Solutions Exam MOL040, Thermodynamics 2
23 January 2019

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.

- Triple point: A point in a phase diagram where three different phases are in mutual equilibrium.

- First order phase transition: A transition between two phases for which the first derivative of the chemical potential with respect to the temperature is discontinuous. Consequently the change in volume, enthalpy, entropy will be non-zero.

- Regular solution: A solution for which the excess enthalpy on mixing $\Delta H^{\mathrm{E}} \neq 0$, but the excess entropy $\Delta S^{\mathrm{E}} = 0$.

- Molality: The amount of a component i in a mixture in terms of its amount in number of moles divided by the mass of the solvent in kg. $m_i = \frac{n_i}{\text{kg of solvent}}$.

- pH: $\mathrm{pH} \equiv -\log a(\mathrm{H}^+)$, where $a(\mathrm{H}^+)$ is the activity of the H^+ ions in the solution.

b)
$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B + E\mathrm{d}q$$

$$\left(\frac{\partial \mu_A}{\partial q}\right)_{P,T,n_A,n_B} = \left(\frac{\partial E}{\partial n_A}\right)_{P,T,n_B,q}$$

c) Partial molar value of X, with respect to component i at constant temperature and pressure.
X: any function, e.g. volume, Gibbs free energy, etc.
i: component i
n: amount/number of moles
P: pressure of the system/mixture
T: temperature of the system/mixture

d) Use the Bolzmann definition of entropy

$$S = k\ln W, \quad \text{so} \quad \Delta_{trs}S = k\ln W' - k\ln W = k\ln\frac{W'}{W}, \quad \text{or} \quad W' = W\exp\left[\frac{\Delta_{trs}S}{k}\right].$$

At the phase transition (Clapeyron equation)

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{trs}S}{\Delta_{trs}V}, \quad \text{so} \quad \Delta S_{trs} = \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)\Delta_{trs}V.$$
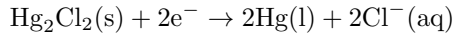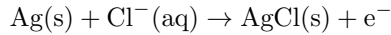
Combining this with the earlier result, we find

$$W' = W\exp\left[\frac{1}{k}\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)\Delta_{trs}V\right].$$

For a transition from solid to gas, the value of $\left(\frac{dP}{dT}\right)$ is negligible for the solid, while for the gas phase it follows from the equation of state $PV = nRT$, so $\left(\frac{dP}{dT}\right) \approx \left(\frac{dP_g}{dT}\right) = \frac{n_g R}{V_g}$, so we get $(nR = Nk)$

$$W' \approx W \exp\left[\frac{n_g R}{k}\frac{\Delta_{trs}V}{V_g}\right] = W \exp\left[N_g \frac{V_g - V_s}{V_g}\right] = W \exp\left[N_g\left(1 - \frac{V_s}{V_g}\right)\right].$$

Problem 2

a)
$$Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$$
$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$$

b)
$$\Delta_r G = -\nu FE = -2 \cdot 9.648 \cdot 10^4 \cdot 0.046 = -8.876 \text{ kJ/mol}.$$

c) At constant pressure $(dP = 0)$:
$$dH = dQ + V dP + E dq = dQ + E dq.$$

Reversibly, so

$$\Delta_r H = Q^{rev} + E\Delta q = Q^{rev} + W^{max} = Q^{rev} - \Delta_r G = 11.08 \text{ kJ/mol}, \quad \text{so} \quad Q^{rev} = 11.08 - (-8.876) = 19.96 \text{ kJ/mol}.$$

d)
$$dG = V dP - S dT + E dq, \quad \text{so} \quad \left(\frac{\partial E}{\partial T}\right)_{P,q} = -\left(\frac{\partial S}{\partial q}\right)_{P,T} = -\frac{1}{T}\left(\frac{\partial Q^{rev}}{\partial q}\right)_{P,T}.$$

$$\left(\frac{\partial E}{\partial T}\right)_{P,q} = -\frac{1}{T}\frac{dQ^{rev}}{dq} = -\frac{1}{298} \cdot \frac{19.96 \cdot 10^3}{-2 \cdot 9.648 \cdot 10^4} = 3.47 \cdot 10^{-4} \text{ V/K} = 0.347 \text{ mV/K}.$$

Problem 3

a) The results can be found in Figure 1 for the various regions:
   1: R-MSA(s) + (R-MSA + S-IPSA)(l)
   2: (R-MSA + S-IPSA)(l)
   3: (R-MSA/S-IPSA)(s) + (R-MSA + S-IPSA)(l)
   4: (R-MSA/S-IPSA)(s) + (R-MSA + S-IPSA)(l)
   5: S-IPSA(s) + (R-MSA + S-IPSA)(l)
   6: S-IPSA(s) + (R-IPSA + S-IPSA)(l)
   7: (R-IPSA + S-IPSA)(l)
   8: (R-IPSA/S-IPSA)(s) + (R-IPSA + S-IPSA)(l)
   9: (R-IPSA/S-IPSA)(s) + (R-IPSA + S-IPSA)(l)
   10: R-IPSA(s) + (R-IPSA + S-IPSA)(l)
   11: (R-IPSA + R-MSA)(l)
   12: R-MSA(s) + (R-MSA/S-IPSA)(s)
   13: (R-MSA/S-IPSA)(s) + S-IPSA(s)
   14: S-IPSA(s) + (S-IPSA/R-IPSA)(s)
   15: (S-IPSA/R-IPSA)(s) + R-IPSA(s)
   16: R-IPSA(s) + (R-IPSA + R-MSA)(l)
   17: R-MSA(s) +(R-IPSA + R-MSA)(l)
   18: R-IPSA(s) + R-MSA(s)
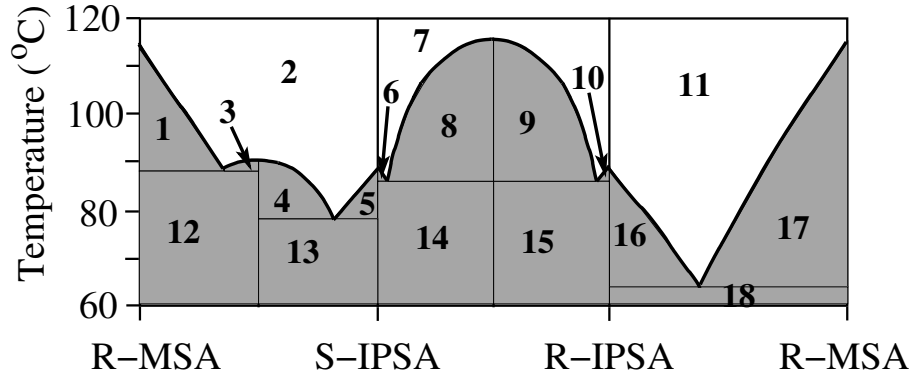   NOTE: Advised but not necessary is putting the further data in the graph (see Figure 2).

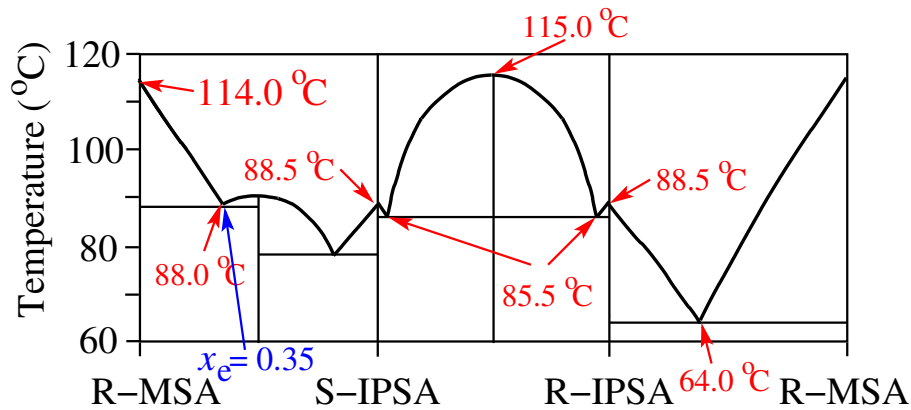Figure 1: NOTE: All shaded areas are two-phase regions.

Figure 2: The futher data have been added to the phase diagram.

b) Because the phase equilibrium can be considered as linear we can use the approximate expression for freezing point depression

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{trs}H} \right) x_B = \left(\frac{R\left(T^*_{\text{R−MSA}}\right)^2}{\Delta_{\text{fus,R−MSA}}H^*} \right) x_{\text{S−IPSA}}.$$

Note: the mole fraction values run between 0 and 1 for each of the three parts of the phase diagram (R-MSA to S-IPSA, S-IPSA to R-IPSA and R-IPSA to R-MSA).
The slope of the linear line is given by

$$\frac{\mathrm{d}\Delta T}{\mathrm{d}x_B} = \frac{RT^{*2}}{\Delta_{\text{fus}}H^*} = \frac{114.0 - 88.0}{0.35 - 0} = 74.29 \text{ degrees K,}$$

so

$$\Delta_{\text{fus}}H* = \frac{RT^{*2}}{\frac{\mathrm{d}\Delta T}{\mathrm{d}x_B}} = \frac{8.314 \cdot (273.15 + 114.0)^2}{74.29} = \frac{1.246 \cdot 10^6}{74.29} = 16.77 \text{ kJ/mol.}$$

Alternatively you can use (see also problem 3d)

$$\ln x_B = \frac{\Delta_{\text{fus}}H^*}{R} \left(\frac{1}{T^*_{\text{fus}}} - \frac{1}{T} \right),$$

leading to the same result.

c)

$$\frac{n_l}{n_s} = \frac{l_s}{l_l} = \frac{1 - 0.7}{0.7 - 0.29} = \frac{0.3}{0.41} = 0.73.$$

d) Use the notation RS = R-ISPA/S-IPSA, R = R-ISPA and S = S-IPSA.

$$\mu_{\text{RS(s)}}^* = \mu_{\text{RS(l)}}^* + RT \ln a_{\text{RS(l)}}, \quad \text{so} \quad -\Delta_{\text{fus}} G_m^*(RS) = RT \ln a_{\text{RS(l)}}.$$

Because for the pure component at T_{fus}^*

$$\Delta_{\text{fus}} G_m^*(RS)(T_{\text{fus}}^*) = 0 \quad \text{it follows that} \quad \Delta_{\text{fus}} H_m^*(RS)(T_{\text{fus}}^*) - T_{\text{fus}}^* \Delta_{\text{fus}} S_m^*(RS)(T_{\text{fus}}^*) = 0,$$

so

$$\Delta_{\text{fus}} S_m^*(RS)(T_{\text{fus}}^*) = \frac{\Delta_{\text{fus}} H_m^*(RS)(T_{\text{fus}}^*)}{T_{\text{fus}}^*},$$

we find

$$-\frac{\Delta_{\text{fus}} H_m^*(RS)(T_{\text{fus}}^*)}{R} \left[\frac{1}{T} - \frac{1}{T_{\text{fus}}^*} \right] = \ln a_{\text{RS(l)}},$$

so for $T = T_e$ we find

$$-\frac{\Delta_{\text{fus}} H_m^*(RS)}{R} \left[\frac{1}{T_e} - \frac{1}{T_{\text{fus}}^*} \right] = \ln a_{\text{RS(l)}} = \ln x_{\text{RS(l)}} + \ln \gamma_{\text{RS(l)}}.$$

plugging in the values we find

$$-\frac{25.05 \cdot 10^3}{8.314} \left[\frac{1}{273.15 + 85.5} - \frac{1}{273.15 + 115} \right] = \ln(1 - 2 \cdot 0.05) + \ln \gamma_{\text{RS(l)}}, \quad \text{so} \quad \ln \gamma_{\text{RS(l)}} = -0.5331, \quad \text{and}$$

$$\gamma_{\text{RS(l)}} = 0.59.$$

Problem 4

a) For that we need the Kelvin equation

$$P = P^* \exp\left[\frac{V_m \Delta P}{RT} \right], \quad \text{with} \quad \Delta P = \frac{2\gamma}{r}$$

$$\log P^*(298 \text{ K}) = 45.465 - \frac{4044}{298} - 13.21 \log 298 + 1.098 \cdot 10^{-7} \cdot 298 + 6.415 \cdot 10^{-6} \cdot 298^2$$
$$= 45.465 - 13.57 - 32.68 + 3.27 \cdot 10^{-5} + 0.570 = -0.215, \quad \text{so}$$

$$P^*(298 \text{ K}) = 0.609 \text{ Torr} = \frac{0.609}{750} = 0.812 \text{ mbar}.$$

$$\Delta P = \frac{2\gamma}{r} = \frac{2 \cdot 43.8 \cdot 10^{-3}}{0.5 \cdot 10^{-6}} = 175.2 \cdot 10^3 \text{ Pa}.$$

$$V_m = \frac{M}{\rho} = \frac{78.13}{1.1004} \text{ cm}^3/\text{mol}.$$

Putting these values into the Kelvin equation results in

$$P = 0.812 \exp\left[\frac{71.0 \cdot 10^{-6} \cdot 175.2 \cdot 10^3}{8.314 \cdot 298} \right] = 0.816 \text{ mbar} = 0.612 \text{ Torr}.$$

b) Because $\gamma = \gamma(T_vap(r))$, we first determine its value

$$\gamma(T_{vap}) = G\left(1 - \frac{T_{vap}}{T_c}\right)^n = 93.26 \cdot 10^{-3}\left(1 - \frac{462.15}{726}\right)^{1.43} = 21.93 \text{ mN/m}.$$

Plugging in all values into the equation for $T'_{vap}(r)$ gives $(P = P^\ominus)$

$$T'_{vap}(0.5 \cdot 10^{-6}) = \frac{462.15}{1 - \frac{8.314 \cdot 462.15}{42.70 \cdot 10^3}\ln\left[1 + \frac{2 \cdot 21.93 \cdot 10^{-3}}{10^5 \cdot 0.5 \cdot 10^{-6}}\right]} = \frac{462.15}{1 - 0.0900\ln 1.877} = 490 \text{ K}.$$

c) For higher temperatures T the surface tension $\gamma(T)$ will be smaller, so T'_{vap} will become closer to T_{vap}.
Furthermore $\Delta_{vap}H_m$ is in reality dependent on T; For increasing temperatures T the vaporization enthalpy will decrease, so T'_{vap} will become closer to T_{vap}.
In practice nucleation of the gas bubble will be heterogeneous, that is, will nucleate on foreign surfaces, like dust or the wall of the vessel, resulting in a smaller effective surface tension.

d) Along the phase boundary line (the liquid-vapour coexistence line)

$$d\mu_g = d\mu_l, \quad \text{so} \quad (V_m dP - S_m dT)_g = (V_m dP - S_m dT)_l, \quad \text{or}$$

$$\left(S_m^g - S_m^l\right) dT = \left(V_m^g - V_m^l\right) dP \approx V_m^g dP.$$

Using the equation of state for a perfect gas $(PV_m = RT)$ we find

$$\left(\frac{RT}{P}dP\right)_g = \left(S_m^g - S_m^l\right) dT, \quad \text{so} \quad R\left(\frac{dP}{P}\right)_g = \left(S_m^g - S_m^l\right)\frac{dT}{T}.$$

On the phase boundary line it also holds that

$$\mu_g = \mu_l, \quad \text{so} \quad H_m^g - TS_m^g = H_m^l - TS_m^l, \quad \text{or} \quad S_m^g - S_m^l = \frac{H_m^g - H_m^l}{T},$$

which we substitute in the equation for $R\left(\frac{dP}{P}\right)_g$:

$$R\left(\frac{dP}{P}\right)_g = \left(H_m^g - H_m^l\right)\frac{dT}{T^2}.$$

Integrating both sides we get (the gas in the bubble will have a higher pressure $P^\ominus + \Delta P = P^\ominus + \frac{2\gamma}{r}$; assume that γ is independent of T)

$$\int_{P^\ominus}^{P^\ominus + \frac{2\gamma}{r}} \frac{dP}{P} = \frac{\left(H_m^g - H_m^l\right)}{R}\int_{T_{vap}}^{T'_{vap}} \frac{dT}{T^2}, \quad \text{so} \quad \ln\frac{P^\ominus + \frac{2\gamma}{r}}{P^\ominus} = \frac{\Delta_{vap}H_m}{R}\left[\frac{1}{T_{vap}} - \frac{1}{T'_{vap}}\right].$$

Rearranging the expression we find

$$T'_{vap} = \frac{T_{vap}}{1 - \frac{RT_{vap}}{\Delta_{vap}H_m}\ln\left[1 + \frac{2\gamma}{P^\ominus r}\right]}.$$