Answers Tutorials 7 Thermodynamics 2, 2025/2026

Exercise 26

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 $\rho g h$ 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

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

c)

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

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.

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

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 27

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 $P = 1$ 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

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

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

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

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 $P = P^\ominus$)

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

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

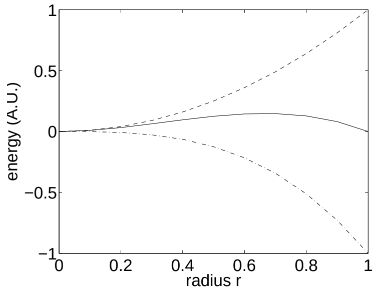

Figure 1: $\Delta G_{bulk}(r) = -Ar^3$ (·-·), $\Delta G_{surf}(r) = Br^2$ (- -) and $\Delta G_{cond}(r) = -Ar^3 + Br^2$ (—)

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

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

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

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

which we can rewrite to

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

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 $\Delta T \to 0$ it follows that $r_c \to \infty$, which implies that only an infinitly 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 $\Delta T \to \Delta T_{crit}$ 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 ($T_b - \Delta T_{crit} = 370.05 - 93.7 = 276$ K).

Exercise 28

For two energy states the partition function is

$$q = \sum_i \exp\left[-\beta\epsilon_i\right] = \exp\left[-\beta\epsilon_0\right] + \exp\left[-\beta\epsilon_1\right] = \exp\left[-\beta\cdot 0\right] + \exp\left[-\beta\epsilon_1\right] = 1 + \exp\left[-\beta\epsilon_1\right].$$

We could translate the question to 'at what temperature is the following equation valid':

$$p_1 \equiv \frac{n_1}{N} = \frac{\exp\left(-\beta\epsilon_1\right)}{q} = \frac{\exp\left(-\beta\epsilon_1\right)}{1+\exp\left(-\beta\epsilon_1\right)} = 0.10,$$

or

$$10\exp\left(-\beta\epsilon_1\right) = 1 + \exp\left(-\beta\epsilon_1\right),$$

or

$$\exp\left(-\beta\epsilon_1\right) = \frac{1}{9}, \quad \text{and} \quad \beta = \frac{1}{kT} = -\frac{1}{\epsilon_1}\ln\left(\frac{1}{9}\right), \quad \text{and} \quad T = \frac{\epsilon_1}{k\ln(9)}.$$

We can calculate ϵ_1 using $\epsilon_1 = hc\nu$, with $\nu = 540\ \text{cm}^{-1}$ so

$$T = \frac{hcv}{k\ln(9)} = 352.6\ \text{K}.$$

Exercise 29

a) Since we set our lowest energy level to 0, also in a magnetic field, both energy levels are raised by $\frac{1}{2}\mu_B B$, so $\epsilon_0 = 0$ and $\epsilon_1 = \mu_B B$.

$$q = \sum_i \exp\left(-\frac{\epsilon_i}{kT}\right) = 1 + \exp\left(-\frac{\mu_B B}{kT}\right)$$

b) The Boltzmann distribution gives

$$n_i = N\frac{\exp\left(-\frac{\epsilon_i}{kT}\right)}{q} \quad (i = 0, 1),$$

so

$$n_0 = N\frac{1}{1+\exp\left(-\frac{\mu_B B}{kT}\right)} \quad \text{and} \quad n_1 = N\frac{\exp\left(-\frac{\mu_B B}{kT}\right)}{1+\exp\left(-\frac{\mu_B B}{kT}\right)}$$

In figure 2, $\frac{n_0}{N}$ and $\frac{n_1}{N}$ are plotted for a magnetic field of $B = 10$ Tesla We can see that occupancy of both levels for $T \to \infty$ goes to 0.5, and that all spins are in the ground state ($n_0(T=0) = N$ and $n_1(T=0) = 0$) for $T \to 0$ We can also see that the occupancy of the two states are $\frac{n_0}{N} = 0.731$ and $\frac{n_1}{N} = 0.269$ if $kT = \mu_B B$ (dotted line in the figure).

c) The average energy per electron due to the magnetic field is

$$<\epsilon> = \frac{1}{N}\sum_i \epsilon_i n_i = \frac{1}{N}\left(\epsilon_0 n_0 + \epsilon_1 n_1\right) = \frac{1}{N}\left(0\cdot n_0 + \mu_B B N\frac{\exp\left(-\frac{\mu_B B}{kT}\right)}{1+\exp\left(-\frac{\mu_B B}{kT}\right)}\right)$$

We have to correct for our earlier shift of $+\frac{1}{2}\mu_B B$, however, resulting in

$$<\epsilon> = \mu_B B\frac{\exp\left(-\frac{\mu_B B}{kT}\right)}{1+\exp\left(-\frac{\mu_B B}{kT}\right)} - \frac{1}{2}\mu_B B.$$

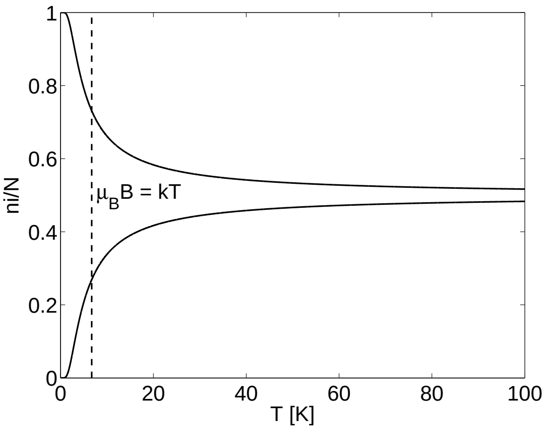

Figure 2: $\frac{n_0}{N}$ and $\frac{n_1}{N}$ for $B = 10$ Tesla

The plot of $< \epsilon >$ has the same shape as the lower line in the graph (apart from the shift of $-\frac{1}{2}\mu_B B$) The effect of the magnetic field thus disappears for $T \to \infty$, because $< \epsilon > \to 0$ (for a finite value of the magnetic field).

d) Before the 180° pulse we have

$$\frac{n_1}{n_0} = \frac{n_1}{N}\frac{N}{n_0} = \frac{\exp(-\beta\mu_B B)}{q}\frac{q}{1} = \exp(-\beta\mu_B B),$$

The distribution after the pulse is inverted, so we have

$$\left(\frac{n_1}{n_0}\right)' = \frac{n_0}{n_1} = [\exp(-\beta'\mu_B B)]^{-1} = \exp(+\beta\mu_B B)$$

which means $\beta' = -\beta$, corresponding to a negative temperature! This is a system out of equilibrium, which in time will spontaneously return to the original distribution, that is, to the equilibrium state with the positive temperature.

Exercise 30

a) Since S is a state function we can choose a reversible process, so $\mathrm{d}W = -P_{ext}\mathrm{d}V = -P\mathrm{d}V$. For an isothermal process and a perfect gas it holds that $\Delta U = 0$ such that $Q = -W$, so $\mathrm{d}Q_{rev} = P\mathrm{d}V$. The result for the entropy change is $\Delta S = \int_{V_1}^{V_2} \frac{\mathrm{d}Q_{rev}}{T} = \int_{V_1}^{V_2} \frac{P\mathrm{d}V}{T} = \int_{V_1}^{V_2} \frac{nRT\mathrm{d}V}{VT} = nR\ln\frac{V_2}{V_1} = nR\ln 2$.

b) The Boltzmann definition of entropy is $S = k\ln W$ in which W is the number of realization possibilities of the system, that is, the number of micro states. Even though we expand isothermally, the distribution of the molecules over the energy levels changes. This is because the energy levels of the particles depend on the volume.
Since $nR = Nk$, in which N is the number of particles, we can write the result of part a) as $\Delta S = Nk\ln 2 = k\ln 2^N$. In terms of the Boltzmann definition this implies that $\Delta S = k\ln W_2 - k\ln W_1 = k\ln\frac{W_2}{W_1}$, so $k\ln\frac{W_2}{W_1} = k\ln 2^N$, or $\frac{W_2}{W_1} = 2^N$.
We can interpret this result as twice the amount of realization possibilities per particle in the system; it is tempting to argue that twice the number of positions can be occupied per particle due to the volume of the final state being twice as large. For N particles there are thus 2^N as many position possibilities. In other words, in this reasoning for the term 'number of realization possibilities' we have to account for not only the number of possibilities to realize the distribution of particles over

the energy states, but also the position possibilities. From a quantum mechanical point of view, this is already covered by the volume dependence of the energy levels (see Study Guide, p.24, eq (121)).