Exercise Classes 5 Physical Chemistry 1 2021/2022

Exercise 15

A mixture of hexane and heptane forms an ideal solution to a good approximation. In what ratio should we mix hexane and heptane to realize the largest entropy of mixing?

a) In terms of number of mol.

b) In terms of mass.

Exercise 16

The boiling point of benzene is 80.15 °C. The heat of evaporation is 30.8 kJ/mol. The molar mass of benzene is 78.11 g/mol. 10 g of a solid is completely dissolved in 100 g benzene. Because of this, the boiling point of benzene increases to 80.95 °C. Calculate the molar mass of the dissolved substance.

Exercise 17

The van 't Hoff expression for the osmotic pressure of very diluted ideal solutions is

$$\Pi = [B]RT.$$

a) Show that the osmotic pressure of a real (non-ideal) solution is given by

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

For an aqueous solution of sucrose ($C_{12}H_{22}O_{11}$) with a molality of 0.300 mol/kg the molarity is 0.282 mol/dm^3 at 20 °C and 1 atm. The density of pure water at 20 °C is $\rho_{H_2O} = 0.998$ g/cm^3.

b) Determine the osmotic pressure using the van 't Hoff expression for very diluted ideal solutions.

c) The measured osmotic pressure for this solution turns out to be 7.61 atm.
Determine the activity and the activity coefficient of the solvent.

Exercise 18

We estimate the inaccuracy in the assumption usually made that the activity of a pure solid i or a pure liquid phase i in a mixture is approximately equal to $a_i = 1$ for not too large pressures P. In the lecture it was shown that the chemical potential of a pure substance i, even if it is part of a multi-component system, as long as it is a *pure* compound in the multi-component system, is equal to its molar Gibbs free energy:

$$\mu_i = G_{m,i} \text{ and } \mathrm{d}\mu_i = \mathrm{d}G_{m,i} = -S_{m,i}\mathrm{d}T + V_{m,i}\mathrm{d}P.$$

The activity a_i of any component i in a multi-component system at a given temperature T is defined by

$$\mu_i \equiv \mu_i^{\ominus} + RT \ln a_i$$

a) Use this definition, in which the pressure P is an implicit variable in a_i as well as in μ_i, to find the following expression for the pressure dependence of the activity, $a_i(P)$, at constant temperature in terms of the molar volume $V_{m,i}$ of component i.

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

where P' is used to avoid confusion between the dummy variable in the integral and the pressure P of the system.

b) A gas in a multi-component system is, of course, only *pure* if the gas does not mix with 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.
Use the result of part a) to calculate the activity of a perfect gas in such a case at pressure $P = 21$ bar and $T = 298$ K.

In contrast to a gas, a fluid or a solid is nearly incompressible. Therefore, the molar volume hardly changes with increasing pressure. As an illustration consider water at 298 K. The isothermal compressibility of water at this temperature is $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = 4.6 \cdot 10^{-10}\ \mathrm{Pa}^{-1}$.
The density at 298 K and $P = P^{\ominus}$ is given by $\rho(H_2O) = 0.997\ \mathrm{g/cm}^3$.

c) First estimate the activity of water at $P = 21$ bar and 298 K by neglecting the compressibility.

d) Next we will include the compressibility, but assume that it is independent of the pressure, i.e. that β is constant for the applied pressures. Then we can determine the volume at pressure P using $V_m(P) = V_m^{\ominus}\,[1 - \beta P]$.
Again, determine the activity of water at $P = 21$ bar and 298 K, now taking account of this expression for the pressure dependence of the volume. Should the result worry us?