

Answers Tutorials 5 Thermodynamics 2, 2024/2025

Exercise 18

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

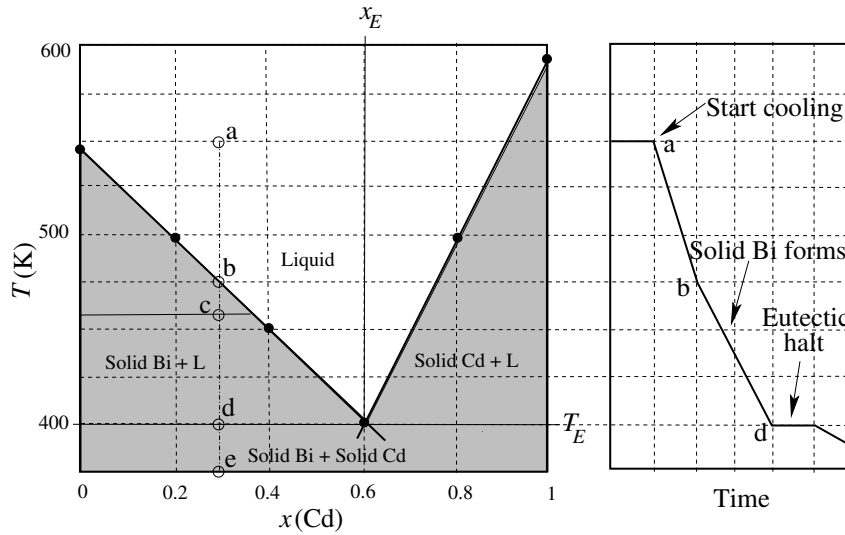
$$\Delta T \approx \frac{RT^{*2}}{\Delta_{fus}H} x_B.$$

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

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

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

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

$$\frac{n_l}{n_s} = \frac{l_s}{l_l} = \frac{0.30 - 0}{0.37 - 0.30} \approx 4.3, \quad \text{so} \quad n = n_l + n_s = 5.3n_s.$$

Therefore, 10/53 of the total amount n in the system is pure solid Bi and 43/53 of the total amount in the system consists of a liquid phase with a mole fraction x_{Cd} .

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) 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 racemic conglomerate, we find an $l-s$ diagram with a similar shape as the one of exercise 18, be it not approximated by the linear melting curves, and more importantly 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 racemic compound 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_{LR} 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 .

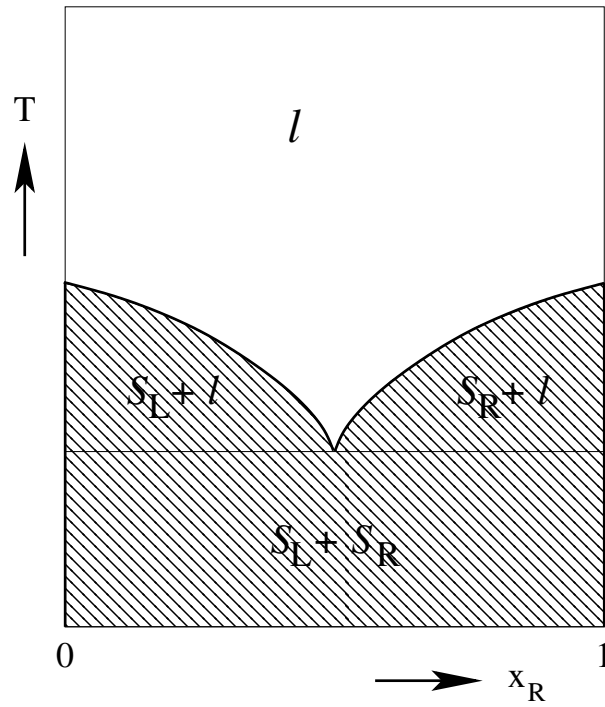


Figure 1: The phase diagram of a racemic conglomerate; the two-phase regions are hatched.

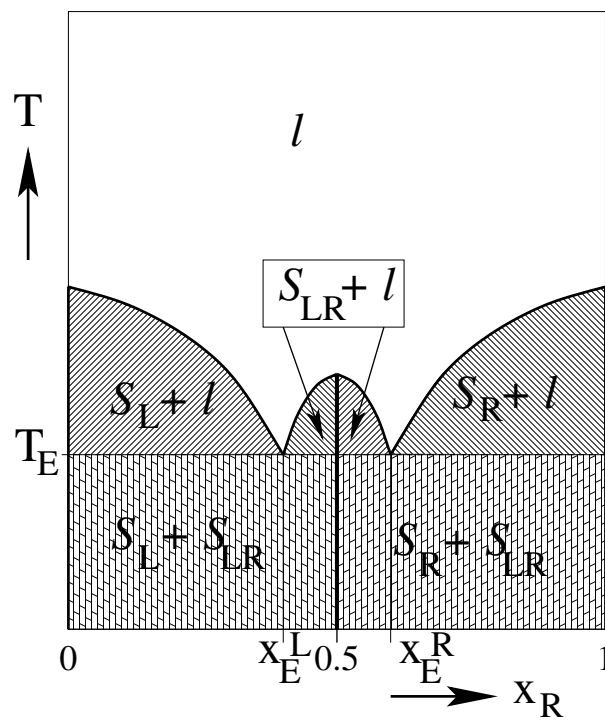


Figure 2: The phase diagram of a racemic compound.

Exercise 20

- a) The phase diagram shows that the salt hydrate $\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ corresponds to approximately 44 wt.% Na_2SO_4 , which melts incongruently at 305.53 K. The molar mass of the salt hydrate is

$$M(\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}) = M(\text{Na}_2\text{SO}_4) + nM(\text{H}_2\text{O}) = 142.04 + n \cdot 18.02 \text{ g/mol.}$$

This mass accounts for approximately 44 wt.% Na_2SO_4 , so

$$\frac{44}{100}(142.04 + n \cdot 18.02) \text{ g/mol} \approx 142.04 \text{ g/mol, so } n \approx \frac{0.56 \cdot 142.04}{0.44 \cdot 18.02} = 10.03,$$

Therefore $n = 10$ and we are dealing with a $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ salt hydrate.

- b) The phase diagram including all phases present is drawn in Figure 3.

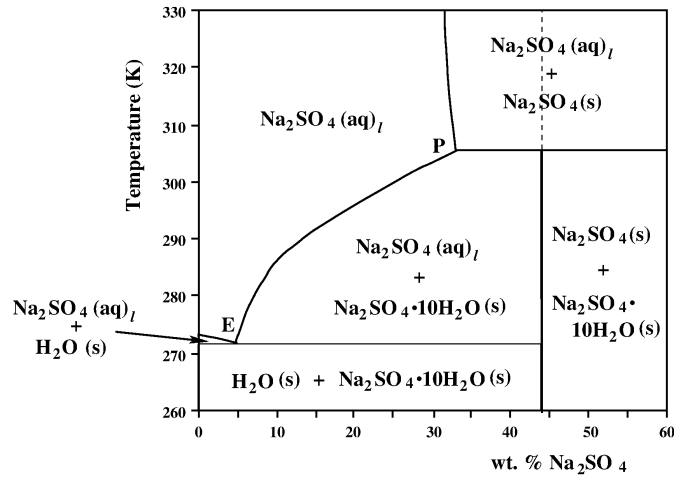


Figure 3: Phase diagram of the $(\text{Na}_2\text{SO}_4, \text{H}_2\text{O})$ system including its salt hydrate $\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$. The isopleth mentioned in part c) is indicated by the dashed vertical line.

- c) Starting at 44 wt.% Na_2SO_4 , from 260 K up to 305.53 K we only have the solid salt hydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. At 305.53 K it melts incongruently into a mixture of solid (so not-dissolved) Na_2SO_4 and a saturated aqueous solution $\text{Na}_2\text{SO}_4(\text{aq})$ of that salt.

We use the lever rule to determine the relative amounts of the two phases for temperatures between 305.53 K and 330 K. For that we need mole fractions. Because we started at 260 K with the salt hydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the total relative amount (in moles) of Na_2SO_4 and H_2O is and stays during heating equal to

$$\frac{n_{\text{Na}_2\text{SO}_4}}{n_{\text{H}_2\text{O}}} = \frac{1}{10} = 0.10, \quad \text{so} \quad x_{\text{Na}_2\text{SO}_4} = \frac{n_{\text{Na}_2\text{SO}_4}}{n_{\text{Na}_2\text{SO}_4} + n_{\text{H}_2\text{O}}} = \frac{1}{1 + 10} = 0.0909.$$

This overall constant composition at 44 wt.% Na_2SO_4 , so at $x_{\text{Na}_2\text{SO}_4} = 0.0909$, is indicated by the dashed isopleth in Figure 3. Because the line starting at point P, upwards is not vertical, the relative amounts of the two phases, the solution $\text{Na}_2\text{SO}_4(\text{aq})$ and the solid $\text{Na}_2\text{SO}_4(\text{s})$ will change on heating. The latter line, which corresponds to the saturated solution, is given by the function $T = 606.87 - 9.063wt$, where wt is the wt.% Na_2SO_4 and T is in Kelvin, so $wt = \frac{606.87 - T}{9.063}$. To rewrite this to a mole fraction $x_{\text{Na}_2\text{SO}_4}$ we first write (m_i is the mass and M_i the molar mass of component i)

$$\frac{wt}{100} = \frac{m_{\text{Na}_2\text{SO}_4}}{m_{\text{Na}_2\text{SO}_4} + m_{\text{H}_2\text{O}}} = \frac{\frac{m_{\text{Na}_2\text{SO}_4}}{M_{\text{Na}_2\text{SO}_4}}}{\frac{m_{\text{Na}_2\text{SO}_4}}{M_{\text{Na}_2\text{SO}_4}} + \frac{m_{\text{H}_2\text{O}}}{M_{\text{Na}_2\text{SO}_4}}} = \frac{n_{\text{Na}_2\text{SO}_4}}{n_{\text{Na}_2\text{SO}_4} + \frac{M_{\text{H}_2\text{O}}}{M_{\text{Na}_2\text{SO}_4}} n_{\text{H}_2\text{O}}}.$$

We can rewrite this to

$$n_{\text{H}_2\text{O}} = n_{\text{Na}_2\text{SO}_4} \frac{100 - wt}{wt} \cdot \frac{M_{\text{Na}_2\text{SO}_4}}{M_{\text{H}_2\text{O}}},$$

so in terms of mole fraction we find

$$x_{\text{Na}_2\text{SO}_4} = \frac{n_{\text{Na}_2\text{SO}_4}}{n_{\text{Na}_2\text{SO}_4} + n_{\text{H}_2\text{O}}} = \frac{M_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}} + \frac{100 - wt}{wt} M_{\text{Na}_2\text{SO}_4}} = \frac{M_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}} + M_{\text{Na}_2\text{SO}_4} \left(\frac{100 - 9.063}{606.87 - T} - 1 \right)}.$$

Filling in the values we find for the temperature dependence of the saturated solution

$$x_{\text{Na}_2\text{SO}_4} = \frac{18.02}{18.02 + 142.04 \left(\frac{906.3}{606.87 - T} - 1 \right)} = \frac{1}{1 + 7.882 \left(\frac{906.3}{606.87 - T} - 1 \right)}$$

The lever rule now gives the relative amounts of the two phases

$$\frac{n_{\text{Na}_2\text{SO}_4(\text{aq})}}{n_{\text{Na}_2\text{SO}_4(\text{s})}} = \frac{1 - x_{\text{Na}_2\text{SO}_4}^{(\text{isopleth})}}{x_{\text{Na}_2\text{SO}_4}^{(\text{isopleth})} - x_{\text{Na}_2\text{SO}_4}^{(\text{sat. solution})}} = \frac{1 - 0.0909}{0.0909 - \left[\frac{1}{1 + 7.882 \left(\frac{906.3}{606.87 - T} - 1 \right)} \right]}.$$

This gives $\frac{n_{\text{Na}_2\text{SO}_4(\text{aq})}}{n_{\text{Na}_2\text{SO}_4(\text{s})}} = 28.90$ at 305.53 K and 23.90 at 330 K.

- d) Just above 305.53 K the system consists of the pure anhydrate $\text{Na}_2\text{SO}_4(\text{s})$ and a saturated aqueous solution of Na_2SO_4 . So all the water for this saturated solution comes from the (pure) salt hydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. At point P $x = 33.25$ wt.%, so for the saturated solution at P we have

$$\frac{33.25}{100} (142.04 + n_{\text{H}_2\text{O}} \cdot 18.02) \text{ g/mol} = 142.04 \text{ g/mol}, \quad \text{so} \quad n_{\text{H}_2\text{O}} = \frac{0.6675 \cdot 142.04}{0.3325 \cdot 18.02} = 15.82.$$

Therefore, the solubility of Na_2SO_4 at 305.53 K as a mole fraction is $x(305.53 \text{ K}) = \frac{1}{1 + 15.82} = 0.059$. At 330 K the wt.% is $\frac{330 - 606.87}{-9.063} = 30.55$ and we find

$$\frac{30.55}{100} (142.04 + n_{\text{H}_2\text{O}} \cdot 18.02) \text{ g/mol} = 142.04 \text{ g/mol}, \quad \text{so} \quad n_{\text{H}_2\text{O}} = \frac{0.6945 \cdot 142.04}{0.3055 \cdot 18.02} = 17.92.$$

Therefore, the solubility of Na_2SO_4 at 330 K as a mole fraction is $x(330 \text{ K}) = \frac{1}{1 + 17.92} = 0.053$. The solubility decreases with increasing temperature, in contrast with most solutes.

Exercise 21

- a) We chose *o*-xylene as component *A* and *p*-xylene as component *B*. At $T = 70$ °C we found $P_A^* = 8.40$ kPa and $P_B^* = 10.65$ 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 4. We 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 $P = 9$ kPa (horizontal line) we find that $z_A = x_A = 0.733$ and $z_A = y_A = 0.684$ (as we found in exercise 11b).

In the entire diagram we have two components, so $C = 2$ in Gibbs' phase rule. Above the liquidus and below the vapourus (gas line) 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 ($T = 70$ °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 ($F' = 1$).

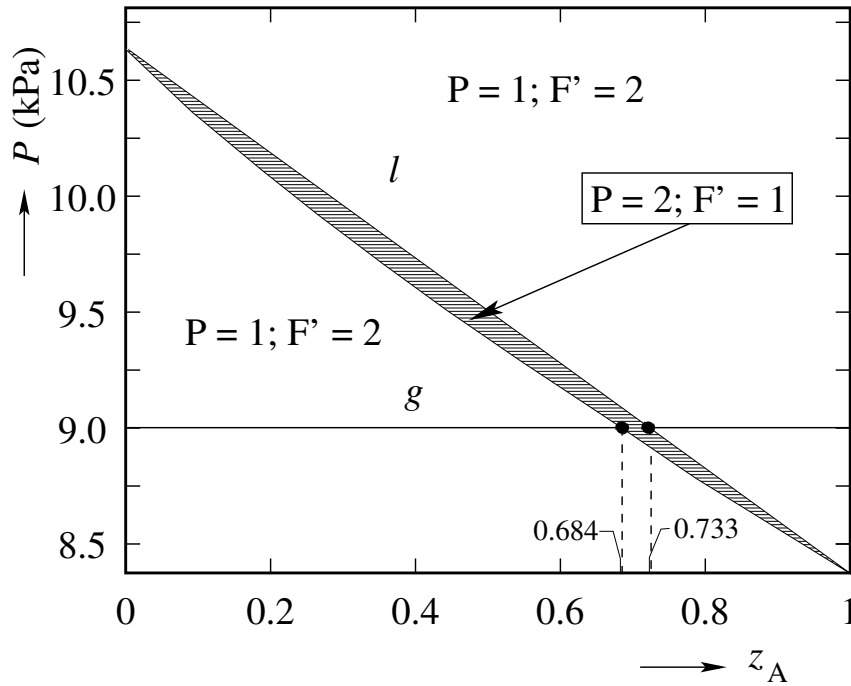


Figure 4: The binary pressure composition diagram of exercise 11a,b.

- b) The point X describes a mixture with composition $(x_A, x_B, x_C) \approx (0.36, 0.48, 0.16)$; the sum of these mole fractions is indeed 1. 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 5. 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 5 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 11. 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 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 11a. At the given pressure and temperature, the mole fractions turned out to be $(x_A = 0.733$ and $x_B = 1 - x_A = 0.267)$, which is indicated in the right part of figure 5. In exercise 11c, 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 $(x_A, x_B, x_C) = (0.733, 0.267, 0)$ 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 $(x_A, x_B, x_C) = (0.4000, 0.1455, 0.4545)$ which we found in exercise 11e.

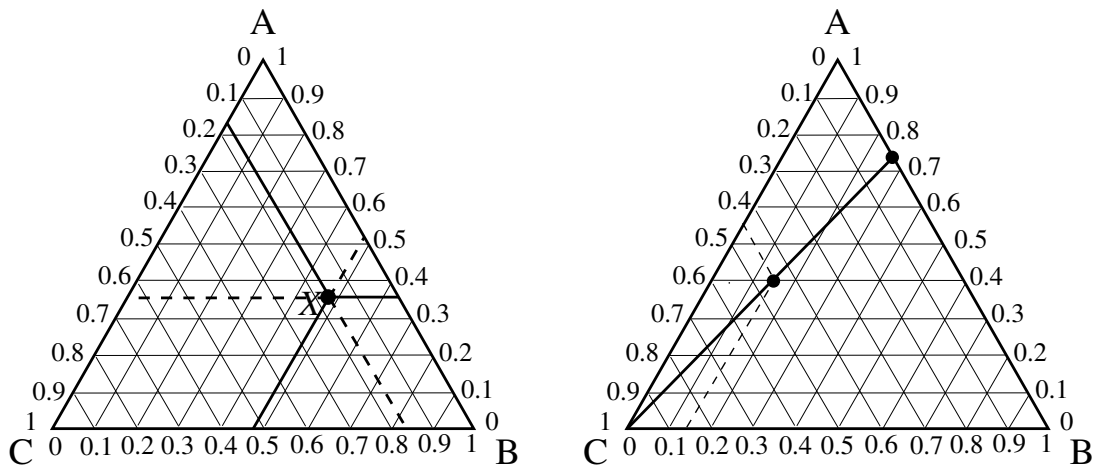


Figure 5: The ternary phase diagram showing the system of exercise 11 is drawn in the graph on the right.