Solutions Exercise Classes 5 Physical Chemistry 1 2021/2022

Exercise 15

For ideal solutions we have found for the entropy of mixing

$$\Delta_{mix}S = -nR\left(x_A \ln x_A + x_B \ln x_B\right) = -nR\left(x_A \ln x_A + (1-x_A)\ln(1-x_A)\right).$$

We find the minimum either by realizing that this is a symmetric function in $x_A = \frac{1}{2}$, or by finding the minimum by putting the derivative with respect to e.g. x_A equal to zero:

$$\frac{\mathrm{d}\Delta_{mix}S}{\mathrm{d}x_A} = -nR\left(\ln x_A + \frac{x_A}{x_A} - \ln(1-x_A) - \frac{1-x_A}{1-x_A}\right) = -nR\ln\frac{x_A}{1-x_A} = 0 \quad \text{for} \quad x_A = \frac{1}{2}.$$

a) Thus in terms of mole fractions we find the maximum entropy of mixing at $x_A = x_B = \frac{1}{2}$. In terms of numbers of mol:

$$\frac{n_{hex}}{n_{hept}} = \frac{\frac{n_{hex}}{n_{hex}+n_{hept}}}{\frac{n_{hept}}{n_{hex}+n_{hept}}} = \frac{x_{hex}}{x_{hept}} = \frac{x_A}{x_B} = 1 \quad \text{or} \quad \mathrm{n_{hex} = n_{hept}}.$$

b) In terms of mass this becomes (using the molar mass M) :

$$\frac{m_{hex}}{m_{hept}} = \frac{n_{hex}M_{hex}}{n_{hept}M_{hept}} = 1 \cdot \frac{M_{hex}}{M_{hept}} = \frac{86.17\ \mathrm{g\ mol^{-1}}}{100.20\ \mathrm{g\ mol^{-1}}} = 0.8600.$$

Exercise 16

We substitute the measured temperature increase into the standard expression for boiling point elevation:

$$\Delta T = K x_B \quad \text{in which} \quad K = \frac{RT^{*2}}{\Delta_{vap}H},$$

or

$$0.80 = \Delta T = \frac{RT^{*2}}{\Delta_{vap}H} \cdot \frac{n_B}{n_{\text{benzene}} + n_B} = \frac{8.314 \cdot 353.30^2}{30.8 \cdot 10^3} \cdot \frac{\frac{10}{M_B}}{\frac{100}{78.11} + \frac{10}{M_B}} = \frac{8.314 \cdot 353.30^2}{30.8 \cdot 10^3 \cdot \left(\frac{10}{78.11}M_B + 1\right)}.$$

With this we find

$$M_B = 321\ \mathrm{g/mol}.$$

Exercise 17

a) For a non-ideal solution the chemical potential of component A is $\mu_A = \mu_A^* + RT\ln a_A$ instead of the ideal solution approximation $\mu_A = \mu_A^* + RT\ln x_A$. This implies that in the derivation for the osmotic pressure we also have to replace $\ln x_A$ by $\ln a_A$, in which a_A is the activity of component A in the solution. So we can continue the original derivation for the osmotic pressure at the equation

$$-RT\ln x_A = V_{m,A}\Pi.$$

Replacing $\ln x_A$ by $\ln a_A$ immediately gives the accurate result for the osmotic pressure

$$\Pi = -\frac{RT}{V_{m,A}}\ln a_A.$$

Note that A represents the solvent, while in the approximated van 't Hoff equation the concentration of the solute B shows up.

b) The osmotic pressure of an ideal solution is given by the van 't Hoff equation $\Pi = [B]RT$. This approximation for very dilute solutions leads to the result $\Pi = [B]RT = 0.282\ \mathrm{mol/dm^3} \cdot 8.314\ \mathrm{J/mol\,K} \cdot 293.2\ \mathrm{K} = 687\ \mathrm{J/dm^3} = 687\ \mathrm{Nm/dm^3} = 687 \cdot 10^3\ \mathrm{N/m^2} = 6.87 \cdot 10^5\ \mathrm{Pa} = 6.87\ \mathrm{bar}$.

c) We use the result of a). The molar volume of water at 20 °C and 1 atm is $V^*_{m,H_2O} = \frac{18.015\ \mathrm{g/mol}}{0.998\ \mathrm{g/cm^3}} = 18.05\ \mathrm{cm^3/mol}$. The osmotic pressure is $\Pi = 7.61\ \mathrm{atm} = 1.01325 \cdot 7.61 = 7.71\ \mathrm{bar} = 7.71 \cdot 10^5\ \mathrm{N/m^2}$. Using this result, we find for the activity of the water (component A)

$$\ln a_A = -\frac{\Pi V_{m,A}}{RT} = -\frac{\Pi V^*_{m,H_2O}}{RT} = -\frac{7.71 \cdot 10^5\ \mathrm{Nm^{-2}} \cdot 18.05 \cdot 10^{-6}\ \mathrm{m^3mol^{-1}}}{8.314\ \mathrm{J\ mol^{-1}\ K^{-1}} \cdot 293.2\ \mathrm{K}} = -5.71 \cdot 10^{-3},$$

so $a_A = 0.9943$.
Note, that by using only SI-units, it is easily checked that $\ln a_A$ is dimensionless (has no units). The activity coefficient γ_{H_2O} of the solvent (on the mole fraction scale) follows with $a_i = \gamma_i x_i$ and is easiest determined via the molality b_i of the components, according to

$$\gamma_{H_2O} = \frac{a_{H_2O}}{x_{H_2O}} = a_{H_2O}\frac{n_{H_2O} + n_B}{n_{H_2O}} = a_{H_2O}\frac{b_{H_2O} + b_B}{b_{H_2O}} = 0.9943\frac{\frac{10^3}{18.015} + 0.300}{\frac{10^3}{18.015}} = \frac{0.9943}{0.9946} = 0.9997.$$

Exercise 18

a) We obtain the pressure dependence of μ by integrating μ with the standard pressure $P^\ominus$ as reference point. For a pure substance we can replace μ_i by $G_{m,i}$ and at constant T the term $-S\mathrm{d}T$ vanishes.

$$\mu_i(P) = \mu_i(P^\ominus) + \int_{P^\ominus}^{P} \mathrm{d}\mu_i = \mu_i(P^\ominus) + \int_{P^\ominus}^{P} \mathrm{d}G_{m,i} = \mu_i(P^\ominus) + \int_{P^\ominus}^{P} V_{m,i}\mathrm{d}P' = \mu_i^\ominus + \int_{P^\ominus}^{P} V_{m,i}\mathrm{d}P',$$

where P' is used to avoid confusion between the dummy variable in the integral and the pressure P of the system. If we combine this result with the definition of the activity a_i we find

$$RT \ln a_i(P) = \mu_i(P) - \mu_i^\ominus = \int_{P^\ominus}^{P} V_{m,i}\mathrm{d}P'.$$

b) A pure perfect gas in a multi-component system is, of course, only relevant if the gas does not mix with any other of the other components, e.g. liquids or solids. In that case the partial pressure of the gas is equal to the total pressure of the system and the equation of state of the perfect gas $PV = nRT$ can be rewritten in terms of the molar volume, $V_{m,i} = \frac{RT}{P_i} = \frac{RT}{P}$, such that

$$RT \ln a_i(P) = \int_{P^\ominus}^{P_i} V_{m,i}\mathrm{d}P' = \int_{P^\ominus}^{P} V_{m,i}\mathrm{d}P' = RT \int_{P^\ominus}^{P} \frac{\mathrm{d}P'}{P'} = RT \ln \frac{P}{P^\ominus}, \quad \text{or} \quad a_i(P) = \frac{P}{P^\ominus}.$$

In other words, for a perfect gas the activity is equal to the pressure in bar. Substituting $P = 21$ bar results in $a_i = 21$. It is, however, questionable whether the perfect gas law still applies at such a pressure, but nevertheless the activity will be much larger than 1.

c) The molar volume of water at 298 K and $P = P^\ominus$ is $V^\ominus_{m,i} = \frac{M}{\rho^\ominus} = 18.02/0.997 = 18.07\ \mathrm{cm^3/mol}$ $= 18.07 \cdot 10^{-6}\ \mathrm{m^3/mol}$. Because the compressibility is considered to have a negligible effect on the volume for the applied pressure difference, we can safely assume $V^\ominus_{m,i}$ to be constant. For the activity we then find

$$\ln a_i(P) = \frac{1}{RT}\int_{P^\ominus}^{P} V_{m,i}\mathrm{d}P' = \frac{V^\ominus_{m,i}}{RT}\left(P - P^\ominus\right) = \frac{18.07 \cdot 10^{-6}}{8.314 \cdot 298}(21 - 1) \cdot 10^5 = 0.0146.$$

So the activity at that pressure is $a_i = 1.0147$, which, despite the large pressure, deviates less than 2 % from the assumption $a_i(s, l) = 1$.

d)

$$\begin{aligned}
\ln a_i(P) &= \frac{1}{RT}\int_{P^\ominus}^{P} V_{m,i}\mathrm{d}P' = \frac{1}{RT}\int_{P^\ominus}^{P} V_m^\ominus\left[1-\beta P'\right]\mathrm{d}P' = \frac{V_m^\ominus}{RT}\left[\left(P-P^\ominus\right)-\frac{\beta}{2}\left(P^2-P^{\ominus 2}\right)\right] \\
&= \frac{18.07\cdot 10^{-6}}{8.314\cdot 298}\left[(21-1)\cdot 10^5\right]-\frac{18.07\cdot 10^{-6}}{8.314\cdot 298}\left[\frac{4.6\cdot 10^{-10}}{2}\left(21^2-1^2\right)\cdot 10^{10}\right] \\
&= 0.0146-7.38\cdot 10^{-6}.
\end{aligned}$$

This result is not very worrying, but if the pressure is much higher than 20 bar the error as a result of the incompressibility assumption can become too large.
The temperature also has a small effect since the thermal expansion is usually very small.
For solid or fluid phases with a large molar volume V_m such as polymers, the assumption might become inadequate.