

# Solutions Exam MOL040, Thermodynamics 2

## 03 November 2021

All 16 subproblems have equal weight for the final grade.  
Sometimes a **NOTE** is added, just meant as an explanation or advise.

### Problem 1

a) Note, that the answers below to part a) are not unique, in some cases overcomplete and are meant to be indicative.

- Equipartition theorem: At high enough temperature the energy per degree of freedom of a system is equal to  $\frac{1}{2}kT$ .
- Henry constant: An effective vapour pressure extrapolated from the vapour pressure dependence on the composition of a dilute solution towards the pure solute axis.
- Isopleth: A line in a temperature-composition or in a pressure-composition phase diagram indicating a constant overall composition, independent of the phases present.
- Critical nucleus: In nucleation of a solid phase from a liquid or a liquid phase from a vapour, too small sized nuclei of the new phase tend to disappear due to the interfacial energy with the mother phase. The critical nucleus has a size, just large enough to overcome this energy barrier.
- Solubility: The maximal amount of solute that can be dissolved in a certain solvent.

b)

$$dA = -PdV - SdT + \mu_A dn_A + \mu_B dn_B + Edq$$

$$\left(\frac{\partial \mu_B}{\partial T}\right)_{V,q,n_A,n_B} = -\left(\frac{\partial S}{\partial n_B}\right)_{V,q,n_A,T}$$

c) The expression is used to calculate the ionic strength of an electrolyte solution. Its value is a measure for the amount and strength of charges in the electrolyte and is used in thermodynamic theories of such solutions, like in the Debye-Hückel limiting law.

$I$ : Ionic strength.

$\Sigma_i$ : sum over all ionic components  $i$  in the electrolyte

$z_i$ : charge of component  $i$

$b_i$ : molality of component  $i$

$b^\ominus$ : standard molality (1 mol/kg)

d)

$$\log \gamma_{\pm} = -|z_+ z_-| A \sqrt{I}$$

$$A = \frac{F^3}{4\pi N_A \ln 10} \left(\frac{\rho b^\ominus}{2\epsilon^3 R^3 T^3}\right)^{\frac{1}{2}} = \frac{F^3}{4\pi N_A \ln 10} \left(\frac{\rho b^\ominus}{2\epsilon^3 R^3}\right)^{\frac{1}{2}} T^{-\frac{3}{2}}$$

For a solution with the same molality only the temperature dependence is relevant:

$$\frac{\log \gamma_{\pm}(275.00 \text{ K})}{\log \gamma_{\pm}(298.15 \text{ K})} = \frac{A(275.00 \text{ K})}{A(298.15 \text{ K})} = \left(\frac{275.00}{298.15}\right)^{-\frac{3}{2}} = 0.9224^{-\frac{3}{2}} = 1.1289$$

$$\log \gamma_{\pm}(275.00 \text{ K}) = 1.1289 \cdot \log(0.900) = -0.051655$$

$$\gamma_{\pm}(275.00 \text{ K}) = 0.888$$

## Problem 2

- 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  $V^E = n V_m^E = (n_A + n_B) V_m^E$ . 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

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

Looking at the symmetry of  $V^E$  and  $V_{ideal}$  on exchanging  $n_A$  and  $n_B$ , or  $x_A$  and  $x_B$ , we can conclude

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

- c) In an equimolar solution we have  $x_A = x_B = 0.5$ . The molar volumes are

$$V_{m,A} = 76.00 \text{ cm}^3 \text{ mol}^{-1} \quad \text{and} \quad V_{m,B} = 77.00 \text{ cm}^3 \text{ mol}^{-1}.$$

Using these values we obtain

$$V_A = 76.00 - 2.4697 \cdot 0.5^2 + 0.0608 \cdot (3 \cdot 0.5 - 0.5) \cdot 0.5^2 = 75.45 \text{ cm}^3 \text{ mol}^{-1} \quad \text{and} \quad V_B = 76.36 \text{ cm}^3 \text{ mol}^{-1}.$$

- d) Putting  $V_A = V_B$  and neglecting the term with  $a_1$  we find

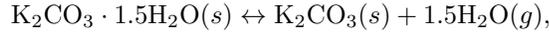
$$V_{m,A} + a_0 (1 - x_A)^2 = V_{m,B} + a_0 x_A^2 \quad \text{so} \quad a_0 (1 - 2x_A + x_A^2) - a_0 x_A^2 = V_{m,B} - V_{m,A} \quad \text{and}$$

$$x_A = \frac{V_{m,B} - V_{m,A} - a_0}{-2a_0} = \frac{77.00 - 76.00 + 2.4679}{-2 \cdot (-2.4679)} = 0.702 \quad \text{and} \quad x_B = 0.298.$$

### Problem 3

The dehydration reaction is

a)



with equilibrium constant (activity of solids  $a(s) \approx 1$ )

$$K = \frac{a_{\text{K}_2\text{CO}_3(s)} \cdot a_{\text{H}_2\text{O}(g)}^{1.5}}{a_{\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}(s)}} \approx a_{\text{H}_2\text{O}(g)}^{1.5}.$$

b)

$$\frac{K(T_1)}{K(T_2)} = \frac{a_{\text{H}_2\text{O}(g)}^{1.5}(T_1)}{a_{\text{H}_2\text{O}(g)}^{1.5}(T_2)} \approx \frac{P^{1.5}(T_1)}{P^{1.5}(T_2)}.$$

Choose in the phase diagram the smallest and largest values on the dehydration transition line:

$$T_1 = 0^\circ \text{C} = 273.15 \text{K}, \quad \text{so} \quad P_1 = 0.1 \text{mbar} = 10 \text{Pa}$$

and

$$T_2 = 92.7^\circ \text{C} = 365.85 \text{K}, \quad \text{so} \quad P_2 = 100 \text{mbar} = 10^4 \text{Pa},$$

leading to

$$\ln \frac{K(T_2)}{K(T_1)} = \ln \left( \frac{10^4}{10} \right)^{1.5} = 1.5 \ln 10^3 = 10.36.$$

The van 't Hoff equation then gives

$$10.36 = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{\Delta H}{8.314} \left( \frac{1}{273.15} - \frac{1}{365.85} \right) = 1.12 \cdot 10^{-4} \Delta H, \quad \text{so}$$

$$\Delta H = +92.9 \text{kJ/mol}.$$

This is an endothermic result, so the heat is stored during the dehydration reaction.

c)

$$\Delta_{trs}G = \Delta_{trs}H - T_{trs}\Delta_{trs}S = 0, \quad \text{so} \quad \Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

Assuming that  $\Delta_{trs}H$  is only weakly dependent on  $T$  we find

$$\Delta_{trs}S(293.15 \text{K}) \approx \frac{92.9 \text{kJ/mol}}{293.15 \text{K}} = 317 \text{J/molK}.$$

d) At  $20^\circ \text{C}$  we read off from the deliquescence line in the phase diagram a partial vapour pressure of  $P_{\text{H}_2\text{O}(g)} = 10 \text{mbar} = 1.0 \text{kPa}$ , and using  $P_{\text{sat}}(\text{H}_2\text{O}(g))$  at  $20^\circ \text{C} = 2.330 \text{kPa}$ , we find

$$RH = \frac{1.0}{2.330} \cdot 100\% = 43\%.$$

## Problem 4

a)

$$c_s = 5.5 \cdot 10^3 \text{ mol/m}^3, \quad \text{and} \quad c_l = \frac{250 \cdot 10^3 \text{ g/m}^3}{282 \text{ g/mol}} = 0.887 \cdot 10^3 \text{ mol/m}^3, \quad \text{so}$$

$$\begin{aligned} \gamma &= \frac{2}{(36\pi)^{\frac{1}{3}}} (5.5 \cdot 10^3 \cdot 6.0 \cdot 10^{23})^{\frac{2}{3}} \cdot 1.38 \cdot 10^{-23} \cdot 340 \ln \left( \frac{5.5 \cdot 10^3}{0.887 \cdot 10^3} \right) \\ &= 0.414 \cdot 0.0104 \cdot 1.825 = 7.86 \cdot 10^{-3} \text{ J/m}^2 \end{aligned}$$

b)

$$P_{\text{in}} = P_{\text{out}} + \frac{2\gamma}{r} \quad \text{and} \quad V(r) = \frac{4\pi}{3} r^3 = n\Omega = \frac{n}{c_s N_A}, \quad \text{so}$$

$$r = \left( \frac{3}{4\pi} \right)^{\frac{1}{3}} V^{\frac{1}{3}} = \left( \frac{3}{4\pi} \right)^{\frac{1}{3}} \cdot \left( \frac{n}{c_s N_A} \right)^{\frac{1}{3}}, \quad \text{and}$$

$$\Delta P = \frac{2\gamma}{r} = \frac{2\gamma}{\left[ \left( \frac{3}{4\pi} \right)^{\frac{1}{3}} \cdot \left( \frac{n}{c_s N_A} \right)^{\frac{1}{3}} \right]}, \quad \text{so}$$

$$\Delta P = \frac{2 \cdot 7.86 \cdot 10^{-3}}{\left( \frac{3}{4\pi} \right)^{\frac{1}{3}} \left( \frac{6}{5.5 \cdot 10^3 \cdot 6.0 \cdot 10^{23}} \right)^{\frac{1}{3}}} = \frac{15.7 \cdot 10^{-3}}{0.620 \cdot 1.22 \cdot 10^{-9}} = 2.07 \cdot 10^7 \text{ N/m}^2, \quad \text{so}$$

$$P_{\text{in}} = 207 \text{ bar.}$$

c)

$$W_c = \gamma\sigma = \gamma 4\pi R^2 \quad \text{and} \quad R(n) = \left( \frac{3}{4\pi} \right)^{\frac{1}{3}} \cdot \left( \frac{n}{c_s N_A} \right)^{\frac{1}{3}}, \quad \text{so}$$

$$W_c(n) = 4\pi \left( \frac{3}{4\pi} \right)^{\frac{2}{3}} \gamma \left( \frac{n}{c_s N_A} \right)^{\frac{2}{3}} = \left( \frac{9}{4\pi} \right)^{\frac{1}{3}} \gamma \left( \frac{n}{c_s N_A} \right)^{\frac{2}{3}}, \quad \text{for } n \geq 2 \quad \text{and.}$$

$$W_c(n) = 0, \quad \text{for } n = 1.$$

d)

$$\frac{C(n)}{C(n=1)} = \frac{\exp[-\beta W_c(n)]}{\exp[-\beta W_c(n=1)]} = \exp[-\beta W_c(n)], \quad \text{so}$$

$$\frac{C(n)}{C(n=1)} = \exp \left[ -\frac{1}{kT} \left( \frac{9}{4\pi} \right)^{\frac{1}{3}} \gamma \left( \frac{n}{c_s N_A} \right)^{\frac{2}{3}} \right].$$

For  $n = 10$  we find

$$\frac{C(10)}{C(n=1)} = \exp \left[ -\frac{1.47 \cdot 10^{-20}}{1.38 \cdot 10^{-23} \cdot 340} \right] = 0.044 = 4.4\%.$$