

Answers Tutorials 5 Thermodynamics 2, 2023/2024

Exercise 18

- a) We use the approximated expression for the freezing point depression ($T^* = T_{fus,A}^*$ and $\Delta_{fus}H = \Delta_{fus,A}H$)

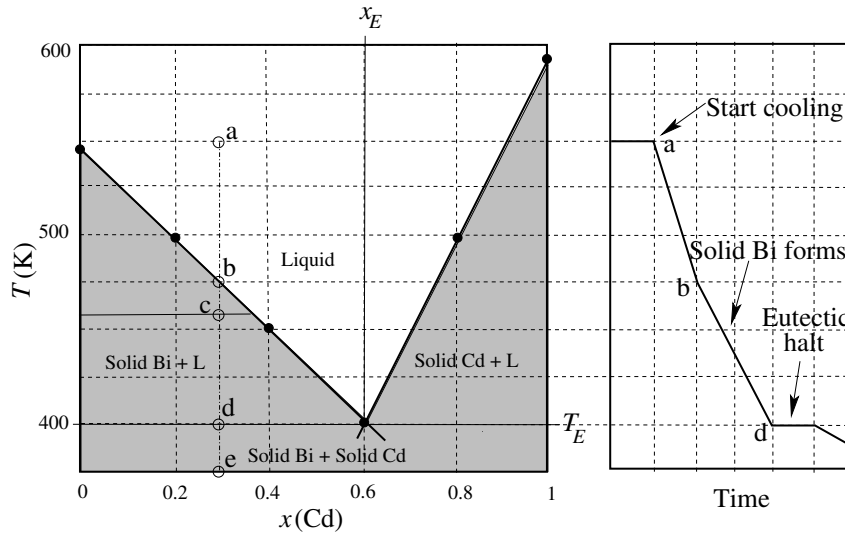
$$\Delta T \approx \frac{RT^{*2}}{\Delta_{fus}H} x_B.$$

The slopes in the (T, x) -phase diagram are therefore

$$\frac{\Delta T}{x_B} = \frac{RT^{*2}}{\Delta_{fus}H} = \frac{8.314 \cdot 544.5^2}{10.88 \cdot 10^3} = 227 \text{ K} \quad \text{when A is bismuth and}$$

$$\frac{\Delta T}{x_B} = \frac{RT^{*2}}{\Delta_{fus}H} = \frac{8.314 \cdot 594^2}{6.07 \cdot 10^3} = 483 \text{ K} \quad \text{when A is cadmium.}$$

Then we determine $T_{fus}(x_B) = T_{fus}^* - \Delta T(x_B) = T_{fus}^* - \frac{RT_{fus}^{*2}}{\Delta_{fus}H} x_B$ for both metals. This results in two straight lines in the phase diagram. The approximate eutectic point can be found at the



intersection of those two lines, so from

$$T_{fus,Bi}^* - \frac{RT_{fus,Bi}^{*2}}{\Delta_{fus,Bi}H} x_{Cd} = T_{fus,Cd}^* - \frac{RT_{fus,Cd}^{*2}}{\Delta_{fus,Cd}H} x_{Bi} = T_{fus,Cd}^* - \frac{RT_{fus,Cd}^{*2}}{\Delta_{fus,Cd}H} (1 - x_{Cd}), \quad \text{so}$$

$$x_{Cd} = \frac{T_{fus,Cd}^* - T_{fus,Bi}^* - \frac{RT_{fus,Cd}^{*2}}{\Delta_{fus,Cd}H}}{-\frac{RT_{fus,Bi}^{*2}}{\Delta_{fus,Bi}H} - \frac{RT_{fus,Cd}^{*2}}{\Delta_{fus,Cd}H}} = \frac{594 - 544.5 - 483.3}{-226.6 - 483.3} = 0.61$$

At this composition the fusion temperature is

$$T_{fus} = T_{fus,Bi}^* - \frac{RT_{fus,Bi}^{*2}}{\Delta_{fus,Bi}H} x_{Cd} = 406 \text{ K.}$$

So the approximated eutectic point is at $T_E \approx 406$ K and $x_E(\text{Cd}) \approx 0.61$.

- b) The cooling path is indicated by the line abcde in the left diagram. On cooling from point a, at point b ($T_b = 476$ K) the liquid phase is divided in solid Bi and a liquid phase richer in Cd. At point d ($T_d = 406$ K) we have Bi(s) together with the liquid phase with composition $x(\text{Cd}) = 0.61$ and therefore $x(\text{Bi}) = 0.39$. Upon further cooling, the remaining liquid will form two separate solid phases of Bi and Cd.
- c) For point c at 460 K and $x(\text{Bi}) = 0.70$, so $x(\text{Cd}) = 0.30$ the system has two phases, a solid Bi phase and a liquid solution (melt). The composition of the solution can be found using the freezing point depression expression, inverted

$$x_{Cd} = \frac{\Delta_{fus,Bi}H}{RT_{fus,Bi}^*2} \Delta T = \frac{\Delta_{fus,Bi}H}{RT_{fus,Bi}^*2} (T_{fus,Bi} - 460) = 0.37.$$

The relative amounts of these phases can be found using the lever rule

$$\frac{n_l}{n_s} = \frac{l_s}{l_l} = \frac{0.30 - 0}{0.37 - 0.30} \approx 4.3.$$

In other words, 10/53 of the total amount in the mixture is pure solid Bi and 43/53 of the total amount consists of a liquid phase with a mole fraction $x_{Cd} \approx 0.37$.

At 375 K (point e) there is no liquid, only solids and the system consists of pure Bi(s) and pure Cd(s). The relative amounts are therefore $n_{Bi(s)}/n_{Cd(s)} = 0.7/0.3 \approx 2.3$

- d) The cooling curve can be found next to the phase diagram.

Exercise 19

- a) 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 . For an ideal solution of B in A we can use

$$\mu_B(l) = \mu_B^*(l) + RT \ln x_B,$$

in which $\mu_B(l)$ is the chemical potential of B in solution. In an equilibrium we have $\mu_B(l) = \mu_B(s) = \mu_B^*(s)$, so

$$\mu_B^*(s) = \mu_B^*(l) + RT \ln x_B.$$

Since only chemical potentials of pure compounds appear in this expression, we can rewrite it in terms of the molar Gibbs free energy $\Delta_{fus}G_{m,B}^*(T)$; we will drop the subscript m in the following, although it is implicitly present. The same holds for the superscript $*$.

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

where we use the assumption that $\Delta_{fus}H_B$ and $\Delta_{fus}S_B$ are independent of T in the last step. Note that the enthalpy and entropy changes refer to the solute B , in contrast to the case of freezing point depression and boiling point elevation, for which the solvent A was in the expressions.

- b) If we plot $\ln x_B$ as a function of $1/T$ we find, given the assumption that, $\Delta_{fus}H$ and $\Delta_{fus}S$ are independent of the temperature, a straight line with slope $-\Delta_{fus}H/R$ and intercept $\Delta_{fus}S/R$, at $1/T = 0$. We could also simply use the values for x_B and T in this equation and solve the system of two linear equations. In either way this results in
- $\Delta_{fus}H_B = 17.35$ kJ/mol and
 $\Delta_{fus}S_B = 28.3$ J/molK.

- c) The expression for the chemical potential of component i in a non-ideal solution is

$$\mu_i = \mu_i^* + RT \ln a_i,$$

in which we take the pure compound as a reference. We therefore find for a saturated solution in contact with the solid of solute $B(s)$

$$\mu_B^*(s) = \mu_B^*(l) + RT \ln a_B.$$

Similar to part a) we find

$$\ln a_B = \ln \gamma_B x_B = \ln \gamma_B + \ln x_B = -\frac{\Delta_{fus} H_B}{RT} + \frac{\Delta_{fus} S_B}{R}, \text{ or}$$

$$\ln x_B = -\frac{\Delta_{fus} H_B}{RT} + \frac{\Delta_{fus} S_B}{R} - \ln \gamma_B.$$

- d) Substituting the values results in

$$\ln \gamma_B = -\frac{18.5 \cdot 10^3}{8.314 \cdot 318.5} + \frac{35.0}{8.314} - \ln 0.0429 = -6.986 + 4.210 + 3.149 = 0.373 \quad \text{so} \quad \gamma = 1.45.$$

Exercise 20

- a) S and R enantiomers have the same physical properties like boiling point, enthalpy of vaporization and vapour pressure. In a binary mixture, both the liquidus and vaporous will be the same horizontal line in an $l-g$ phase diagram, in a (P, x) as well as in a (T, x) diagram. As a consequence, the mole fractions of the enantiomers will be the same in both phases ($y_R = x_R$ and $y_S = x_S$).
- b) If the solid phase forms a conglomerate, we find an $l-s$ diagram with a similar shape as the one of exercise 18, be it with the same melting point on both sides. Also the liquidus will now be (mirror) symmetrical in $x = \frac{1}{2}$. As a consequence, we will find the eutectic point at $x_R = x_S = \frac{1}{2}$. The phase diagram can be found in figure 1.
- c) For a racemate there are three solid phases, the two pure enantiomers, S_L and S_R , as well as a solid phase with a 1-1 ratio of both enantiomers, S_{LR} . A phase diagram with all the phase information can be found in figure 2. In the non-shaded area only the liquid phase (melt) is present, and in each of the shaded areas there are two phases. Cooling the melt with a composition left of the left eutectic point ($x_R < x_E^L$) will, once the liquidus is passed, result in a pure solid S_L in contact with a liquid, which becomes richer in R . Upon further cooling, as soon as the eutectic temperature at $T = T_E$ is passed, the remaining liquid will form both crystals of S_L and S_{RL} . A similar situation occurs for compositions at the right side of the right eutectic point $x_R > x_E^R$.
When cooling a liquid mixture with initial composition $x_E^L < x_R < 0.5$ the solid S_{LR} together with a liquid mixture poorer in R is formed, as soon as the liquidus is passed. Further cooling results for $T < T_E$ in solid S_L and solid S_{RL} . A similar situation occurs for $0.5 < x_R < x_E^R$.
For $x_R = 0.5$ only solid S_{RL} is formed on passing the top of the liquidus.
- d) The discussion in part c) shows that pure solid S_L can only be obtained for cooling a melt with composition $x_R < x_E^L$ and cooling not further than T_E , while pure solid S_R can only be obtained by cooling a melt with composition $x_R > x_E^R$ and cooling not further than T_E .

Exercise 21

- a) We will chose *o*-xylene as component A and *m*-xylene as component B . At $T = 90$ °C, $P_A^* = 18.5$ kPa is and $P_B^* = 21.9$ kPa. The liquid solution behaves ideal so Raoult's law can be applied; $P = P_A + P_B = x_A P_A^* + (1 - x_A) P_B^*$, which gives a straight liquidus (upper curve) in figure 3. We

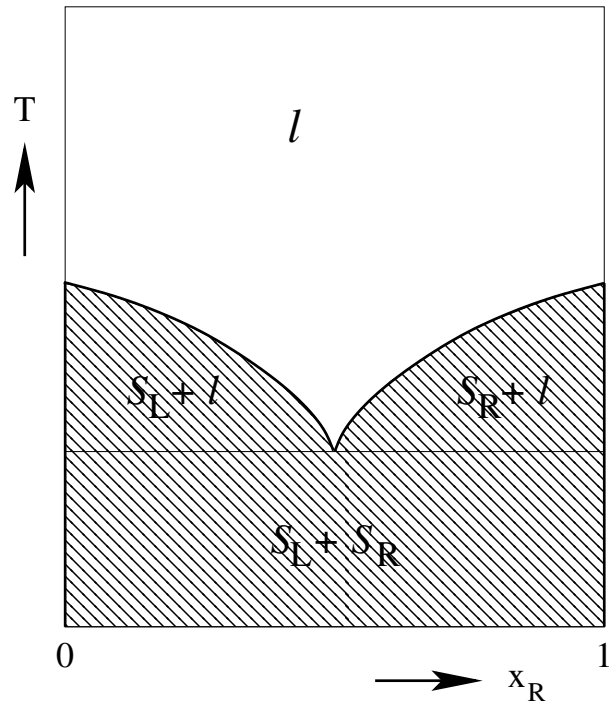


Figure 1: The phase diagram of a conglomerate.

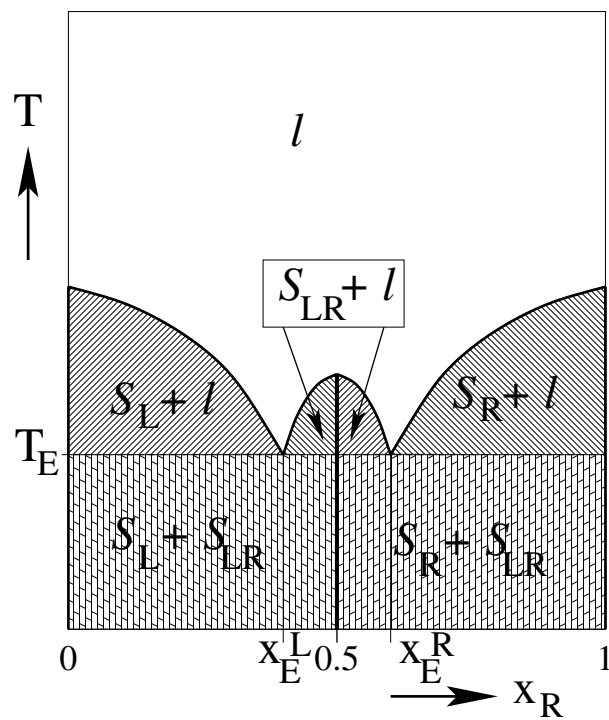


Figure 2: The phase diagram of a racemate.

have derived the total vapour pressure of y_A for such a solution as $P = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) y_A}$, which gives the curved line (lower curve) in the diagram. At a pressure of $P = 20.2$ kPa (horizontal line) we find that $z_A = x_A = 0.5$ and $z_A = y_A = 0.458$ (as we have seen in exercise 15).

In the entire diagram we have two components, so $C = 2$ in Gibbs' phase rule. Above the

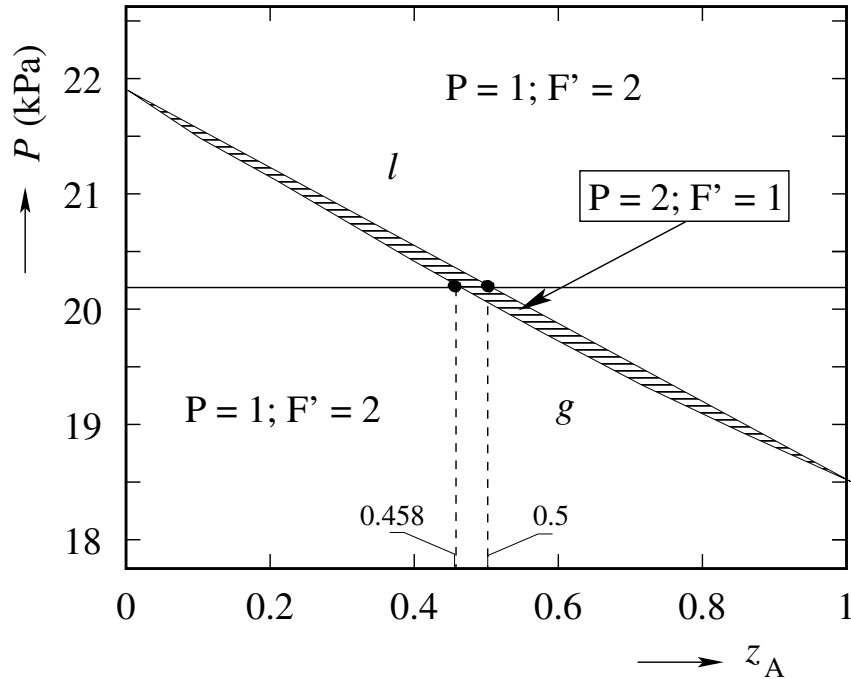


Figure 3: The binary pressure composition diagram of exercise 15.

liquidus and below the vapourus we find the liquid and vapour respectively. We thus have $P = 1$, and therefore $F = C - P + 2 = 3$ in these regions. We have already chosen the temperature ($T = 90^\circ\text{C}$), so we have two remaining variables, P and z_A , which we can freely choose ($F' = 2$). In the region between the two lines, both vapour and liquid are present. At a given pressure P the corresponding horizontal line intersects the liquidus and vapourus. At these intersections the vapour and liquid are in equilibrium. The ratio between the amount of vapour and liquid can be found using the lever rule. In this area we have $P = 2$, and therefore $F = 2$. The temperature was already chosen, so upon choosing the pressure the composition of the vapour and liquid are determined and vice-versa ($F' = 1$).

- b) The point X describes a mixture with composition $(x_A, x_B, x_C) = (0.36, 0.48, 0.17)$; the sum of these mole fractions is indeed almost 1, the deviation being due to rounding errors. That this is valid for the whole plot can be seen without mathematical prove. Examine the three segments parallel to the borders of the diagram that run from point X to the edge of the diagram; these are the bold segments in the left part of figure 4. The length of the segments are x_A , x_B and x_C respectively. Construct an equilateral triangle with the corresponding edge for each of the segments. You can find these in the left part of figure 4 looking at the combinations of a bold and bold dashed line. If you slide all three triangles to one edge, you can see that the sum of the lengths of the triangles is equal to the length of the edge of the diagram. The length of each of the triangles is the same as the length of the bold segments (since it is an equilateral triangle). Each edge has a length of 1, so for all X : $x_A + x_B + x_C = 1$.
- c) Compare your answer to part d) of exercise 15. There are three components in the whole diagram (with the exception of the edges), so for Gibbs' phase rule we have $C = 3$ and $F = 5 - P$. We have

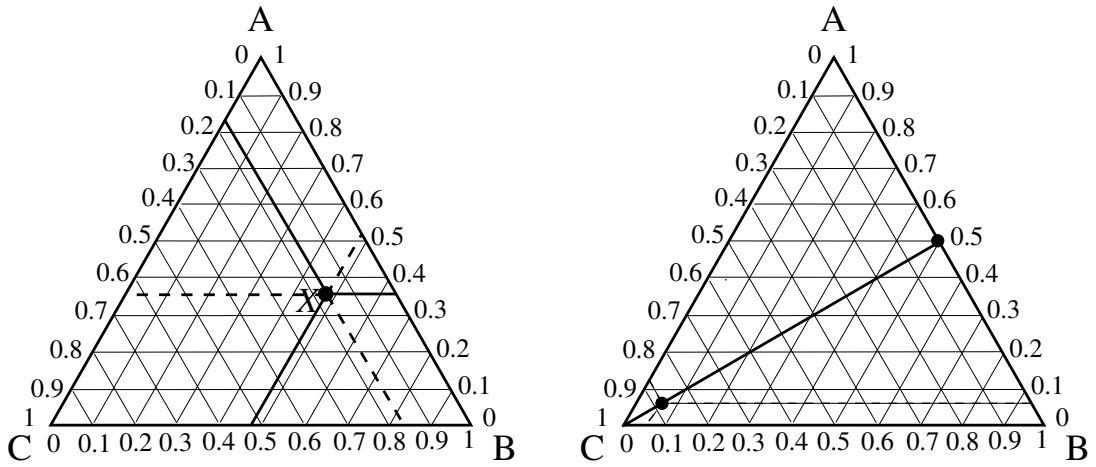


Figure 4: The ternary pressure composition diagram of exercise 15.

already chosen the pressure and temperature, which reduces the amount of variables to $F'' = 3 - P$, which implies $F'' = 2$ for the liquid and the vapour phase regions, and $F'' = 1$ for the region where the two are in equilibrium.

- d) We started with a binary mixture (A and B) in exercise 15a. At the given pressure and temperature, the mole fractions turned out to be $x_A = x_B = 0.5$, which is indicated in the right part of figure 4. In exercise 15c, a third component C was added to the binary mixture. This means that in the ternary phase diagram we get a composition somewhere on the line between $(x_A, x_B, x_C) = (0.5, 0.5, 0)$ and $(x_A, x_B, x_C) = (0, 0, 1)$. The last value corresponds to an infinite amount of C added. Somewhere on this line we find point $(x_A, x_B, x_C) = (0.0618, 0.0618, 0.8765)$ which we found in exercise 15e.