

## Tutorials 7 Thermodynamics 2, 2025/2026

### Exercise 26

At 20 °C the vapour pressure of bulk water is 2.330 kPa, the density 0.9982 gcm<sup>-3</sup> and the surface tension 72.75 mNm<sup>-1</sup>.

- Calculate the vapour pressure of a spherical droplet of water with a radius of 10.0 nm at 20 °C.
- The contact angle of water on clean glass is very small.  
Calculate to what height the water rises in a glass capillary with diameter 0.300 mm at 20 °C.

The relative humidity at temperature  $T$  is defined as the actual partial pressure of water vapour in the air as a fraction of the maximum (equilibrium) partial pressure of water vapour at that temperature:

$$RH = \frac{P_{H_2O}}{P_{H_2O}^{sat}} \times 100 \%$$

- Calculate the mole fraction of water vapour in the air at  $T = 293$  K,  $P = P^\ominus$  and  $RH = 50 \%$ .

The following equation is a good approximation for the temperature dependence of the equilibrium surface tension of water

$$\gamma(T) = \gamma_0 \left(1 - \frac{T}{T_c}\right)^{\frac{11}{9}},$$

in which  $\gamma_0 = 152.0 \cdot 10^{-3}$  N/m and  $T_c = 647$  K.

- Explain the presence of  $T_c$  in the expression for  $\gamma(T)$ .
- Calculate the change in capillary action of water in a glass capillary of diameter 0.300 mm at  $RH = 100 \%$  if the temperature is raised from 20 °C to 90 °C. Assume that the contact angle and the thermal expansion of the water and glass are negligible.

### Exercise 27

We will examine the nucleation of spherical water droplets in a supercooled vapour at a pressure of  $P = 1$  bar. The chemical potential in the vapour and liquid are  $\mu_g$  en  $\mu_l$  respectively.

At 100 °C, water has a surface tension of  $\gamma = 58$  mNm<sup>-1</sup>, and a density of 18.8 mLmol<sup>-1</sup>. We assume that these values are independent of the temperature in the temperature range of the supercooling.

The formation enthalpies and entropies for the two phases of water at 298 K are:

$\Delta_f H_l^\ominus = -285.83$  kJ/mol,  $\Delta_f H_g^\ominus = -241.82$  kJ/mol,  $S_l^\ominus = 69.9$  J/molK and  $S_g^\ominus = 188.83$  J/molK.

- Determine the boiling point  $T_b$  of water, by using the equilibrium condition for the chemical potentials of the two phases at  $T_b$ .  
Assume that the molar enthalpies and entropies of formation are independent of the temperature between 298 K and 393 K and check afterwards if this was a reasonable assumption, by comparing the result with the literature value for  $T_b$ .
- The Gibbs free energy of the condensation,  $\Delta G_{cond} = \Delta G_{bulk} + \Delta G_{surf}$ , contains a surface and a volume (bulk) term.  
Give an expression for  $\Delta G_{cond}(r)$ , in terms of the radius of the droplet  $r$ , the chemical potential of both phases, the molar volume of water  $V_m$  and the surface tension  $\gamma$ .  
Draw  $\Delta G_{bulk}(r)$  and  $\Delta G_{surf}(r)$  as a function of the radius in one figure, as well as the total condensation energy. Discuss the situation on the right and left side of the maximum and at the maximum of  $\Delta G_{cond}$ .

- c) We are looking for the critical radius,  $r_c$ , at which the droplet is in a quasi-equilibrium with the vapour, as a function of the supercooling  $\Delta T = T_b - T$ . Use the result for  $T_b$  from part a) to find the following relation

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

- d) Determine the supercooling  $\Delta T_{crit}$  at which the critical radius of the droplet is about the radius of a water molecule.
- e) Discuss the condensation process at the limits of the expression for the critical radius for  $\Delta T \rightarrow 0$  and for  $\Delta T \rightarrow \Delta T_{crit}$ .

## Exercise 28

A certain molecule has two energy states, the ground state and an excited state at  $540 \text{ cm}^{-1}$ . At what temperature will 10 % of the molecules be in the excited state?

## Exercise 29

We will use the Boltzmann distribution to determine the occupancy of two spin states of electrons in a magnetic field  $B$ . In zero magnetic field the spin states are degenerate and have therefore equal energy. When a magnetic field is applied the degenerate spin states, with energy  $\epsilon$ , split up into two states with energies  $\epsilon_0 = -\frac{1}{2}\mu_B B$  and  $\epsilon_1 = +\frac{1}{2}\mu_B B$ , in which  $\mu_B = \frac{e\hbar}{2m_e} = 9.27 \cdot 10^{-24} \text{ J/Tesla}$  is the so-called Bohr magneton. We only take into account the states of the electrons since we can consider them to be independent of the other energy states. We furthermore set our state with the lowest energy to 0.

- a) Determine the partition function  $q$ .
- b) Determine the distribution of  $N$  electrons over the two energy states as a function of the temperature. Plot this distribution for a magnetic field of  $B = 10 \text{ Tesla}$  and determine the occupancy if the thermal energy ( $kT$ ) is equal to the magnetic energy.
- c) Determine the average energy per electron as a function of temperature and plot this for a magnetic field of  $B = 10 \text{ Tesla}$ . At what temperature does the influence of the magnetic field on the average energy disappear?
- d) The system is placed in an Electron Spin Resonance (ESR) machine at a temperature of  $\beta = 1/kT$ . The distribution over the two energy states is inverted by applying a so-called  $180^\circ$  pulse. Determine the temperature of the system and interpret the result.

## Exercise 30

Consider the Boltzmann definition of entropy for  $n$  mol of a perfect mono-atomic gas that expands isothermally from a volume  $V_1$  to a volume  $V_2 = 2V_1$ .

- a) First calculate the entropy change  $\Delta S$  of the perfect gas for this process with the classical definition of entropy  $dS = \frac{dQ_{rev}}{T}$ .
- b) Interpret the result from the previous part in terms of the Boltzmann definition of entropy.