Additional tutorial A, Thermodynamics 2, 2023/2024

Exercise A1

The densities of aqueous solutions of $CuSO_4$ at 20 °C have been determined experimentally. The findings are listed below (weight % means the amount of gram $CuSO_4$ per 100 g solution)

conc (weight%)	ρ (gcm^{-3})
5	1.051
10	1.107
15	1.167
20	1.230

The molar mass of $CuSO_4$ is $m = 159.6$ g/mol and that of water is $m = 18$ g/mol.

a) Determine the total volume of the four solutions with 1000 g water.

b) Determine the amount of mole $n_{\mathrm{CuSO_4}}$ for the four solutions with 1000 g water.

c) Plot the volume (in cm^3) as a function of $n_{\mathrm{CuSO_4}}$.

d) A decent fit for this graph is
$V = a + bn + cn^{2.5}$ with $a = 1000.5882$ cm^3, $b = 2.159$ cm^3/mol and $c = 4.0002$ cm^3/mol$^{2.5}$.
Determine the partial molar volume of the $CuSO_4$ in the four solutions.

e) Determine the partial molar volume of the water in the four solutions.

Exercise A2

The vapour pressures of toluene and benzene at 27 °C are 100 mm Hg en 60 mm Hg respectively. Benzene and toluene form an ideal mixture; Raoult's law can therefore be used for any mixture of the two.

a) Draw the P, x-diagram at 27 °C.

b) At 27 °C 4 moles of benzene and 6 moles of toluene are mixed.
Calculate the ΔH, ΔG and ΔS of this mixing process.

c) Calculate the composition of the vapour which is in equilibrium with the liquid mixture.

Exercise A3

The equilibrium vapour pressure of acetone and chloroform at 27 °C are respectively 300 mm Hg and 200 mm Hg. Chloroform and acetone form a non-ideal mixture, which near the edges of the phase diagram follow Raoult's law for the majority component, while the minority component follws Henry's law in those regions.
The Henry-constants at 27 °C are 170 mm Hg en 166 mm Hg for acetone and chloroform respectively.

a) Sketch the P, x-diagram for mixtures of acetone en chloroform at 27 °C.

b) At 27 °C acetone and chloroform are mixed, such that 99 mol acetone and 1 mol chloroform are present in the mixture. Calculate $\Delta_{mix}G$.

c) Is it possible to calculate $\Delta_{mix}S$ and $\Delta_{mix}H$ as well with these data?

d) Determine the composition of the vapour above the mixture of part b) in terms of the mole fractions y_A and y_B.

Exercise A4

We consider non-ideal solutions. For non-ideal solutions the deviation from ideal behaviour is expressed in terms of the so-called excess-value of a quantity X:

$$X^{E(xcess)} = \Delta_{mix}X - \Delta_{mix}X^{ideal}.$$

a) Determine for a binary mixture $X^{E(xcess)}$ as far as possible for $X = G$, S and H.

Consider a binary mixture for which $G^E = gRTx(1-x)$, where g is a constant.

b) What are the units of g?

c) Determine the chemical potential of the components using the definition of μ_i.

d) Determine the activities and activity coefficients of the components.

e) Sketch the chemical potential for both components as a function of x_1.

f) Determine the entropy and enthalpy of mixing.

g) Discuss, using the result of part f), in what respect the mixture behaves as non-ideal.

Exercise A5

Calculate the freezing point of 250 cm^3 of water, in which 7.5 g sucrose is dissolved at 25 °C .
Some data: $T^*_{\mathrm{H_2O}} = 273.15$ K, $\Delta_{fus}H_{\mathrm{H_2O}} = 6.008$ kJ/mol, $M_{\mathrm{H_2O}} = 18.015$ g/mol, $\rho_{\mathrm{H_2O}} = 0.997$ g/cm^{-3} en $M_{\mathrm{sucrose}} = 342.30$ g/mol.

Exercise A6

Calculate how many grams of the following substances you need to add to lower the melting point of water by 1 °C. Use the following values:
$T^*_{\mathrm{H_2O}} = 273.15$ K, $\Delta_{fus}H_{\mathrm{H_2O}} = 6.008$ kJ/mol, $M_{\mathrm{H_2O}} = 18.015$ g/mol en $\rho_{\mathrm{H_2O}} = 0.997$ g·cm^{-3}.

a) DMSO ($(CH_3)_2SO$),

b) sucrose ($C_{12}H_{22}O_{11}$),

c) 1 M hydrochloric acid.