TKJ4215 Statistisk termodynamikk i kjemi og biologi
Eksamen 19.05.2014, 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 fire oppgaver. Se parentes etter oppgavenummer for antall poeng per deloppgave.

Exercise 1 (15, 15, 10)

a) Self-assembly is used in nanoscience to construct devices on a molecular scale. Here we use a surface as a carrier material, and we have two types of molecules A and B with $N_A = N_B = 20$. The A molecules bind favourably to the u sites with an interaction energy, w_{Au}, and the B molecules bind favourably to the v sites with an interaction energy, w_{Bv}, respectively. For simplicity we can set $w_{Av} = w_{Bu} = 0$. The molecules also interact with each other, but we assume that $w_{AA} = w_{BB} = w_{AB}$. Give an expression for Helmholtz free energy, F, for a perfect match of the A and B molecules on the surface, i.e. that all the A molecules bind to u sites and all the B molecules bind to v sites.

u	v	u	v	u	v	u	v
v	u	v	u	v	u	v	u
u	v	u	v	u	v	u	v
v	u	v	u	v	u	v	u
u	v	u	v	u	v	u	v

b) Assume that we have a mismatch so that one of the central (i.e. with 4 neighbours) A molecules and one of the central B molecules have swapped positions as compared to a). Derive an expression for the difference in Helmholtz free energy as compared to the case in a)

c) Here, we will discuss the effects of the size of the system. If $N_A = N_B$ is increased, will the probability for a mismatch, p_b, increase or decrease as compared to the probability for the perfect match, p_a. Give an expression for p_b/p_a.

Exercise 2 (15)

In the course, we talk about *driving forces*. What is a *driving force*? Explain briefly the relation between a driving force and temperature, pressure, and chemical potential, respectively. This exercise is easiest to explain in the microcanonical ensemble. What is an ensemble, and in particular what is the microcanonical ensemble?

Exercise 3 (15)

We will try to mix two liquids A and B. In terms of the Helmholtz free energy, what is the distinction between a mixture and a two-phase system? For a two-phase system, briefly explain (not derive) how the composition of the two phases and the relative amount of each phase can be obtained, respectively. What is the definition of the critical temperature for a two-phase system?

Exercise 4 (15, 15)

a) We will consider a rubber band, with a retracive force, f, given as

$$f = kT(L - L_0)$$

where k is a constant, L is the length of the rubber band and L_0 is its equilibrium length. Derive expressions for

$$\left(\frac{\partial S}{\partial L}\right)_{T,p} \quad \text{and} \quad \left(\frac{\partial H}{\partial L}\right)_{T,p}$$

b) If we adiabatically stretch the rubber band from L_0 to L_1, explain why

$$dU = fdL$$

assuming also that the volume, V, does not change. The temperature will change from T_0 to T_1, and express this temperature change in terms of the heat capacity C_V, k, L_1 and L_0.