

## Tutorials 4 Thermodynamics 2, 2025/2026

### 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 <sub>2</sub> ) [%]	0	10	34	54	70	82	92	100
$y$ (O <sub>2</sub> ) [%]	0	2	11	22	35	52	73	100
$P^*$ (O <sub>2</sub> ) [Torr]	154	171	225	294	377	479	601	760

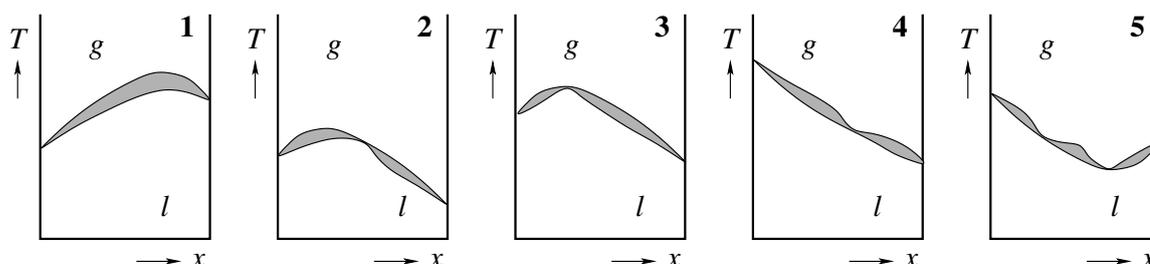
- a) Plot the temperature-composition diagram for the liquid and vapour in one diagram and indicate which phase can be found where. Where do both phases coexist?
- b) The partial vapour pressure is described by  $P_A = x_A P_A^*$  in case of an ideal solution. Deviations from ideal behavior are generally described by the activity  $a_A$  according to  $P_A = a_A P_A^* = \gamma_A x_A P_A^*$ , in which  $\gamma_A$  is the activity coefficient. Find the activity coefficient of O<sub>2</sub> for each of the compositions in the table. Would you, based on your findings, consider this mixture to be an ideal solution?

### Exercise 15

- a) (exam 2020, problem 1d)

In the figure below 5 isobaric, temperature-mol fraction equilibrium phase diagrams, labeled 1 to 5, have been drawn for a binary system. In the vapour phase the two components form an ideal mixture.

Indicate which of the diagrams is thermodynamically possible and which is not; An explanation is not needed.



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

- b) Construct (draw) the chlorobenzene-rich part of the temperature-composition phase diagram **and** hatch the two-phase region in the diagram.

- c) 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 16

In this exercise we study the solubility of a solid (solute  $B$ ) in a solvent  $A$ . With that we are studying a solution (l)-solid (s) phase diagram.

The solubility of a compound is reached when on adding an increasing amount of solute to the solution, the solute no longer dissolves. This means that solid (non-dissolved solute) is in equilibrium with the solute in the saturated solution. Thus the solubility of  $B$  in  $A$  is determined by the equilibrium between pure  $B(s)$  and  $B$  dissolved in  $A$ .

- a) Derive the following expression for the solubility of a solute  $B$  in terms of the mole fraction  $x_B$  as a function of the molar fusion enthalpy  $\Delta_{fus}H$  and the molar fusion entropy  $\Delta_{fus}S$  of the solute for an ideal solution of  $B$  in  $A$  (Assume that  $\Delta_{fus}H$  and  $\Delta_{fus}S$  are independent of the temperature).

$$\ln x_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT} = -\frac{\Delta_{fus}H_B}{RT} + \frac{\Delta_{fus}S_B}{R}.$$

Hint: A saturated solution corresponds to an equilibrium situation, so  $\mu_B(l) = \mu_B(s) = \mu_B^*(s)$ .

- b) As an example we take a compound with the mysterious name  $7\alpha MNa$ , a hormone which suppresses menopausal complaints. The solubility of  $7\alpha MNa$  in acetone is  $x_B = 0.0429$  at  $T = 318.5$  K and  $x_B = 0.0171$  at  $T = 279.3$  K. Calculate the molar fusion enthalpy and entropy of  $7\alpha MNa$ .
- c) For non-ideal solutions we need to revert to the activity in the expression for  $\mu_B(l)$ . Examine what the expression will be; use that  $a_B(s) \approx 1$ , meaning that we are still dealing with a pure solid  $B(s)$ .
- d) In a measurement, the molar fusion enthalpy and entropy of  $7\alpha MNa$  at  $T = 318.5$  K turn out to be  $\Delta_{fus}H = 18.5$  kJ/mol and  $\Delta_{fus}S = 35.0$  J/molK respectively. Calculate the activity coefficient  $\gamma_B$  at that temperature.

## Exercise 17

In this exercise we consider once more the regular solution of Exercise 12, 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. ( $x \equiv x_A = 1 - x_B$ )

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

in which  $\beta > 0$ .  $G$  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  $\beta$ .

- a) Determine the critical value for  $\beta$ , 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  $\beta$  often depends on the temperature according to ( $k$  is the Boltzmann constant).

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

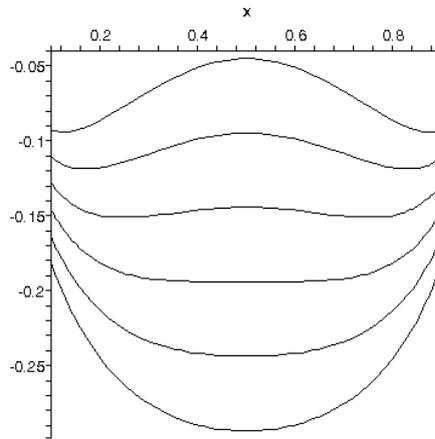


Figure 1:  $\frac{\Delta_{mix}G}{nRT}$  for  $\beta = 1.6, 1.8, 2.0, 2.2, 2.4$  en  $2.6$

- b) 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  $x$ .
- c) Determine the amount of extrema for a negative value of  $\beta$ , and interpret the thermodynamic relevance of  $\beta$ , for both positive and negative values, in terms of the excess enthalpy and excess entropy of a mixing.