

Answers Tutorials 3 Thermodynamics 2, 2024/2025

Exercise 10

We consider $m = 100$ g of the mixture. The volume of this mixture then follows from the density $\rho = \frac{m}{V}$, so $V = \frac{100}{0.914} = 109.4$ cm³. Since we have a 50% weight percent mixture, we have 50 g of each component per 100 g.

We can determine the amount of moles of each component using $n_i = \frac{m_i}{M_i}$.

The volume in terms of partial molar volumes V_i is

$$V = V_{alc}n_{alc} + V_{water}n_{water} = V_{alc}\frac{m_{alc}}{M_{alc}} + V_{water}\frac{m_{water}}{M_{water}}.$$

so

$$V_{alc} = \frac{V - V_{water}\frac{m_{water}}{M_{water}}}{\frac{m_{alc}}{M_{alc}}} = \frac{109.4 - 17.4\frac{50}{18}}{\frac{50}{46}} = 56.2 \text{ cm}^3/\text{mol}.$$

Note that we could have used m g solution instead of the 100 g, leading to the more general expression

$$V_{alc} = \frac{\frac{m}{\rho} - V_{water}\frac{m_{water}}{M_{water}}}{\frac{m_{alc}}{M_{alc}}} = \frac{\frac{m}{\rho} - V_{water}\frac{m}{2M_{water}}}{\frac{m}{2M_{alc}}} = \frac{2M_{alc}}{\rho} - V_{water}\frac{M_{alc}}{M_{water}}.$$

Exercise 11

- a) An ideal solution follows Raoult's law, $P_j = x_j P_j^*$. We choose $j = A$ for *o*-xylene and $j = B$ for *p*-xylene. We use the approximated form (in which $\Delta_{vap}H$ is considered to be independent of the temperature) of the Clausius-Clapeyron equation to find the vapour pressures of pure *A* and *B* at 70 °C (P^* and P both represent vapour pressures of pure compounds, but at 90 and 70 °C respectively)

$$P = P^* \exp(-\chi) \quad \text{where} \quad \chi = \frac{\Delta_{vap}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right),$$

which gives for the pure compounds *A* and *B*

$$\chi_A = \frac{40.9 \cdot 10^3}{8.314} \left(\frac{1}{343.15} - \frac{1}{363.15} \right) = 0.790 \quad \text{resp.} \quad \chi_B = \frac{39.2 \cdot 10^3}{8.314} \left(\frac{1}{343.15} - \frac{1}{363.15} \right) = 0.757,$$

so we have (* now indicates that it is the vapour pressure of a pure compound (at 70 °C), so $P_{A,B}^*$ is what we previously called $P_{A,B}$ since the meaning of * has changed)

$$P_A^* = 18.5 \exp(-0.790) = 8.40 \text{ kPa} \quad \text{and} \quad P_B^* = 22.7 \exp(-0.757) = 10.65 \text{ kPa}.$$

At 70 °C we still have an ideal solution follows Raoult's law, with $P_j = x_j P_j^*$.

The total pressure is $P = P_A + P_B = x_A P_A^* + (1 - x_A) P_B^*$, so $x_A = \frac{P - P_B^*}{P_A^* - P_B^*}$.

The mixture is boiling when $P = P_{ext} = 9.00$ kPa and $T = 70$ °C, so we find $x_A = \frac{9.00 - 10.65}{8.40 - 10.65} = 0.733$ and $x_B = 1 - x_A = 0.267$.

- b) We will use the the symbol y_i for the mole fraction of component *i* in the vapour.

$$y_A = \frac{P_A}{P_A + P_B} = \frac{x_A P_A^*}{x_A P_A^* + x_B P_B^*} = \frac{0.733 \cdot 8.40}{0.733 \cdot 8.40 + 0.267 \cdot 10.65} = 0.684. \quad \text{and} \quad y_B = 1 - y_A = 0.316.$$

- c) $P_j = x_j P_j^*$ with $j = A, B, C$. The total pressure remains the sum of the partial pressures, $P = P_A + P_B + P_C$, and the sum of the mole fractions remains $x_A + x_B + x_C = 1$.

d) $F = C - P + 2$ with $C = 3$. $P = 2$ for an equilibrium between a liquid- and vapour mixture, so $F = 3$. At a given pressure and temperature we are left with $F'' = 1$ (in part a) this was $F'' = 0$. This means we can still choose one of the variables, e.g. x_A . This suggests that we could construct an x_A, x_B diagram (P and T have already been chosen and x_C follows from $x_A + x_B + x_C = 1$) in which the mixture boils for the points on a line. Since we however chose to add *m*-xylene to the mixture with the composition found in a) (for which the relative amounts n_A and n_B were already fixed), we have also no free variables left; $F'' = 0$.

e) We simplify the ternary mixture to a binary mixture by treating a mixture of components *A* and *B* as one 'component' *D*. *p*-xylene (*C*) is then the second component (actually the third). From question a) we already know the vapour pressure of 'compound' *D*, $P_D^*(70^\circ\text{C}) = 9.00$ kPa.

For the ternary mixture boiling at 70°C and 9.5 kPa we can therefore write

$$P = P_C + P_D = x_C P_C^* + (1 - x_C) P_D^* \text{ so } x_C = \frac{P - P_D^*}{P_C^* - P_D^*} = \frac{9.5 - 9.0}{10.1 - 9.0} = 0.4545 \text{ and } x_D = 1 - x_C = 0.5455.$$

For the vapour we find $y_C = \frac{P_C}{P} = \frac{x_C P_C^*}{P} = \frac{0.4545 \cdot 10.1}{9.5} = 0.4832$ so $y_D = 1 - y_C = 0.5168$.

What remains is to calculate x_A, x_B, y_A and y_B from x_C, x_D, y_C en y_D .

We use $x_D = x_A + x_B$ and $y_D = y_A + y_B$.

Because $P = P_A + P_B + P_C$ we can use Raoult:

$$P = x_A P_A^* + x_B P_B^* + (1 - x_A - x_B) P_C^* = x_A (P_A^* - P_C^*) + x_B (P_B^* - P_C^*) + P_C^*, \text{ so (still at } 70^\circ\text{C)}$$

$$x_A = -x_B \frac{P_B^* - P_C^*}{P_A^* - P_C^*} + \frac{P - P_C^*}{P_A^* - P_C^*} = -\frac{10.65 - 10.1}{8.40 - 10.1} x_B + \frac{9.5 - 10.1}{8.40 - 10.1} = 0.3235 x_B + 0.3529.$$

If we combine the last expression with $x_A + x_B = x_D = 0.5455$ we find

$$0.3235 x_B + 0.3529 + x_B = 0.5455, \text{ so}$$

$$x_B = \frac{0.5455 - 0.3529}{1.3235} = 0.1455 \text{ and}$$

$$x_A = 1 - x_C - x_B = 1 - 0.4545 - 0.1455 = 0.4000.$$

$$\text{For the vapour we find } y_A = \frac{x_A P_A^*}{P} = \frac{0.4000 \cdot 8.40}{9.5} = 0.3537 \text{ and } y_B = \frac{x_B P_B^*}{P} = \frac{0.1455 \cdot 10.65}{9.5} = 0.1631.$$

$$\text{Check: } \sum y_i = y_A + y_B + y_C = 0.3537 + 0.1631 + 0.4832 = 1.$$

Exercise 12

a)

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

In the lecture we found for an ideal solution

$$\Delta_{mix} G^{ideal} = nRT (x_A \ln x_A + x_B \ln x_B),$$

which can be written as (use $x \equiv x_A = 1 - x_B$)

$$\Delta_{mix} G^{ideal} = nRT [x \ln x + (1 - x) \ln(1 - x)].$$

Before mixing we have the pure liquids, so

$$G_{no\ mix} = n_A \mu_A^*(l) + n_B \mu_B^*(l).$$

Therefore

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

$$G^E = nRT [\beta x(1 - x)],$$

$$\Delta_{mix} G = nRT [x \ln x + (1 - x) \ln(1 - x) + \beta x(1 - x)],$$

$$\Delta_{mix} G^{ideal} = nRT [x \ln x + (1 - x) \ln(1 - x)].$$

- b) Although not asked for we will show how G_A has been determined.
The partial molar Gibbs free energy of component i is defined as

$$G_i \equiv \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq i}, \quad \text{so} \quad G_A \equiv \left(\frac{\partial G}{\partial n_A} \right)_{T,P,n_B},$$

and an analogous expression for G_B . Therefore, we first rewrite $G(x)$ to $G(n_A, n_B)$ (use $x_i \equiv n_i/n$)

$$G = n_A \mu_A^*(l) + n_B \mu_B^*(l) + RT \left[n_A \ln \frac{n_A}{n_A + n_B} + n_B \ln \frac{n_B}{n_A + n_B} \right] + RT\beta \frac{n_A n_B}{n_A + n_B}.$$

Differentiation with respect to n_A leads to

$$\begin{aligned} G_A = \mu_A^*(l) + & \\ + RT & \left[\ln \frac{n_A}{n_A + n_B} + n_A \frac{n_A + n_B}{n_A} \left(\frac{1}{n_A + n_B} - \frac{n_A}{(n_A + n_B)^2} \right) + n_B \frac{n_A + n_B}{n_B} \cdot \frac{-n_B}{(n_A + n_B)^2} \right] \\ + RT\beta & \left[\frac{n_B}{n_A + n_B} - \frac{n_A n_B}{(n_A + n_B)^2} \right], \end{aligned}$$

which simplifies in a two steps to first

$$G_A = \mu_A^*(l) + RT \left[\ln \frac{n_A}{n_A + n_B} + (n_A + n_B) \left(\frac{n_B}{(n_A + n_B)^2} \right) - \frac{n_B}{n_A + n_B} \right] + RT\beta \left[\frac{n_B^2}{(n_A + n_B)^2} \right],$$

and finally

$$G_A = \mu_A^*(l) + RT \ln \frac{n_A}{n_A + n_B} + RT\beta \frac{n_B^2}{(n_A + n_B)^2}.$$

Using this result for G_A we can find the expression for G_B , as suggested, in two ways

1. The general expression we found in the lecture

$$G|_{T,P} = \sum_i n_i G_i = n_A G_A + n_B G_B, \quad \text{so} \quad G_B = \frac{G|_{T,P} - n_A G_A}{n_B}.$$

This gives (use G written as $G(n_A, n_B)$ in b))

$$\begin{aligned} G_B = & \frac{n_A \mu_A^*(l) + n_B \mu_B^*(l) + RT \left[n_A \ln \frac{n_A}{n_A + n_B} + n_B \ln \frac{n_B}{n_A + n_B} \right] + RT\beta \frac{n_A n_B}{n_A + n_B}}{n_B} \\ - & \frac{n_A \mu_A^*(l) - n_A RT \ln \frac{n_A}{n_A + n_B} - n_A RT\beta \left[\frac{n_B^2}{(n_A + n_B)^2} \right]}{n_B} \\ = & \mu_B^*(l) + RT \ln \frac{n_B}{n_A + n_B} + RT\beta \frac{n_A^2}{(n_A + n_B)^2}. \end{aligned}$$

2. G is symmetric in exchanging x and $(1-x)$. To find G_B we can therefore simply swap the subscripts A and B in the expression of problem b):

$$G_B = \mu_B^*(l) + RT \ln \frac{n_B}{n_A + n_B} + RT\beta \frac{n_A^2}{(n_A + n_B)^2}.$$

Exercise 13

Since we have an ideal-dilute solution, we can use Henry's law for the solute (HCl) and Raoult's law for the solvent (benzene). This means that the vapour pressure of the solute is given by $P_{HCl} = x_{HCl}K_{HCl}$, in which x_{HCl} is the mole fraction of HCl in solution and K_{HCl} is the Henry-constant.

At $P_{HCl} = 760$ mm Hg, the mole fraction HCl in benzene is $x_{HCl} = 0.040$.

We can use this value to calculate the Henry-constant: $K_{HCl} = \frac{P_{HCl}}{x_{HCl}} = \frac{760}{0.040} = 19 \cdot 10^3$ mm Hg = 19 m Hg.

We determine the vapour pressure of b(enzene) for the mixture using Raoult's law. The mole fraction benzene is $x_b = 1 - x_{HCl}$. According to Raoult's law we have $P_b = x_b P_b^* = (1 - x_{HCl})200$ mm Hg.

We have to calculate the mole fraction of HCl if the total vapour pressure is 760 mm Hg;

$$P = P_b + P_{HCl} = (1 - x_{HCl})200 + x_{HCl}19 \cdot 10^3 = 760, \quad \text{so} \quad x_{HCl} = \frac{760 - 200}{19 - 0.2} 10^{-3} = 0.030.$$

In the figure below you can see the phase diagram and a magnification for $x_{HCl} \ll 1$, in which H represents Henry's law and the subscript b is used for benzene. The line with label H_{HCl} intersects the $x_{HCl} = 1$ -axis at $19 \cdot 10^3$ mm Hg.

