CHEM-E6105 Thermodynamics of solutions (5 cr)

Examination February 23, 2021, 9:00-13:00 Responsible teacher: prof. Daniel Lindberg All five questions must be replied and all will be marked.

Return the answers in the return box in MyCourses latest at 13:00. It is not possible to return after that time. Remember to submit the answers. Answers can be written directly in this paper or in a separate document. Scanned documents or pictures are accepted if the quality is high enough to be easily read. All relevant calculation steps must be included in the responses. An equation sheet from previous exams is provided at the end of the document. All questions give a maximum 5 points each, maximum score is 30 points.

Responsible teacher: Daniel Lindberg (Daniel.k.lindberg@aalto.fi)

Gas constant R = 8.314 J / (mol K)

- 1. Explain shortly following terms and their importance.
 - a) Standard state
 - b) Activity coefficient
 - c) Gibbs-Duhem equation
 - d) Ideal solution
 - e) Regular solution
- 2. The Margules equations for a binary A-B regular solution is given by the following equations

 $ln \gamma(A) = \Omega^* x(B)^2$ $ln \gamma(B) = \Omega^* x(A)^2$

Derive the function for the Gibbs energy of mixing to form 1 mol of a nonideal, regular solution of A and B.

 Copper and gold form a complete solid solution at temperatures between 410 °C and 889 °C, and at 700 °C, the excess molar gibbs energy of mixing is given by

 $g^E = -30000 \cdot x(Au) \cdot x(Cu) J.$

The vapour pressure (atm) of pure copper and pure gold, respectively, is given by

$$\label{eq:rescaled} \begin{split} ln(P_{Cu}) &= -40920/T - 0.86*ln(T) + 21.67\\ ln(P_{Au}) &= -45650/T - 0.306*ln(T) + 10.81\\ where \ T \ is \ temperature \ [K]. \end{split}$$

What is the vapour pressure at 700 °C of copper and gold over copper-gold alloy which contains 70 at% (mol %) of copper? Gas phase can be assumed ideal.

4. The phase diagram of Au-Si (gold-silicon) is shown in the figure below. The system is a simple eutectic system, with no solid solubility, and no intermediate phases. The stable phases are solid gold, solid silicon and a binary liquid phase. For the composition x(Si)=0.9, the two phase equilibria between the liquid phase and solid silicon occurs between 636 and 1630 K. The composition of the liquid phase in equilibrium with solid silicon was measured between 700 K and 1500 K for every 200 K, and is given in the table below. The molar Gibbs energy of pure solid and liquid Au and Si is also known, and given in the table. The symbols in the phase diagram are as follows: Filled circles: composition of liquid; Empty circle: bulk composition; dotted lines: tie lines.

Based on these data, calculate the activity and activity coefficient of Si in the liquid phase, for the liquid phase in equilibrium with solid silicon at 700, 900, 1100, 1300, and 1500 K.

Т/К	x(Si) of liquid phase in equilibrium with solid Si	G _m (solid Si) / (J/mol)	G _m (liquid Si) / (J/mol)	G _m (solid Au) / (J/mol)	G _m (liquid Au) / (J/mol)
700	0.2142	-17483.8	12143.1	-38301.3	-32319.4
900	0.2812	-25784.7	-2176.85	-52975.8	-48871.1
1100	0.3715	-35242.3	-17651.2	-68901.9	-66674.4
1300	0.5076	-45677.7	-34097.5	-85896.7	-85546.3
1500	0.7154	-56966.0	-51383.1	-103870.0	-105396.8



Au - Si

5. The excess Gibbs energies of solutions of methylcyclohexane (MCH) and tetrahydrofuran (THF) at 303.15 K were found to fit the expression

 $G^{E} = RTx(1-x)(0.4857-0.1077(2x-1)+0.0191(2x-1)^{2}) (J/mol)$

where x is the mole fration of the methylcyclohexane. Calculate the Gibbs energy of mixing when a mixture of 1.00 mol of MCH and 3.00 mol of THF is prepared.

NECESSARY FORMULAS ARE ON THE NEXT TWO PAGES

Formula Sheet for CHEM-E6100 and CHEM-E6105 exam

1. Z = PV/nRT

2. $\Delta U = Q - W$ 3. H = U + PV

4.
$$C = dQ/dT$$

5. $G = H - T \cdot S$
6. $\Delta G = V\Delta P - S\Delta T$
7. $\Delta U = T\Delta S - P\Delta V$
8. $\Delta H = V\Delta P + T\Delta S$
9. $\Delta A = -P\Delta V - S\Delta T$
10. $G(T) = [H^{\circ}(298K) + \int_{298K}^{T} c_{p} \cdot dT] - T \cdot [S^{\circ}(298K) + \int_{298K}^{T} c_{p} \cdot dT]$
11. $c_{p} = a + bT + cT^{-2} + dT^{2}$
12. $H(T) = [H^{\circ}(298K) + [aT + \frac{1}{2}bT^{2} - cT^{-1} + \frac{1}{3}dT^{3}]^{T}_{298K}$
13. $S(T) = \int \frac{c_{p}}{T} \cdot dT$
14. $\Delta S = \frac{\Delta H}{T}(equilibrium)$
15. $S(T) = S^{\circ}(298K) + [a\ln(T) + bT - \frac{1}{2}cT^{-2} + \frac{1}{2}dT^{2}]^{T}_{298K}$
17. $T \cdot S(T) = T \cdot S^{\circ}(298K) + [T \cdot a\ln(T) + bT^{2} - \frac{1}{2}cT^{-1} + \frac{1}{2}dT^{3}]^{T}_{298K}$
18. $\Delta H_{R}(T) = \sum v \cdot H_{i}(T)_{products} - \sum v \cdot H_{i}(T)_{reactants}$
19. $\Delta G = -RT \cdot \ln(K)$
20. $K = \frac{\Pi a^{v}(products)}{\Pi a^{v}(reactants)}$
21. $\Delta G_{R}(T) = \sum v \cdot G_{i}(T)_{products} - \sum v \cdot G_{i}(T)_{reactants}$
22. $\xi = \frac{n_{i} - n_{i,0}}{v_{i}}$

NOTE: In formulas 12, 16 and 17 the]^{*T*}_{298 *K*} means temperature range 298 K – T K

Additional Formulas CHEM-E6105 exam

Mixing functions

 ${}^{M}Z_{i} \equiv Z_{i} - {}^{\circ}Z_{i}$ Z=general thermodynamic property, e.g. G, H

$$\begin{split} G_i &= {}^\circ G_i + RT \, ln \, a_i \\ \mu_i &= {}^\circ \mu_i + RT \, ln \, a_i \\ G_i &= {}^\circ G_i + RT \, ln \, x_i + RT \, ln \, \gamma_i, \qquad \text{where} \, a_i \equiv \gamma_i \times x_i \\ G &= \Sigma \, x_i G_i = \Sigma \, x_i {}^\circ G_i + RT \, \Sigma \, x_i \, ln \, x_i + RT \, \Sigma \, x_i \, ln \, \gamma_i \\ {}^{Ex}G &= RT \, \Sigma x_i \, ln \, \gamma_i \end{split}$$

 $\mu_i = {}^\circ\!\mu_i(1) + RT \ln a_i(1) = {}^\circ\!\mu_i(2) + RT \ln a_i(2) = \mu_i \quad \text{for standard state 1 and 2}$

$\Sigma_k n_k d\mu_k = 0$	Gibbs-Duhem equation		
$p_A = x_A \cdot p^*_A$	Raoult's law		
$p_B = x_B \cdot K_B$	Henry's law		