

## Answers Tutorials 3 Thermodynamics 2, 2023/2024

### 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  $V = \frac{100}{0.914} = 109.4$  cm<sup>3</sup>. 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) We label the two compounds A and B. For an ideal mixture (a mixture in which there is no difference between the interactions between A and A, B and B or A and B), the total volume will simply be the sum of the two original volumes. So in terms of the molar volumes  $V_{m,A}$  en  $V_{m,B}$  we get

$$V = V_{ideal} = n_A V_{m,A} + n_B V_{m,B}, \quad \text{so} \quad V_A = \left( \frac{\partial V}{\partial n_A} \right)_{T,P,n_B} = V_{m,A} \quad \text{and} \quad V_B = V_{m,B}.$$

N.B., the partial molar volume  $V_A = \left( \frac{\partial V}{\partial n_A} \right)_{T,P,n_B}$  is not to be confused with the molar volume  $V_{m,A} = \frac{V^*}{n_A}$ . The latter is defined on the basis of the volume  $V^*$  of the pure compound A.; only for an ideal solution  $V_A = V_{m,A}$ .

- b)

$$V = V_{ideal} + V^E \quad \text{with} \quad V_{ideal} = n_A V_{m,A} + n_B V_{m,B}.$$

To calculate the partial molar volumes, we first need to translate the molar excess volume to an excess volume according to  $V^E = nV_m^E = (n_A + n_B)V_m^E$ . If we rewrite  $V^E$  in terms of  $n_A$  and  $n_B$ , we get

$$V^E = (n_A + n_B)V_m^E = (n_A + n_B)\frac{n_A n_B}{(n_A + n_B)^2} \left( a_0 + a_1 \frac{n_A - n_B}{n_A + n_B} \right) \quad \text{so}$$

$$V = n_A V_{m,A} + n_B V_{m,B} + \frac{n_A n_B}{n_A + n_B} \left( a_0 + a_1 \frac{n_A - n_B}{n_A + n_B} \right).$$

We can find the partial molar volume of propionic acid using

$$V_A = \left( \frac{\partial V}{\partial n_A} \right)_{T,P,n_B} = V_{m,A} + \frac{a_0 n_B^2}{(n_A + n_B)^2} + \frac{a_1 (3n_A - n_B) n_B^2}{(n_A + n_B)^3} = V_{m,A} + a_0 x_B^2 + a_1 (3x_A - x_B) x_B^2.$$

In the same way we find for  $V_B$

$$V_B = V_{m,B} + a_0 x_A^2 + a_1 (x_A - 3x_B) x_A^2.$$

c) In an equimolar solution we have  $x_A = x_B = 0.5$ . The molar volumes can be calculated using

$$V_{m,A} = \frac{M_A}{\rho_A} = \frac{74.08 \text{ g/mol}}{0.97174 \text{ g/cm}^3} = 76.23 \text{ cm}^3 \text{ mol}^{-1} \quad \text{and} \quad V_{m,B} = \frac{86.13 \text{ g/mol}}{0.86398 \text{ g/cm}^3} = 99.69 \text{ cm}^3 \text{ mol}^{-1}.$$

Using these values we obtain

$$V_A = 76.23 - 2.4697 \cdot 0.5^2 + 0.0608 \cdot (3 \cdot 0.5 - 0.5) \cdot 0.5^2 = 75.63 \text{ cm}^3 \text{ mol}^{-1} \quad \text{and} \quad V_B = 99.06 \text{ cm}^3 \text{ mol}^{-1}.$$

## Exercise 12

We choose  $j = A$  for *o*-xylene and  $j = B$  for *m*-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 22 °C ( $P^*$  and  $P$  both represent vapour pressures of pure compounds, but at 90 and 22 °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*

$$\chi_A = \frac{36.24 \cdot 10^3}{8.314} \left( \frac{1}{295.15} - \frac{1}{363.15} \right) = 2.765 \quad \text{resp.} \quad \chi_B = \frac{35.66 \cdot 10^3}{8.314} \left( \frac{1}{295.15} - \frac{1}{363.15} \right) = 2.721,$$

so we have (\* now indicates that it is the vapour pressure of a pure compound (at 22 °C), so  $P_{A,B}^*$  is what we previously called  $P_{A,B}$  since the meaning of \* has changed)

$$P_A^* = 18.5 \exp(-2.765) = 1.17 \text{ kPa} \quad \text{and} \quad P_B^* = 21.9 \exp(-2.721) = 1.44 \text{ kPa}.$$

a) An ideal solution follows Raoult's law,  $P_j = x_j P_j^*$ . 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  $P = P_{ext} = 1.24 \text{ kPa}$  and  $T = 22 \text{ °C}$ .

$$\text{We find } x_A = \frac{1.24 - 1.44}{1.17 - 1.44} = 0.741 \quad \text{and} \quad x_B = 1 - x_A = 0.259.$$

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

$$y_A = \frac{P_A}{P_A + P_B} = \frac{x_A P_A^*}{x_A P_A^* + x_B P_B^*} = \frac{0.741 \cdot 1.17}{0.741 \cdot 1.17 + 0.259 \cdot 1.44} = \frac{0.8670}{1.240} = 0.699. \quad \text{and} \quad y_B = 1 - y_A = 0.301.$$

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

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

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

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

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

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  $19 \cdot 10^3 \text{ mm Hg}$ .

