Tutorials 4 Thermodynamics 2, 2023/2024

Exercise 14

Results of measurements at 100 kPa on the liquid-vapour equilibrium of mixtures of oxygen and nitrogen can be found in the following table (x and y represent the liquid and vapour composition respectively).

T [K]	77.3	78	80	82	84	86	88	90.2
x (O_2) [%]	0	10	34	54	70	82	92	100
y (O_2) [%]	0	2	11	22	35	52	73	100
$P^*(O_2)$ [Torr]	154	171	225	294	377	479	601	760

a) Plot the temperature-composition diagram for the liquid and vapour in one diagram and indicate which phase can be found where. Where do both phases coexist?

b) The partial vapour pressure is described by $P_A = x_A P_A^*$ in case of an ideal solution. Deviations from ideal behavior are generally described by the activity a_A according to $P_A = a_A P_A^* = \gamma_A x_A P_A^*$, in which γ_A is the activity coefficient. Find the activity coefficient of O_2 for each of the compositions in the table. Would you, based on your findings, consider this mixture to be an ideal solution?

Exercise 15

o-xylene and *m*-xylene form an ideal solution, and their vapour pressures at 90 °C are 18.5 kPa and 21.9 kPa, respectively.

a) Determine the composition of a mixture of these two liquids, which boils at a temperature of 90 °C and a pressure of 20.2 kPa.

b) What is the composition of the vapour of this mixture?

If we add toluene to this mixture, it will still behave like an ideal solution.
The vapour pressure of pure toluene at 90 °C is 54.2 kPa.

c) Generalize Raoult's law for a ternary mixture.

d) What is the implication of Gibbs' phase rule for the number of free variables in this ternary mixture at a given pressure and temperature.

e) Determine the composition of the ternary mixture that boils at a temperature of 90 °C and a pressure of 50.0 kPa.
Determine the composition of the vapour of this mixture.
Hint: we add toluene to the mixture of *o*-xylene and *m*-xylene with the composition found in a).

Exercise 16

Mixtures of 1-Butanol and chlorobenzene form a low-boiling azeotrope. The mole fractions of 1-butanol, x in the liquid and y in the vapour, are given in the table below for various boiling temperatures and at a pressure of $P = 1.000$ atm. The boiling point of chlorobenzene at 1.000 atm is 404.86 K.

T [K]	396.57	393.94	391.60	390.15	389.03	388.66	388.57
x	0.1065	0.1700	0.2646	0.3687	0.5017	0.6091	0.7171
y	0.2859	0.3691	0.4505	0.5138	0.5840	0.6409	0.7070

a) Construct (draw) the chlorobenzene-rich part of the temperature-composition phase diagram.

b) Estimate the temperature at which a solution with a mole fraction of $x = 0.300$ starts to boil.

c) Determine the composition and relative quantities of the two phases present when a solution with an initial mole fraction of $x = 0.300$ is heated to a temperature of 393.94 K.

Exercise 17

In this exercise we consider a non-ideal solution of two liquids A and B at a constant pressure P. The non-ideal nature of this mixture is expressed in an excess term G^E in the Gibbs free energy. ($x \equiv x_A = 1 - x_B$)

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

in which $\beta > 0$. G as a function of the composition x can have either one or three extrema, depending on he value of β and T. In figure 1 you can find a plot of $\frac{\Delta_{mix}G}{nRT}$ for different values of β.

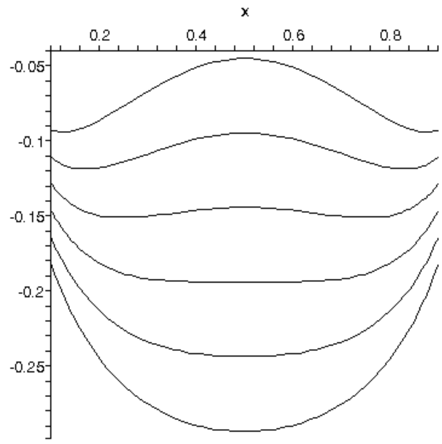

Figure 1: $\frac{\Delta_{mix}G}{nRT}$ for β =1.6, 1.8, 2.0, 2.2, 2.4 en 2.6

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

b) Determine the critical value for β, which is the value below which $\Delta_{mix}G$ has one and above which $\Delta_{mix}G$ has three extrema.
Hint: The critical value will depend on the number of inflection points the function has. You can find this number by differentiating the function twice, and setting the result equal to zero.

The above mentioned expression is a good model for the mixing behaviour of certain binary liquid mixtures. The parameter β often depends on the temperature according to (k is the Boltzmann constant).

$$\beta = \frac{b}{kT}.$$

c) What is the behaviour of such a mixture as a function of the temperature. Make a sketch of the $T - x$ phase diagram of the liquid mixture, and examine the consequences of the Gibbs phase rule for the different phases.
Hint: As a consequence of the second law of thermodynamics, a mixture will always adopt the lowest value of G at a given T, P and (overall) composition x.

d) Determine the amount of extrema for a negative value of β, and interpret the thermodynamic relevance of β, for both positive and negative values, in terms of the excess enthalpy and excess entropy of a mixing.