

# TKJ4215 Statistisk termodynamikk i kjemi og biologi

## Eksamen 31.05.2013, 09.00-13.00

Norges Teknisk-Naturvitenskapelige Universitet

Hjelpemiddelkode A. (Alle trykte og håndskrevne hjelpemidler tillatt. Alle kalkulatorer tillatt.)

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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, 10)

a) For calculating the Helmholtz free energy,  $F$ , we use either  $F = U - TS$  or  $F = -k_B T \ln Q$ . Which are the properties and constants entering the two equations? Briefly explain how to calculate  $F$  for four model systems: i) the free energy of a single molecule; ii) a lattice model for a set of  $N$  interacting molecules described with an interaction energy,  $w_{AB}$ , iii) a system with  $m$  energy levels, each level with an energy  $\epsilon_j$ , iv) an ideal gas.

b) Given that you know  $F$  in terms of  $F = -k_B T \ln Q$ , explain how you would calculate the pressure,  $p$ , and the chemical potential,  $\mu$ . What would be the approach to calculate  $U$  in the canonical ensemble?

### Exercise 2 (10, 5, 5)

a) In a chemical reaction, what is the transition state and the activation energy? What is the fundamental concept in catalysis? In heterogeneous catalysis, explain Sabatier's principle and what a volcano curve is, respectively.

b) As an example, we take the reaction for dissociation of methane,



and the same reaction for deuterated methane,



Which reaction is faster? Motivate the answer.

c) Your fellow organic chemist would like to chlorinate butane,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$ , but he/she is uncertain about if the result will be 1-chlorobutane,  $\text{CH}_2\text{Cl-CH}_2\text{-CH}_2\text{-CH}_3$ , and/or 2-chlorobutane,  $\text{CH}_3\text{-CHCl-CH}_2\text{-CH}_3$ . Based on the discussion in b), advise on a strategy to find out what the product is.

### Exercise 3 (20, 20)

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  $B$  that we expect to assemble on the surface according to the pattern in the figure, i.e. with only  $A - B$  interactions.

	A	B	A	B	A	B	A	B
	B	A	B	A	B	A	B	A
	A	B	A	B	A	B	A	B
	B	A	B	A	B	A	B	A
	A	B	A	B	A	B	A	B

We have  $N_A = N_B$  molecules which can be assumed to be a large number. The temperature is 300 K. Calculate the free energy difference,  $\Delta F$ , between the pattern in the figure and a random distribution of the molecules on the surface in terms of the interaction energies. We use  $w_{AA}$ ,  $w_{BB}$  and  $w_{AB}$  for the intermolecular interactions and  $w_{As}$  and  $w_{Bs}$  for the molecule-surface interactions. Is it important in this task to assume that we have a large number of molecules? Motivate the answer.

b) The Boltzmann distribution may be written as

$$p_j = \frac{g_j e^{-\beta E_j}}{Q}$$

where  $g_j$  is the degeneracy (multiplicity) of energy level  $j$ . Show by using this equation as a starting point that the ratio between the probabilities to be at two energy levels can be given in terms of  $\Delta F$  as

$$\frac{p_j}{p_i} = e^{-\beta \Delta F}$$

What is the condition in terms of the interaction energies to get a ratio larger than 1000/1 between the correct assembly (in the figure) and a random configuration? Does the result depend on the number of molecules? Motivate the answer. Here we can assume that  $w_{AA} = w_{BB}$ . This condition may be difficult to achieve for some systems, so can you suggest some approaches to improve the preference for the correct assembly?

### Exercise 4 (15)

a) What is the most important difference between a lattice model for a regular solution of molecules (with about equal size) and a lattice model for a polymer solution? Why do we use volume fractions instead of mole fractions for polymer solutions? Let us next regard a solution between a polymer  $A$  and a molecule  $B$ , where the volume fraction of the molecule  $B$  is 99%. How will the vapour pressure of the molecules  $B$  be affected by i) the length of the polymer  $A$ , and ii) the interaction energies  $w_{AA}$ ,  $w_{BB}$  and  $w_{AB}$ , respectively? Explain why and discuss the relative importance of the contributions at the given volume fraction. Finally, what would you regard as an *ideal polymer solution* in comparison to a *regular polymer solution*?