

Answers Tutorials 6 Thermodynamics 2, 2023/2024

Exercise 22

- a) We use the Kelvin equation for the vapour pressure of a droplet with radius r

$$P = P^* \exp\left(\frac{2\gamma V_m}{rRT}\right).$$

The molar volume is

$$V_m = \frac{M}{\rho} = \frac{18.02 \text{ gmol}^{-1}}{0.9982 \text{ gcm}^{-3}} = 1.805 \cdot 10^{-5} \text{ m}^3\text{mol}^{-1},$$

so

$$\frac{2\gamma V_m}{rRT} = \frac{2 \cdot 72.75 \cdot 10^{-3} \text{ Nm}^{-1} \cdot 1.805 \cdot 10^{-5} \text{ m}^3\text{mol}^{-1}}{10 \cdot 10^{-9} \text{ m} \cdot 8.314 \text{ JK}^{-1}\text{mol}^{-1} \cdot 293 \text{ K}} = 0.1078,$$

which gives

$$P = 2.3\text{kPa} \cdot \exp(0.1078) = 2.6 \text{ kPa}.$$

- b) If we neglect the contact angle, since it is very small, we can assume that the curvature of the meniscus is that of a semi circle (in fact a semi sphere) with as radius that of the capillary. The hydrostatic pressure ρgh is equal to the difference in pressure $\frac{2\gamma}{r}$ due to the curvature of the meniscus, so we can find the height using

$$h = \frac{2\gamma}{\rho gr} = \frac{2 \cdot 72.75 \cdot 10^{-3} \text{ Nm}^{-1}}{0.9982 \cdot 10^3 \text{ kgm}^{-3} \cdot 9.807 \text{ ms}^{-2} \cdot \frac{1}{2} \cdot 0.300 \cdot 10^{-3} \text{ m}} = 9.91 \cdot 10^{-2} \text{ m} = 9.91 \text{ cm}.$$

- c)

$$y_{H_2O} = \frac{P_{H_2O}}{P} = \frac{P_{H_2O}}{P_{H_2O}^{sat}} \frac{P_{H_2O}^{sat}}{P} = RH \frac{P_{H_2O}^{sat}}{P} = 0.5 \frac{2330}{10^5} = 0.0117.$$

- d) T_c is the critical temperature of water. When $T \geq T_c$, the liquid and vapour phase cannot be distinguished from one another. This means there is no meniscus anymore, so $\gamma(T = T_c) = 0$. If $T > T_c$, the equation cannot be used anymore.
- e) At $RH = 100\%$ we can use the expression for the equilibrium surface tension.

$$\rho gh = \frac{2\gamma}{r} \quad \text{so} \quad h = \frac{2}{\rho gr} \gamma = \frac{2}{0.9982 \cdot 10^3 \cdot 9.81 \cdot 0.15 \cdot 10^{-3}} \gamma = 1.36 \gamma = 0.207 \left(1 - \frac{T}{T_c}\right)^{\frac{11}{9}}.$$

This results in a height difference of

$$\Delta h = h(363 \text{ K}) - h(293 \text{ K}) = 0.207 \left[\left(1 - \frac{363}{647}\right)^{\frac{11}{9}} - \left(1 - \frac{293}{647}\right)^{\frac{11}{9}} \right] = -0.023 \text{ m}.$$

An increasing temperature results in a lower surface tension, which decreases the height h of the column, found in part b.

Exercise 23

- a) The chemical potential of a pure compound is equal to the molar Gibbs free energy, so

$$\mu(T, P) = G_m(T, P) = H_m(T, P) - TS_m(T, P).$$

At constant pressure $P = 1 \text{ bar} = P^\ominus$ this becomes

$$\mu^\ominus(T) = G_m^\ominus(T) = H_m^\ominus(T) - TS_m^\ominus(T).$$

We can find the boiling point T_b using the equilibrium condition $\mu_l^\ominus(T_b) = \mu_g^\ominus(T_b)$, implying

$$H_{m,l}^\ominus(T_b) - T_b S_{m,l}^\ominus(T_b) = H_{m,g}^\ominus(T_b) - T_b S_{m,g}^\ominus(T_b) \quad \text{so} \quad T_b = \frac{H_{m,g}^\ominus(T_b) - H_{m,l}^\ominus(T_b)}{S_{m,g}^\ominus(T_b) - S_{m,l}^\ominus(T_b)}.$$

If we assume that the numerator and denominator are independent of the temperature (which is a less strict assumption than that all the terms are independent of the temperature), and use the given values for the enthalpies and entropies of formation we find

$$T_b = \frac{H_{m,g}^\ominus - H_{m,l}^\ominus}{S_{m,g}^\ominus - S_{m,l}^\ominus} \approx \frac{\Delta_f H_{m,g}^\ominus(298 \text{ K}) - \Delta_f H_{m,l}^\ominus(298 \text{ K})}{S_{m,g}^\ominus(298 \text{ K}) - S_{m,l}^\ominus(298 \text{ K})} = \frac{(-241.82 - (-285.83)) \cdot 10^3}{188.83 - 69.9} = 370.05 \text{ K}.$$

This value is not too far off from the usual 100°C . Our assumptions seem reasonable, even though we used the relatively low reference temperature of 298 K .

- b) ΔG_{bulk} is the gain in energy of a (bulk) droplet compared to the same material in the supercooled vapour, so

$$\Delta G_{bulk} = n_l (\mu_l - \mu_g) = \frac{V_{\text{droplet}}}{V_m} (\mu_l - \mu_g) = \frac{4\pi}{3V_m} r^3 (\mu_l - \mu_g),$$

in which n_l is the amount (mole) in the droplet and V_m the molar volume of water. The contribution ΔG_{bulk} is negative for $T < T_b$, so the vapour tends to condense spontaneously. This tendency is counteracted by the (positive) surface tension equal to

$$\Delta G_{surf} = 4\pi r^2 \gamma.$$

The total Gibbs free energy of a droplet is therefore

$$\Delta G_{cond}(r) = \frac{4\pi}{3V_m} r^3 (\mu_l - \mu_g) + 4\pi r^2 \gamma.$$

In figure 1 it can be seen that $\Delta G_{cond}(r)$ has a maximum at $r = r_c$. Droplets with a radius $r < r_c$ will evaporate; if $r > r_c$ a droplet will grow towards a bulk liquid phase. Droplets with $r = r_c$ are in a quasi-stationary equilibrium.

- c) The maximum of $\Delta G_{cond}(r)$ at critical radius $r = r_c$ follows from

$$0 = \frac{d\Delta G_{cond}}{dr} = \frac{4\pi r^2}{V_m} (\mu_l - \mu_g) + 8\pi \gamma r \quad \text{so} \quad r_c = \frac{2\gamma V_m}{\mu_g - \mu_l}.$$

The denominator is 0 at the boiling point ($T = T_b$), which results in a critical radius of $r_c(T_b) = \infty$, while for an arbitrary temperature (and given pressure $P = P^\ominus$)

$$\mu_g - \mu_l = (H_{m,g}^\ominus - TS_{m,g}^\ominus) - (H_{m,l}^\ominus - TS_{m,l}^\ominus) = (H_{m,g}^\ominus - H_{m,l}^\ominus) - T (S_{m,g}^\ominus - S_{m,l}^\ominus), \quad \text{so}$$

$$r_c = \frac{2\gamma V_m}{(H_{m,g}^\ominus - H_{m,l}^\ominus) - T (S_{m,g}^\ominus - S_{m,l}^\ominus)}$$

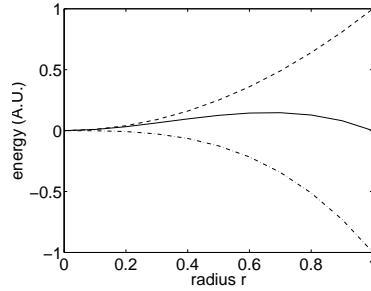


Figure 1: $\Delta G_{bulk}(r) = -Ar^3$ (---), $\Delta G_{surf}(r) = Br^2$ (- · -) and $\Delta G_{cond}(r) = -Ar^3 + Br^2$ (—)

If we define the supercooling as $\Delta T = T_b - T$, so $T = T_b - \Delta T$, in which T_b is the temperature at which the bulk liquid and the vapour phase are in equilibrium (implying $\mu_g - \mu_l = 0$, so $\Delta G(T_b) = \Delta H - T_b \Delta S = (H_{m,g} - H_{m,l}) - T_b(S_{m,g} - S_{m,l}) = 0$) we find

$$r_c(\Delta T) = \frac{2\gamma V_m}{(H_{m,g}^\ominus - H_{m,l}^\ominus) - (T_b - \Delta T)(S_{m,g}^\ominus - S_{m,l}^\ominus)} = \frac{2\gamma V_m}{\Delta T(S_{m,g}^\ominus - S_{m,l}^\ominus)}.$$

- d) The molecular volume is $\frac{V_m}{N_A}$, so the critical radius has the size of a molecule when $\frac{4\pi}{3}r_c^3 \approx \frac{V_m}{N_A}$, so

$$\frac{4\pi}{3} \left(\frac{2\gamma V_m}{\Delta T_{crit}(S_{m,g}^\ominus - S_{m,l}^\ominus)} \right)^3 \approx \frac{V_m}{N_A},$$

which we can rewrite to

$$\Delta T_{crit} = T_b - T_{crit} = \frac{2\gamma V_m}{S_{m,g}^\ominus - S_{m,l}^\ominus} \left(\frac{3V_m}{4\pi N_A} \right)^{-\frac{1}{3}}.$$

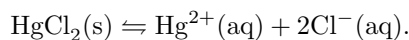
If we insert the known values we get

$$\Delta T_{crit} = \frac{2 \cdot 58 \cdot 10^{-3} \cdot 18.8 \cdot 10^{-6}}{188.83 - 69.91} \left(\frac{3 \cdot 18.8 \cdot 10^{-6}}{4\pi \cdot 6.02 \cdot 10^{23}} \right)^{-\frac{1}{3}} = 1.83 \cdot 10^{-8} \cdot 5.12 \cdot 10^9 = 93.7 \text{ K}.$$

- e) For $\Delta T \rightarrow 0$ it follows that $r_c \rightarrow \infty$, which implies that only an infinitely large volume of water (without a curved surface), has the same boiling point as T_b . Since every (seed of) a droplet has some curvature, it will immediately evaporate. Only seeds with a radius equal or larger than r_c will grow to a full-sized droplet. The larger the supercooling, the smaller the critical radius becomes. For $\Delta T \rightarrow \Delta T_{crit}$ the supercooling is so large that it compensates the surface tension of a droplet of the size of a molecule. This is however not realistic since the γ of such small 'droplets' of a single molecule will be significantly different from the γ of finite sized droplets. ΔT_{crit} does give a good approximation of how large the supercooling needs to be to form droplets without heterogeneous nucleation sources (like dust particles). The value we found would suggest that pure water vapour could be supercooled to values almost reaching the melting point of ice ($T_b - \Delta T_{crit} = 370.05 - 93.7 = 276 \text{ K}$).

Exercise 24

The reaction is



The equilibrium constant is defined as

$$K = \prod_i a_i^{\nu_i}.$$

We can assume that the activity is equal to the molality for a poorly soluble salt (and we use $a_{\text{HgCl}_2(\text{s})} \approx 1$):

$$K = \frac{a_{\text{Hg}^{2+}(\text{aq})} a_{\text{Cl}^{-}(\text{aq})}^2}{a_{\text{HgCl}_2(\text{s})}} \approx a_{\text{Hg}^{2+}(\text{aq})} a_{\text{Cl}^{-}(\text{aq})}^2 \approx \frac{b_{\text{Hg}^{2+}}}{b^\ominus} \left(\frac{b_{\text{Cl}^{-}}}{b^\ominus} \right)^2.$$

The relation between the solubility, s , and the molalities is $b_{\text{Cl}^{-}} = 2b_{\text{Hg}^{2+}} = 2s$, so

$$K = \frac{4s^3}{(b^\ominus)^3}, \quad \text{therefore} \quad s = \left(\frac{1}{4} K \right)^{\frac{1}{3}} b^\ominus.$$

K follows from $RT \ln K = -\Delta_r G^\ominus$, in which

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{Hg}^{2+}, \text{aq}) + 2\Delta_f G^\ominus(\text{Cl}^{-}, \text{aq}) - \Delta_f G^\ominus(\text{HgCl}_2, \text{s}) = 164.40 - 2 \cdot 131.23 + 178.6 = 80.54 \text{ kJ/mol}.$$

From this result the equilibrium constant follows:

$$\ln K = \frac{-80.54 \cdot 10^3}{8.314 \cdot 298.15} = -32.49, \quad \text{so} \quad K = 7.758 \cdot 10^{-15},$$

and therefore

$$s = 1.25 \cdot 10^{-5} \text{ mol/kg},$$

which indeed corresponds to a very dilute solution.

Exercise 25

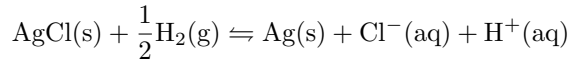
- a) The electrical work is given by $dW_e = Edq$, in which E is the potential difference over which the charge dq is transferred. This results in the following relation for the Gibbs free energy (at constant pressure)

$$dG = -SdT + VdP + dW_e = -SdT + Edq.$$

From this characteristic equation the following Maxwell relation can be derived

$$\left(\frac{\partial E}{\partial T} \right)_{q,P} = - \left(\frac{\partial S}{\partial q} \right)_{T,P}.$$

- b) The overall reaction is



The standard potential of a standard hydrogen electrode is, per definition, $E^\ominus(\text{Pt}|\text{H}_2(\text{g})|\text{H}^{+}(\text{aq})) = 0 \text{ V}$ for any T . The standard conditions for this expression are $P = P^\ominus = 1 \text{ bar}$ and $a_{\text{H}^{+}} = 1$. Realize that the *choice* to set the standard potential of the standard hydrogen electrode to zero for all temperatures, does not mean that the standard potential of other electrodes are also independent of the temperature.

Because of that choice for $E^\ominus(\text{Pt}|\text{H}_2(\text{g})|\text{H}^{+}(\text{aq}))$, only the $\text{Ag}/\text{AgCl}/\text{Cl}^{-}$ electrode determines the temperature dependence for this cell. Under standard conditions we thus find for the standard potential ($t \text{ [}^\circ\text{C]} = T - 273.15 \text{ [K]}$) so $\partial/\partial T = \partial/\partial t$):

$$\left(\frac{\partial E^\ominus}{\partial T} \right)_{q,P} = \left(\frac{\partial E^\ominus(\text{Ag}/\text{AgCl}/\text{Cl}^{-})}{\partial T} \right)_{q,P} = -4.8564 \cdot 10^{-4} - 2 \cdot 3.4205 \cdot 10^{-6} t + 3 \cdot 5.869 \cdot 10^{-9} t^2 \quad [\text{V/K}].$$

At $t = 25\text{ }^\circ\text{C}$ we find $E^\ominus = 0.2224\text{ V}$ and $\left(\frac{\partial E^\ominus}{\partial T}\right)_{q,P} = -6.457 \cdot 10^{-4}\text{ V/K}$.

Per mole we have a charge transfer of $-N_A e = -F = -96485\text{ C/mol}$ so ($P = P^\ominus$)

$$\Delta_r G = \Delta_r G^\ominus = -\nu F E^\ominus = -1 \cdot 96485 \cdot 0.2224 = -21458\text{ J/mol}$$

and using the Maxwell relation we find for the reaction entropy

$$\Delta_r S = \Delta_r S^\ominus = -\left(\frac{\partial E^\ominus}{\partial T}\right)_{q,P} \Delta q = -(-6.457 \cdot 10^{-4}) \cdot (-96485) = -62.30\text{ J/molK},$$

so

$$\Delta_r H = \Delta_r H^\ominus = \Delta_r G^\ominus + T \Delta_r S^\ominus = -21458 + 298.15 \cdot (-62.30)\text{ J/mol} = -40.03\text{ kJ/mol}.$$

- c) $E^\ominus(\text{Pt}|\text{H}_2(\text{g})|\text{H}^+(\text{aq})) = 0$ per definition for any T , implying for the half reaction $\frac{1}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{H}^+(\text{aq}) + e^-$ (with $P = P^\ominus$, so $a_{\text{H}_2(\text{g})} = 1$)

$$E(\text{Pt}|\text{H}_2(\text{g})|\text{H}^+(\text{aq})) = E^\ominus - \frac{RT}{\nu F} \ln Q = 0 - \frac{RT}{1 \cdot F} \ln \frac{a_{\text{H}^+}}{a_{\text{H}_2(\text{g})}^{1/2}} = -\frac{RT}{F} \ln a_{\text{H}^+}.$$

For the other half reaction $\text{AgCl}(\text{s}) + e^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$ (with $a_{\text{AgCl}(\text{s})} = a_{\text{Ag}(\text{s})} = 1$) we find at $T = 323.2\text{ K}$ ($50\text{ }^\circ\text{C}$) $E^\ominus(\text{AgCl}/\text{Ag}, \text{Cl}^-(\text{aq})) = 0.2045\text{ V}$, so

$$E(\text{AgCl}/\text{Ag}, \text{Cl}^-(\text{aq})) = E^\ominus - \frac{RT}{\nu F} \ln Q = 0.2045 - \frac{8.314 \cdot 323.2}{1 \cdot 96485} \ln a_{\text{Cl}^-}.$$

For the total cell without added KCl we take the **sum** of the two half cell potentials

$$E = 0.2045 - \frac{8.314 \cdot 323.2}{96485} \ln a_{\text{Cl}^-} - \frac{8.314 \cdot 323.2}{96485} \ln a_{\text{H}^+} = 0.2045 - \frac{8.314 \cdot 323.2}{96485} \ln a_{\text{Cl}^-} a_{\text{H}^+}.$$

For the total cell with added KCl we find analogously

$$E' = 0.2045 - \frac{8.314 \cdot 323.2}{96485} \ln a'_{\text{Cl}^-} a'_{\text{H}^+}.$$

The change in the product of the activities follows with

$$0.200 = \Delta E = E' - E = -\frac{8.314 \cdot 323.2}{96485} \ln a'_{\text{Cl}^-} a'_{\text{H}^+} + \frac{8.314 \cdot 323.2}{96485} \ln a_{\text{Cl}^-} a_{\text{H}^+},$$

so

$$\frac{a'_{\text{Cl}^-} a'_{\text{H}^+}}{a_{\text{Cl}^-} a_{\text{H}^+}} = \exp \left[-0.200 \frac{96485}{8.314 \cdot 323.2} \right] = \exp[-7.18] = 7.6 \cdot 10^{-4}.$$