Tutorials 6 Thermodynamics 2, 2023/2024

Exercise 22

At 20 °C the vapour pressure of bulk water is 2.330 kPa, the density 0.9982 gcm^{-3} and the surface tension 72.75 mNm^{-1}.

a) Calculate the vapour pressure of a spherical droplet of water with a radius of 10.0 nm at 20 °C.

b) 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:

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

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.

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

d) Explain the presence of T_c in the expression for $\gamma(T)$.

e) 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 23

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 μ_g en μ_l respectively.
At 100 °C, water has a surface tension of $\gamma = 58$ mNm^{-1}, and a density of 18.8 mLmol^{-1} . 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.

a) 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 afterwords if this was a reasonable assumption, by comparing the result with the literature value for T_b.

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 γ.
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 ΔG_{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 ΔT_{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 $\Delta T \to 0$ and for $\Delta T \to \Delta T_{crit}$.

Exercise 24

Calculate the solubility s in mol/kg of $HgCl_2$ in water at 298.15 K and $P = P^{\ominus}$.
Hint: Use the Gibbs free energy of formation for the components given in the table and the dissolution reaction to calculate the equilibrium constant K. Assume that the solubility is small enough to approximate the activity of the ions by their molalities, and check the poor solubility afterwards.

	$\Delta_f G^{\ominus}$(kJ/mol)
$HgCl_2(s)$	-178.6
$Hg^{2+}(aq)$	164.40
$Cl^-(aq)$	-131.23

Exercise 25

The standard potential (in V) of the $Ag/AgCl/Cl^-$ electrode as a function of the temperature at 1 bar is

$$E^{\ominus} = 0.23659 - 4.8564 \cdot 10^{-4}t - 3.4205 \cdot 10^{-6}t^2 + 5.869 \cdot 10^{-9}t^3,$$

where t is the temperature in °C.

a) Derive a Maxwell relation between E, T, S and q.

b) Use the Maxwell relation to determine $\Delta_r G^{\ominus}$, $\Delta_r H^{\ominus}$ en $\Delta_r S^{\ominus}$ at $T = 25$ °C for an electrochemical cell with a silver chloride- and a standard hydrogen electrode.

c) An unknown quantity of KCl is added to the half cell with the silver chloride electrode at a temperature of 323.2 K. As a result the potential of the cell turns out to increase by 0.200 V.
Find an indication for the change in the activities of Cl^- and H^+ in the cell with KCl (indicated with a prime) by determining $\frac{a'_{Cl-}a'_{H+}}{a_{Cl-}a_{H+}}$.