

## Tutorials 3 Thermodynamics 2, 2025/2026

### Exercise 10

The density of an alcohol-water mixture (50 weight percent) is  $\rho = 0.914 \text{ g cm}^{-3}$  at  $25 \text{ }^\circ\text{C}$ . The partial molar volume of water in this mixture is  $V_{water} = 17.4 \text{ cm}^3\text{mol}^{-1}$ . The molar masses of alcohol and water are  $M = 46 \text{ g/mol}$  and  $M = 18 \text{ g/mol}$  respectively. Calculate the partial molar volume of alcohol in this mixture.

### Exercise 11

Binary mixtures of *ortho*-xylene and *para*-xylene form ideal solutions. The pure vapor pressures at  $90 \text{ }^\circ\text{C}$  are  $18.5 \text{ kPa}$  and  $22.7 \text{ kPa}$ , respectively. At  $80 \text{ }^\circ\text{C}$  the enthalpy of vaporization of *o*-xylene and *p*-xylene are  $\Delta_{vap}H = 40.9 \text{ kJ/mol}$  and  $\Delta_{vap}H = 39.2 \text{ kJ/mol}$ , respectively. Assume that these enthalpies are independent of the temperature between  $70 \text{ }^\circ\text{C}$  and  $90 \text{ }^\circ\text{C}$ .

- Determine the composition of the liquid mixture that boils at a temperature of  $70 \text{ }^\circ\text{C}$  and a pressure of  $9.00 \text{ kPa}$ . Note that the above mentioned values are based on a different temperature.
- What is the composition of the vapour of the mixture.

Next we add *meta*-xylene to this mixture boiling at  $70 \text{ }^\circ\text{C}$  and  $9.00 \text{ kPa}$ . The resulting ternary mixture will still behave like an ideal solution.

The vapour pressure of pure *m*-xylene at  $70 \text{ }^\circ\text{C}$  is  $10.1 \text{ kPa}$ .

- Generalize Raoult's law for a ternary mixture.
- What is the implication of Gibbs' phase rule for the number of free variables in this ternary mixture at a given pressure and temperature.
- Determine the composition of the ternary mixture that boils at a temperature of  $70 \text{ }^\circ\text{C}$  and a pressure of  $9.5 \text{ kPa}$ .  
Determine the composition of the vapour of this mixture.  
Hint: we add *m*-xylene to the mixture of *o*-xylene and *p*-xylene with the composition found in a).

### Exercise 12

The non-ideal nature of a mixture is expressed in an excess term  $G^E$  in the Gibbs free energy. In this exercise we consider a non-ideal solution of two liquids *A* and *B* at a constant pressure *P*, which is an example of a so-called regular solution for which the excess entropy  $S^E = 0$  and the excess enthalpy  $H^E \neq 0$ . The Gibbs free energy of the mixture in the present example is given by ( $x \equiv x_A = 1 - x_B$ )

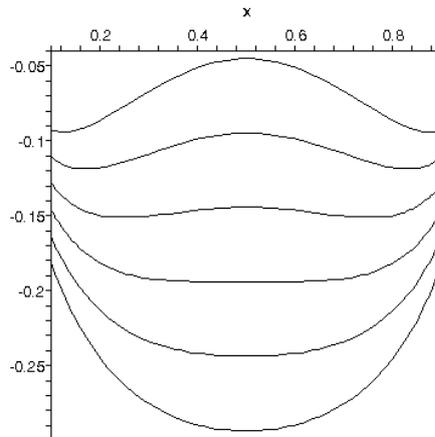
$$G = G^{ideal} + G^E = n_A \mu_A^*(l) + n_B \mu_B^*(l) + nRT [x \ln x + (1 - x) \ln(1 - x)] + n\beta RT x(1 - x),$$

in which the parameter  $\beta > 0$ . *G* as a function of the composition *x* can have either one or three extrema, depending on the value of  $\beta$  and *T*. In figure 1 you can find a plot of  $\frac{\Delta_{mix}G}{nRT}$  for different values of  $\beta$ . In lecture 4 we will show that depending on the value of  $\beta$  the excess term can lead to a phenomenon called liquid-liquid separation or oiling out.

- Which terms in the expression for *G* correspond to  $G^{ideal}$ ,  $G^E$ ,  $\Delta_{mix}G$  and  $\Delta_{mix}G^{ideal}$ ?

The chemical potential  $\mu_i$  of component *i*, which is the partial molar Gibbs free energy  $G_i$  of component *i*, is defined as

$$\mu_i \equiv G_i \equiv \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}}, \quad \text{so} \quad \mu_A = G_A = \left( \frac{\partial G}{\partial n_A} \right)_{T, P, n_B},$$



Figuur 1:  $\frac{\Delta_{mix}G}{nRT}$  for  $\beta = 1.6, 1.8, 2.0, 2.2, 2.4$  en  $2.6$

Determining  $G_A$  is a bit tedious, but the result is

$$G_A = \mu_A^*(l) + RT \ln \frac{n_A}{n_A + n_B} + RT\beta \frac{n_B^2}{(n_A + n_B)^2}.$$

In the solutions to the problem this will be shown.

b) Given this expression for  $G_A$  the partial molar Gibbs free energy  $G_B$  can now be obtained in two ways

1. by using the general expression we found in the lecture

$$G|T, P = n_A G_A + n_B G_B,$$

2. by using the symmetry of  $G$  in terms of  $n_A$  and  $n_B$ .  
Check that these two options lead to the same result.

### Exercise 13

At a partial pressure of HCl of 760 mm Hg, the HCl-gas will dissolve in benzene upto a mole fraction of 0.040.

The vapour pressure of pure benzene is 200 mm Hg.

This solution in benzene behaves like an ideal-dilute solution.

Calculate the mole fraction HCl in the solution if the total pressure of HCl-gas and benzene vapour is 760 mm Hg.