

Tutorials 3 Thermodynamics 2, 2024/2025

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 kPa and 22.7 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 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 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 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 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 ($x \equiv x_A = 1 - x_B$)

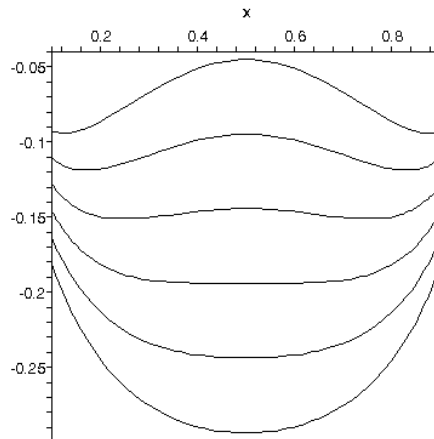
$$G = G^{ideal} + G^E = n_A \mu_A^*(l) + n_B \mu_B^*(l) + nRT [x \ln x + (1 - x) \ln(1 - x)] + n\beta RT x(1 - x),$$

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 β and T . In figure 1 you can find a plot of $\frac{\Delta_{mix}G}{nRT}$ for different values of β . In lecture 4 we will show that depending on the value of β 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 μ_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.