

## CHEM-E6105 Thermodynamics of solutions (5 cr)

Examination

February 24, 2022, 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 6 points each, maximum score is 30 points.

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**Gas constant  $R = 8.314 \text{ J / (mol K)}$**

1. Explain shortly following terms and their importance.
  - a) Standard state
  - b) Activity coefficient
  - c) Gibbs-Duhem equation
  - d) Ideal solution
  - e) Regular solution
  - f) Associate model
  
2.  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$  form a complete solid solution at high temperatures. Enthalpy of mixing for the solid solution can be described by the following equation

$$\Delta H^{\text{mix}} = x(\text{Na}_2\text{CO}_3) \cdot x(\text{Na}_2\text{SO}_4) \cdot (2000 + 3000x(\text{Na}_2\text{SO}_4)) \text{ (J/mol)}$$

Calculate the partial molar enthalpies of mixing of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$  at  $x(\text{Na}_2\text{SO}_4)=0.2$

3. In this task, the phase equilibrium of Ag-Si system is to be calculated.

It is assumed that the liquid components Ag and Si can mix and form a homogeneous phase, whereas solid Ag and solid Si only form stoichiometric phases (Ag(s) and Si(s)).

- a) Based on the Gibbs energy functions, calculate the melting point of Ag and Si
  
- b) Calculate the liquidus lines for crystallization of Ag(s) and Si(s), and based on this, estimate the eutectic point of the system if the liquid phase behaves like a Raoultian ideal solution.

The molar Gibbs energy of solid and liquid Ag, and solid and liquid Si are given below:  
Molar Gibbs energy (units J/mol and K)

G(Ag,solid)

$$-4794.7508 + 90.0937T - 19.731744T \ln T - 0.004799048T^2 - 266520.8T^{-1}$$

G(Ag,liquid)

$$-3577.53265 + 180.81324T - 33.472T \ln T$$

G(Si,solid)

$$-8156.5395 + 137.08626 T - 22.809187 T \ln T - 0.001935343T^2 + 176496.0355T^{-1}$$

G(Si,liquid)

$$42043.4605 + 107.29397 T - 22.809187 T \ln T - 0.001935343T^2 + 176496.0355T^{-1}$$

4. Francesconi et al. (1996) studied the liquid-vapour equilibria of trichloromethane (A) and 1,2-epoxybutan (B) at several temperatures. Among their data are the following measurements of the the mole fractions of trichloromethane in the liquid phase ( $x_T$ ) and the vapour phase ( $y_T$ ) at 298.15 K as a function of pressure.

p/kPa	23.40	21.75	20.25	18.75	18.15	20.25	22.50	26.30
$x_T$	0	0.129	0.228	0.353	0.511	0.700	0.810	1
$y_T$	0	0.065	0.145	0.285	0.535	0.805	0.915	1

Calculate the activity coefficients of both trichloromethane and 1,2-epoxybutan on the basis of Raoult's law. The gas phase can be assumed to be ideal.

5. The activity coefficient of Ag in solid Ag-Au alloy has been measured by Santoso et al. ([Thermodynamic properties of Ag–Au alloys measured by a solid-state electrolyte EMF method - ScienceDirect](#)). At T=1000 K, the activity coefficient is fitted by the following equation:

$$\ln \gamma(\text{Ag}) = -1.45x(\text{Au})^2 + 0.30x(\text{Au})^3$$

Find an expression for  $\ln \gamma(\text{Au})$  as a function of composition at 1000 K.

## **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.  $G(T) = [H^\circ(298K) + \int_{298K}^T c_p \cdot dT] - T \cdot [S^\circ(298K) + \int_{298K}^T \frac{c_p}{T} \cdot dT]$
11.  $c_p = a + bT + cT^{-2} + dT^2$
12.  $H(T) = [H^\circ(298K) + \left[ aT + \frac{1}{2}bT^2 - cT^{-1} + \frac{1}{3}dT^3 \right]_{298K}^T]$
13.  $S(T) = \int \frac{c_p}{T} \cdot dT$
14.  $\Delta S = \frac{\Delta H}{T}(\text{equilibrium})$
15.  $S(T) = S^\circ(298K) + \left( \int_{298K}^T \frac{a}{T} + b + cT^{-3} + dT \right) dT$
16.  $S(T) = S^\circ(298K) + \left[ a \ln(T) + bT - \frac{1}{2}cT^{-2} + \frac{1}{2}dT^2 \right]_{298K}^T$
17.  $T \cdot S(T) = T \cdot S^\circ(298K) + \left[ T \cdot a \ln(T) + bT^2 - \frac{1}{2}cT^{-1} + \frac{1}{2}dT^3 \right]_{298K}^T$
18.  $\Delta H_R(T) = \sum \nu \cdot H_i(T)_{\text{products}} - \sum \nu \cdot H_i(T)_{\text{reactants}}$
19.  $\Delta G = -RT \cdot \ln(K)$
20.  $K = \frac{\prod a^{\nu}(\text{products})}{\prod a^{\nu}(\text{reactants})}$
21.  $\Delta G_R(T) = \sum \nu \cdot G_i(T)_{\text{products}} - \sum \nu \cdot G_i(T)_{\text{reactants}}$
22.  $\xi = \frac{n_i - n_{i,0}}{\nu_i}$

NOTE: In formulas 12, 16 and 17 the  $\int_{298K}^T$  means temperature range 298 K – T  
K

## **Additional Formulas CHEM-E6105 exam**

Mixing functions

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

$$G_i = {}^\circ G_i + RT \ln a_i$$

$$\mu_i = {}^\circ \mu_i + RT \ln a_i$$

$$G_i = {}^\circ G_i + RT \ln x_i + RT \ln \gamma_i, \quad \text{where } a_i \equiv \gamma_i x_i$$

$$G = \sum x_i G_i = \sum x_i {}^\circ G_i + RT \sum x_i \ln x_i + RT \sum x_i \ln \gamma_i$$

$$^{Ex} G = RT \sum x_i \ln \gamma_i$$

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

$$\sum_k n_k d\mu_k = 0$$

Gibbs-Duhem equation

$$p_A = x_A \cdot p_A^*$$

Raoult's law

$$p_B = x_B \cdot K_B$$

Henry's law