# Answers Tutorials 4 Thermodynamics 2, 2025/2026

Exercise 14

Pure nitrogen has a boiling point of 77.3 K at 1 atm. The corresponding boiling point of oxygen is 90.2 K. All the values in the table of the exercise are therefore between the boiling points of the two components. The first two rows, indicated by x and y, represent the composition of the liquid mixture and the composition of the corresponding vapour mixture, respectively at different temperatures and a total pressure of 100 kPa. The last row gives the vapour pressure of pure (liquid) oxygen at the indicated temperatures.

a) We can simply use the data from the table to construct the temperature-composition diagram; see figure below. If the combination of the (total) composition and temperature lies between the two lines (the grey area), both phases are present. The mole fractions of the liquid phase can be found on the bottom curve (liquidus). In the same way, the mole fractions of the vapour can be found using the upper curve. 760 Torr = the pressure of a column Hg of 760 mm height, which is equal to 1 atm = 101325 Pa.
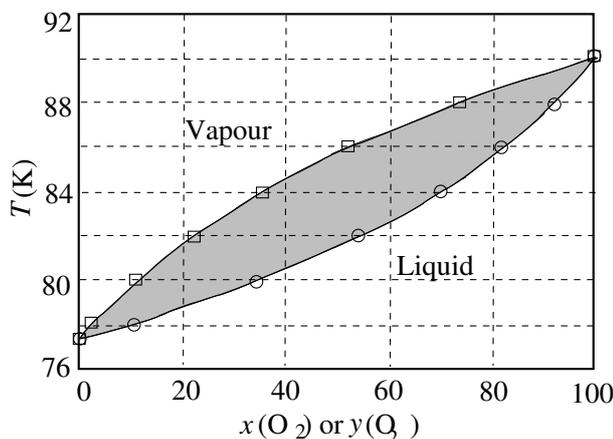
b) The activity a_A of O_2 can be found using $P_A = a_A P_A^* = \gamma_A x_A P_A^*$. We perform the calculation at 80 K as an example:

$$\gamma_{O_2}(80 \text{ K}) = \frac{P_A}{x_A P_A^*} = \frac{y_A P}{x_A P_A^*} = \frac{0.11 \cdot 100 \text{ [kPa]}}{0.34 \cdot 225 \text{ [Torr]}} \left(\frac{760 \text{ [Torr]}}{101.325 \text{ [kPa]}} \right) = 1.079.$$
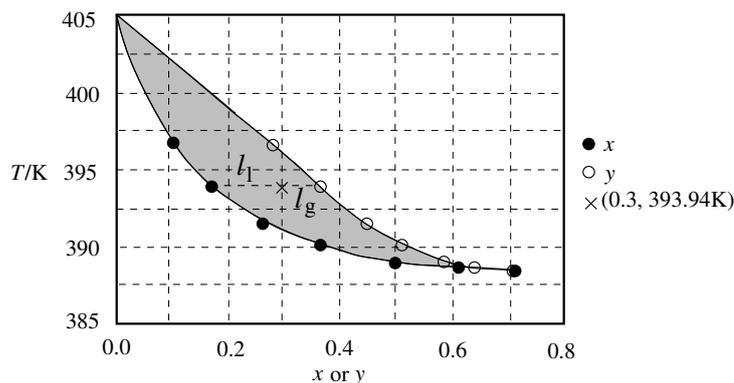
The results can be found in the table below. The solution seems to behave almost ideal for the

T [K]	77.3	78	80	82	84	86	88	90.2
γ_{O_2}	-	0.877	1.079	1.039	0.995	0.993	0.990	0.987

majority of the measured points ($\gamma \approx 1$), except for the questionable point at 78 K. This would be best visible in a (P, x_A) plot (at constant T), since we should get a straight line with slope P_A^*, for an ideal solution according to Raoult's law.

Exercise 15

a) The answer is no, no, yes, yes, yes.
The argument is that you cannot have a local minimum or local maximum for the gas line without it touching there the liquidus, as this would lead to g-g separation or l-l separation, which is at least very unlikely. (see slide 39 of Lecture 4).

b) The values from the table can be found in the figure below. The hatched (grey) region is the two-phase region.

c) The lower curve, which represents the boiling point, has a value of $T = 391.0K$ at $x = 0.300$.

d) The mole fractions of 1-butanol are $x = 0.1700$ and $y = 0.3691$ for the liquid and vapour phase respectively, according to the table.
So $\frac{n_{l,but}}{n_{l,Clbenz}} = \frac{x}{1-x} = \frac{0.1700}{0.8300} = 0.20$ and $\frac{n_{g,but}}{n_{g,Clbenz}} = \frac{y}{1-y} = \frac{0.3691}{0.6309} = 0.5850$.
Using the lever rule we find the relative amounts of the two phases

$$\frac{n_l}{n_g} = \frac{l_g}{l_l} = \frac{0.3691 - 0.300}{0.300 - 0.1700} = 0.532.$$

Exercise 16

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.

2

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

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

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

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 17

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

a) We can find the extrema using

$$0 = \frac{\partial \Delta_{mix} G}{\partial x} = nRT \left[\ln x + \frac{x}{x} - \ln(1-x) - \frac{1-x}{1-x} + \beta(1-2x) \right] = nRT \left[\ln x - \ln(1-x) + \beta(1-2x) \right].$$

We cannot solve this equation analytically. We can however set the second derivative to zero, since if there is one extremum $\Delta_{mix} G$ must have zero inflection points and if there are three extrema the function must have two inflection points.

$$0 = \frac{\partial^2 \Delta_{mix} G}{\partial x^2} = nRT \left[\frac{1}{x} + \frac{1}{1-x} - 2\beta \right] \quad \text{so} \quad x(1-x) - \frac{1}{2\beta} = 0 \quad \text{so} \quad x = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 - \frac{2}{\beta}}.$$

The implies that if $\beta < 2$ there are no solutions, so no inflection points.
If $\beta > 2$ there are two solutions (inflection points).
If $\beta = 2$ we have $x = \frac{1}{2}$, which means that $\Delta_{mix} G(\beta)$ as a function of β changes from having one minimum at $x = \frac{1}{2}$ to a maximum at the same value of x, while the minima (for $\beta > 2$) slide symmetrically outward.

b) In figure 1 the minima of $\Delta_{mix} G$ as a function of x have been plotted vs. T.
If $\beta = 2$ we have $T = \frac{b}{2k}$.
If $\beta < 2$, so $T > \frac{b}{2k}$ there is only one minimum for $\Delta_{mix} G(\beta)$ ($x = \frac{1}{2}$). For any value of x the mixture will have one liquid phase.
If $\beta > 2$, so $T < \frac{b}{2k}$ there are two minima for $\Delta_{mix} G$. They have the same value for $\Delta_{mix} G$ because the function is symmetrical around $x = \frac{1}{2}$.
For a total composition outside of the two minima, it will always be unfavorable to reach one minimum by separating into two phases. This is because the increase in $\Delta_{mix} G$ for the second phase will be higher than the decrease for the first one, due to the slope being lower near the minima. The total $\Delta_{mix} G$ would increase upon demixing, so this will not happen.
For a mixture of total composition between the two minima (grey area in the plot) however, both minima will be reached upon forming two phases (one rich in A and poor in B, the other rich in B and poor in A). This lowers the total $\Delta_{mix} G$, which makes the phase separation favourable.

3

Gibbs' phase rule is $F = C - P + 2$. $C = 2$ for a binary system, and since we have already chosen a pressure we are left with $F' = 2 - P + 1 = 3 - P$. For $T > \frac{b}{2k}$, we have $P = 1$, so $F' = 2$ which means we can vary both T and x. For $T < \frac{b}{2k}$ and the total composition lying between the two minima, we have $P = 2$, so $F' = 1$. This means that for any value of T, the mole fractions of the two phases are fixed. We than have two phases of which the composition can be found by the boundary of the grey area (at the given temperature). The quantities of each of the phases can be found using the lever rule.
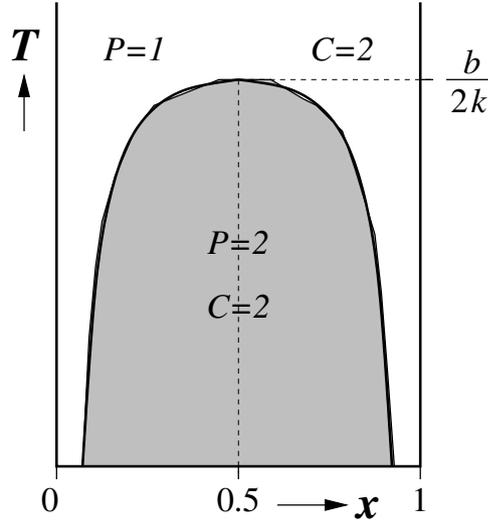

Figure 1: The $T - x$ phase diagram with the bell shaped area in which we have l-l demixing.

c) Setting the second derivative equal to zero ($x = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 - \frac{2}{\beta}}$) for negative values of β results in a value of $x > 1$ or $x < 0$, which is not possible for a mole fraction, implying that there is no inflection point and there is always just one minimum at $x = \frac{1}{2}$.

The Gibbs free energy is $G^E = nRT\beta x_A x_B$. In the case of $\beta = b/kT$ this becomes $G^E = \frac{nbR}{k}x_A x_B$. When we compare this expression with the definition of the Gibbs free energy, $G = H - TS$, we can interpret the excess Gibbs free energy as an excess enthalpy. A mixture for which $H^E \neq 0$ and $S^E = 0$ is called a regular solution.

If we however interpret β as temperature independent, the excess term becomes an excess entropy term with $S^E = nR\beta x_A x_B$. Such a mixture is generally referred to as an athermal solution, for which $H^E = 0$ and $S^E \neq 0$. A negative value for β in an athermal solution implies a larger value for the entropy than the entropy of ideal mixing, which only deepens the minimum of $\Delta_{mix}G$ at $x = \frac{1}{2}$, while a positive value will bring the value closer to zero like we have seen in the exercise. The latter could for instance occur due to clustering of components A and B in a mixture. An increase of the entropy can only occur by an increase in the molar volume of the components in a mixture, through which furthermore the vibrations and rotations of the components increase, which also increases the entropy. Here we run into a problem however for an athermal solution; since an increase in the molar volume suggests that the interactions between A and B become smaller, so the enthalpy will become smaller, implying $H^E \neq 0$. In other words, real solutions will never be pure regular or pure athermal solutions, as both H^E and S^E will differ from zero and β will always be somewhat temperature dependent. Purely regular or purely athermal solutions are therefore not easily realizable, and should be considered theoretical limits (models) of mixtures. We call a solution in which both $S^E \neq 0$ and $H^E \neq 0$ either a quasi-regular solution or a general solution.