. Totalt er 100 poeng fordelt på tre oppgaver. Se parentes etter oppgavenummer for antall poeng per deloppgave.

Exercise 1 (10,10,10,10)

a) How is an *ensemble* defined in statistical thermodynamics? Discuss briefly the differences between the *microcanonical*, *canonical* and *isobaric-isothermal* ensembles. Which are the variables, fundamental function and extremum principle for each ensemble, respectively? Which ensembles are preferred experimentally (motivate the answer)?

b) For which ensemble is the Boltzmann distribution,

$$p_j = \frac{g_j e^{-E_j/k_B T}}{Q} \tag{1}$$

derived? What is g_j (we have also used the notation W_j) in eq. (1)? How is Q defined? What does the magnitude of Q tell us?

c) Assume that we have three molecules, $N = 3$, and also assume that only the two lowest molecular states, $\varepsilon_0 = \varepsilon$ and $\varepsilon_1 = 2\varepsilon$, can be occupied. What is the probability for that the total energy, E, is 5ε? The temperature, $T = 300$ K and $\varepsilon = 10$ kJ/mol.

d) The equilibrium constant, K,

$$K = \frac{x_1}{x_2}$$

is investigated. Show that it can be written both in terms of the energy difference, $\Delta E = E_1 - E_2$, as

$$K = Ae^{-\Delta E/k_B T}$$

and in terms of the Helmholtz free energy difference, $\Delta F = F_1 - F_2$, as

$$K = e^{-\Delta F/k_B T}$$

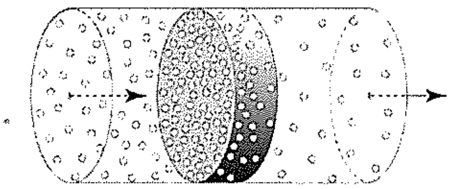
Use eq. (1) as a starting point. Define A in terms of properties used in eq. (1).

Exercise 2 (10,10,15)

a) When studying transport processes, we often use the approximation of *steady-state.* Explain what we mean by a system being in steady-state. How would you in a few sentences define what a *flux of particles* is? What is the distinction between a system being in steady-state or being at equilibrium?

b) Assume that we have a two-phase system and we add a solute, s, that may partition between the two phases to reach equilibrium. What is the definition of the partition coefficent in terms of the molar fractions, x, of the solute in the two phases? What is the condition for equilibrium expressed in terms of chemical potentials? Is the partitioning of the solute between the two phases an entropy-driven or an energy-driven process (motivate the answer)?

c) Particles flow from a reservoir to the left with a concentration, c_1, through a membrane, and leaves the system to the right with an imposed concentration, c_2 (see figure). Assuming steady-state, draw the concentration profile, $c(l)$, where l is the length of the tube (from left to right). Explain each part of the graph with a few sentences.



Exercise 3 (10,15)

Regard a lattice model of an alloy with two components A and B (e.g Cu and Zn), where one atom occupies a lattice point. Assume that each atom has a spin, s_i, with two possible values, $\frac{1}{2}$ or $-\frac{1}{2}$. The interaction energy, V, between the spins and an external magnetic field, H, is given as

$$V = -\mu_B \mu_0 H \sum_i^N s_i \tag{2}$$

where μ_B and μ_0 are constants (with positive values). Including only nearest-neighbour interactions (assume a cubic lattice with $z = 6$), the spin-spin interaction energy is given as

$$V_{ij} = -J s_i s_j$$

where J is a spin-spin coupling constant (here we assume that J has a *negative* value).

a) Extend the fundamental equation for the internal energy, dU, with the interaction between the spins and the external magnetic field. Which is the *intensive* and *extensive* variable, respectively, in eq. (2)? Within the canonical ensemble, give the Maxwell relations including the magnetic field, H.

b) Regard two limiting cases: i) all the spins are aligned by the external magnetic field; ii) completely random values of the spins, $\frac{1}{2}$ or $-\frac{1}{2}$, without an external magnetic field. Derive an equation for the difference in Helmholtz free energy, ΔF, between the two cases. Discuss and show how a phase transition between the two cases can be induced by modifying the external conditions.