# Tutorials 5 Thermodynamics 2, 2024/2025

## Exercise 18

The phase diagram of Bi and Cd is important in metallurgy. These metals are mutually insoluble (immiscible) as solids. In other words, there is no composition for the solids to form a solid solution. Such behaviour leads to a eutectic phase diagram. The general shape of the phase diagram can be approximated by the usual equation for the freezing point depression. Use the following data:
$T_{fus}$(Bi) = 544.5 K, $T_{fus}$(Cd) = 594 K, $\Delta_{fus}H$(Bi) = 10.88 kJ/mol en $\Delta_{fus}H$(Cd) = 6.07 kJ/mol.

a) Construct the phase diagram using the expression for the freezing point depression and determine the location of the eutectic point in an approximation by extrapolating both freezing point depression lines in the phase diagram and calculating the intersection point.

b) Examine the change in phases present if the liquid phase with composition $x$(Bi) = 0.70 at 550 K is slowly cooled.

c) Determine the composition as well as the relative amounts of the phases of the system for an overall composition $z$(Bi) = 0.70 at 460 K and at 375 K.

d) Make a sketch of the cooling curve for the mixture at $z$(Bi) = 0.70 in a temperature-time diagram, assuming that the system is cooled by continuously withdrawing a constant amount of heat.

## Exercise 19

Chiral molecules have two enantiomers, a left (S or L) and a right (R or D) one, which are each others mirror image. In the pharmaceutical industry and related industries, it is often essential that the final product is enantiopure. This is mostly achieved through enantioselective synthesis. If this is not possible or too expensive, crystallization can provide an alternative.
We will examine the *l-s* phase diagram for two different mixtures, *racemic conglomerates* (R- and S-enantiomers form separate crystals) and *racemic compounds*, sometimes incorrectly called racemates (R- and S- enantiomers are present in the same crystal in a 1:1 ratio). We assume that the enantiomers form an ideal solution in the liquid phase.

a) Why is it not possible to separate enantiomers using distillation?

b) Draw the *l-s* phase diagram of a racemic conglomerate as an $x, T$ diagram at constant pressure; hatch the two-phase regions and indicate melting temperatures and phases present in the various areas of the phase diagram.
Hint: look at the result of exercise 18.

In Figure 1 you can find a typical $x, T$ phase diagram for a racemic compound.

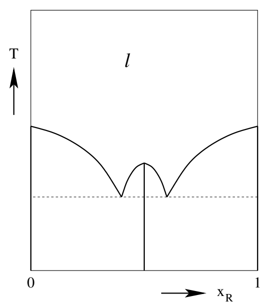


Figure 1: Phase diagram of a racemic compound.

c) Determine which phase can be found where in the diagram of Figure 1 and examine what happens if a liquid solution with an initial composition of $x_R \neq 0.5$ is cooled until it is completely solid.

d) Find the conditions (temperature and initial composition) which allow to purify a mixture of enantiomers using cooling crystallization.

# Exercise 20

(exam 2015, Problem 3)
The ($Na_2SO_4$, $H_2O$) phase diagram is drawn as a temperature-composition diagram in Figure 2 at $P = P^{\ominus}$. The composition is expressed in terms of the weight percentage $Na_2SO_4$. The phase diagram includes a stable compound as the salt hydrate $Na_2SO_4{\cdot}nH_2O$ (where $n$ is an integer number).
The horizontal line starting at P (peritecticum) runs on until 100 wt. % $Na_2SO_4$, as a phase boundary between the hatched areas above and below the line.
The point P is at (33.25 wt.% $Na_2SO_4$, 305.53 K).
The phase boundary line starting at P running upwards can be considered as a linear line described by the function
$T = 606.87 - 9.063wt$, where $wt$ is the wt.% $Na_2SO_4$ (in %) and $T$ is in Kelvin.
All two-phase regions are hatched (grey shaded) in the Figure.
The following data can be used
$T_{fus}(H_2O) = 273.15$ K.
$T_{fus}(Na_2SO_4{\cdot}nH_2O) = 305.53$ K.
$M(Na_2SO_4) = 142.04$ g/mol.
$M(H_2O) = 18.02$ g/mol.

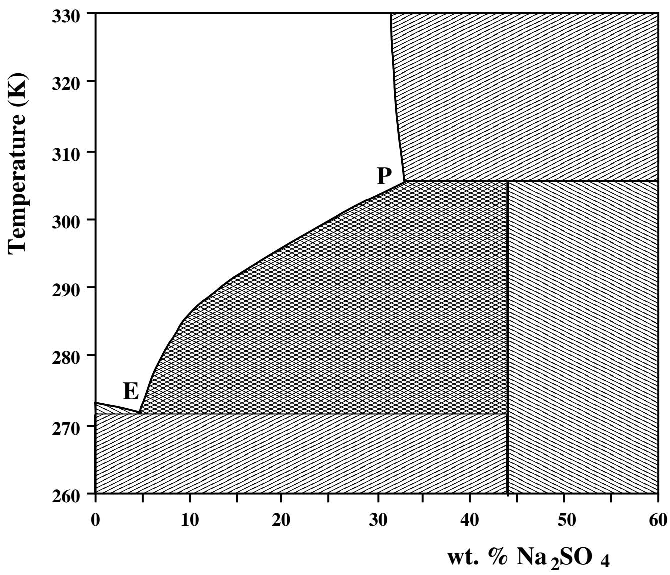


Figure 2: Phase diagram of the ($Na_2SO_4$, $H_2O$) system including its salt hydrate $Na_2SO_4 \cdot nH_2O$.

a) Determine the value of $n$ in $Na_2SO_4{\cdot}nH_2O$. Explain how you obtained the answer.

b) Redraw the phase diagram, without hatching and indicate which phases are present in the various areas of the phase diagram.

c) We gradually increase the temperature from 260 to 330 K, starting at the vertical line in the phase diagram (i.e the line at approximately 44 wt. % $Na_2SO_4$). Determine the composition of the system as the relative amounts (in moles) of the phases present as a function of the temperature during this heating process.

d) Determine the solubility of $Na_2SO_4$ as a mole fraction at 305.53 K and at 330 K.
The temperature dependence of this curve is somewhat unexpected; explain why it is unexpected and try to find an explanation for it.

# Exercise 21

We look back at the situation of exercise 11.

a) Draw the $(P, z_A)$ phase diagram at $T = 70$ °C of the binary mixture of that exercise. The two compounds were *o*-xylene as component $A$ and *p*-xylene as component $B$. At $T = 70$ °C we found in exercise 11a for the pure compound vapour pressures $P_A^* = 8.40$ kPa and $P_B^* = 10.65$ kPa. Indicate the different phases in the diagram and examine the situation of each region (especially the two-phase region) using Gibbs' phase rule.

b) A ternary phase diagram is often drawn for constant pressure and temperature. In such a diagram, each side of the equilateral triangle represents the mole fraction of one of the three components.
Show that for each point $X$ in such a diagram (like in figure 3) the following equation is valid

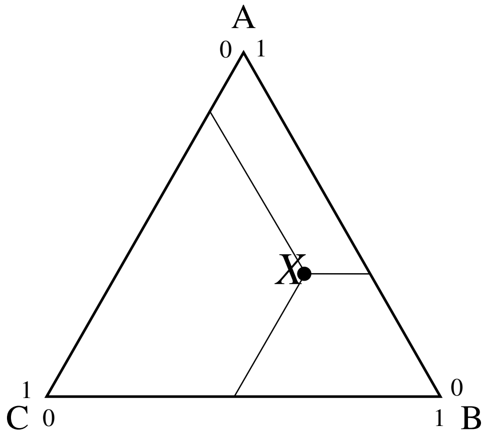


Figure 3: Example ternary phase diagram at chosen $P$ and $T$.

$x_A + x_B + x_C = 1$, in which the line $A, B$ represents a composition with $x_C = 0$ and analogously for the two other sides.
Hint: this can be done by constructing triangles within the phase diagram.

c) Examine Gibbs' phase rule for the ternary phase diagram corresponding to the system of exercise 11d.

d) Draw the results of exercise 11a ($x_A = 0.733$ and $x_B = 1 - x_A = 0.267$) and 11e $(x_A, x_B, x_C) = (0.4000, 0.1455, 0.4545)$ in a ternary phase diagram.