Solutions

Exercises of Chapter 2

2.1 We calculate the total mass of air M. The mass is equal to the volume multiplied by the density. It is proper to notice the units used here: 1 g cm^{-3} and $1 \text{ L} = 1000 \text{ cm}^3$, whose product gives the unit of mass, i.e., 1 kg. We get

$$M = V\rho = 22 \times 1000 \text{ cm}^3 \times 10^{-3} \text{ g cm}^{-3} = 22 \text{ g} = 0.022 \text{ kg}.$$

We neglect the fact that air is composed mainly of N_2 (78 %) and O_2 (21 %). Then we use the expression for the kinetic energy. Assuming that all molecules have an average speed of about $v = 300 \text{ m s}^{-1}$, which corresponds roughly to the speed of sound in air, we obtain the kinetic energy:

$$E = \frac{Mv^2}{2} = 22 \text{ g} \times (300)^2 \text{ m}^2 \text{ s}^{-2}/2 = 1980 \text{ J}/2 \approx 1 \text{ kJ}.$$

It is proper to notice here the way we calculate numerical values. We can represent each number in the following form: $a10^b$, where a is of the order 1, and b is an integer. If we have large numbers (b is positive) or small numbers (b is negative), then this way of representation of numbers save us a lot of time during calculation and also improves its quality, because multiplication of two numbers can be written as $a10^b \times c10^d = ac \times 10^{b+d}$. In the equation above, we have $0.022 \times 90000 = 2.2 \times 10^{-2} \times 9 \times 10^4 = 9 \times 2.2 \times 10^{-2+4} = 1980$. As we can see, when a and c are small, of the order 1, then this way of calculation is quick. The second remark concerns rounding off. Sometimes we need very accurate numbers, but most often we want only to find out the order of magnitude of a given quantity and for this reason, we write $1980 \text{ J} \approx 2 \text{ kJ}$. The value of 2 kJ is also easier to remember than 1980 J, and the rounding-off error amounts to 1 % only.

2.2 We use the formula for the potential energy of a body in the gravitational field of the earth, calculated with respect to the earth surface (at $h = 0$). In thermodynamics, we do not know the internal energy of a body. We can only calculate changes in its internal energy with respect to some reference states, as in the case of this exercise.

Here the initial state corresponds to the energy E_i at $h = 0$, and the final state corresponds to the energy E_f at $h = 5$ km $= 5000$ m $= 5 \times 10^3$ m. The mass of one mole of water (H_2O) $m = 18$ g. The change in its potential energy, ΔE, amounts to

$$E_f - E_i = mgh = 18 \times 10^{-3} \text{ kg} \times 9.81 \text{ m s}^{-2} \times 5 \times 10^3 \text{ m} = 882.9 \text{ J} \approx 0.9 \text{ kJ}.$$

Why is the difference in the potential energy ΔE independent of the way we reach the height $h = 5$ km? We often hear about climbers who have found a new and more difficult route to the top of a known mountain, K2 for instance. However, no matter which way they choose and how much effort it requires to get to the top, each time they do it, their potential energy increases exactly by the same amount. We say that the potential energy is a function of the height above sea level, and not a function of the path along which we move, to reach a given height. The essence of thermodynamics consists in investigation of quantities, e.g., the internal energy, which depend only on the state of a system and not on the way the given state is reached. We note by chance that the kinetic energy of one mole of air is comparable with the change in its gravitational energy when it is lifted a few kilometers above sea level. This means that in a typical chemical experiment, the potential energy can be neglected.

2.3 Heat of evaporation amounts to 40 kJ mol^{-1}. To evaporate 1 mol of water, 40 kJ of heat is to be supplied to the system. We denote this heat by Δh, because it is related to a state function called the *enthalpy*, H (see Chap. 3). The molar mass of water is $M = 18 \text{ g mol}^{-1}$. Since the mass of water amounts to $m = 9$ g, the total heat needed to evaporate this mass of water amounts to

$$Q = \frac{m}{M} \Delta h = \frac{9 \text{ g}}{18 \text{ g mol}^{-1}} \times 40 \text{ kJ mol}^{-1} = 20 \text{ kJ}.$$

Molecules in liquid water are close to one another (density of liquid water is 1 g cm^{-3}) and they strongly interact (forming hydrogen bonds). The density of water vapour, which escapes from the kettle, for instance, amounts to 10^{-3} g m^{-3}, thus, it is 1000 times smaller than the density of liquid water. It means, that water molecules in the vapour are 10 times farther away from one another than in liquid water (think how to determine this ratio from the ratio of the densities of liquid water and water vapour). 1 mol of water contains $N_A = 6.022 \times 10^{23}$ molecules, and each H_2O molecule has 4 neighbours (oxygen forms two hydrogen bonds and each hydrogen atom in the molecule takes part in one hydrogen bond with another water molecule). Measuring the heat of evaporation (40 kJ mol^{-1}), we can estimate the energy of interaction of water molecules (see Fig. 3.2), i.e., $40 \text{ kJ}/(4N_A) = 3.2 \times 10^{-20}$ J $= 0.1$ eV (we divide by 4, to take into account the number of neighbours of a molecule). We notice by chance that the energy of intermolecular interactions is much larger than the gravitational energy or the kinetic energy of molecules in water vapour (see the previous two exercises).

2.4 The mass of 1 mol of argon amounts to $M = 40$ g. We have $\Delta h = 6 \text{ kJ mol}^{-1}$, hence, to evaporate the mass $m = 40$ g of argon, we need

$$Q = \frac{m}{M} \Delta h = \frac{40 \text{ g}}{40 \text{ g mol}^{-1}} \times 6 \text{ kJ mol}^{-1} = 6 \text{ kJ}.$$

Now we want to find the energy of interaction between argon atoms which follows from this value of Q. We calculate it in a similar way as in the previous exercise, i.e., 6 kJ/$12N_A = 0.17 \times 10^{-20}$ J ≈ 0.005 eV (we divide by 12, to take into account the number of neighbours of a single argon atom). The number of the closest neighbours of one atom, i.e., the atoms that are sufficiently close to the given atom to interact with it, follows from the local structure of a substance (arrangement of atoms or molecules in space). Argon at low temperature forms a crystalline structure in which each argon atom is surrounded by 12 closest neighbours. Water molecules interact with one another almost 20 times stronger than argon atoms. The interactions between argon atoms are weak because they result from the interaction of induced electric dipoles.

2.5 This exercise allows us to estimate how much the energy of molecular interactions differs from the energy contained in chemical bonds that binds atoms in a molecule. The heat of combustion amounts to $\Delta h = 400$ kJ mol^{-1}. The molar mass of carbon $M = 12$ g mol^{-1}, and the mass used for the combustion $m = 12$ g, hence, the amount of heat given off during the combustion amounts to

$$Q = \frac{m}{M}\, \Delta h = \frac{12 \text{ g}}{12 \text{ g mol}^{-1}} \times 400 \text{ kJ mol}^{-1} = 400 \text{ kJ}.$$

The reaction of combustion has the following form:

$$C + O_2 \rightarrow CO_2.$$
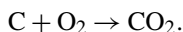
In this reaction, the double bond between two oxygen atoms is broken and two double bonds between two oxygen atoms and one carbon atom are formed. Due to the reconstruction of the chemical bonds, 400 kJ of heat per mole of carbon is given off. By comparison with the previous source of energy, we can see that the energy hidden in chemical bonds, i.e., in the electronic structure of molecules and interactions between negative electrons and positive nuclei of atoms, is tens of times larger than the energy of intermolecular interactions in a liquid (cf. the previous exercises).

2.6 Protons and neutrons are bound in the atom nuclei through interactions called the *nuclear* or *strong* interactions. The energy of nuclear interactions is released inside the sun at a temperature of millions degrees centigrade. Hans Bethe (1906–2005), a great physicist and a Nobel prize winner, was the first to propose these interactions as a source of the solar energy. A cycle of nuclear reactions inside the sun can be presented in short in the form of one nuclear reaction:

$$4\,^1\text{H} + 2e \rightarrow {}^4\text{He} + 2\nu + 6\gamma.$$
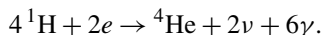
Four hydrogen nuclei (protons) and two electrons form one helium nuclei, which is composed of two protons and two neutrons, and some energy is released in the form of two neutrinos (ν) and six photons in the range of gamma-rays. The energy released in this nuclear reaction amounts to about 26 MeV, which gives 26 MeV/4 = 6.5 MeV per each hydrogen atom used in the reaction. Thus, in the reaction of 1 mol of protons (^{1}H), the energy

$$\Delta U = 6.022 \times 10^{23} \times 6.5 \times 10^6 \times 1.6 \times 10^{-19} \text{ J} = 6.26 \times 10^{11} \text{ kJ}$$

is released. Due to the nuclear synthesis, 1.5×10^9 times more heat is released than during carbon combustion. Construction of a device for a controllable thermonuclear synthesis would give the mankind practically inexhaustible source of energy and allow to achieve a great leap forward.

2.7 We make use of the Einstein formula. The speed of light in vacuum $c \approx 300\,000$ km s^{-1}. Annihilation changes the whole mass into the energy of photons. The mass to be changed into pure energy amounts to $m = 12$ g. We calculate the energy contained in 12 g of carbon:

$$E = mc^2 = 12 \times 10^{-3} \text{ kg} \times 9 \times 10^{16} \text{ m}^2 \text{ s}^{-2} = 1.08 \times 10^{12} \text{ kJ mol}^{-1}.$$

Thus, the annihilation of 1 mol of carbon provides almost 10^{10} times more energy than its combustion. Possibility of getting such a process under control would give the mankind the greatest access to energy resources.

2.8 We begin with writing down the parameters of the initial and final equilibrium states. In the initial state, 1 mol of water vapour, of the mass $m = 18$ g and density $\rho_i = 10^{-3}$ g cm^{-3}, occupies the volume $V_i = m/\rho_i = 18 \times 10^3$ cm^3. In the final state, liquid water has the same mass, and its density $\rho_f = 1$ g cm^{-3}, hence, the final volume $V_f = m/\rho_f = 18$ cm^3. Thus, the change in the volume amounts to

$$\Delta V = V_f - V_i = 18 \text{ cm}^3 - 18000 \text{ cm}^3 = -17982 \text{ cm}^3.$$

The change is negative, since the volume in the final state is smaller than the volume in the initial state.

2.9 In the initial state, we have separate compounds N_2 and H_2, and their mole numbers are $n_{N_2} = 1$ and $n_{H_2} = 3$. The total mole number in the initial state is

$$n_i = n_{H_2} + n_{N_2} = 1 + 3 = 4.$$

In the final state, we have only NH_3, and its mole number is $n_{NH_3} = 2$, hence, the final mole number is

$$n_f = n_{NH_3} = 2.$$

Note that in equilibrium, we would have a mixture of three compounds in the final state, but here we ignore this fact and assume that all reactants have been used up in the reaction, giving a pure product. The total mole number in the system has changed by

$$\Delta n = n_f - n_i = 2 - 4 = -2.$$

The total mole number has decreased by 2. The mole number of NH_3 has increased by 2, the mole number of H_2 has decreased by 3, and the mole number of N_2 has decreased by 1.

2.10 In the initial state, we have $V_{1i} = 100$ L, $n_{1i} = 3 + 4 + 1 = 8$ mol in vessel 1, and $V_{2i} = 100$ L, $n_{2i} = 5 + 2 + 1 = 8$ in vessel 2. In the final state, we have $V_f = V_{1i} + V_{2i} = 200$ L and $n_f = n_{1i} + n_{2i} = 16$ mol in the fused vessels.

2.11 The internal energy, volume and mole number are extensive parameters, thus, in the final state, after the fusion of the vessels, we have the following values of the state parameters: $U_f = 4U$, $V_f = 4V$, $n_f = 4n$ (cf. Fig. 2.4).

2.12 The heat given off by a man amounts to $Q = 2\,000$ kcal $= 8368$ kJ. A day and night have $t = 24 \times 60 \times 60$ s. Dividing a daily consumption of energy by time, we get the power, i.e., $Q/t = 96.85$ J s^{-1} $= 96.85$ W. It means that a man consumes approximately the same amount of energy as a 100 W bulb. Lavoisier compared the heat of carbon combustion with the heat given off by living beings and with the amounts of carbon dioxide and water produced. His study became a basis for establishing of a detailed energetic balance of the human organism.

2.13 Water evaporates too quickly and its density is too small (1 g cm^{-3}), to be a good working substance in the barometer. It is easy to calculate how high the barometer would have to be if we used flaxseed oil (density $\rho_{oil} = 0.94$ g cm^{-3}) instead of mercury, to measure atmospheric pressure. The density of mercury $\rho_{Hg} = 13.6$ g cm^{-3}. First, we measure atmospheric pressure p, using flaxseed oil in the barometer, and then we measure p with the mercury barometer. Since the liquid density is different in each case, the height of the liquid column is also different. We calculate this difference, using the formula for the pressure measured with the barometer:

$$p = \rho_{oil} g h_{oil} = \rho_{Hg} g h_{Hg}.$$

Since $h_{Hg} = 760$ mm at the pressure of 1 atm, we get

$$h_{oil} = \frac{\rho_{Hg}}{\rho_{oil}} h_{Hg} = \frac{13.6}{0.94} \times 760 \text{ mm} = 10995.7 \text{ mm} \approx 11 \text{ m}.$$

As we can see, the oil barometer would have the height of 11 m and no doubt it would not be a very practical device.

2.14 The pressure in a car tyre amounts to about 2 atm, and a car weighing 1 ton stands on four wheels. In a mountain bicycle, we pump the wheels up to 4 atm. The pressure at the depth of 1000 km amounts to about 250 000 atm. As one can see, the question is not correctly formulated, as in order to say that something is small or large we have to compare it with other things. No quantity exists that could be said to be large or small *in itself*, as Immanuel Kant might have said.

Let us calculate the force acting on our bodies. First, we have to estimate the area of the body, A. We assume it to be equal to 2 m^2. By definition, the force is the product of p and A, hence, $F = pA = 101325$ N m^{-2} $\times$ 2 m^2 ≈ 200000 N. It means that air acts on the body with a force corresponding to the weight of 20 ton (1 kG $\approx$ 10 N). It is really a lot! We do not feel it because the pressure of our blood and other body fluids is exactly the same as atmospheric pressure, in accord with mechanical equilibrium, i.e., $p_{body} = p$. If the external pressure would fall down to zero our bodies would burst due to the internal pressure, the blood would boil and partially evaporate (the boiling point decreases with lowering of the pressure) and the remaining blood and body fluids would freeze, because they would give the heat off to the vapour causing their temperature to fall below the freezing point.

Fig. S2.1 To draw a liquid
with a straw, we have to
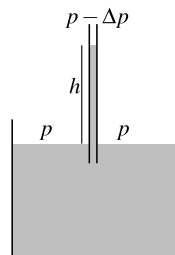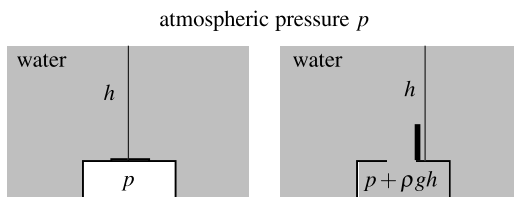produce the underpressure
Δp with the mouth

Fig. S2.2 To lift the lid, a
sailor would have to lift a
whole column of water above
the lid. When the sluice-gate
is filled with water the
pressure above and below the
lid is the same and equal to
$p + \rho gh$

atmospheric pressure p

water

water

h

h

p

$p + \rho gh$

2.15 The liquid must rise 20 cm above its surface in the glass, to reach the mouth.
The liquid in the glass is at atmospheric pressure p, and the pressure above the
liquid in the straw amounts to $p_0 < p$. From the balance of forces, it follows that
to make the liquid (its density $\rho = 1 \text{ g cm}^{-3}$) in the straw rise to the level h, the
pressure difference $\Delta p = p - p_0$ must be equal to (see Fig. S2.1):

$$\Delta p = \rho gh = 1 \text{ g cm}^{-3} \times 9.81 \text{ m s}^{-2} \times 20 \text{ cm} = 1962 \text{ Pa}.$$

This underpressure we have to produce in the straw, to draw the liquid into the
mouth. The pressure difference is about 50 times smaller than atmospheric pressure.

2.16 A column of water, of the height $h = 10$ m, presses on the lid (Fig. S2.2). It
exerts the pressure

$$p_0 = \rho gh = 10^3 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2} \times 10 \text{ m} = 9.81 \times 10^4 \text{ N m}^{-2}.$$

Since the lid area amounts to $A = 2 \text{ m}^2$, the total force is equal to

$$F = p_0 A = 9.81 \times 10^4 \text{ N m}^{-2} \times 2 \text{ m}^2 = 19.62 \times 10^4 \text{ N}.$$

This is the force the sailor has to use to lift the lid (we neglect the weight of the lid).
It is about 20 ton, which is not surprising, since lifting the lid, the sailor lifts at the
same time a column of water 10 m in height. If the sluice-gate is filled with water,
the pressure on both sides of the lid is the same and then the force needed to lift the
lid is equal to its weight minus its buoyancy, which is about 10–20 kg. This is why
the sluice-gate must be filled with water before the access door is opened.

2.17 We have to invert relation (2.18) between the Fahrenheit and Celsius scale:

$$t_F/°\text{F} = \frac{9}{5} t_C/°\text{C} + 32,$$

hence

$$t_C/°C = \frac{5}{9}(t_F/°F - 32).$$

The temperature of 0 °F corresponds to -17.8 °C (the lowest temperature of supercooled water obtained by Fahrenheit in his laboratory), 70 °F corresponds to 21.1 °C (room temperature), and 451 °F corresponds to 232.8 °C (the autoignition temperature of paper and the title of the famous sf novel by Ray Bradbury).

2.18 The Celsius and Kelvin scales are related to each other with the formula

$$T/K = t_C/°C + 273.15,$$

hence, $t_C = -273.15$ °C corresponds to $T = 0$ K, the absolute zero temperature, unattainable experimentally.

2.19 We know that 0 K corresponds to -273.15 °C. Converting to the Fahrenheit scale, we get -459.67 °F.

2.20 From the expression

$$t_C/°C = \frac{5}{9}(t_F/°F - 32),$$

we get $t_C = 37.8$ °C. The body temperature of a healthy man amounts to 36.6 °C, which means that Fahrenheit calibrated his thermometer, measuring the temperature of a sick person. In general, it is not a good idea to use living organisms to calibrate thermometers. For instance, the temperature of the human body can vary by even a few degrees, depending on the condition of the organism. It means that if we calibrate the thermometer one day we can get a result which differs by a few degrees from the result obtained another day. Therefore, the calibration of thermometers is usually based on reproducible phenomena, which occur always at the same temperature, such as coexistence of the vapour, liquid and solid of a pure substance at its triple point. At the triple point of water (water vapour, liquid water and ice coexist), the temperature and pressure amount always to 273.16 K (0.01 °C) and 611 Pa (4.6 torr), respectively.

2.21 We take a body with the characteristics corresponding to the perfect blackbody and put it into a mixture of ice, liquid water and water vapour (the triple point of water). Then we measure the electromagnetic radiation emitted by the body and use the formula

$$U = \gamma V T^4,$$

where the internal energy U is proportional to the intensity of radiation. In this way, we determine the quantity $U_0 = U(T_0 = 273.16)$ K. To determine the given temperature T, we use the relation between T and U, hence

$$T = 273.16 \text{ K} \left(\frac{U}{U_0}\right)^{1/4}.$$

2.22 The internal energy per mole for the system of the internal energy U and mole number n is given by

$$u = \frac{U}{n}.$$

When we join together m identical systems, each of the internal energy U and mole number n, we obtain a composite system of the internal energy mU and mole number mn, since the internal energy and amount of substance are extensive quantities. The internal energy per mole of the composite system amounts to

$$\frac{mU}{mn} = \frac{U}{n} = u,$$

thus, it does not depend on the size of the composite system. It has the same value for the system composed of m subsystems and for each of the subsystems.

2.23 The molar mass of water amounts to $M = 18$ g mol^{-1}. The volume $V_1 = 18$ cm^3 contains the mass

$$m_1 = V_1 \rho = 18 \text{ g},$$

hence, the mole number of water amounts to

$$n_1 = \frac{m_1}{M} = 1 \text{ mol}.$$

For the second vessel, we find $m_2 = 36$ g and $n_2 = 2$ mol. The molar density in both vessels amounts to

$$\rho_n = \frac{n_1}{V_1} = \frac{n_2}{V_2} = \frac{1}{18} \text{ mol cm}^{-3}.$$

The total volume after the fusion:

$$V = V_1 + V_2 = 54 \text{ cm}^3$$

and the total mole number:

$$n = n_1 + n_2 = 3,$$

hence, for the molar density, we get

$$\rho_n = \frac{n}{V} = \frac{1}{18} \text{ mol cm}^{-3}.$$

The molar density is an intensive quantity, since it does not depend on the size of the system. The volume and amount of substance are extensive quantities. The mass density ρ is an intensive quantity, because

$$\rho = \frac{m}{V} = \frac{nM}{V} = M\rho_n.$$

2.24 We denote by v the volume occupied by 1 mol of water, i.e., its molar volume. It is obtained from the formula

$$v = \frac{M}{\rho} = 18 \text{ cm}^3 \text{ mol}^{-1}.$$

To determine the volume per molecule, v_m, we divide v by N_A, which gives

$$v_m = \frac{v}{N_A} = \frac{18}{6.022 \times 10^{23}} \text{ cm}^3 \approx 3 \times 10^{-23} \text{ cm}^3.$$

We can express this volume, using $1 \text{ Å} = 10^{-8}$ cm as a unit of length, which corresponds roughly to the atom size. We obtain $v_m = 30 \text{ Å}^3$. We can estimate the linear size of the molecule, l_m, assuming that $v_m = l_m^3$, which gives $l_m \approx 3 \text{ Å}$. In reality, the size of water molecule amounts to 2.76 Å. Liquids are very dense and the crowd of molecules resembles the crowds of people travelling in Tokyo by underground during the rush-hour, when people almost seat on one another. In a liquid, one molecule touches other molecules and altogether they fill up the space rather closely.

2.25 We express V for the ideal gas as a function of T, p and n:

$$V(T, p, n) = \frac{nRT}{p}.$$

According to the definition of an infinitesimal change of a state function, dV depends on dp and dT as follows:

$$dV = V(T + dT, p + dp, n) - V(T, p, n) = \left(\frac{\partial V}{\partial T}\right)_{p,n} dT + \left(\frac{\partial V}{\partial p}\right)_{T,n} dp.$$

Since

$$\left(\frac{\partial V}{\partial T}\right)_{p,n} = \frac{nR}{p}, \qquad \left(\frac{\partial V}{\partial p}\right)_{T,n} = -\frac{nRT}{p^2},$$

we get

$$dV = \frac{nR}{p} dT - \frac{nRT}{p^2} dp.$$

2.26 For a monatomic van der Waals gas, we have

$$U(T, V, n) = \frac{3}{2} nRT - \frac{an^2}{V}.$$

The increase in the internal energy at constant mole number amounts to

$$dU = U(T + dT, V + dV, n) - U(T, V, n) = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV.$$

Since

$$\left(\frac{\partial U}{\partial T}\right)_{V,n} = \frac{3}{2} nR, \qquad \left(\frac{\partial U}{\partial V}\right)_{T,n} = \frac{an^2}{V^2},$$

we get

$$dU(T, V, n) = \frac{3}{2} nR dT + \frac{an^2}{V^2} dV.$$

2.27 The relation between the pressure and temperature of the photon gas is

$$p = \frac{1}{3}\gamma T^4,$$

hence, we get an infinitesimal increase in the pressure

$$\mathrm{d}p = p(T + \mathrm{d}T) - p(T) = \frac{\partial p}{\partial T}\mathrm{d}T.$$

Since

$$\frac{\partial p}{\partial T} = \frac{4}{3}\gamma T^3,$$

we find that

$$\mathrm{d}p = \frac{4}{3}\gamma T^3\mathrm{d}T.$$

2.28 For $đ\omega = \omega_x\mathrm{d}x + \omega_y\mathrm{d}y$, we have to check if $\partial\omega_x/\partial y = \partial\omega_y/\partial x$. In case (1), we have

$$\frac{\partial\omega_x}{\partial y} = 6xy^2, \qquad \frac{\partial\omega_y}{\partial x} = 6xy^2,$$

thus, the equality of the derivatives is satisfied, which means that $đ\omega = \mathrm{d}f$, where f is a function of x and y. It is easy to verify that $f(x, y) = x^2y^3 + const.$ In case (2), we have

$$\frac{\partial\omega_x}{\partial y} = 4xy^3, \qquad \frac{\partial\omega_y}{\partial x} = 2xy^2,$$

thus, the derivatives differ. No function f exists, whose differential $\mathrm{d}f$ would be equal to $đ\omega$.

2.29 We consider a differential form $đ\omega = \omega_x(x, y)\mathrm{d}x + \omega_y(x, y)\mathrm{d}y$, defined in the xy plane, hence

$$\int_i^f đ\omega = \int_i^f \left[\omega_x(x, y)\mathrm{d}x + \omega_y(x, y)\mathrm{d}y\right],$$

where the path linking the initial point with the final point is to be defined. Both paths of integration are shown in Fig. S2.3. In case (1), we have

$$\int_i^f đ\omega = \int_0^1 \omega_x(x, 0)\mathrm{d}x + \int_0^1 \omega_y(1, y)\mathrm{d}y,$$

since we integrate first along the x axis, at $y = 0$, and then along the y axis, at $x = 1$. In the previous exercise, we showed that $đ\omega = xy^4\mathrm{d}x + x^2y^2\mathrm{d}y$ is not a function differential, hence, we substitute $\omega_x = xy^4$ and $\omega_y = x^2y^2$. The first integral vanishes, since $\omega_x(x, 0) = 0$. In the second integral, $\omega_y(1, y) = y^2$, hence

$$\int_i^f đ\omega = \int_0^1 y^2\mathrm{d}y = \frac{1}{3}.$$

Fig. S2.3 Two paths linking
the point $(0,0)$ with the point
$(1,1)$
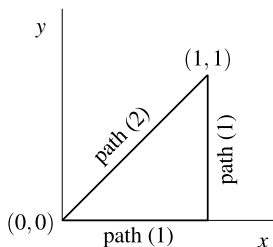
In case (2), we have to substitute $y = x$ and $dy = dx$, hence

$$\int_i^f đ\omega = \int_0^1 [\omega_x(x,x) + \omega_y(x,x)]dx = \int_0^1 (x^5 + x^4)dx = \frac{11}{30}.$$

Thus, we have shown that the value of the integral depends on the path between the points i and f.

Now we integrate along the same paths the differential $df = 2xy^3 dx + 3x^2 y^2 dy$, where $f(x,y) = x^2 y^3 + const$. For path (1), we get

$$\int_i^f df = \int_0^1 3y^2 dy = 1,$$

and for path(2), we get

$$\int_i^f df = \int_0^1 5x^4 dx = 1.$$

In both cases, the value of the integral is the same, equal to $\Delta f = f(1,1) - f(0,0) = 1$.

Below we give a general method of integration of differential forms $đ\omega$. We restrict ourselves to two variables but it is easy to generalize the result. A path of integration is defined by a certain curve, which can be expressed in the parametric form: $\tau \mapsto (x(\tau), y(\tau))$, where the parameter τ changes from the initial value τ_i to the final value τ_f. The path may consist of several parts, as in case (1), but we assume for simplicity that the curve is smooth. If it is not, then we integrate along each smooth part of the curve and add the integrals. The parameter τ_i corresponds to the initial point (x_i, y_i), where $x_i = x(\tau_i)$, $y_i = y(\tau_i)$, and analogously for the final point (x_f, y_f). The integral of $đ\omega$ along the curve is defined as follows:

$$\int_i^f đ\omega = \int_{\tau_i}^{\tau_f} \left[\omega_x(x(\tau), y(\tau)) \frac{dx}{d\tau} + \omega_y(x(\tau), y(\tau)) \frac{dy}{d\tau} \right] d\tau.$$

Thus, we have reduced the problem to the integration of a function of one variable. Note that if $đ\omega = df$, then

$$\int_i^f df = \int_{\tau_i}^{\tau_f} \left(\frac{\partial f}{\partial x} \frac{dx}{d\tau} + \frac{\partial f}{\partial y} \frac{dy}{d\tau} \right) d\tau = \int_{\tau_i}^{\tau_f} \frac{df(x(\tau), y(\tau))}{d\tau} d\tau$$

$$= f(x(\tau_f), y(\tau_f)) - f(x(\tau_i), y(\tau_i)) = f(x_f, y_f) - f(x_i, y_i),$$

which means that the value of the integral depends only on the initial and final points, and not on the path linking these points.

Finally, we notice that if the curve can be presented as a set of points $(x, y(x))$, then $\tau = x$ and

$$\int_i^f đ\omega = \int_{x_i}^{x_f} \left[\omega_x\big(x, y(x)\big) + \omega_y\big(x, y(x)\big) \frac{dy}{dx} \right] dx.$$

2.30 We use the equation of state of the ideal gas. In general, we should use an equation of state which describes gases better, e.g., the van der Waals equation of state. Then, however, we would have to know which gas it is, and find the parameters a and b for this gas in the tables. Since this information is not provided, we assume the equation of state independent of the gas, i.e., the ideal gas equation of state:

$$pV = nRT.$$

The initial state: $V_i = 120$ L, $T_i = (273.15 + 25)$ K $= 298.15$ K, $n_i = 5$ mol.
The final state: $V_f = 120$ L $= 120 \times 10^{-3}$ m^3, $T_f = 298.15$ K, $p_f = 0.5$ atm.

Substituting the parameters of the final state into the equation of state, we get the final value of the mole number n_f, i.e.,

$$n_f = \frac{p_f V_f}{RT_f} = \frac{0.5 \times 101325 \text{ N m}^{-2} \times 120 \times 10^{-3} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{mol}^{-1} \times 298.15 \text{ K}} = 2.453 \text{ mol},$$

hence

$$\Delta n = n_f - n_i = 2.453 - 5 = -2.547 \text{ mol}.$$

Δn is negative because the mole number has decreased; 2.547 mol of the gas has escaped from the vessel.

2.31 From the equation of state of the ideal gas, we get

$$p = \frac{nRT}{V} = \frac{1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{10^{-4} \text{ m}^3} \approx 2.48 \times 10^7 \text{ Pa}.$$

The internal energy of a two-atomic gas is given by

$$U = \frac{5}{2} nRT = 2.5 \times 1 \text{ mol} \times 8.314 \text{ mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} = 6193.9 \text{ J}.$$

2.32 The van der Waals equation of state describes nitrogen better than the ideal gas equation of state. Performing calculations for both equations of state, we want to learn how good an approximation to a real gas the ideal gas is. From the van der Waals equation of state, we get

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2} = \frac{8.314 \text{ J K}^{-1} \times 298 \text{ K}}{10^{-4} \text{ m}^3 - 3.85 \times 10^{-5} \text{ m}^3} - \frac{0.1358 \text{ J m}^3}{10^{-8} \text{ m}^6}$$
$$\approx 4.029 \times 10^7 \text{ Pa} - 1.358 \times 10^7 \text{ Pa} \approx 2.67 \times 10^7 \text{ Pa}.$$

Thus, the pressure of the ideal gas differs by a few percent from the pressure obtained from the van der Waals equation of state. We notice, however, that this good agreement is fortuitous. It results from partial cancellation of two large terms in the

van der Waals equation of state. Note that when the molar volume $v = V/n$ is small, i.e., comparable with the constant b, then the first term in the van der Waals equation is large and dominates over the second term.

To calculate the internal energy, we use the expression

$$U = \frac{5}{2}nRT - \frac{an^2}{V} = 6193.9 \text{ J} - 1358 \text{ J} \approx 4836 \text{ J}. \tag{S2.1}$$

The first term is the same as for the ideal gas. This part of the internal energy comes from the kinetic energy of N_2 molecules. The second term comes from the potential energy of intermolecular attraction. At large densities and low temperatures, its absolute value becomes large compared to the first term, which leads to condensation of the gas.

2.33 When the gas density is small, as in this case, we obtain practically the same result for the pressure and internal energy, using the ideal gas and van der Waals equations of state. In the previous exercise, we assumed the volume $V = 0.1$ L, which corresponds to the molar density of 10 mol L^{-1}. In the present case, the molar density amounts only to 0.001 mol L^{-1}. We calculate the pressure and internal energy of the gas, using the van der Waals equation:

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2} = \frac{8.314 \text{ J K}^{-1} \times 298 \text{ K}}{1 \text{ m}^3 - 3.85 \times 10^{-5} \text{ m}^3} - \frac{0.1358 \text{ J m}^3}{1 \text{ m}^6}$$
$$\approx 2477.67 \text{ Pa} - 0.1358 \text{ Pa} \approx 2477.53 \text{ Pa},$$

$$U = \frac{5}{2}nRT - \frac{an^2}{V} = 6193.93 \text{ J} - 0.1358 \text{ J} \approx 6193.79 \text{ J}.$$

For the ideal gas, we get $p = 2477.57$ Pa and $U = 6193.93$ J. Thus, in the case of small molar densities, the corrections coming from intermolecular interactions are very small and can be neglected.

2.34 We use the expression for the internal energy of the photon gas: $U = \gamma V T^4$, where $\gamma = 7.56 \times 10^{-16}$ J m^{-3} K^{-4}. For $T = 298$ K, we get

$$U = 7.56 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4} \times 1 \text{ m}^3 \times 298^4 \text{ K}^4 \approx 6 \times 10^{-6} \text{ J},$$

and for $T = 400$ K, we get $U \approx 2 \times 10^{-5}$ J. The pressure is determined from the expression: $p = \gamma T^4/3 = U/(3V)$. For $T = 298$ K, we get $p \approx 2 \times 10^{-6}$ Pa, and for $T = 400$ K, $p \approx 6.5 \times 10^{-6}$ Pa.

Therefore, the internal energy of radiation contained in the photon gas is very small compared to the internal energy of the ideal gas, and the same concerns the pressure. The photon gas can be used to a fast transfer of energy (in lasers). We can imagine that the energy $E = 10^{-5}$ J is transferred during the time $t = 1$ fs $= 10^{-15}$ s (femtosecond lasers). It requires the power $P = E/t = 10^{10}$ W $= 10$ GW, which is the power generated by a big power station. For instance, the Bełchatów power station in Poland, generating the power of 4 GW, is the biggest conventional power station in Europe (it uses brown coal as fuel). The biggest water power stations in Brasil or USA generate the power of about 10 GW. Thus, to generate great power from a small amount of energy, the energy has to be delivered in a very short time.

2.35 For the ideal gas, we have $pV = nRT$ and $U = fnRT/2$, where f is the number of degrees of freedom per molecule ($f = 3$ for one atom), hence

$$p(U, V, n) = \frac{2U}{fV} = \frac{2mU}{fmV} = p(mU, mV, mn).$$

In the case of the van der Waals gas, we determine T from the expression for the internal energy, i.e.,

$$T = \frac{2}{fnR}\left(U + \frac{an^2}{V}\right),$$

and then substitute it into the expression for the pressure, hence

$$p = \frac{2U}{f(V - nb)} + \frac{2an^2}{fV(V - nb)} - \frac{an^2}{V^2}.$$

Using the last formula we verify that $p(mU, mV, mn) = p(U, V, n)$.

2.36 For the ideal gas $V(T, p, n) = nRT/p$, hence

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,n} = \frac{nRT}{Vp^2} = \frac{1}{p}.$$

In the case of the van der Waals gas, to find the relation $V = V(T, p, n)$, the equation of state is to be written in the form of a third order equation for V, i.e.,

$$pV^2(V - nb) - nRTV^2 + an^2(V - nb) = 0,$$

and then the root of this equation is to be determined.[1] However, it is more convenient to calculate the derivative

$$\left(\frac{\partial p}{\partial V}\right)_{T,n} = -\frac{nRT}{(V - nb)^2} + \frac{2an^2}{V^3},$$

hence, we get

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,n} = \left[\frac{nRTV}{(V - nb)^2} - \frac{2an^2}{V^2}\right]^{-1}.$$

In the case of the photon gas, the mole number n is not a thermodynamic variable, and from the equation of state $p = \gamma T^4/3$, it follows that $(\partial p/\partial V)_T = 0$, thus, $(\partial V/\partial p)_T$ is not well defined. However, we can express V as a function of U and p, i.e., $V = U/(3p)$, hence

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_U = \frac{1}{p}.$$

Thus, we obtain the same result as for the ideal gas, for which we differentiated at constant temperature. Note that from the equations of state for the ideal gas: $pV = nRT$ and $U = fnRT/2$, the relation $V = 2U/(fp)$ follows, hence

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_U = \frac{1}{p}.$$

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[1]The equation has only one real root at sufficiently high temperatures.

2.37 For the ideal gas,

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,n} = \frac{nR}{pV} = \frac{1}{T}.$$

In the case of the photon gas, fixing pressure, we also fix temperature. Therefore, the above expression does not make sense. However, we can calculate

$$\frac{1}{V}\left(\frac{\partial V}{\partial U}\right)_{p} = \frac{1}{3Vp} = \frac{1}{U}.$$

2.38 For the ideal gas,

$$\left(\frac{\partial U}{\partial T}\right)_{V,n} = \frac{f}{2}nR,$$

and we obtain the same result for the van der Waals gas. In the case of the photon gas, we get

$$\left(\frac{\partial U}{\partial T}\right)_{V} = 4\gamma V T^3.$$

2.39 We make an assumption that the atmosphere is in thermodynamic equilibrium. This is not quite correct, since neither the temperature nor pressure of the atmosphere are constant, and also a macroscopic flow of air exists. Nevertheless, the assumption is good enough to estimate the amount of oxygen in the atmosphere. We calculate the volume V occupied by air. It is the volume of a spherical layer whose internal radius amounts to $R = 6500$ km (radius of the earth), and the external radius is equal to $R + h$, where $h = 10$ km. The temperature amounts to $T = 273.15 + 14$ K, and the pressure $p = 1$ atm. Since $h \ll R$, we get

$$V = \frac{4}{3}\pi(R + h)^3 - \frac{4}{3}\pi R^3 \approx 4\pi R^2 h \approx 5.3 \times 10^{18} \text{ m}^3.$$

The mole number is determined from the ideal gas equation of state:

$$n = \frac{pV}{RT} = \frac{101325 \text{ Pa} \times 5.3 \times 10^{18} \text{ m}^3}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 287.15 \text{ K}} \approx 2 \times 10^{20} \text{ mol}.$$

Since oxygen makes 21 % of the whole, the amount of oxygen in the atmosphere is equal to $n_{O_2} = 0.21n \approx 0.4 \times 10^{20}$ mol. The amount of 0.5×10^{16} mol of oxygen is used up yearly by living organisms, which means that even if the oxygen supply was not renewed it would disappear from the atmosphere only after $n_{O_2}/0.5 \times 10^{16} = 8000$ years. Obviously, if the concentration of oxygen fell well below 21 % we would have serious problems with breathing. After a few hundred years, we would begin to feel the lack of oxygen in the atmosphere.

2.40 The data: $R = 700\,000$ km, $T = 6000$ K, $c = 3 \times 10^8$ m/s, $\gamma = 7.56 \times 10^{-16}$ J K^{-4} m^{-3}. Using the expression for u, we obtain the power per unit area, i.e.

$$I = \frac{uc}{4} = \frac{\gamma T^4 c}{4}.$$

Substituting the numbers, we get

$$I = \frac{7.56}{4} \times 10^{-16} \, \text{J}\,\text{K}^{-4}\,\text{m}^{-3} \times 3 \times 10^8 \, \text{m}\,\text{s}^{-1} \left(6 \times 10^3 \, \text{K}\right)^4 \approx 7 \times 10^7 \, \text{W}\,\text{m}^{-2}.$$

The total power radiated from the sun surface, of the area $A = 4\pi R^2$, amounts to

$$P = AI = 4\pi \left(7 \times 10^8 \, \text{m}\right)^2 \times 7 \times 10^7 \, \text{W}\,\text{m}^{-2} \approx 4 \times 10^{26} \, \text{W}.$$

It is an unimaginably great number. By comparison, the total energy consumption in 2008 amounted to 4.74×10^{20} J $\approx 132\,000$ TWh. With this level of energy consumption, the energy radiated by the sun during 1 second only would be enough for us for 840 000 years.

Exercises of Chapter 3

3.1 The process takes place at constant pressure p, hence, the heat absorbed by the system due to the change in the temperature from T_i to T_f amounts to

$$Q = nc_p(T_f - T_i) = nc_p\Delta T,$$

provided that the molar heat capacity at constant pressure, c_p, does not depend on temperature. Here we consider a monatomic ideal gas, for which $c_p = 5R/2$. The temperature difference follows from the equation of state $pV = nRT$:

$$\Delta T = \frac{p\Delta V}{nR},$$

hence

$$Q = \frac{5}{2}p\Delta V.$$

This result can also be derived directly from the first law of thermodynamics: $Q = \Delta U - W$. The change in the internal energy of the gas amounts to

$$\Delta U = \frac{3}{2}nR\Delta T = \frac{3}{2}p\Delta V,$$

and the work done on the gas in an isobaric process is equal to $W = -p\Delta V$, hence, $Q = (5/2)p\Delta V$. Substituting the data: $p = 1$ bar and $\Delta V = 30$ L, we get

$$Q = 2.5 \times 10^5 \, \text{Pa} \times 30 \times 10^{-3} \, \text{m}^3 = 7500 \, \text{J}.$$

3.2 In this case, the external pressure p_{ext} is fixed, but the gas pressure changes during the process from the initial value $p_i = 2$ atm to the final value $p_f = p_{\text{ext}} = 1$ atm. The process is not quasi-static, thus, it is not reversible. However, if the system performs work on a reversible source of work, then we can calculate the work in the same way as in the previous exercise, i.e., $W = -p_{\text{ext}}\Delta V$. The change in the volume is obtained from the equation of state $pV = nRT$ as follows:

$$\Delta V = V_f - V_i = nR\left(\frac{T_f}{p_{\text{ext}}} - \frac{T_i}{p_i}\right).$$

Fig. S3.1 Volume of the
vessel doubles at constant
temperature and the pressure
of the ideal gas decreases by a
factor of two
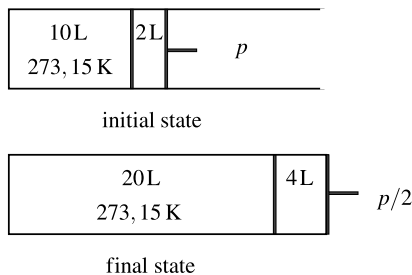
The change in the internal energy of the gas is equal to $\Delta U = (3/2)nR(T_f - T_i)$, hence

$$Q = \Delta U - W = nR\left[\frac{3}{2}(T_f - T_i) + \left(T_f - \frac{T_i\, p_{\text{ext}}}{p_i}\right)\right],$$

where $n = 5$, $T_i = 298.15$ K, $T_f = 293.15$ K. Substituting the data, we get $\Delta U = -311.8$ J and $W = -5989.2$ J, hence, $Q = 5677.4$ J. Thus, the system performs work ($W < 0$) and absorbs heat from the surroundings ($Q > 0$).

3.3 The system considered is shown in Fig. S3.1. Since the subsystems are in equilibrium, the gas pressure must be the same, hence

$$pV^{(1)} = n^{(1)}RT,$$
$$pV^{(2)} = n^{(2)}RT.$$

The temperature and mole numbers in the subsystems do not change, thus

$$p_i V_i^{(1)} = p_f V_f^{(1)},$$
$$p_i V_i^{(2)} = p_f V_f^{(2)},$$

hence

$$p_i V_i = p_f V_f,$$

where V_i and V_f denote the total volume of the system in the initial and final states. Thus, we have

$$\frac{V_f^{(1)}}{V_i^{(1)}} = \frac{V_f^{(2)}}{V_i^{(2)}} = \frac{p_i}{p_f} = \frac{V_f}{V_i} = 2.$$

The work done by each subsystem in the isothermal process amounts to

$$W^{(1)} = -n^{(1)}RT \ln \frac{V_f^{(1)}}{V_i^{(1)}} = -n^{(1)}RT \ln 2,$$

$$W^{(2)} = -n^{(2)}RT \ln \frac{V_f^{(2)}}{V_i^{(2)}} = -n^{(2)}RT \ln 2.$$

The work done by the whole system amounts to

$$W = W^{(1)} + W^{(2)} = -nRT \ln 2 = -nRT \ln \frac{V_f}{V_i},$$

where n denotes the total mole number of the gas. We know that $n^{(1)} = 10$, and $n^{(2)}$ is determined from the relation

$$\frac{n^{(2)}}{n^{(1)}} = \frac{V_i^{(2)}}{V_i^{(1)}} = \frac{1}{5},$$

hence $n^{(2)} = 2$ mol. Substituting the data, we get

$$W^{(1)} = -15741 \text{ J}, \qquad W^{(2)} = -3148 \text{ J}, \qquad W = -18889 \text{ J}.$$

The internal energy of the subsystems and whole system does not change, since $T = const$ and we consider the ideal gas, thus

$$Q = \Delta U - W = -W = 18889 \text{ J}.$$

3.4 Due to the condition of mechanical equilibrium, the gas pressure is the same in each subsystem. The temperature is also the same, since the system is in thermal equilibrium with the surroundings, hence

$$p_i V_i^{(j)} = n^{(j)} RT_i,$$
$$p_f V_f^{(j)} = n^{(j)} RT_f,$$

where $j = 1, 2, 3$ numbers the subsystems. Summing up over all subsystems, we get

$$p_i V = nRT_i,$$
$$p_f V = nRT_f,$$

where n denotes the total number of moles of the gas in the system, thus

$$\frac{T_i}{p_i} = \frac{T_f}{p_f},$$

hence it follows that

$$V_f^{(j)} = n^{(j)} R \frac{T_f}{p_f} = n^{(j)} R \frac{T_i}{p_i} = V_i^{(j)}.$$

The gas in the subsystems does not perform any work because the volume does not change. The mole number for each subsystem is determined from the equation of state

$$n^{(j)} = \frac{p_i V_i^{(j)}}{RT_i}.$$

The change in the internal energy of each subsystem amounts to

$$\Delta U^{(j)} = \frac{3}{2} n^{(j)} R(T_f - T_i) = \frac{3}{2} p_i V_i^{(j)} \left(\frac{T_f}{T_i} - 1 \right).$$

Since the system performs no work, the heat Q absorbed by the system is equal to the change in its internal energy, i.e.

$$Q = \Delta U = \sum_{j=1}^{3} \Delta U^{(j)} = \frac{3}{2} p_i V \left(\frac{T_f}{T_i} - 1 \right).$$

Therefore, it does not matter if we heat up subsystems, which are thermally insulated from one another but remain in thermal contact with the surroundings, or if we heat up the whole system of the volume $V = V^{(1)} + V^{(2)} + V^{(3)}$.

3.5 We solve this problem in a similar way as in Exercise 3.3. The process is isothermal and the pressure is the same in each subsystem. From the isotherm equation $pV = const$, it follows that

$$p_f V_f^{(j)} = p_i V_i^{(j)},$$

for each subsystem j. Since $V_f^{(1)}/V_i^{(1)} = 4$, we have

$$\frac{V_f^{(j)}}{V_i^{(j)}} = \frac{p_i}{p_f} = 4$$

for all subsystems. The work done in a reversible isothermal process by the jth subsystem amounts to

$$W^j = -n^{(j)} RT \ln \frac{V_f^{(j)}}{V_i^{(j)}} = -n^{(j)} RT \ln 4.$$

To calculate the work done by the whole system, we sum up over all subsystems, hence

$$W = \sum_{i=1}^{3} W^{(i)} = -nRT \ln 4,$$

where n is the total mole number of the gas in the system. Since we know the initial volume of each subsystem, hence, also the total volume ($V_i = 16$ L), the initial pressure ($p_i = 1$ atm) and the temperature $T = 273.15$ K, we can determine n from the equation of state

$$n = \frac{p_i V_i}{RT}.$$

Substituting it into the expression for the work, we get

$$W = - p_i V_i \ln 4 = -101325 \text{ Pa} \times 16 \times 10^{-3} \text{ m}^3 \ln 4 \approx -2247 \text{ J}.$$

We notice that actually the temperature is not needed in this exercise. The internal energy does not change in the isothermal process, thus, the heat supplied to the system $Q = -W$.

3.6 The gas expanding to the vacuum performs no work ($W = 0$), since the external pressure $p_{ext} = 0$. The process is adiabatic, thus, by definition no heat is transferred

between the system and surroundings ($Q = 0$), hence, the internal energy of the system does not change either ($\Delta U = Q + W = 0$). Since the internal energy in the initial state, U_i, is the same as in the final state, U_f, we have

$$U_f = \frac{3}{2}nRT_f = \frac{3}{2}nRT_i - \frac{an^2}{V_i} = U_i,$$

where we have used the assumption that $V_f = \infty$. From the above equation, we determine the change in the temperature

$$\Delta T = T_f - T_i = -\frac{2an}{3RV_i}.$$

Why does the temperature decrease when the van der Waals gas expands, even though it performs no work? Attractive intermolecular interactions cause molecules to slow down when they move away. Since the speed of molecules decreases, the gas temperature, which is proportional to the average kinetic energy of molecules, also decreases.

3.7 The work done against the constant external pressure p_{ext} amounts to $W = -p_{\text{ext}}\Delta V$, hence, the change in the internal energy in an adiabatic process is $\Delta U = W = -p_{\text{ext}}\Delta V$. For 1 mol of the ideal gas, $\Delta U = 3R\Delta T/2$, hence, also the work $W = 3R\Delta T/2$. Comparing both expressions for W, we determine the change in the volume:

$$\Delta V = -\frac{3R\Delta T}{2p_{\text{ext}}}.$$

3.8 Since we consider a reversible adiabatic process, we can make use of the adiabat equation: $TV^{2/3} = const$, hence

$$\frac{V_f}{V_i} = \left(\frac{T_i}{T_f}\right)^{3/2} = 4^{3/2} = 8,$$

for $T_f = T_i/4$. In this process, the volume has increased 8 times. The work done by the gas is equal to the change in its internal energy, hence

$$W = \Delta U = \frac{3}{2}nR(T_f - T_i) = -\frac{9}{8}nRT_i.$$

3.9 Substituting the temperature determined from the ideal gas equation of state, $T = pV/(nR)$, to the adiabat equation expressed in the variables T and V (see the previous exercise), we obtain the adiabat equation in the variables p and V, i.e.,

$$pV^{5/3} = const,$$

hence

$$\frac{p_f}{p_i} = \left(\frac{V_i}{V_f}\right)^{5/3} = \left(\frac{1}{4}\right)^{5/3} \approx 0.1.$$

For the initial pressure $p_i = 1$ bar, we get the final pressure $p_f \approx 0.1$ bar.

Fig. S3.2 Evaporation of
water at the external pressure
p_{ext}. In the initial state, water
is a liquid, and in the final
state, we have water vapour.
Q is the heat supplied to
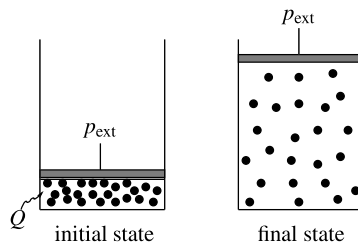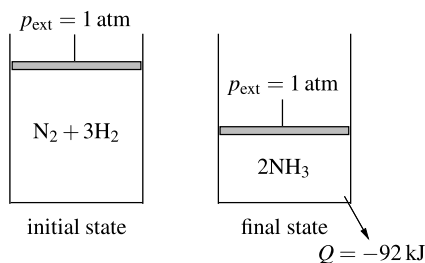change liquid water into
vapour

initial state   final state

Fig. S3.3 Synthesis of
ammonia occurs at the
pressure $p_{ext} = 1$ atm. As a
result of the reaction, the heat
$Q = -92$ kJ is given off to
the surroundings and the final
volume of the system is half
of the initial volume

initial state   final state

$Q = -92$ kJ

3.10 The process of water evaporation at constant pressure is shown schematically
in Fig. S3.2. In the initial state, 1 mol of liquid water occupies the volume $V_i = 18$ cm^3 and fills up the whole available space of the vessel. The pressure is constant
and equals $p_{ext} = 1$ atm. In the final state, only water vapour is present, which
occupies the volume $V_f = 30.6$ L. A change of 1 mol of liquid water into vapour
at the pressure of 1 atm requires supply of the heat $Q = 40670$ J. Moreover, when
liquid water evaporates it performs the work W against the external pressure $p_{ext} = 1$ atm, where

$$W = -p_{ext}(V_f - V_i).$$

The change in the internal energy of the system amounts to

$$\Delta U = Q + W = Q - p_{ext}(V_f - V_i).$$

Substituting the data, we get

$$\Delta U = 40670 \text{ J} - 101325 \text{ Pa} \times \left(30.6 \times 10^{-3} - 18 \times 10^{-6}\right) \text{ m}^3 \approx 37569 \text{ J}.$$

Thus, the work done by the system is much smaller then the heat supplied.

3.11 The process considered is shown schematically in Fig. S3.3. The heat given
off in this reaction, $Q = -92$ kJ, comes from the energy of chemical bonds. $Q < 0$
since the system gives off the heat. In the energetic balance, we have to take into
account also the work done by (or on) the system due to the change in its volume.
All substances are treated as ideal gases. In the initial state, there are 3 mol of H_2
and 1 mol of N_2, which gives the total mole number $n_i = 4$ mol. In the final state,
there are $n_f = 2$ mol of ammonia (NH_3). The temperature and pressure have the
same values in the initial and final states: $T = 298$ K and $p_{ext} = 1$ atm. The change
in the internal energy

$$\Delta U = Q + W = Q - p_{ext}(V_f - V_i) = Q - RT(n_f - n_i),$$

where we have used the ideal gas equation of state. Substituting the data, we get

$$\Delta U = -92 \times 10^3 \, \text{J} + 2 \, \text{mol} \times 8.314 \, \text{J K}^{-1} \, \text{mol}^{-1} \times 298 \, \text{K} \approx -87 \, \text{kJ}.$$

3.12 In the initial state, we have two isolated systems with the total internal energy $U_i^{(1)} + U_i^{(2)} = 30$ kJ. Their mole numbers are constant and equal to $n^{(1)} = 2$ and $n^{(2)} = 3$, respectively. Both systems are isolated from the surroundings, thus, their total internal energy does not change, hence, $U_f^{(1)} + U_f^{(2)} = 30$ kJ. The temperature of the final equilibrium state is T_f. We determine T_f from the equation

$$U_f^{(1)} + U_f^{(2)} = \left(\frac{3}{2}n^{(1)} + \frac{5}{2}n^{(2)}\right)RT_f = 30 \, \text{kJ},$$

hence

$$T_f = \frac{30 \, \text{kJ}}{10.5 \, \text{mol} \times 8.314 \, \text{J K}^{-1} \, \text{mol}^{-1}} \approx 343.65 \, \text{K}.$$

Then we calculate the internal energy of each system:

$$U_f^{(1)} = \frac{3}{2}n^{(1)}RT_f \approx 8571 \, \text{J},$$

$$U_f^{(2)} = \frac{5}{2}n^{(2)}RT_f \approx 21429 \, \text{J}.$$

3.13 The total internal energy in the final state is the same as in the initial state, hence

$$U_i = \gamma V\left(T^{(1)4} + T^{(2)4}\right) = U_f = 2\gamma V T_f^4,$$

and for the final temperature, we get

$$T_f = \left(\frac{T^{(1)4} + T^{(2)4}}{2}\right)^{1/4}.$$

3.14 The initial temperatures of the metal and water amount to $T_{1i} = 400$ K and $T_{2i} = 294$ K. The final temperature of water and the metal immersed in it amounts to $T_f = 300$ K. The mass of the metal and water is $m_1 = 1$ kg and $m_2 = 0.3$ kg, respectively. For the change in their internal energy, we get

$$\Delta U_1 = c_1 m_1 (T_f - T_{1i}),$$

$$\Delta U_2 = c_2 m_2 (T_f - T_{2i}),$$

respectively, where c_1 and c_2 denote their specific heat. The SI derived unit of the specific hit is $\text{J kg}^{-1} \, \text{K}^{-1}$. The whole system, i.e., the metal and water, is isolated from the surroundings, hence, $\Delta U_1 + \Delta U_2 = 0$, and we can determine the ratio

$$\frac{c_2}{c_1} = -\frac{m_1(T_f - T_{1i})}{m_2(T_f - T_{2i})}.$$

Substituting the data, we get

$$\frac{c_2}{c_1} = \frac{1 \text{ kg} \times 100 \text{ K}}{0.3 \text{ kg} \times 6 \text{ K}} \approx 55.6.$$

Thus, the specific heat of water is 55.6 times bigger than the specific heat of the metal. Substances of good cooling capabilities are those of high specific heat in the given temperature range, which means that they are difficult to warm up. Evaporation of a liquid can also be used for cooling. In the latter case, we choose substances of high heat of evaporation.

3.15 Since the internal energy is an extensive quantity, we have

$$U(T, V, n) = nu(T, V/n) = nu(T, v),$$

where u denotes the molar internal energy, and $v = V/n$ is the molar volume. For $n = 4$, we have

$$U(T, V, 4 \text{ mol}) = ATV^3 = AT(4v)^3 \text{ mol}^3 = (4 \text{ mol})u(T, v),$$

hence, $u(T, v) = BTv^3$, where $B = 16A \text{ mol}^2 = 160 \text{ J mol}^2 \text{ K}^{-1} \text{ cm}^{-9}$, and

$$U(T, V, n) = nu(T, V/n) = BT\frac{V^3}{n^2}.$$

3.16 This exercise is solved in a similar way as the previous one

$$U(T, V, 2 \text{ mol}) = aVT^4 = (2 \text{ mol})avT^4 = (2 \text{ mol})u(T, v),$$

hence $u(T, v) = avT^4$, where a is independent of n. Thus, the expression $U = aVT^4$ holds for any n.

3.17 The total energy transferred to the substance in the form of heat, i.e.,

$$Q = 12 \text{ V} \times 1 \text{ A} \times 3000 \text{ s} = 36 \text{ kJ},$$

caused the substance temperature to increase by $\Delta T = 5.5$ K. If we assume that in this range of temperature, the heat capacity of the substance, C, is independent of temperature, then we can calculate it from the formula: $C = Q/\Delta T \approx 6545 \text{ J K}^{-1}$.

3.18 Infinitesimal work performed by the gas is equal to $đW^* = -đW = pdV$, hence, in the process of isothermal expansion from the volume V_i to $V_f > V_i$, we get

$$W^* = nRT \int_{V_i}^{V_f} \left(\frac{1}{V} + \frac{n^2 B(T)}{V^2} \right) dV = nRT \ln \frac{V_f}{V_i} - n^2 RT B(T) \left(\frac{1}{V_f} - \frac{1}{V_i} \right).$$

The work done by the ideal gas amounts to $W^* = nRT \ln(V_f/V_i)$. At high temperatures $B(T) > 0$, and the work done by the real gas is greater than in the case of the ideal gas.

3.19 To calculate the work done by the gas, we integrate $đW^* = pdV$ from the initial volume V_i to the final volume $V_f > V_i$. For the van der Waals equation of state, we get

$$W^* = \int_{V_i}^{V_f} \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2} \right) dV = nRT \ln \left(\frac{V_f - nb}{V_i - nb} \right) + an^2 \left(\frac{1}{V_f} - \frac{1}{V_i} \right).$$

The constants a and b are positive. The presence of a lowers the gas pressure in relation to the ideal gas pressure, and the presence of b increases the gas pressure. The same tendency holds for the work done by the gas. Then we expand the term $1/(V - nb)$ in a power series of nb/V:

$$\frac{1}{V - nb} = \frac{1}{V(1 - nb/V)} = \frac{1}{V}\left[1 + \frac{nb}{V} + \left(\frac{nb}{V}\right)^2 + \cdots\right].$$

For $V \gg nb$, we have

$$\frac{1}{V - nb} = \frac{1}{V(1 - nb/V)} \approx \frac{1}{V} + \frac{nb}{V^2}.$$

Substituting this approximation into the van der Waals equation of state, we get the expression for the function $B(T)$ introduced in the previous exercise:

$$B(T) = b - \frac{a}{RT}.$$

The above approximation can be used when the molar volume of the gas, $v = V/n$, is large compared to the parameter b. We notice also that $B(T)$ is negative at low temperatures and positive at high temperatures.

3.20 We use the form of the internal energy differential at constant volume: $dU = nc_v dT$. Integrating this relation from the temperature T_i to T_f, we find the change in the molar internal energy:

$$\Delta u = u_f - u_i = \int_{T_i}^{T_f} c_v dT = A(T_f - T_i) + \frac{1}{2}B(T_f^2 - T_i^2).$$

3.21 We proceed in the same way as in the previous exercise, hence

$$\Delta u = u_f - u_i = \int_{T_f}^{T_i} c_v dT = A(T_f - T_i) + \frac{1}{2}B(T_f^2 - T_i^2) + C\left(\frac{1}{T_f} - \frac{1}{T_i}\right).$$

3.22 In this case, the heat capacity per unit volume is given, thus, $dU = Vc_v dT$, and

$$\Delta U = U_f - U_i = V\int_{T_f}^{T_i} c_v dT = V\gamma(T_f^4 - T_i^4).$$

3.23 To avoid damaging of the vessel, the maximum pressure obtained by heating of the gas cannot exceed 100 atm, i.e., $p_f < 100$ atm. From the equation of state, we get

$$\frac{p_i}{T_i} = \frac{p_f}{T_f},$$

hence, the final temperature must satisfy the inequality

$$T_f = \frac{p_f T_i}{p_i} < 100 T_i = 29800 \text{ K}.$$

The molar heat capacity at constant volume amounts to $c_v = 5R/2$, and the mole number $n = p_i V / R T_i$. The heat to be delivered to warm up the gas from $T_i = 298$ K to $T_f = 29800$ K amounts to

$$Q = \frac{5}{2} n R(T_f - T_i) = \frac{5}{2} p_i V \left(\frac{T_f}{T_i} - 1 \right) \approx 601.87 \text{ kJ}.$$

Note that the maximum final temperature is much higher than the melting point of any material on the earth. Therefore, it is not possible, in practice, to warm up the gas in the vessel, to achieve the pressure of 100 atm.

3.24 In the initial state, $U_i = 3n_i RT/2$, and in the final state, $U_f = 3n_f RT/2$. The change in the internal energy caused by the reduction of the mole number $\Delta n = n_f - n_i$ amounts to

$$\Delta U = U_f - U_i = \frac{3}{2} RT \Delta n.$$

3.25 As in the previous exercise, the change in the internal energy amounts to

$$\Delta U = \frac{3}{2} RT \Delta n.$$

The process occurs at constant pressure, hence, the work done in the process amounts to

$$W = -p\Delta V = -RT \Delta n,$$

where we have used the equation of state $pV = nRT$. According to the first law of thermodynamics, $\Delta U = Q + W + Z$. The change in the internal energy at constant temperature is related to the change in the mole number of the gas, hence, $\Delta U = Z$, from which it follows that

$$Q = -W = RT \Delta n.$$

Since $\Delta n < 0$, we have $W > 0$ and $Q < 0$, i.e., the work is performed on the system, and the system gives off the heat.

Exercises of Chapter 4

4.1 The process considered is shown in Fig. S4.1. At the first stage, $V = V_1$, hence $W_1 = 0$. The change in the temperature amounts to $\Delta T = V_1(p_2 - p_1)/R$, and the internal energy changes by

$$\Delta U_1 = \frac{3}{2} V_1(p_2 - p_1),$$

hence

$$Q_1 = \Delta U_1 - W_1 = \frac{3}{2} V_1(p_2 - p_1).$$

Fig. S4.1 Isochoric–isobaric
cycle
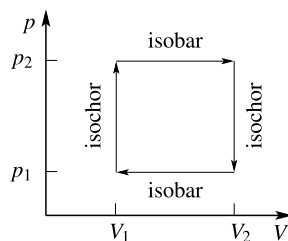
At the second stage, $p = p_2$, the work amounts to

$$W_2 = -p_2(V_2 - V_1),$$

and the temperature changes by $\Delta T = p_2(V_2 - V_1)/R$, hence

$$\Delta U_2 = \frac{3}{2}p_2(V_2 - V_1),$$

$$Q_2 = \Delta U_2 - W_2 = \frac{5}{2}p_2(V_2 - V_1).$$

At the third stage, $V = V_3$, $W_3 = 0$ and

$$\Delta U_3 = \frac{3}{2}V_2(p_1 - p_2),$$

$$Q_3 = \Delta U_3 - W_3 = \frac{3}{2}V_2(p_1 - p_2).$$

At the fourth stage, we have $p = p_1$,

$$W_4 = -p_1(V_1 - V_2),$$

$$\Delta U_4 = \frac{3}{2}p_1(V_1 - V_2),$$

$$Q_4 = \Delta U_4 - W_4 = \frac{5}{2}p_1(V_1 - V_2).$$

The process is a cycle, thus

$$\Delta U = \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4 = 0.$$

The total work

$$W = W_1 + W_2 + W_3 + W_4 = -(p_2 - p_1)(V_2 - V_1),$$

and the total heat

$$Q = Q_1 + Q_2 + Q_3 + Q_4 = \Delta U - W = (p_2 - p_1)(V_2 - V_1).$$

Thus, the system performs work ($W < 0$) due to the heat absorbed.

4.2 The engine efficiency η_e is equal to the ratio of the work done by the engine, $W^* = -W$, to the heat absorbed. In the cycle considered, the engine absorbs the

Fig. S4.2 Carnot cycle
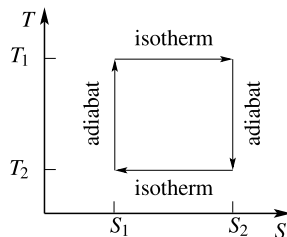
heat $Q_1 = (3/2)V_1(p_2 - p_1) > 0$ during the isochoric warming up of the gas, and the heat $Q_2 = (5/2)p_2(V_2 - V_1) > 0$ during the isobaric expansion, hence

$$\eta_e = \frac{2(p_2 - p_1)(V_2 - V_1)}{3V_1(p_2 - p_1) + 5p_2(V_2 - V_1)}.$$

As we can see, the efficiency depends on the working substance used in the engine, because the heat absorbed depends on the molar heat capacity. For instance, in the case of a two-atomic ideal gas, the engine efficiency is smaller than in the case of a monatomic gas.

4.3 The cycle can be a combination of isothermal, isobaric, adiabatic and isochoric processes. Most common is the combination of isochoric or isobaric processes with adiabatic processes, for instance, an adiabatic–isochoric cycle (Otto cycle). An interesting combination is used in the jet engine, in which air flows through a combustion chamber, and the cycle is not closed. It has two adiabatic stages and the stage of combustion, which occurs at constant pressure.

4.4 The Carnot cycle is shown in Fig. S4.2. The changes in the entropy in the isothermal processes at the temperatures T_1 and T_2 amount to $\Delta S = S_2 - S_1$ and $-\Delta S = S_1 - S_2$, respectively. The heat absorbed by the system at $T = T_1$ is equal to $Q_1 = T_1(S_2 - S_1)$, and the heat given off to the thermostat at $T = T_2$ is equal to $Q_2 = T_2(S_1 - S_2)$. Since $\Delta U = 0$ in a cyclic process, we have

$$\Delta U = Q_1 + Q_2 - W^* = 0,$$

where $W^* = -W$ is the work done by the system, hence

$$W^* = T_1(S_2 - S_1) + T_2(S_1 - S_2) = (T_1 - T_2)(S_2 - S_1), \qquad \text{(S4.1)}$$

which is the area of the rectangle shown in Fig. S4.2.

4.5 The change in the entropy of the ideal gas in the isothermal process amounts to

$$\Delta S_{\text{sys}} = nR \ln \frac{V_f}{V_i} = nR \ln \frac{p_i}{p_f},$$

hence, for $n = 5$ mol, $p_i = 2$ atm, $p_f = 1$ atm, we get $\Delta S_{\text{sys}} = (5 \, \text{mol}) R \ln 2$. Since the process is reversible, we have

$$\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0, \qquad \text{(S4.2)}$$

hence $\Delta S_{\text{sur}} = -\Delta S_{\text{sys}}$.

4.6 The external pressure $p_{ext} = 1$ atm is constant, and the final pressure of the ideal gas $p_f = p_{ext}$, hence

$$W = -p_{ext}(V_f - V_i) = -nRT\left(1 - \frac{p_f}{p_i}\right),$$

where $n = 5$ mol, $T = 298$ K and $p_i = 2$ atm. The internal energy of the ideal gas does not change ($\Delta U = 0$), because the temperature does not change, thus, the heat absorbed by the system $Q = -W$. The change in the entropy of the system is the same as in the previous exercise, i.e.,

$$\Delta S_{sys} = nR\ln\frac{V_f}{V_i} = nR\ln\frac{p_i}{p_f} = (5\text{ mol})R\ln 2,$$

because the initial and final states of the system are also the same. However, the change in the entropy of the surroundings, which supply the heat Q to the system at constant temperature T, is different. Since the surroundings are treated as a reservoir of heat and volume, it can be assumed that they are in thermodynamic equilibrium all the time, and the change in their entropy amounts to

$$\Delta S_{sur} = -\frac{Q}{T} = -nR\left(1 - \frac{p_f}{p_i}\right) = -\left(\frac{5}{2}\text{ mol}\right)R. \tag{S4.3}$$

The total change in the entropy of the system and surroundings amounts to

$$\Delta S = \Delta S_{sys} + \Delta S_{sur} = (5\text{ mol})R\left(\ln 2 - \frac{1}{2}\right) > 0.$$

Thus, the process is irreversible, since $\Delta S > 0$.

4.7 So far we have considered the Carnot engine working between two thermostats of infinite heat capacity. Here, we assume that the heat capacity of the system at higher temperature, i.e., the system we want to cool down, is finite. This means that the temperature of the system decreases with each cycle of the engine. The engine operates until the temperature of the system becomes equal to the temperature of the radiator. Then the engine efficiency η_e reaches zero. We assume that the work done in one cycle is small compared to the total work needed to lower the system temperature to the value T_2. This assumption allows us to treat the work done by the engine in one cycle, W^*, and the heat drawn from the system by the working substance in the engine, Q_1, as infinitesimal quantities. We denote by T the actual temperature of the system, thus, the engine efficiency at T amounts to $\eta_e(T) = 1 - T_2/T$. According to the definition of η_e, we have

$$đW^* = \eta_e(T)đQ_1 = -\eta_e(T)nc_v dT.$$

Integrating this equality from the initial temperature of the system, T_1, to the final temperature T_2, we obtain the total work required to cool down the system, i.e.

$$W^* = -nc_v\int_{T_1}^{T_2}\eta_e(T)dT = nc_v\int_{T_2}^{T_1}\left(1 - \frac{T_2}{T}\right)dT = nc_v\left(T_1 - T_2 + T_2\ln\frac{T_2}{T_1}\right).$$

The work W^* is positive, since we integrate a non-negative function $\eta_e(T)$.

4.8 Both systems and the working substance in the Carnot engine form an adiabatically isolated system which performs work on the surroundings. The system at higher temperature is treated as a heat container, and the system at lower temperature is treated as a radiator. Since the engine works reversibly, the total entropy of the composite system does not change. The change in the entropy of the heat container and radiator during one cycle is denoted by dS_1 and dS_2, respectively. The change in the entropy of the working substance in one cycle equals zero, hence, also $dS_1 + dS_2 = 0$. Denoting by T' and T'' the actual temperatures of the heat container and radiator, respectively, and using the relation between the heat capacity and entropy, we get the following equation:

$$dS_1 + dS_2 = C_V \frac{dT'}{T'} + C_V \frac{dT''}{T''} = 0.$$

It is easy to verify that the solution of the above equation can be presented as follows:

$$\ln \frac{T'}{T_1} + \ln \frac{T''}{T_2} = 0,$$

because the value $T' = T_1$ corresponds to $T'' = T_2$. At the final temperature T_f, we have $T' = T'' = T_f$, hence, $T_f = \sqrt{T_1 T_2}$ is the geometric mean of the initial temperatures of the heat container and radiator. In the case of direct thermal contact of the heat container and radiator, we have

$$C_V (T_1 - T_f) = C_V (T_f - T_2),$$

hence, the final temperature $T_f = (T_1 + T_2)/2$ is the arithmetic mean of the initial temperatures. For $T_1 \neq T_2$, the inequality $\sqrt{T_1 T_2} < (T_1 + T_2)/2$ holds, thus, the final temperature obtained by means of the Carnot engine is lower than in the case of direct thermal contact. It is so because a part of the internal energy is transferred to the surroundings in the form of work.

4.9 The change in the molar entropy follows from the relation $c_v = T(\partial s/\partial T)_v$, hence

$$\Delta s = \int_{T_i}^{T_f} \left(A + BT - CT^{-2} \right) \frac{dT}{T} = A \ln \frac{T_f}{T_i} + B(T_f - T_i) + \frac{C}{2} \left(\frac{1}{T_f^2} - \frac{1}{T_i^2} \right).$$

4.10 Since $đQ = V c_v dT$, from the relation $đQ = T dS$, we get

$$\Delta S = V \int_{T_i}^{T_f} c_v \frac{dT}{T} = V 4\gamma \int_{T_i}^{T_f} T^2 dT = \frac{4}{3} V\gamma \left(T_f^3 - T_i^3\right).$$

4.11 We supply the heat Q to the system, using either an electric heater or a heat pump. We assume that the whole work of the electric current in the heater, W_h, changes into heat, hence $Q = W_h$. In the case of a heat pump, the work of the electric current, W_p, is related to the heat supplied to the system, Q, by

$$Q = \eta_p W_p = \frac{T_1}{T_1 - T_2} W_p,$$

where η_p denotes the efficiency of the heat pump, $T_1 = 23\,°C$ is the temperature we want to maintain at home, and $T_2 = 0\,°C$ is the outdoor temperature. For the given temperatures, we have $\eta_p \approx 12.9$. This is a theoretical factor by which we can lower the electricity bill, using a heat pump instead of an electric heater. In practice, the profit is smaller and the installation of a heat pump is expensive.

4.12 The artesian well serves here as a radiator at the temperature $T_2 = 278.15\,K$, whereas air above the Australian desert serves as a heat container at the temperature $T_1 = 293.15\,K$. In these conditions, the efficiency of the Carnot engine $\eta_e \approx 0.05$. The heat Q_1 drawn by the working substance in the engine is obtained from the formula

$$Q_1 = \frac{W^*}{\eta_e}, \qquad (S4.4)$$

where W^* is the work done by the engine. The heat Q_2 which flows to the radiator (the well) follows from the relation

$$Q_1 + W + Q_2 = Q_1 - W^* - Q_2^* = 0, \qquad (S4.5)$$

hence

$$Q_2^* = \left(\frac{1}{\eta_e} - 1\right) W^* = \frac{T_2}{T_1 - T_2} W^*.$$

Substituting $W^* = 500\,kJ$, we get $Q_2^* \approx 9272\,kJ$.

4.13 We use the relations:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n} = 3B\frac{S^2}{nV},$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,n} = B\frac{S^3}{nV^2}.$$

Then, from the equation of state $U = BS^3/(nV)$, we determine the entropy as a function of U, V and n, i.e.,

$$S = \left(\frac{UVn}{B}\right)^{1/3}.$$

Substituting S into the expressions for T and p, we get:

$$T = 3\left(\frac{BU^2}{nV}\right)^{1/3},$$

$$p = \frac{U}{V}.$$

4.14 From the extensiveness of entropy, we have $S(U, V) = Vs(u)$, where $s = S/V$ and $u = U/V$. Using the relation

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \frac{ds}{du} = \frac{ds}{dT}\frac{dT}{du},$$

and the equation of state $u = \gamma T^4$, we get

$$\frac{\mathrm{d}s}{\mathrm{d}T} = \frac{1}{T}\frac{\mathrm{d}u}{\mathrm{d}T} = 4\gamma T^2,$$

hence

$$S = Vs = \frac{4}{3}\gamma V T^3.$$

Then, expressing T as a function of U and V, we get

$$S = \frac{4}{3}(\gamma V)^{1/4}U^{3/4}.$$

The pressure of the photon gas is determined from the relation

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_U = \frac{1}{3}\gamma^{1/4}\left(\frac{U}{V}\right)^{3/4} = \frac{1}{3}\gamma T^3,$$

hence, $p = \gamma T^4/3$. This is the second of the two equations of state for the photon gas.

4.15 We use the relation

$$\mathrm{d}s = \frac{1}{T}\mathrm{d}u + \frac{p}{T}\mathrm{d}v.$$

From the equation of state $u = 3RT/2 - a/v$, we obtain $\mathrm{d}u = (3R/2)\mathrm{d}T + (a/v^2)\mathrm{d}v$, which is then substituted into the expression for $\mathrm{d}s$. Using the second equation of state, we get eventually

$$\mathrm{d}s = \frac{3R}{2T}\mathrm{d}T + \frac{R}{v-b}\mathrm{d}v.$$

Integrating both sides of this equation, we obtain the molar entropy as a function of T and v:

$$s(T, v) = s_0 + \frac{3}{2}R\ln\left(\frac{T}{T_0}\right) + R\ln\left(\frac{v-b}{v_0-b}\right), \qquad \text{(S4.6)}$$

where the constants T_0, v_0 and $s_0 = s(T_0, v_0)$ define the reference state. To express the molar entropy as a function of u and v, we determine $T = 2(u + a/v)/(3R)$, hence

$$s(u, v) = s_0 + \frac{3}{2}R\ln\left(\frac{u+a/v}{u_0+a/v_0}\right) + R\ln\left(\frac{v-b}{v_0-b}\right),$$

where $u_0 = 3RT_0/2 - a/v_0$. It is easy to verify that differentiating $s(u, v)$ with respect to u and v, and using the relations $(\partial s/\partial u)_v = 1/T$ and $(\partial s/\partial v)_u = p/T$, we recover both equations of state.

4.16 First, we introduce the molar quantities: $s_A = S_A/n_A$, $u_A = U_A/n_A$ and $v_A = V_A/n_A$, and analogously for the system B. Then we have

$$s_A = \left(\frac{u_A v_A}{D}\right)^{1/3}, \qquad s_B = \left(\frac{u_B v_B}{D}\right)^{1/3},$$

hence

$$\left(\frac{\partial s_A}{\partial u_A}\right)_{v_A} = \frac{1}{3}\left(\frac{v_A}{Du_A^2}\right)^{1/3} = \frac{1}{T_A},$$

$$\left(\frac{\partial s_A}{\partial v_A}\right)_{u_A} = \frac{1}{3}\left(\frac{u_A}{Dv_A^2}\right)^{1/3} = \frac{p_A}{T_A},$$

and analogous expressions hold for the system B. From the equality of pressures and temperatures, the following equations result:

$$\frac{v_A}{u_A^2} = \frac{v_B}{u_B^2}, \qquad \frac{u_A}{v_A^2} = \frac{u_B}{v_B^2},$$

hence

$$\left(\frac{u_A}{u_B}\right)^2 = \frac{v_A}{v_B}, \qquad \left(\frac{v_A}{v_B}\right)^2 = \frac{u_A}{u_B}.$$

They are satisfied only if $u_A = u_B$ and $v_A = v_B$, hence, also $s_A = s_B$. Since we have $U = U_A + U_B = n_A u_A + n_B u_B = n u_A$ for the total internal energy, thus, $u = U/n = u_A = u_B$. In a similar way we show that $v = V/n = v_A = v_B$. The molar entropy of the fused system, $s = S/n$, must also satisfy the equilibrium conditions:

$$\left(\frac{\partial s}{\partial u}\right)_v = \frac{1}{T_A} = \frac{1}{T_B} = \frac{1}{3}\left(\frac{v}{Du^2}\right)^{1/3},$$

$$\left(\frac{\partial s}{\partial v}\right)_u = \frac{p_A}{T_A} = \frac{p_B}{T_B} = \frac{1}{3}\left(\frac{u}{Dv^2}\right)^{1/3},$$

where we have used the equalities $u_A = u_B = u$ and $v_A = v_B = v$. Therefore, we conclude that the function $s(u, v)$ has the same form as $s_A(u_A, v_A)$ and $s_B(u_B, v_B)$, i.e.,

$$s = \left(\frac{uv}{D}\right)^{1/3}.$$

Since $s = s_A = s_B$, we show eventually that

$$S = ns = (n_A + n_B)s = n_A s_A + n_B s_B = S_A + S_B.$$

4.17 Since no external lateral force acts on the vessel, the total momentum of the system is conserved and equal to zero. In Fig. S4.3, the gas occupies initially the left half of the vessel. When the internal wall is removed, the mass center of the gas shifts to the right. To maintain the zero value of the total momentum, the vessel shifts to the left, that is, in the opposite direction to the gas motion in the vessel. The gas motion causes the vessel to oscillate on the surface without friction. The oscillatory motion decays because according to the fundamental law of thermodynamics every isolated system reaches eventually an equilibrium state. In equilibrium, there is no macroscopic flow, therefore, the mass center of the gas must be at rest. Since the total momentum is conserved, the mass center of the vessel must also be at rest. Thus, the motion of the gas and vessel stops eventually.

Fig. S4.3 Broken line shows the mass center position of the vessel filled with a gas

initial state

vessel gas

final state
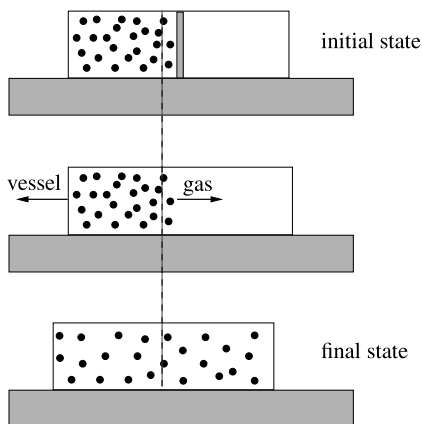
Exercises of Chapter 5

5.1 The derivative of the function $Y = Ax^2 + Bx + C$:

$$\frac{dY}{dx} = 2Ax + B,$$

is a monotonic function of the variable x, thus, the relation $dY/dx = z$ can be inverted, i.e.,

$$x = \frac{z - B}{2A}.$$

The Legendre transform of $Y(x)$ is the function

$$\Psi(z) = Y(x) - zx.$$

Substituting x expressed by z, we get

$$\Psi(z) = -\frac{z^2}{4A} + \frac{Bz}{2A} - \frac{B^2}{2A} + C,$$

hence, $d\Psi/dz = -(z - B)/(2A) = -x$. In the case of the function $Y = x + ae^x$, we have $z = dY/dx = 1 + ae^x$, hence

$$x = \ln\frac{z - 1}{a}$$

and

$$\Psi(z) = z - 1 - (z - 1)\ln\frac{z - 1}{a}, \qquad \frac{d\Psi}{dz} = -\ln\frac{z - 1}{a} = -x.$$

5.2 Since the process occurs at constant pressure, we have $H_i = U_i + pV_i$ at the beginning of the process and $H_f = U_f + pV_f$ at the end. Thus, the change in the enthalpy of the system is equal to

$$\Delta H = H_f - H_i = U_f - U_i + p(V_f - V_i) = \Delta U + p\Delta V.$$

5.3 We have $F_i = U_i - T S_i$ at the beginning of the process and $F_f = U_f - T S_f$ at the end, thus, the change in the Helmholtz free energy is equal to

$$\Delta F = F_f - F_i = U_f - U_i - T(S_f - S_i) = \Delta U - T\Delta S.$$

5.4 We use the definitions of thermodynamic potentials and their derivatives with respect to the natural variables. For instance, $F = U - TS$, $(\partial F/\partial T)_{V,n} = -S$, hence

$$\left(\frac{\partial F/T}{\partial T}\right)_{V,n} = \frac{1}{T}\left(\frac{\partial F}{\partial T}\right)_{V,n} - \frac{F}{T^2} = -\frac{1}{T^2}(F + TS) = -\frac{U}{T^2}.$$

In the case of the Gibbs free energy, we have $G = U - TS + pV = H - TS$, $(\partial G/\partial T)_{p,n} = -S$, hence

$$\left(\frac{\partial G/T}{\partial T}\right)_{p,n} = -\frac{S}{T} - \frac{G}{T^2} = -\frac{H}{T^2}.$$

The last relation is called the *Gibbs–Helmholtz relation*. In a similar way, we prove the remaining relations.

5.5 We make use of the Gibbs–Helmholtz relation derived in the previous exercise. Integrating both sides of the relation over T, from T_i to T_f, we get

$$\frac{G_f}{T_f} - \frac{G_i}{T_i} = -\int_{T_i}^{T_f} \frac{H}{T^2}\mathrm{d}T = -H\int_{T_i}^{T_f} \frac{1}{T^2}\mathrm{d}T = H\left(\frac{1}{T_f} - \frac{1}{T_i}\right),$$

hence

$$G_f = G_i\frac{T_f}{T_i} + H\left(1 - \frac{T_f}{T_i}\right).$$

5.6 Differentiating U with respect to S and V, we get

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n} = 3B\frac{S^2}{nV},$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,n} = B\frac{S^3}{nV^2}.$$

The Gibbs free energy is defined as $G = U - TS + pV$, and its natural variables are T, p and n. Therefore, we have to express S and V in terms of T, p and n, i.e.,

$$S = \frac{T^2 n}{9Bp},$$

$$V = \frac{T^3 n}{27Bp^2}.$$

We notice that $U = pV$, hence

$$G = U - TS + pV = 2pV - TS = \frac{2T^3 n}{27Bp} - \frac{T^3 n}{9Bp} = -\frac{T^3 n}{27Bp}.$$

Alternatively, we obtain the chemical potential from the relation $\mu = (\partial U/\partial n)_{S,V}$, and then express μ as a function of T and p, and make use of the relation $G = \mu n$.

5.7 The internal energy of the photon gas per unit volume is equal to $u = U/V = \gamma T^4$. From the definition of temperature, we have $T \, ds = du = 4\gamma T^3 dT$, where s is the entropy of the system per unit volume, hence

$$ds = 4\gamma T^2 dT,$$

which gives $S = (4/3) V \gamma T^3$. Then we determine the Helmholtz free energy

$$F(T, V) = U - TS = -\frac{1}{3}\gamma V T^4,$$

and the pressure as a function of T, i.e.,

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{3}\gamma T^4.$$

Now we can calculate the Gibbs free energy

$$G = U - TS + pV = \gamma V T^4 - \frac{4}{3}\gamma V T^4 + \frac{1}{3}\gamma V T^4 = 0.$$

The Gibbs free energy is equal to zero because the number of photons is not a thermodynamic parameter. Finally, we calculate the enthalpy

$$H = U + pV = \frac{4}{3}\gamma V T^4 = TS.$$

The natural variables of the enthalpy are S and p, therefore, we have to express T as a function of pressure, i.e.,

$$T = \left(\frac{3p}{\gamma}\right)^{1/4},$$

hence

$$H = S\left(\frac{3p}{\gamma}\right)^{1/4}.$$

5.8 We use the relation

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,n} = -\left(\frac{\partial \phi}{\partial v}\right)_T,$$

where $\phi = F/n$ denotes the molar Helmholtz free energy. Since

$$p = \frac{RT}{v - b} - \frac{a}{v^2},$$

we obtain

$$\phi(T, v) = \phi_0(T) + \int_{v_0}^{v} p(T, v')dv' = \phi_0(T) + RT \ln \frac{v - b}{v_0 - b} + a\left(\frac{1}{v} - \frac{1}{v_0}\right),$$

where v_0 is the molar volume of the reference state, and $\phi_0(T) = \phi(T, v_0)$. The Helmholtz free energy $F(T, V, n) = n\phi(T, v)$. To determine the function $\phi_0(T)$, we have to know the dependence of the molar internal energy on T and v.

5.9 We use the relation (see (5.132))

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = -p + T\left(\frac{\partial p}{\partial T}\right)_{V,n},$$

into which we substitute the van der Waals equation of state

$$p = \frac{nRT}{V - nb} - \frac{an^2}{v^2},$$

which gives

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = \frac{an^2}{V^2}.$$

Integrating the last relation over V and making use of extensiveness of the internal energy, we get

$$U(T, V, n) = nf(T) + \int \frac{an^2}{V^2} dV = nf(T) - \frac{an^2}{V},$$

where $f(T)$ is a function of temperature to be determined. Since

$$\left(\frac{\partial U}{\partial T}\right)_{n,V} = nc_v,$$

we obtain $f(T) = 3RT/2$, hence, the internal energy is given by the formula

$$U(T, V, n) = \frac{3}{2}nRT - \frac{an^2}{V}.$$

5.10 For a system heated at constant pressure, we have

$$\Delta H = \int_{T_i}^{T_f} c_p dT = a(T_f - T_i) + \frac{b}{2}(T_f^2 - T_i^2)$$

and

$$\Delta S = \int_{T_i}^{T_f} \frac{c_p}{T} dT = a \ln \frac{T_f}{T_i} + b(T_f - T_i).$$

5.11 We have

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,n},$$

hence

$$\left(\frac{\partial C_p}{\partial p}\right)_{T,n} = T\left(\frac{\partial^2 S}{\partial T \partial p}\right)_n = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{p,n},$$

where we have used the Maxwell relation

$$\left(\frac{\partial S}{\partial p}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{p,n}.$$

5.12 We write the differential of $V(T, p)$ at constant mole number:

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp = V\alpha dT - V\kappa_T dp.$$

Since κ_T and α are assumed constant, we can easily integrate dV. Dividing both sides by V and then integrating, we get

$$\ln\frac{V}{V_0} = \alpha(T - T_0) - \kappa_T(p - p_0),$$

hence

$$V = V_0 e^{[\alpha(T-T_0)-\kappa_T(p-p_0)]},$$

where V_0, T_0 and p_0 define the reference state.

5.13 We use the differential of the potential Ψ, i.e.,

$$d\Psi = TdS - pdV - nd\mu.$$

From the equality of mixed second order partial derivatives, we derive the following Maxwell relations:

$$\left(\frac{\partial T}{\partial V}\right)_{S,\mu} = -\left(\frac{\partial p}{\partial S}\right)_{V,\mu},$$

$$\left(\frac{\partial T}{\partial \mu}\right)_{S,V} = -\left(\frac{\partial n}{\partial S}\right)_{V,\mu},$$

$$\left(\frac{\partial p}{\partial \mu}\right)_{S,V} = \left(\frac{\partial n}{\partial V}\right)_{S,\mu}.$$

In the case of the potential Θ, we have

$$d\Theta = TdS + Vdp - nd\mu,$$

hence, the Maxwell relations follow:

$$\left(\frac{\partial T}{\partial p}\right)_{S,\mu} = \left(\frac{\partial V}{\partial S}\right)_{p,\mu},$$

$$\left(\frac{\partial T}{\partial \mu}\right)_{S,p} = -\left(\frac{\partial n}{\partial S}\right)_{p,\mu},$$

$$\left(\frac{\partial V}{\partial \mu}\right)_{S,p} = -\left(\frac{\partial n}{\partial p}\right)_{S,\mu}.$$

5.14 The potential $\Psi(S, V, \mu)$ is an extensive quantity, thus, $\psi = \Psi/V = \Psi(s, 1, \mu)$, where $s = S/V$. The natural variables are the entropy per unit volume and chemical potential. At constant volume, we have

$$d\Psi = TdS - nd\mu.$$

Dividing both sides by V, we get

$$d\psi = T ds - \rho d\mu,$$

where $\rho = n/V = 1/v$.

5.15 It follows from the Euler relation $U = TS - pV + \mu n$ that

$$\Theta = U + pV - \mu n = TS,$$

hence, $T = \Theta/S$. At constant entropy, we have

$$d\Theta = V dp - n d\mu,$$

hence, dividing both sides by S, we get

$$dT = \frac{V}{S} dp - \frac{n}{S} d\mu.$$

We notice that it is simply a different form of the Gibbs–Duhem equation: $d\mu = -s dT + v dp$, with $s = S/n$ and $v = V/n$.

5.16 We have

$$\left(\frac{\partial v}{\partial \mu}\right)_T = \left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial \mu}\right)_T = \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = -\kappa_T,$$

where we have used the Gibbs–Duhem equation. The second derivative is calculated in a similar way, i.e.,

$$\left(\frac{\partial s}{\partial \mu}\right)_T = \left(\frac{\partial s}{\partial p}\right)_T \left(\frac{\partial p}{\partial \mu}\right)_T = \frac{1}{v}\left(\frac{\partial s}{\partial p}\right)_T.$$

It follows from the Gibbs–Duhem equation that

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p,$$

hence

$$\left(\frac{\partial s}{\partial \mu}\right)_T = -\alpha.$$

5.17 The inversion temperature in the Joule–Thomson process satisfies the condition $T\alpha = 1$, therefore, we have to calculate the thermal expansion coefficient:

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p,$$

for

$$pv = RT\big[1 + b(T)p\big].$$

Since we differentiate at constant pressure, we get

$$T\alpha = \frac{RT}{pv}\left(\frac{\partial pv/R}{\partial T}\right)_p = \frac{1}{1 + bp}\left(\frac{\partial T(1 + bp)}{\partial T}\right)_p = 1 + \frac{Tb'(T)p}{1 + b(T)p},$$

where $b'(T) = db/dT$. Thus, the inversion temperature satisfies the equation

$$b'(T) = 0.$$

Exercises of Chapter 6

6.1 Since T and p are treated as independent variables, we have $\mu = \mu(T, v)$ and $p = p(T, v)$. Chemical potentials and pressures of coexisting phases are equal, i.e.,

$$\mu^\alpha(T, v^\alpha) = \mu^\beta(T, v^\beta) = \dots,$$
$$p^\alpha(T, v^\alpha) = p^\beta(T, v^\beta) = \dots,$$

where $\alpha, \beta, \dots$ correspond to different phases. Thus, we have $2(P-1)$ equations and $P+1$ variables, since the molar volume is different for different phases, in general. Subtracting the number of equations from the number of variables, we get

$$f = P + 1 - 2(P - 1) = 3 - P.$$

Since $f \geq 0$, the number of coexisting phases P cannot exceed three. For instance, when two phases coexist, we can change their temperature, and the molar volumes v^α and v^β are functions of T.

6.2 It follows from the Gibbs-Duhem equation that pressure can be treated as a function of T and μ. Therefore, for the phases α and β, we have $p^\alpha(T, \mu)$ and $p^\beta(T, \mu)$, respectively. The pressures are equal on the coexistence line, hence

$$p^\alpha(T, \mu_{\text{coex}}(T)) = p^\beta(T, \mu_{\text{coex}}(T)).$$

Differentiating both sides of this equality with respect to T, we get

$$\left(\frac{\partial p^\alpha}{\partial T}\right)_{\mu_{\text{coex}}} + \left(\frac{\partial p^\alpha}{\partial \mu_{\text{coex}}}\right)_T \frac{d\mu_{\text{coex}}}{dT} = \left(\frac{\partial p^\beta}{\partial T}\right)_{\mu_{\text{coex}}} + \left(\frac{\partial p^\beta}{\partial \mu_{\text{coex}}}\right)_T \frac{d\mu_{\text{coex}}}{dT}.$$

From the Gibbs-Duhem equation: $d\mu = -s\,dT + v\,dp$, the relations $(\partial p/\partial T)_\mu = s\rho$ and $(\partial p/\partial \mu)_T = \rho$ follow, where $\rho = n/V = 1/v$, hence

$$\frac{d\mu_{\text{coex}}}{dT} = -\frac{s^\alpha \rho^\alpha - s^\beta \rho^\beta}{\rho^\alpha - \rho^\beta} = -\frac{\Delta(s\rho)}{\Delta\rho}.$$

6.3 Chemical potentials of two coexisting phases are equal. We know the chemical potential of the monatomic ideal gas (see (5.52)):

$$\mu^g(T, p) = \mu_0 \frac{T}{T_0} - \frac{5}{2} RT \ln \frac{T}{T_0} + RT \ln \frac{p}{p_0},$$

thus, $\mu_{\text{coex}}(T) = \mu^g(T, p_{\text{coex}}(T))$, where $p_{\text{coex}}(T)$ denotes the pressure on the liquid–vapour coexistence line. Since the molar volume of the vapour is much bigger than the molar volume of the liquid, we have $\Delta v \approx v^g$, where $v^g = RT/p$ for the ideal gas. Then, the pressure $p_{\text{coex}}(T)$ satisfies the Clausius-Clapeyron equation (6.41), which can be integrated if the enthalpy of transition does not depend on temperature, and we obtain see (6.42)):

$$p_{\text{coex}}(T) = p_{\text{coex}}(T_0) \exp\left[\frac{\Delta h}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right].$$

Substituting $p_{\text{coex}}(T)$ into the expression for the chemical potential μ^g, we obtain

$$\mu_{\text{coex}}(T) = \mu_0 \frac{T}{T_0} - \frac{5}{2} RT \ln \frac{T}{T_0} + \Delta h \left(\frac{T}{T_0} - 1 \right).$$

6.4 Before we start to supply heat to the system only the phase α is present, therefore, we determine the mole number of the phase β from the ratio

$$n^\beta = Q/\Delta h.$$

Hence, the ratio of the mole numbers of the two phases amounts to

$$\frac{n^\beta}{n^\alpha} = \frac{n^\beta}{n - n^\beta} = \frac{Q}{n\Delta h - Q},$$

which can also be written in the form of a lever rule:

$$n^\beta (n\Delta h - Q) = n^\alpha Q.$$

It follows from this expression that if $Q = n\Delta h$ then $n^\alpha = 0$, which means that the phase α has changed completely into the phase β.

6.5 The average molar volume is defined as

$$v = x^\alpha v^\alpha + x^\beta v^\beta,$$

where $x^\alpha = n^\alpha/n$, $x^\beta = n^\beta/n$, $n^\alpha + n^\beta = n$, hence

$$v = x^\alpha v^\alpha + (1 - x^\alpha) v^\beta = v^\beta - x^\alpha \Delta v,$$

where $\Delta v = v^\beta - v^\alpha$. The molar fraction of the phase α at the end of the process, $x_f^\alpha = n_f^\alpha/n$, is given, whereas to calculate the average molar volume v_i at the beginning of the process, we have to find x_i^α first. It follows from the context that the amount of the phase α at the beginning of the process, n_i^α, was grater than the amount of α at the end, n_f^α, thus

$$Q = \left(n_i^\alpha - n_f^\alpha \right) \Delta h,$$

hence

$$Q/n = q = \left(x_i^\alpha - x_f^\alpha \right) \Delta h.$$

Substituting x_i^α from this equation into the expression for v, we get eventually

$$v_i = v^\beta - \left(x_f^\alpha + q/\Delta h \right) \Delta v = v_f - q\Delta v/\Delta h,$$

where $v_f = v^\beta - x_f^\alpha \Delta v$.

6.6 We use the equation (see (6.39))

$$p_{\text{coex}}(T) = p_{\text{coex}}(T_0) + \frac{\Delta h}{\Delta v} \ln \frac{T}{T_0}.$$

Substituting the numbers, we get

$$\Delta h/\Delta v = -3.54 \times 10^9 \, \text{N} \, \text{m}^{-2} = -3.54 \times 10^4 \, \text{bar}$$

and $T/T_0 = 263.15/273.15$, hence $\ln(T/T_0) = -0.0373$. Finally, we get

$$p_{\text{coex}}(T) = p_{\text{coex}}(T_0) + 1320 \, \text{bar}.$$

Thus, to lower the melting point of ice by 10 °C, we have to apply a pressure approximately 1300 times bigger than atmospheric pressure.

6.7 Since we want to determine Δh, we only need to transform the expression used in Exercise 6.6, i.e.,

$$\Delta h = \frac{[p_{\text{coex}}(T) - p_{\text{coex}}(T_0)]\Delta v}{\ln(T/T_0)}.$$

We have $\Delta v = v^l - v^s = 3 \, \text{cm}^3 \, \text{mol}^{-1}$, $T_0 = 350 \, \text{K}$, $T = 351 \, \text{K}$, $p_{\text{coex}}(T_0) = 1 \, \text{bar}$, $p_{\text{coex}}(T) = 100 \, \text{bar}$, $\ln(T/T_0) = 2.85 \times 10^{-3}$, hence, $\Delta h = 1.04 \, \text{kJ} \, \text{mol}^{-1}$.

6.8 Since a liquid–gas transition is concerned, we use the equation (see (6.42))

$$p_{\text{coex}}(T) = p_{\text{coex}}(T_0) \exp\left[\frac{\Delta h}{RT_0}\left(1 - \frac{T_0}{T}\right)\right],$$

which we transform to the following form:

$$\frac{1}{T_0} - \frac{1}{T} = \frac{R}{\Delta h}\ln\left[\frac{p_{\text{coex}}(T)}{p_{\text{coex}}(T_0)}\right] = \frac{8.314 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1}}{14.4 \, \text{kJ} \, \text{mol}^{-1}}\ln 2 = 4 \times 10^{-4} \, \text{K}^{-1},$$

hence $T = 194 \, \text{K}$.

6.9 We have two coexistence lines: the liquid–vapour line and solid–vapour line. The coordinates of the triple point, (T_3, p_3), are obtained from the intersection of these lines, i.e.,

$$15.16 - 3063 \, \text{K}/T_3 = 18.70 - 3754 \, \text{K}/T_3,$$

hence, $T_3 = 195.2 \, \text{K}$, $p_3 = 0.588 \, \text{atm}$. To find the enthalpy of evaporation and sublimation, we notice that the coefficient at $-1/T$ in the function $\ln[p_{\text{coex}}(T)/p_{\text{coex}}(T_0)]$ is equal to $\Delta h/R$ (see Exercise 6.8), hence

$$\Delta h_{\text{vap}} = 3063 \, \text{K} \times 8.314 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1} = 25.466 \, \text{kJ} \, \text{mol}^{-1},$$

$$\Delta h_{\text{sub}} = 3754 \, \text{K} \times 8.314 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1} = 31.211 \, \text{kJ} \, \text{mol}^{-1}.$$

Since enthalpy is a state function, we can obtain the solid–liquid transition as a combination of the solid–vapour and vapour–liquid transitions, hence

$$\Delta h_{\text{mel}} = \Delta h_{\text{sub}} - \Delta h_{\text{vap}} = 5.745 \, \text{kJ} \, \text{mol}^{-1}.$$

6.10 First, we calculate the pressure on the sublimation line corresponding to the temperature of $-5 \, °C$ ($T \approx 268 \, \text{K}$), using the expression (see Exercise 6.8)

$$\ln\left[\frac{p_{\text{coex}}(T)}{p_{\text{coex}}(T_3)}\right] = \frac{\Delta h_{\text{sub}}}{R}\left(\frac{1}{T_3} - \frac{1}{T}\right),$$

where for the triple point temperature we assume 273 K. Substituting $p_{\text{coex}}(273) = p_3 = 0.006 \, \text{bar}$, we get

$$p_{\text{coex}}(268) = p_{\text{coex}}(273) \exp(-0.419) = 0.004 \, \text{bar}.$$

The pressure of water vapour equal to $2\,\mathrm{Tr} = 0.0027$ bar is well below the pressure of sublimation at the temperature of $-5\,°\mathrm{C}$. Frost can remain only if the vapour pressure is close to the pressure of sublimation at a given temperature. Thus, the frost will disappear from the car glass.

6.11 First, we derive the barometric formula, i.e., the relation between the gas pressure and the altitude. The gravity of a gas column, of the height $\mathrm{d}z$ and the mass density ρ_m, is balanced by the pressure difference $\mathrm{d}p = -\rho_m(p)g\mathrm{d}z$, where g is the earth gravity. Using the relation $\rho_m = M\rho$, where ρ is the molar density and M denotes the molar mass, and assuming the ideal gas equation of state, $p = RT\rho$, we get

$$\mathrm{d}p = -Mg\rho\mathrm{d}z = -Mg\frac{p}{RT}\mathrm{d}z.$$

Integrating this equation, we obtain the barometric formula:

$$p(z) = p_0 \exp\left[-\frac{Mg(z - z_0)}{RT}\right].$$

Deriving this formula, we make an assumption that the temperature T does not change with the altitude. Although it is not true, in general, such an approximation is sufficient for the present purpose.

Boiling consists in formation of vapour bubbles in the whole volume of a liquid. It occurs when the vapour pressure at the liquid–vapour coexistence equals atmospheric pressure. The boiling temperatures T_0 and $T_{\mathcal{H}}$ result from the equations $p_{\mathrm{coex}}(T_0) = p_0$ and $p_{\mathrm{coex}}(T_{\mathcal{H}}) = p_{\mathcal{H}}$, where p_0 and $p_{\mathcal{H}}$ denote the pressures at the foot of the mountain and at the altitude $\mathcal{H}$, respectively. Thus, we have

$$\ln\frac{p_{\mathrm{coex}}(T_{\mathcal{H}})}{p_{\mathrm{coex}}(T_0)} = \ln\frac{p_{\mathcal{H}}}{p_0} = -\frac{Mg\Delta\mathcal{H}}{RT},$$

where $\Delta\mathcal{H}$ is the height of the mountain. Using expression (6.42), we obtain the equation

$$\frac{\Delta h}{R}\left(\frac{1}{T_0} - \frac{1}{T_{\mathcal{H}}}\right) = -\frac{Mg}{RT}\Delta\mathcal{H},$$

from which we determine $\Delta\mathcal{H}$:

$$\Delta\mathcal{H} = \frac{\Delta h}{Mg}\left(\frac{T}{T_{\mathcal{H}}} - \frac{T}{T_0}\right).$$

Substituting $T = 293\,\mathrm{K}$ ($20\,°\mathrm{C}$) and $M = 28\,\mathrm{g\,mol^{-1}}$ (for N_2 molecule), we get

$$\Delta\mathcal{H} = \frac{45\,\mathrm{kJ\,mol^{-1}}}{28\,\mathrm{g\,mol^{-1}} \times 9.81\,\mathrm{m\,s^{-2}}}\left(\frac{293}{368} - \frac{293}{378}\right) = 3.45\,\mathrm{km}.$$

In principle, we should take into account that air is a mixture of gases, mainly nitrogen (78 %) and oxygen (21 %), and apply the barometric formula to each gas separately and then add the partial pressures of the gases. Since nitrogen predominates, and the molecular mass of O_2 (32) does not differ much from the molecular mass of N_2 (28), we do not make a big error, approximating air by nitrogen alone.

6.12 We calculate the derivative with respect to temperature of the function

$$\Delta s(T) = s^\beta\left(T, p_{\text{coex}}(T)\right) - s^\gamma\left(T, p_{\text{coex}}(T)\right),$$

where $p_{\text{coex}}(T)$ is the pressure of coexisting phases at the temperature T. We have

$$\frac{ds^\beta}{dT} = \left(\frac{\partial s^\beta}{\partial T}\right)_{p_{\text{coex}}} + \left(\frac{\partial s^\beta}{\partial p_{\text{coex}}}\right)_T \frac{dp_{\text{coex}}}{dT} = \frac{c_p^\beta}{T} - v^\beta \alpha^\beta \frac{dp_{\text{coex}}}{dT},$$

where c_p^β and α^β denote the molar heat capacity at constant pressure and thermal expansion coefficient of the phase β, respectively. Deriving the above relation, we have used the Maxwell relation $(\partial s/\partial p)_T = -(\partial v/\partial T)_p$. An analogous expression holds for the phase γ. Since $dp_{\text{coex}}/dT = \Delta s/\Delta v$, we get

$$\frac{d\Delta s}{dT} = \frac{\Delta c_p}{T} - \Delta(v\alpha)\frac{\Delta s}{\Delta v},$$

where $\Delta c_p = c_p^\beta - c_p^\gamma$, $\Delta v = v^\beta - v^\gamma$, $\Delta(v\alpha) = v^\beta \alpha^\beta - v^\gamma \alpha^\gamma$.

6.13 The enthalpy $H = U + pV = TS + \mu n$, hence, the molar enthalpy $h = Ts + \mu$. At the coexistence of phases β and γ, we have $\Delta h = T\Delta s$, since $\mu^\beta = \mu^\gamma$. Substituting $\Delta s = \Delta h/T$ in Exercise 6.12 and neglecting thermal expansion, we get

$$\frac{d(\Delta h/T)}{dT} = \frac{\Delta c_p}{T}.$$

Then, we integrate the above equality from T_0 to T, hence

$$\frac{\Delta h(T)}{T} - \frac{\Delta h(T_0)}{T_0} = \int_{T_0}^T \frac{\Delta c_p(T')}{T'}dT' = \Delta a(T - T_0) + (\Delta b - T_0\Delta a)\ln\frac{T}{T_0},$$

where $\Delta a = a^\beta - a^\gamma$ and $\Delta b = b^\beta - b^\gamma$. Using this formula, we can calculate the enthalpy of transition at the temperature T if we know Δh at the reference temperature T_0.

6.14 The infinitesimal heat absorbed by the system in a reversible process equals $đQ = TdS$. Since the process occurs at constant V and n, and the parameter that we control is temperature, the appropriate thermodynamic potential is the Helmholtz free energy $F(T, V, n)$. From the Euler relation, we get $F = U - TS = -pV + \mu n$. The system considered is a two-phase system, the pressure $p = p_{\text{coex}}$ and the chemical potential $\mu = \mu_{\text{coex}}$ are functions of temperature, thus (see (6.14))

$$F = U - TS = -p_{\text{coex}}(T)V + \mu_{\text{coex}}(T)n.$$

To calculate the heat Q absorbed by the system heated from the temperature T_0 to T_1, we notice that the change in the internal energy $\Delta U = Q$, since the volume is constant, thus, the work $W = 0$. Using the relation (see Exercise 5.4)

$$\left(\frac{\partial F/T}{\partial T}\right)_{V,n} = -\frac{U}{T^2},$$

we get

$$Q = \Delta U = -\Delta\left[T^2\left(\frac{\partial F/T}{\partial T}\right)_{V,n}\right] = -n\Delta\left[T^2\left(\frac{\partial \phi_{\text{coex}}/T}{\partial T}\right)_v\right],$$

where $\phi_{\text{coex}}(T, v) = -p_{\text{coex}}(T)v + \mu_{\text{coex}}(T)$ denotes the molar Helmholtz free energy of the system at the temperature T and at the average molar volume $v = V/n$. We can proceed with the calculation if we know the explicit form of the functions $p_{\text{coex}}(T)$ and $\mu_{\text{coex}}(T)$. For instance, for the liquid–vapour coexistence, and with the additional assumptions specified in this exercise, we have

$$p_{\text{coex}}(T) = p_{\text{coex}}(T_0)\exp\left[\frac{\Delta h}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right],$$

$$\mu_{\text{coex}}(T) = \mu_0\frac{T}{T_0} - \frac{5}{2}RT\ln\frac{T}{T_0} + \Delta h\left(\frac{T}{T_0} - 1\right).$$

6.15 We have (see (6.58))

$$T_{\text{cr}} = \frac{8a}{27Rb} = \frac{8 \times 0.15}{27 \times 8.314 \times 4 \times 10^{-5}}\,\text{K} = 133.6\,\text{K},$$

$$p_{\text{cr}} = \frac{a}{27b^2} = \frac{0.15}{27 \times 16 \times 10^{-10}}\,\text{Pa} = 34.7\,\text{bar},$$

$$v_{\text{cr}} = 3b = 3 \times 4 \times 10^{-5}\,\text{m}^3\,\text{mol}^{-1} = 0.12\,\text{L}\,\text{mol}^{-1}.$$

6.16 We use the relations:

$$v_{\text{cr}} = 3b, \qquad p_{\text{cr}} = \frac{a}{27b^2}, \qquad T_{\text{cr}} = \frac{8a}{27Rb}.$$

Since

$$u = \frac{f}{2}RT - \frac{a}{v},$$

at the critical point, we have

$$u_{\text{cr}} = \frac{f}{2}RT_{\text{cr}} - \frac{a}{v_{\text{cr}}} = \frac{a}{27b}(4f - 9).$$

Dividing u by u_{cr}, we get

$$\bar{u} = \frac{4f}{4f - 9}\bar{T} - \frac{9}{4f - 9}\frac{1}{\bar{v}}.$$

For $f = 3, 5$ and 6, we obtain, respectively:

$$\bar{u} = 4\bar{T} - \frac{3}{\bar{v}},$$

$$\bar{u} = \frac{20}{11}\bar{T} - \frac{9}{11\bar{v}},$$

$$\bar{u} = \frac{8}{5}\bar{T} - \frac{3}{5\bar{v}}.$$

6.17 We use expression (6.51):

$$\phi(T, v) = \left(\frac{1}{2}fR - s_0\right)T - \frac{a}{v} - \frac{1}{2}fRT\ln\frac{T}{T_0} - RT\ln\frac{v-b}{v_0-b},$$

where $\phi = F/n$ is the molar Helmholtz free energy. From the Euler relation, we get $F = U - TS = -pV + \mu n$, hence, $\mu = \phi + pv$. Assuming that $T > T_{cr}$, we can determine $v = v(T, p)$ from the van der Waals equation of state:

$$p = \frac{RT}{v-b} - \frac{a}{v^2},$$

hence

$$\mu(T, p) = pv(T, p) + \left(\frac{1}{2}fR - s_0\right)T - \frac{a}{v(T, p)} - \frac{1}{2}fRT\ln\frac{T}{T_0}$$

$$- RT\ln\frac{v(T, p) - b}{v_0 - b}.$$

As the limit $p \to 0$ corresponds to $v \to \infty$, we have

$$p = \frac{RT}{v}\left(\frac{1}{1 - b/v} - \frac{a}{RTv}\right) \approx \frac{RT}{v},$$

i.e., the ideal gas equation of state, hence

$$\mu(T, p) - RT\ln\frac{p}{p_0} \to \left[\frac{1}{2}(f+2)R - s_0\right]T - \frac{1}{2}fRT\ln\frac{T}{T_0} - RT\ln\frac{RT}{(v_0 - b)p_0}.$$

Taking $(v_0 - b)p_0 = RT_0$, we get eventually

$$\mu_0(T) = \left[\frac{1}{2}(f+2)R - s_0\right]T - \frac{1}{2}(f+2)RT\ln\frac{T}{T_0}.$$

Comparing $\mu_0(T)$ with the chemical potential of the ideal gas, μ^{id} (see (4.70)), we note that $\mu_0(T) = \mu^{id}(T, p_0)$. The chemical potential of the van der Waals gas can be presented as follows:

$$\mu(T, p) = \mu_0(T) + pv - RT - \frac{a}{v} + RT\ln\frac{RT}{p_0(v-b)},$$

where $v = v(T, p)$ is obtained from the van der Waals equation of state. Using the relation

$$pv - RT = \frac{RTb}{v-b} - \frac{a}{v},$$

we can eliminate p and express the chemical potential as a function of T and v:

$$\mu(T, v) = \mu_0(T) + \frac{RTb}{v-b} - \frac{2a}{v} + RT\ln\frac{RT}{p_0(v-b)}.$$

Exercises of Chapter 7

7.1 The volume of the solution amounts to

$$V = n_A v_A + n_B v_B = n(x_A v_A + x_B v_B).$$

As v_A, v_B and x_B are given, it remains to determine $n = n_A + n_B$. The mass of the solution is given by the relation

$$m = n_A M_A + n_B M_B = n(x_A M_A + x_B M_B)$$
$$= n(0.55 \times 58 + 0.45 \times 118)\,\mathrm{g\,mol^{-1}} = n \times 85\,\mathrm{g\,mol^{-1}},$$

and for $m = 0.85\,\mathrm{kg}$, we get $n = 10\,\mathrm{mol}$. For the volume V, we obtain

$$V = 10(0.55 \times 74 + 0.45 \times 80)\,\mathrm{cm^3} = 767\,\mathrm{cm^3}.$$

7.2 According to the general definition of a partial molar quantity, we have

$$h_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_{j\neq i}}.$$

The differential of enthalpy

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \sum_{i=1}^{C} \mu_i \mathrm{d}n_i,$$

hence

$$\left(\frac{\partial h_i}{\partial p}\right)_{T,x} = \left(\frac{\partial^2 H}{\partial n_i \partial p}\right)_{T,n_{j\neq i}}.$$

We use the relation

$$\left(\frac{\partial H}{\partial p}\right)_{T,n_j} = V + T\left(\frac{\partial S}{\partial p}\right)_{T,n_j},$$

and from the differential of the Gibbs free energy

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \sum_{i=1}^{C} \mu_i \mathrm{d}n_i,$$

we obtain the Maxwell relation

$$\left(\frac{\partial S}{\partial p}\right)_{T,n_j} = -\left(\frac{\partial V}{\partial T}\right)_{p,n_j},$$

thus,

$$\left(\frac{\partial H}{\partial p}\right)_{T,n_j} = V - T\left(\frac{\partial V}{\partial T}\right)_{p,n_j} = -T^2\left(\frac{\partial V/T}{\partial T}\right)_{p,n_j}.$$

Differentiating both sides of the above equality with respect to n_i at constant T, p and $n_{j\neq i}$, we get the relation

$$\left(\frac{\partial h_i}{\partial p}\right)_{T,x} = -T^2\left(\frac{\partial^2 V/T}{\partial T \partial n_i}\right)_{p,n_{j\neq i}} = -T^2\left(\frac{\partial v_i/T}{\partial T}\right)_{p,x}.$$

7.3 The Gibbs–Duhem equation at constant T and p has the following form:

$$\sum_{i=1}^{C} x_i d\mu_i = 0.$$

From the form of the chemical potential: $\mu_i = \mu_i^*(T, p) + RT \ln x_i$, it follows that at constant T and p, we have $d\mu_i = RT dx_i/x_i$, hence

$$\sum_{i=1}^{C} x_i d\mu_i = RT \sum_{i=1}^{C} dx_i = RT d\sum_{i=1}^{C} x_i = 0,$$

as the molar fractions sum up to unity. This shows that the Gibbs–Duhem equation is satisfied.

7.4 From the form of the chemical potentials, it follows that at $T = const$ and $p = const$, we have

$$x_A d\mu_A + x_B d\mu_B = RT dx_A + x_A W'(x_B)dx_B + RT dx_B + x_B W'(x_A)dx_A,$$

where $W'(x)$ denotes the derivative. Taking into account the relations $x_A + x_B = 1$ and $dx_B = -dx_A$, we get

$$x_A d\mu_A + x_B d\mu_B = \left[(1 - x_A)W'(x_A) - x_A W'(1 - x_A)\right]dx_A.$$

Since $W(x) = \sum_{n=1}^{N} W_n x^n$, the right-hand side of the above equation vanishes if

$$\sum_{n=1}^{N} n W_n\left[(1 - x_A)x_A^{n-1} - x_A(1 - x_A)^{n-1}\right] = 0.$$

It is easy to show that the expression in the brackets vanishes only if $n = 2$, thus, the polynomial must be of the form $W(x) = W_2 x^2$, where W_2 depends on T and p, in general.

7.5 According to the definition of the Gibbs free energy of mixing, we have

$$\frac{\Delta_M G}{n} = x_A\left(\mu_A - \mu_A^*\right) + x_B\left(\mu_B - \mu_B^*\right)$$

$$= RT(x_A \ln x_A + x_B \ln x_B) + x_A W(x_B) + x_B W(x_A).$$

As $W(x) = W_2 x^2$, and $x_A x_B^2 + x_B x_A^2 = x_A x_B(x_A + x_B) = x_A x_B$, we get

$$\frac{\Delta_M G}{n} = RT(x_A \ln x_A + x_B \ln x_B) + W_2 x_A x_B.$$

7.6 At constant T and p, the Gibbs–Duhem equation $x_A \mathrm{d}v_A + x_B \mathrm{d}v_B = 0$ must hold. Treating x_A as an independent variable, we get

$$x_A \frac{\partial v_A}{\partial x_A} + x_B \frac{\partial v_B}{\partial x_A} = 0.$$

The first term vanishes at $x_A = 0$, and since $x_B = 1 - x_A = 1$, we get $\partial v_B / \partial x_A = 0$ at $x_A = 0$. Analogously, treating x_B as an independent variable, we show that $\partial v_A / \partial x_B = 0$ at $x_B = 0$. Thus, the Taylor expansion of the function $v_A(x_B)$ around $x_B = 0$, and the function $v_B(x_A)$ around $x_A = 0$, has the following form:

$$v_A(x_B) = v_A^* + a_A x_B^2 + \cdots,$$
$$v_B(x_A) = v_B^* + a_B x_A^2 + \cdots,$$

where we have neglected higher order terms.

7.7 We calculate $x_A \mathrm{d}v_A + x_B \mathrm{d}v_B$, substituting the expressions for v_A and v_B:

$$x_A \mathrm{d}v_A + x_B \mathrm{d}v_B = x_A \left[2ax_B - 2(a-b)x_B^2 \right] \mathrm{d}x_B + x_B \left[2bx_A + 2(a-b)x_A^2 \right] \mathrm{d}x_A$$
$$= 2x_A x_B \left[-a + (a-b)(1-x_A) + b + (a-b)x_A \right] \mathrm{d}x_A = 0.$$

The molar volume of mixing is given by the formula

$$\Delta_M v = \frac{\Delta_M V}{n} = x_A \left(v_A - v_A^* \right) + x_B \left(v_B - v_B^* \right),$$

where $\Delta_M V$ is the volume of mixing. Substituting v_A and v_B, we get

$$\Delta_M v = x_A x_B \left[ax_B + bx_A + \frac{2}{3}(a-b)\left(x_A^2 - x_B^2 \right) \right].$$

Then, we make use of the relation $x_A + x_B = 1$, which gives

$$\Delta_M v = \frac{x_A x_B}{3} \left[(2a+b)x_A + (a+2b)x_B \right].$$

7.8 Substituting the molar fractions into the formula for the entropy of mixing of an ideal mixture:

$$\Delta_M S = -nR \sum_i x_i \ln x_i,$$

we get

$$\frac{\Delta_M S}{n} = -8.314(0.781 \ln 0.781 + 0.21 \ln 0.21 + 0.009 \ln 0.009) \, \mathrm{J \, K^{-1} \, mol^{-1}}$$
$$= 4.682 \, \mathrm{J \, K^{-1} \, mol^{-1}}.$$

7.9 The total pressure of air results from the ideal gas equation of state

$$p = \frac{RT}{v} = \frac{8.314 \times 273.15}{0.0224} \, \mathrm{Pa} = 101383 \, \mathrm{Pa}.$$

The partial pressure of nitrogen, oxygen and argon amounts to, respectively

$$p_{N_2} = 0.781\,p = 79180.12 \text{ Pa},$$

$$p_{O_2} = 0.210\,p = 21290.43 \text{ Pa},$$

$$p_{Ar} = 0.009\,p = 912.45 \text{ Pa}.$$

7.10 For the entropy of mixing, we have

$$\Delta_M S = -nR \sum_i x_i \ln x_i.$$

The Gibbs free energy of mixing:

$$\Delta G_M = \Delta_M H - T \Delta_M S,$$

depends only on temperature and on the mixture composition, because both terms on the right-hand side do not depend on pressure. Therefore, the volume of mixing vanishes:

$$\Delta_M V = \left(\frac{\partial \Delta_M G}{\partial p} \right)_{T, n_j} = 0,$$

and the internal energy of mixing equals the enthalpy of mixing:

$$\Delta_M U = \Delta_M H - p \Delta_M V = \Delta_M H.$$

7.11 We use the relations

$$\left(\frac{\partial \Delta_M G}{\partial p} \right)_{T, n_j} = \Delta_M V,$$

$$\left(\frac{\partial \Delta_M G}{\partial T} \right)_{p, n_j} = -\Delta_M S.$$

Using the equality of mixed second order partial derivatives of the function $\Delta_M G$, we obtain the Maxwell relation

$$\left(\frac{\partial \Delta_M S}{\partial p} \right)_{T, n_j} = -\left(\frac{\partial \Delta_M V}{\partial T} \right)_{p, n_j}.$$

If the volume of mixing does not change with temperature then the entropy of mixing does not depend on pressure.

7.12 We use the relation (see (7.102))

$$\ln \frac{f(T, p)}{p} = \frac{1}{RT} \int_0^p [v(T, p') - v^{\text{id}}(T, p')] \mathrm{d}p',$$

where $v^{\text{id}}(T, p') = RT/p'$ denotes the molar volume of the ideal gas. Substituting

$$\frac{v(T, p')}{RT} = \frac{1}{p'} + B(T) + C(T)p',$$

we get

$$\ln \frac{f(T, p)}{p} = B(T)p + \frac{1}{2}C(T)p^2,$$

hence

$$f(T, p) = p \exp\left[B(T)p + \frac{1}{2}C(T)p^2\right].$$

7.13 From the van der Waals equation of state,

$$p = \frac{RT}{v - b} - \frac{a}{v^2},$$

it follows that for temperatures higher than the critical temperature, v is a function of temperature and pressure which can be expressed in the following form:

$$v(T, p) = \frac{RT}{p} + v^E(T, p).$$

The first term on the right-hand side is the molar volume of the ideal gas, v^{id}, and the function $v^E(T, p)$ characterizes deviations from the ideal behaviour. Substituting $v(T, p)$ into the van der Waals equation of state and dividing both sides by p^2, we obtain the equation for $v^E(T, p)$:

$$\frac{v^E - b}{RT + p(v^E - b)} + \frac{a}{(RT + pv^E)^2} = 0,$$

hence

$$RT\left[(v^E - b)RT + a\right] + (v^E - b)(2RTv^E + a)p + (v^E - b)v^{E^2}p^2 = 0.$$

We assume that v^E can be expanded in a Taylor series in p, around $p = 0$, i.e.

$$\frac{v^E(T, p)}{RT} = B(T) + C(T)p + \cdots.$$

Substituting this expansion into the above equation, we can calculate the coefficients at consecutive powers of p:

$$B(T) = \frac{b}{RT} - \frac{a}{(RT)^2},$$

$$C(T) = \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right).$$

For $a = 0.15 \, \mathrm{J\,m^3\,mol^{-2}}$, $b = 4 \times 10^{-5} \, \mathrm{m^3\,mol^{-1}}$ and $T = 273.13$ K, we get

$$B = -1.147 \times 10^{-3} \, \mathrm{bar^{-1}}, \qquad C = 1.786 \times 10^{-6} \, \mathrm{bar^{-2}},$$

hence

$$Bp + \frac{1}{2}Cp^2 = -5.71 \times 10^{-3},$$

which gives

$$\Phi = \exp\left(Bp + \frac{1}{2}Cp^2\right) = 0.994.$$

Note that for the given values of the constants a and b, we have (see Exercise 6.15) $T_{cr} = 133.6$ K and $p_{cr} = 34.7$ bar. Thus, for $T = 273.15$ K and $p = 5$ bar, the gas behaves almost as the ideal gas.

7.14 From the solution of Exercise 6.17, we know that the chemical potential of the van der Waals gas has the following form:

$$\mu(T, v) = \mu^0(T) + \frac{RTb}{v - b} - \frac{2a}{v} + RT \ln \frac{RT}{p^0(v - b)}.$$

The gas fugacity is defined as

$$\mu(T, p) = \mu^0(T) + RT \ln \frac{f(T, p)}{p^0}.$$

As above the critical temperature the relation between p and v is unique, we can treat f as a function of T and v. From the comparison of the two expressions, it follows that

$$\ln \frac{f}{p^0} = \ln \frac{RT}{p^0(v - b)} + \frac{b}{v - b} - \frac{2a}{RTv},$$

hence

$$f(T, v) = \frac{RT}{v - b} \exp\left(\frac{b}{v - b} - \frac{2a}{RTv} \right).$$

In the limit $v \to \infty$, we obtain $f(T, v) \approx p$. The fugacity coefficient $\Phi = f/p$, hence, for T_{cr} and p_{cr}, we have $v = v_{cr}$ and

$$\Phi_{cr} = \frac{f(T_{cr}, v_{cr})}{p_{cr}} = \frac{RT_{cr}}{p_{cr}(v_{cr} - b)} \exp\left(\frac{b}{v_{cr} - b} - \frac{2a}{RT_{cr}v_{cr}} \right).$$

Substituting the values of the critical parameters of the van der Waals gas (see (6.58)):

$$v_{cr} = 3b, \qquad p_{cr} = \frac{a}{27b^2}, \qquad T_{cr} = \frac{8a}{27Rb},$$

we get

$$\Phi_{cr} = 4 \exp(-7/4) \approx 0.695.$$

Thus, the deviation of the van der Waals gas at the critical point from the ideal gas behaviour ($\Phi = 1$) amounts to about 30 %.

7.15 We have $P = 3$ and $C = 4$, hence, $f = C - P + 2 = 3$.

7.16 We have $P = 5$, and the minimum number of components corresponds to $f = 0$, thus, it amounts to $C_{min} = P - 2 = 3$.

Exercises of Chapter 8

8.1 We find the liquid composition x_A from the formula $p = p_B^* + (p_A^* - p_B^*)x_A$, which for $p = (p_A^* + p_B^*)/2$ gives $x_A = 0.5$. The relation between the liquid com-

position x_A and the vapour composition y_A follows from Raoult's law, $p_A = p_A^* x_A$, and Dalton's law, $p_A = p y_A$, hence

$$y_A = x_A \frac{p_A^*}{p} = \frac{p_A^*}{p_A^* + p_B^*}.$$

8.2 When the external pressure p is fixed, the temperature of the liquid–vapour coexistence at that pressure is called the boiling point. We want to derive relations between the boiling point of the solution $A + B$ and its composition x_A and the composition of the vapour above the solution, y_A. According to Raoult's law the vapour pressure above the solution with the composition x_A amounts to

$$p = p_B^*(T) + \left[p_A^*(T) - p_B^*(T) \right] x_A,$$

where $p_A^*(T)$ and $p_B^*(T)$ denote the pressures of the liquid–vapour coexistence for pure components at the temperature T. Hence, we determine the composition of the solution which boils at the given temperature T at constant pressure p:

$$x_A(T) = \frac{p - p_B^*(T)}{p_A^*(T) - p_B^*(T)}.$$

To find the function $x_A(T)$, we have to know the functions $p_A^*(T)$ and $p_B^*(T)$. It follows from the Clausius–Clapeyron equation that in the case of a pure substance, if the enthalpy of evaporation Δh does not depend on temperature, then the pressure on the liquid–vapour coexistence line, p_{coex}, is given by the formula

$$p_{\text{coex}}(T) = p_{\text{coex}}(T_0) \exp\left[(\Delta h/R)(1/T_0 - 1/T) \right],$$

where T_0 is the temperature of a reference state. First, we use this formula to the pure component A, substituting p_A^* for p_{coex} and the enthalpy of evaporation Δh_A^* for Δh. As the reference temperature, we assume the boiling point of the pure A at the pressure p, which we denote by T_A^*. It follows from the definition of the boiling point that $p = p_A^*(T_A^*)$, hence

$$p_A^*(T) = p \, e^{(\Delta h_A^*/R)(1/T_A^* - 1/T)}.$$

Using analogous reasoning for the component B, we get

$$p_B^*(T) = p \, e^{(\Delta h_B^*/R)(1/T_B^* - 1/T)},$$

where T_B^* denotes the boiling point of the pure B at the pressure p. Substituting $p_A^*(T)$ and $p_B^*(T)$ into the formula for $x_A(T)$, we get

$$x_A(T) = \frac{1 - e^{(\Delta h_B^*/R)(1/T_B^* - 1/T)}}{e^{(\Delta h_A^*/R)(1/T_A^* - 1/T)} - e^{(\Delta h_B^*/R)(1/T_B^* - 1/T)}}.$$

This is the relation between the boiling point of the solution at constant pressure p and the liquid composition.

To find the composition of the vapour above the solution, y_A, we use the relation $y_A = p_A/p$ (see Dalton's law), where p_A is the partial vapour pressure of the component A, and then Raoult's law $p_A = p_A^* x_A$, hence

$$y_A(T) = e^{(\Delta h_A^*/R)(1/T_A^* - 1/T)} x_A(T).$$

To obtain the inverse relations, i.e., the temperature as a function of the liquid or vapour composition, we need to expand the exponential function: $e^y \approx 1 + y$, assuming that y is sufficiently small. Using the approximation $1/T_A^* - 1/T \approx (T - T_A^*)/(T_A^*)^2$, we get, e.g., for $\Delta h_A^* = 20$ kJ and $T_A^* = 300$ K:

$$\frac{\Delta h_A^*}{R(T_A^*)^2} = 0.027 \text{ K}^{-1}.$$

Thus, if the difference $T - T_A^*$ amounts to a few kelvins than the argument of the exponential function is really small. It happens when the temperatures T_A^* and T_B^* are not very different. We leave this simple exercise to the reader, to invert the relations $x_A = x_A(T)$ and $y_A = y_A(T)$ in the case when the approximation $e^y \approx 1 + y$ can be used.

8.3 We use the relations derived in Exercise 8.2. For pure substances, at the temperature $T = 350$ K, we get: $p_A^*(T)/p = 1.224$, $p_B^*(T)/p = 0.788$. For the solution $A + B$, the liquid composition results from Raoult's law, and the vapour composition, from Dalton's law, hence: $x_A = 0.486$ and $y_A = 0.595$. Thus, the vapour composition is richer in the more volatile component A, which in the pure state boils at a lower temperature.

8.4 First, we convert the concentration of O_2 in water from milligrams per litre to the molar fraction. We assume water to be the component A, and oxygen to be the component B. Since the solution is dilute, the molar fraction of oxygen in the solution, at the liquid–gas equilibrium, satisfies the inequality $x_B \ll 1$, hence, we get

$$x_B \approx n_B/n_A = v_A^* n_B/V_A,$$

where V_A denotes the volume of water. The molar volume of water $v_A^* = 0.018$ L mol^{-1}. The concentration of O_2 is equal to 4 mg L^{-1}, which corresponds to $n_B/V_A = 1.25 \times 10^{-4}$ mol L^{-1}, hence

$$x_B = 0.018 \times 1.25 \times 10^{-4} = 2.25 \times 10^{-6}.$$

Multiplying x_B by the Henry constant for oxygen in water, $k_B = 3.3 \times 10^7$ torr, we get the partial pressure of oxygen above water surface:

$$p_B = 3.3 \times 10^7 \times 2.25 \times 10^{-6} \text{ torr} = 74.25 \text{ torr}.$$

This is the pressure needed to sustain the assumed concentration of oxygen in water at the temperature of 25 °C.

8.5 We use expression (8.43) for the Ostwald absorption coefficient:

$$\frac{V_B}{V_A} = \frac{RT}{k_B v_A^*}.$$

Substituting the values $k_B = 3.3 \times 10^7$ torr and $v_A^* = 0.018$ L mol^{-1}, for $T = 298$ K, we get

$$V_B/V_A = \frac{8.314 \times 298.15 \text{ J mol}^{-1}}{3.3 \times 10^7 \times 133.322 \text{ Pa} \times 1.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}} = 0.031.$$

8.6 The elevation h of the column of water in the capillary corresponds to the osmotic pressure

$$\Pi = \rho g h,$$

where g is the gravity of earth, and ρ denotes the density of water. For a dilute solution, we can use formula (8.57):

$$\Pi = \frac{RT n_B}{V},$$

where B denotes the solute. The mole number of B, i.e., polyethylglicol, equals $n_B = m/M$. From the equality

$$\Pi = \frac{RT m}{V M} = \rho g h,$$

we determine the elevation of water level:

$$h = \frac{RT m}{V M \rho g}.$$

We notice that this formula can also be used to determine the molar mass of the solute

$$M = \frac{RT m}{V \rho g h}.$$

8.7 The boiling point elevation amounts to $\Delta T_b = 1.8$ K, hence, using formula (8.35):

$$\Delta T_b = K_b m_B,$$

we determine the molality of the solute

$$m_B = \frac{\Delta T_b}{K_b} = \frac{1.8}{2.53} \ \mathrm{mol\,kg^{-1}} = 0.711 \ \mathrm{mol\,kg^{-1}}.$$

Using the definition of the molality:

$$m_B = \frac{n_B}{n_A M_A},$$

where $M_A = 78 \ \mathrm{g\,mol^{-1}}$ is the molar mass of benzene, we get $n_B/n_A = 0.055$. As the mass of the solution amounts to

$$m = M_A n_A + M_B n_B = n_A \left(M_A + M_B \frac{n_B}{n_A} \right) = n_A \times 81.52 \ \mathrm{g\,mol^{-1}},$$

for $m = 100$ g, we get $n_A = 1.227$ mol and $n_B = 0.067$ mol. Thus, the mass of the non-volatile component amounts to

$$M_B n_B = 64 \times 0.067 = 4.29 \ \mathrm{g}.$$

8.8 First, we calculate the mole number of ethanol (component B), of the molar mass $M_B = 46 \ \mathrm{g\,mol^{-1}}$:

$$n_B = \frac{24 \ \mathrm{g}}{46 \ \mathrm{g\,mol^{-1}}} = 0.522 \ \mathrm{mol}.$$

As the mass of the solvent (water) amounts to 1 kg, the molality of ethanol amounts to

$$m_B = 0.522 \ \text{mol kg}^{-1}.$$

The freezing point depression amounts to $\Delta T_f = -0.97$ K, hence, for the cryoscopic constant of water we get

$$K_f = -\frac{\Delta T_f}{m_B} = 1.86 \ \text{K kg mol}^{-1}.$$

8.9 The freezing point depression $\Delta T_f = -0.5$ K, hence, the molality of acetone (component B) amounts to

$$m_B = -\frac{\Delta T_f}{K_f} = \frac{0.5}{3.70} \ \text{mol kg}^{-1} = 0.135 \ \text{mol kg}^{-1},$$

and the mole number of B in 1.5 kg of acetic acid amounts to

$$n_B = 0.135 \times 1.5 \ \text{mol} = 0.203 \ \text{mol}.$$

The molar mass of acetone $M_B = 58$ g/mol, thus, the mass of $n_B M_B = 11.77$ g of acetone should be dissolved in 1.5 kg of acetic acid.

8.10 The solvent (benzene) is denoted by A and the solute (naphthalene) is denoted by B. It follows from the assumptions that we can use formula (8.51):

$$\ln x_B = \frac{\Delta h_B^*}{R} \left(\frac{1}{T_B^*} - \frac{1}{T} \right),$$

where $T_B^* = 352.3$ K is the melting point of pure naphthalene, and $\Delta h_B^* = 19.0 \ \text{kJ mol}^{-1}$ is its enthalpy of melting. This relation, called the solubility line, defines the molar fraction of the solute in saturated solution, above which the solute precipitates from the solution as a solid. For the temperature $T = 298$ K, we get

$$\ln x_B = \frac{19000}{8.314} \left(\frac{1}{352.3} - \frac{1}{298} \right) = -1.18.$$

Thus, the solubility of naphthalene in benzene at 298 K amounts to $x_B = 0.307$.

8.11 It follows from the assumptions that both lines of liquid–solid coexistence have the following form (see (8.52) and (8.53)):

$$\ln x_A = \frac{\Delta h_A^*}{R} \left(\frac{1}{T_A^*} - \frac{1}{T} \right),$$

$$\ln x_B = \frac{\Delta h_B^*}{R} \left(\frac{1}{T_B^*} - \frac{1}{T} \right),$$

where $x_B = 1 - x_A$. If we set x_A on one axis and T on the other axis we obtain two lines which intersect at the eutectic point. The temperature $T = T_e$ lies below the freezing points of both components in the pure state. Substituting the data: $x_A = x_e = 0.4$, $T_e/T_A^* = 0.9$, $T_e/T_B^* = 0.84$, we get

$$\ln x_A = \ln 0.4 = \frac{\Delta h_A^*}{RT_e}(0.9 - 1) = -0.1 \frac{\Delta h_A^*}{RT_e},$$

$$\ln x_B = \ln 0.6 = \frac{\Delta h_B^*}{RT_e}(0.84 - 1) = -0.16 \frac{\Delta h_B^*}{RT_e},$$

hence, the ratio of the enthalpy of melting amounts to

$$\frac{\Delta h_A^*}{\Delta h_B^*} = 1.6 \times \frac{\ln 0.4}{\ln 0.6} = 2.87.$$

Exercises of Chapter 9

9.1 We use the generalized form of Raoult's law (see (9.6) and (9.7)):

$$p_A = p_A^* \gamma_A x_A,$$

$$p_B = p_B^* \gamma_B x_B,$$

where γ_A and γ_B denote the activity coefficients (see Definition 7.15). We can determine γ_A and γ_B from measurements of the vapour pressure above the solution and above pure components. We have $p_A^* = 0.031$ bar, $p_B^* = 0.029$ bar, $x_A = 0.2$, $y_A = 0.44$ and $p = 0.041$ bar. Since vapour is treated as an ideal gas, we can use Dalton's law. Thus, the partial pressures amount to $p_A = y_A p = 0.018$ bar and $p_B = y_B p = 0.023$ bar, hence, we get

$$\gamma_A = \frac{p_A}{p_A^* x_A} = 2.9,$$

$$\gamma_B = \frac{p_B}{p_B^* x_B} = 0.99.$$

The activity coefficient of the component B is very close to unity, thus, Raoult's law is better satisfied for that component. Note that here B is a solvent because $x_B \gg x_A$.

9.2 From Dalton's law, $p_A = p y_A$, $p_B = p y_B$, where p is the vapour pressure above the solution, and p_A and p_B denote the partial pressures, hence

$$p y_A = p_A^* \gamma_A x_A, \qquad p y_B = p_B^* \gamma_B x_B.$$

At the azeotropic point, the vapour composition is the same as the liquid composition, i.e., $y_A = x_A = x_a$ and $y_B = x_B = 1 - x_a$, therefore

$$p = p_A^* \gamma_A = p_B^* \gamma_B,$$

hence

$$\frac{\gamma_B}{\gamma_A} = \frac{p_A^*}{p_B^*}.$$

Using expressions (9.13) and (9.14) for activity coefficients in the simple solution:

$$\gamma_A = \exp\big(g_{AB}x_B^2/RT\big),$$
$$\gamma_B = \exp\big(g_{AB}x_A^2/RT\big),$$

we get

$$\ln \frac{p_A^*}{p_B^*} = \ln \frac{\gamma_B}{\gamma_A} = \frac{g_{AB}(2x_a - 1)}{RT},$$

hence

$$\frac{g_{AB}}{RT} = \frac{\ln 2.5}{0.4} \approx 2.29.$$

For $T = 298$ K, we obtain $g_{AB} \approx 5675$ J mol^{-1}. As $g_{AB} > 0$, the activity coefficients are grater than one, which means positive deviation from Raoult's law.

9.3 If the mixture is an azeotrope, then the composition at the azeotropic point, $x_A = x_a$, follows from the formula (see Exercise 9.2):

$$2x_a - 1 = \frac{RT}{g_{AB}} \ln \frac{p_A^*}{p_B^*} = \frac{\ln 3}{0.9} = 1.22.$$

This gives $x_a = 1.11$, which is in contradiction with the condition $x_a \leq 1$. Thus, the mixture considered does not form an azeotrope.

9.4 The condition for the critical temperature (see 9.2.2) has the following form:

$$g_{AB}(T)/RT = 5(T - T_0)\,\text{K}^{-1} - 2(T - T_0)^2\,\text{K}^{-2} = 2.$$

This equation has two roots: $T_1 = T_0 + 0.5$ K and $T_2 = T_0 + 2$ K, hence, $g_{AB}/RT < 2$, if either $T < T_1$ or $T > T_2$, and $g_{AB}/RT > 2$, if $T_1 < T < T_2$. Thus, for temperatures lower than T_1 or higher than T_2, the condition of intrinsic stability is satisfied, i.e., the components are completely miscible, whereas for temperatures $T_1 < T < T_2$, a miscibility gap exists. Thus, the miscibility curve is closed, T_1 is the lower critical temperature and T_2 is the upper critical temperature.

9.5 According to the definition of the Henry constant we have (see Exercise 9.2)

$$k_B = \lim_{x_B \to 0} \frac{p_B}{x_B},$$

where p_B is the partial pressure of B in the vapour above the solution, and x_B is the molar fraction of B in the solution. Since $p_B = p_B^* \gamma_B x_B$, where γ_B denotes the activity coefficient of B in the solution, in the case of the simple solution, we get

$$k_B = p_B^* \gamma_B(T, x_A = 1) = p_B^* \exp\left[\frac{g_{AB}(T)}{RT}\right].$$

At the composition of the azeotropic point, we have (see Exercise 9.2)

$$\frac{g_{AB}(T)}{RT} = \frac{1}{2x_a - 1} \ln \frac{p_A^*}{p_B^*},$$

hence

$$k_B = p_B^* \left(\frac{p_A^*}{p_B^*} \right)^{1/(2x_a - 1)}.$$

9.6 Since the solution is ideal, Raoult's law holds. We also assume that vapour is an ideal gas. From Raoult's and Dalton's laws, the relation between the solution composition, x_A, and the vapour pressure above the solution follows:

$$p = p_A + p_B = p_B^* + (p_A^* - p_B^*) x_A,$$

hence

$$x_A(p) = \frac{p - p_B^*}{p_A^* - p_B^*}.$$

The vapour composition results from the relation $p_A = p y_A$:

$$y_A(p) = \frac{p_A^* x_A(p)}{p}.$$

Here, we treat pressure as an independent parameter and express the bubble point and dew point isotherms accordingly, i.e.,

$$\left(\frac{\partial x_A}{\partial p} \right)_T = \frac{y_A \Delta v_A + y_B \Delta v_B}{(y_A - x_A) g_{xx}},$$

$$\left(\frac{\partial y_A}{\partial p} \right)_T = \frac{x_A \Delta v_A + x_B \Delta v_B}{(y_A - x_A) g_{yy}}.$$

The molar Gibbs free energy of an ideal mixture is given by (see (9.43))

$$g = g^{id} = \mu_A^* x_A + \mu_B^* x_B + RT(x_A \ln x_A + x_B \ln x_B),$$

hence

$$g_{xx} = \left(\frac{\partial^2 g}{\partial x_A^2} \right)_{T,p} = \frac{RT}{x_A x_B},$$

$$g_{yy} = \left(\frac{\partial^2 g}{\partial y_A^2} \right)_{T,p} = \frac{RT}{y_A y_B}.$$

Substituting these expressions into the equations of the bubble point and dew point isotherms, we get

$$\left(\frac{\partial \ln x_A}{\partial p} \right)_T = \frac{x_B(y_A \Delta v_A + y_B \Delta v_B)}{RT(y_A - x_A)},$$

$$\left(\frac{\partial \ln y_A}{\partial p} \right)_T = \frac{y_B(x_A \Delta v_A + x_B \Delta v_B)}{RT(y_A - x_A)}.$$

As $\ln y_A = \ln x_A - \ln(p/p_A^*)$, we have

$$\left(\frac{\partial \ln x_A}{\partial p} \right)_T - \left(\frac{\partial \ln y_A}{\partial p} \right)_T = \frac{1}{p},$$

and after simple transformations we get

$$\frac{\Delta v_A}{RT} = \frac{1}{p}, \qquad \frac{\Delta v_B}{RT} = \frac{1}{p};$$

to obtain the second relation we have replaced A with B in the equations of the isotherms. Note that the above relations are in accord with the assumption that vapour is an ideal gas and that the molar volumes of the liquids A and B can be neglected in Δv_A and Δv_B.

Exercises of Chapter 10

10.1 To prove the stability condition, we use the form of the chemical potential for the ideal gas:

$$\mu_i(T, p, x_i) = \mu_i^0(T) + RT \ln(p/p^0) + RT \ln x_i.$$

From the definition of the affinity of reaction, we get

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p} = -\left(\frac{\partial A}{\partial \xi}\right)_{T,p} = \sum_i v_i \left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,p}.$$

The molar fractions as functions of ξ are defined by

$$x_i(\xi) = \frac{n_i(\xi)}{n(\xi)} = \frac{n_i(0) + v_i \xi}{n(\xi)},$$

where $n(\xi) = \sum_i n_i(\xi) = n(0) + \xi \Delta n$, and $\Delta n = \sum_i v_i$. Since

$$\sum_i v_i \left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,p} = RT \sum_i v_i \frac{\partial \ln x_i}{\partial \xi} = RT \sum_i v_i \left[\frac{v_i}{n_i(0) + v_i \xi} - \frac{\Delta n}{n(\xi)}\right],$$

we have

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p} = \frac{RT}{n(\xi)}\left[\sum_i \frac{v_i^2}{x_i(\xi)} - (\Delta n)^2\right].$$

To transform the sum on the right-hand side, we use the identity $\sum_j x_j = 1$, hence

$$\sum_i \frac{v_i^2}{x_i} = \sum_{i,j} \frac{v_i^2 x_j}{x_i} = \frac{1}{2}\sum_{i,j}\left(\frac{v_i^2 x_j}{x_i} + \frac{v_j^2 x_i}{x_j}\right) = \frac{1}{2}\sum_{i,j} \frac{(v_i x_j - v_j x_i)^2}{x_i x_j} + \sum_{i,j} v_i v_j,$$

where

$$\sum_{i,j} v_i v_j = \left(\sum_i v_i\right)^2 = (\Delta n)^2,$$

which gives

$$\sum_i \frac{v_i^2}{x_i} - (\Delta n)^2 = \frac{1}{2}\sum_{i,j} \frac{(v_i x_j - v_j x_i)^2}{x_i x_j} \geq 0.$$

Although the equality holds for $x_i = const \times v_i$, this case is unphysical, however, because the condition $x_i \geq 0$ is not satisfied either for reactants or products. Thus, in the case of ideal gases, the stability condition holds for all acceptable values of the molar fractions, which means that G is a convex function of ξ at constant T and p.

10.2 We have $T = const$ and $pV = nRT$, hence

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + RT\,\Delta n,$$

where $\Delta n = \sum_i v_i$ denotes the change in the total mole number of gases in the given reaction.

10.3 From the definition of the constant $K_x(T, p)$, we obtain

$$\frac{K_x(T, p_2)}{K_x(T, p_1)} = \left(\frac{p_2}{p_1}\right)^{-\Delta n}.$$

In the first reaction, $\Delta n = 0$, hence, K_x does not change. In the second reaction, $\Delta n = -1$, thus, for $p_2/p_1 = 2$, K_x at p_2 is twice as big as K_x at p_1.

10.4 The initial amounts of the reactants and products, expressed in moles, are: $n_A(0) = 2$, $n_B(0) = 1/3$, $n_C(0) = 1$, $n_D(0) = 1/2$, hence (see (10.5))

$$n_A = 2 - 3\xi, \qquad n_B = \frac{1}{3} - \xi, \qquad n_C = 1 + \xi, \qquad n_D = \frac{1}{2} + 2\xi.$$

Since all mole numbers must be positive, we obtain the condition for ξ:

$$-\frac{1}{4} \leq \xi \leq \frac{1}{3},$$

which specifies the minimum and maximum value of the extent of reaction. Substituting $\xi_{eq} = 1/4$ mol, we get (in moles): $n_A = 5/4$, $n_B = 1/12$, $n_C = 5/4$, $n_D = 1$, hence, the molar fractions in the state of chemical equilibrium amount to: $x_A = 15/43$, $x_B = 1/43$, $x_C = 15/43$, $x_D = 12/43$. Using the law of mass action, we get

$$K_x(T, p) = \frac{x_C x_D^2}{x_A^3 x_B} = 27.52.$$

10.5 The compounds A, B and C are ideal gases, thus, the law of mass action for this reaction has the following form:

$$\frac{x_C^2}{x_A x_B} = K_x = K^0 = 1,$$

as the pressure $p = p^0 = 1$ bar. The molar fractions depend on the extent of reaction ξ:

$$x_A(\xi) = x_A(0) - x, \qquad x_B(\xi) = x_B(0) - x, \qquad x_C(\xi) = 2x,$$

where $x = \xi/n(0)$. Thus, we obtain a quadratic equation for x, i.e.,

$$4x^2 = [x_A(0) - x][x_B(0) - x],$$

which has two roots:

$$x = \frac{1}{6}\left[-1 \pm \sqrt{1 + 12x_A(0)x_B(0)}\right].$$

The negative root is unphysical, because the molar fractions cannot be negative, and for $x_C(0) = 0$, we have $x_C \geq 0$ only if $x \geq 0$. In case (a), $x_A(0) = x_B(0) = 1/2$, hence $x_{eq} = 1/6$, and the equilibrium molar fractions amount to: $x_A = x_B = x_C = 1/3$. In case (b), $x_A(0) = 1/4$, $x_B(0) = 3/4$, hence, $x_{eq} = 0, 134$, and in chemical equilibrium we have $x_A = 0.116$, $x_B = 0.616$ and $x_C = 0.268$.

10.6 For convenience, we denote the compounds PCl_5, PCl_3 and Cl_2, by A, B and C, respectively. The molar mass of PCl_5 amounts to $M_A = 208$ g mol^{-1}, hence, the initial mole number $n(0) = n_A(0) = 0.91 \times 10^{-2}$ mol. The mole number in the state of chemical equilibrium, $n_{eq} = n(\xi_{eq})$, results from the ideal gas equation of state:

$$n_{eq} = \frac{pV_{eq}}{RT} = \frac{0.314 \times 10^5 \times 2.4 \times 10^{-3}}{8.314 \times 593.15} = 1.53 \times 10^{-2} \text{ mol.}$$

The changes in the mole numbers of all compounds during the reaction amount to:

$$n_A(\xi) = n(0) - \xi, \qquad n_B(\xi) = \xi, \qquad n_C(\xi) = \xi,$$

hence, $n(\xi) = n(0) + \xi$ and $\xi_{eq} = n_{eq} - n(0) = 0.62 \times 10^{-2}$ mol. The percentage of decomposed PCl_5 molecules is equal to

$$\frac{n_A(0) - n_A(\xi_{eq})}{n_A(0)} = \frac{\xi_{eq}}{n(0)} = 0.68,$$

i.e., 68 %. To calculate the equilibrium constant K^0, we have to find the molar fractions of all compounds in chemical equilibrium:

$$x_A = \frac{n_A(\xi_{eq})}{n_{eq}} = 0.190, \qquad x_B = x_C = \frac{\xi_{eq}}{n_{eq}} = 0.405.$$

As in the state of chemical equilibrium we have

$$\frac{x_B x_C}{x_A} = \left(\frac{p}{p^0}\right)^{-\Delta n} K^0(T) = \left(\frac{p}{p^0}\right)^{-1} K^0(T),$$

thus

$$K^0(320\,°C) = 0.314 \times 0.863 = 0.271.$$

10.7 According to the Le Chatelier-Braun principle, in case (a) the position of chemical equilibrium shifts in the direction of heat absorption by the system. Since the decomposition reaction is endothermic, the equilibrium shifts in the direction of higher products concentration, i.e., in the new equilibrium state, $x_A(T_1, p_0) < x_A(T_0, p_0)$. In case (b), the equilibrium shifts in the direction of decreasing volume. Due to the decomposition reaction, one mole of the gas is replaced by two moles, thus, the equilibrium shifts in the direction of higher reactant concentration, i.e., $x_A(T_0, p_1) > x_A(T_0, p_0)$.

10.8 If the temperatures T_1 and T_0 do not differ too much, then, as a first approximation, we can assume that $\Delta_r H^0$ is constant in the range $T_0 < T < T_1$. Then, from the van 't Hoff equation, we get

$$\ln K^0(T_1) = \ln K^0(T_0) + \int_{T_0}^{T_1} \frac{\Delta_r H^0}{RT^2} dT = \ln K^0(T_0) + \frac{\Delta_r H^0}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right),$$

and the same formula holds also for $T_1 < T_0$.

10.9 We assume that $\Delta_r H^0$ is independent of temperature in the temperature range of interest, thus

$$\ln \frac{K^0(T_1)}{K^0(T_0)} = \frac{32000}{8.314}\left(\frac{1}{298} - \frac{1}{310}\right) = 0.50,$$

hence, $K^0(T_1) = 1.65 K^0(T_0)$.

10.10 Since $x_B = x_C = (1 - x_A)/2$, and $\Delta n = 0$, the law of mass action for this reaction has the following form:

$$\frac{(1 - x_A)^2}{4x_A^2} = K_x(T, p) = K^0(T).$$

We have $1 - x_A = 0.40$, at $T_1 = 300$ K, and $1 - x_A = 0.42$, at $T_2 = 315$ K, hence

$$K^0(T_1) = 0.111, \qquad K^0(T_2) = 0.131.$$

We calculate the enthalpy of reaction, using the formula (see Exercise 10.8)

$$\Delta_r H^0 = \frac{R \ln[K^0(T_2)/K^0(T_1)]}{1/T_1 - 1/T_2},$$

hence, $\Delta_r H^0 = 8.68\ \text{kJ mol}^{-1}$.

10.11 The law of mass action for this reaction has the following form:

$$\frac{(p_B/p^0)^{\nu_B}(p_C/p^0)^{\nu_C}}{p_A/p_0} = K^0(T),$$

where $p_A = px_A$, $p_B = px_B$ and $p_C = px_C$ denote the partial pressures. Substituting these expressions for the partial pressures, we obtain the law of mass action expressed in terms of the molar fractions:

$$\frac{x_B^{\nu_B} x_C^{\nu_C}}{x_A} = \left(\frac{p}{p^0}\right)^{-\Delta n} K^0(T) = K_x(T, p),$$

where $\Delta n = \nu_B + \nu_C - 1$. Then, we express the molar fractions, using the degree of dissociation α. The total number of moles in the system in chemical equilibrium amounts to

$$n = n_A + n_B + n_C,$$

where, according to the definition of α, we have $n_A = n_i - n_d = (1 - \alpha)n_i$. From the reaction equation, it follows that $n_B = \nu_B n_d$, $n_C = \nu_C n_d$, hence, $n_B = \nu_B \alpha n_i$, $n_C = \nu_C \alpha n_i$ and

$$n = (1 - \alpha + \nu_B \alpha + \nu_C \alpha)n_i = (1 + \alpha \Delta n)n_i.$$

Substituting $x_A = n_A/n$, $x_B = n_B/n$, $x_C = n_C/n$, we get

$$x_A = \frac{1 - \alpha}{1 + \alpha \Delta n}, \qquad x_B = \frac{\nu_B \alpha}{1 + \alpha \Delta n}, \qquad x_C = \frac{\nu_C \alpha}{1 + \alpha \Delta n}.$$

Thus, we obtain the following relation between the degree of dissociation and the equilibrium constant

$$\frac{(\nu_B \alpha)^{\nu_B} (\nu_C \alpha)^{\nu_C}}{1 - \alpha} (1 + \alpha \Delta n)^{-\Delta n} = K_x(T, p).$$

When $\alpha \ll 1$, the above expression can be simplified as follows:

$$K_x(T, p) \approx \nu_B^{\nu_B} \nu_C^{\nu_C} \alpha^{\nu_B + \nu_C}.$$

10.12 In this sort of problems, we treat the symbol $\rightarrow$ in the same way as the equality sign, and add the reactions as if they were algebraic equations. The standard enthalpies of reactions are treated in the same way. It is easy to verify that adding both sides of the first and second reaction, and then subtracting the third reaction from the sum, we obtain the reaction of our interest. Therefore, $\Delta_r H^0$ for that reaction amounts to

$$\Delta_r H^0 = (-1411.3 - 285.8 + 1559.8) \text{ kJ mol}^{-1} = -137.3 \text{ kJ mol}^{-1}.$$

A negative value of $\Delta_r H^0$ means that the reaction is exothermic, because the enthalpy of the final state is smaller than the enthalpy of the initial state, i.e., the system gives off heat to the surroundings.

10.13 The reaction of N_2O_5 formation from the elements is given by the equation

$$N_2(g) + \frac{5}{2} O_2(g) \rightarrow N_2O_5(g).$$
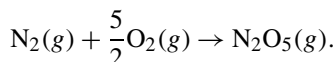
Multiplying the first and second reaction by 2 and then adding all three reactions, we get

$$2N_2(g) + 5O_2(g) \rightarrow 2N_2O_5(g).$$
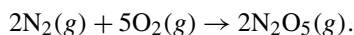
We do the same with their standard enthalpies:

$$(-2 \times 114.1 - 110.2 + 2 \times 180.5) \text{ kJ mol}^{-1} = 2\Delta_f H^0_{N_2O_5},$$

hence, $\Delta_f H^0_{N_2O_5} = 11.3 \text{ kJ mol}^{-1}$. The reaction is endothermic, since the enthalpy of the final state of the system is bigger than the enthalpy of the initial state, i.e., the system absorbs heat.

10.14 We substitute the enthalpies of formation of individual compounds, with the plus sign for products and the minus sign for reactants, and with the appropriate stoichiometric coefficient. Thus, the standard enthalpy of reaction of propane combustion amounts to

$$\Delta_r H^0 = (-3 \times 393.5 - 4 \times 285.8 + 103.7) \text{ kJ mol}^{-1} = -2220 \text{ kJ mol}^{-1}.$$

Note that $\Delta_f H^0_{O_2} = 0$, since O_2 is an element. Before the reaction started there were 6 mol of gases and 0 mol of liquids, whereas after the reaction there are 3 mol of

gaseous carbon dioxide and 4 mol of liquid water. The change in the volume of ideal gases amounts to

$$\Delta V = \frac{RT \Delta n}{p} = -\frac{3RT}{p} = -74.3 \text{ L},$$

where $p = 1$ bar, and $\Delta n = -3$ is the change in the mole number of gases. The amount of liquid water has increased by 4 mol, i.e., by 72 g, which occupy 72 cm^3. The volume of the liquid formed in the reaction is more than 1000 times smaller than the change in the gas volume, therefore, it can be neglected. The enthalpy $H = U + pV$, hence, the change in the internal energy at constant pressure amounts to

$$\Delta U = \Delta H - p\Delta V = \Delta H + 3RT = (-2220 + 7.4) \text{ kJ} = -2212.6 \text{ kJ}.$$

10.15 To obtain 1 mol of ammonia from this reaction, we have to take 2 mol of hydrogen and nitrogen altogether. The change in the enthalpy amounts to $\Delta H = \Delta_f H_{NH_3}^0 = -46.1$ kJ mol^{-1}. The work done by the system per 1 mol of NH$_3$ amounts to

$$W = -p\Delta V = -RT \Delta n = 2.5 \text{ kJ},$$

hence

$$\Delta U = \Delta H + W = (-46.1 + 2.5) \text{ kJ} = -43.6 \text{ kJ}.$$

10.16 We multiply the reaction of water formation by 2 and add the reaction of CO$_2$ formation, and then subtract the reaction of methane combustion, to get the reaction of methane formation, hence

$$\Delta_f H_{CH_4}^0 = 2\Delta_f H_{H_2O}^0 + \Delta_f H_{CO_2}^0 - \Delta_r H^0 = -74.8 \text{ kJ mol}^{-1}.$$

For the reaction occurs at constant pressure, the heat $Q = \Delta H$, whereas for the reaction at constant volume, $Q = \Delta U$, as the system performs no work. Thus, we have

$$Q = \Delta H - \Delta(pV) \approx \Delta H - RT \Delta n,$$

where Δn is the increase in the total mole number of gases taking part in the reaction. Note that if liquids or solids also take part in a given reaction, then their contribution to pV is usually much smaller than the contribution of gases because of their much smaller molar volumes. In the reaction considered, 2 mol of hydrogen are replaced by 1 mol of methane, hence, $\Delta n = 1 - 2 = -1$ and

$$Q = \Delta_f H_{CH_4}^0 + RT = -72.3 \text{ kJ mol}^{-1}.$$

10.17 We know from statistical physics (equipartition of kinetic energy) that the molar internal energy of an ideal gas is equal to the product of $RT/2$ and the number of degrees of freedom per molecule, which is treated as a solid body without internal structure. A linear molecule has 5 degrees of freedom, hence, $U_A = 5n_A RT/2$ and $U_B = 5n_B RT/2$, whereas a molecule of C has 6 degrees of freedom, hence, $U_C =$

$3n_C RT$. For all ideal gases, the equation of state has the same form: $pV = nRT$. For the molar enthalpies of individual gases, we get

$$h_A = h_B = \frac{7}{2}RT, \qquad h_C = 4RT,$$

hence, we calculate the molar heat capacity at constant pressure, c_p, differentiating the enthalpy with respect to T:

$$c_{p,A} = c_{p,B} = \frac{7}{2}R, \qquad c_{p,C} = 4R.$$

Thus, c_p depends neither on pressure nor temperature. For $\Delta_r c_p^0$, we have

$$\Delta_r c_p^0 = 3c_{p,C} - 2c_{p,A} - c_{p,B} = \frac{3}{2}R.$$

Integrating the Kirchhoff equation, we get (see (10.55))

$$\Delta_r H^0(T_2) = \Delta_r H^0(T_1) + \frac{3}{2}R(T_2 - T_1).$$

Substituting $T_1 = 298$ K and $T_2 = 340$ K, we obtain

$$\Delta_r H^0(340 \text{ K}) = -19.48 \text{ kJ mol}^{-1}.$$

10.18 The number of components in the system $C = 3$ and one chemical reaction takes place, hence, $R = 1$. The substance D is a gas, and the substances A and B are liquids. In case (1), A and B form a homogeneous mixture, thus, the number of phases $P = 2$. In case (2), A and B form two liquid phases, which are in equilibrium with the gaseous phase, thus, $P = 3$. The number of independent parameters in the system is the number of degrees of freedom, $f = C + 2 - P - R$. In case (1), $f = 3 + 2 - 2 - 1 = 2$, and in case (2), $f = 3 + 2 - 3 - 1 = 1$.

10.19 The liquids A and B form an ideal solution, thus, Raoult's law can be applied to them, i.e., $p_A = p_A^*(T)x_A$, $p_B = p_B^*(T)x_B$, where p_A and p_B denote the partial pressures of the vapour above the solution. The chemical potentials of the components of the ideal solution are given by

$$\mu_A(l) = \mu_A^*(l) + RT \ln x_A, \qquad \mu_B(l) = \mu_B^*(l) + RT \ln x_B,$$

where $\mu_A^*(l)$ and $\mu_B^*(l)$ are the chemical potentials of pure liquids A and B. Making use of Raoult's law (see Sect. 8.1.1), we get for the liquid–vapour coexistence:

$$\mu_A(l) = \mu_A(g) = \mu_A^0 + RT \ln \frac{p_A}{p^0} = \mu_A^*(T) + RT \ln x_A,$$

where $\mu_A^*(T)$ denotes the chemical potential of pure substance A on the liquid–vapour coexistence line. An analogous relation holds for the component B, i.e.,

$$\mu_B(l) = \mu_B^*(T) + RT \ln x_B.$$

The component C is an ideal gas, thus

$$\mu_C = \mu_C^0(T) + RT \ln \frac{p_C}{p^0}.$$

The condition of chemical equilibrium adopts the following form:

$$\mu_A(l) - \mu_B(l) - \mu_C(g) = \mu_A^*(T) - \mu_B^*(T) - \mu_C^0(T) + RT \ln \frac{x_A p^0}{x_B p_C} = 0.$$

Using the equilibrium constant defined by

$$\mu_A^*(T) - \mu_B^*(T) - \mu_C^0(T) = RT \ln K(T),$$

we obtain the law of mass action:

$$\frac{x_B(p_C/p_0)}{x_A} = K(T).$$

The total pressure of the gaseous phase above the solution, p, is the sum of three partial pressures:

$$p = p_A + p_B + p_C = p_A^* x_A + p_B^* x_B + p_C.$$

As the presence of the component C in the solution can be neglected, we have

$$x_A + x_B + x_C \approx x_A + x_B = 1.$$

Substituting this relation into the law of mass action, we get

$$(1 - x_A)p_C = p^0 K(T)x_A,$$

hence

$$x_A = \frac{p_C}{p^0 K + p_C}, \qquad x_B = \frac{p^0 K}{p^0 K + p_C}.$$

Finally, we obtain

$$p = \frac{p_A^* p_C + p_B^* p^0 K}{p^0 K + p_C} + p_C.$$

According to the phase rule, we have $f = C + 2 - P - R = 3 + 2 - 2 - 1 = 2$. In this case, the independent parameters are T and p_C.

10.20 First, we write the condition of chemical equilibrium (see Exercise (10.11)):

$$\mu_{CuO}(s) + \mu_{H_2}(g) - \mu_{Cu}(s) - \mu_{H_2O}(g) = 0,$$

where

$$\mu_{H_2}(g) = \mu_{H_2}^0 + RT \ln \frac{p_{H_2}}{p^0}, \qquad \mu_{H_2O}(g) = \mu_{H_2O}^0 + RT \ln \frac{p_{H_2O}}{p^0}.$$

Cu and CuO are pure substances in the solid phase. We recall that in general we can express the chemical potential of the i-the component in terms of its activity (see (7.116)), i.e.

$$\mu_i = \mu_i^0(T) + RT \ln a_i.$$

In the case of a pure substance, $\mu_i = \mu_i^*$ depends on temperature and pressure. However, liquids and solids are hardly compressible, therefore, the dependence of the chemical potential on pressure is often neglected, provided the pressure p does

not differ too much from the standard pressure p^0. In the case of chemical reactions, it is usually assumed that the activity of a pure liquid or solid is equal to unity. Thus, for the reaction considered, we have $a_{\text{CuO}}^*(s) = 1$, $a_{\text{Cu}}^*(s) = 1$, and the condition of chemical equilibrium adopts the following form:

$$\mu_{\text{CuO}}^0 + \mu_{\text{H}_2}^0 - \mu_{\text{Cu}}^0 - \mu_{\text{H}_2\text{O}}^0 + RT \ln \frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} = 0,$$

where the standard chemical potentials depend only on temperature. According to the definition of the standard equilibrium constant, we have

$$\mu_{\text{CuO}}^0 + \mu_{\text{H}_2}^0 - \mu_{\text{Cu}}^0 - \mu_{\text{H}_2\text{O}}^0 = RT \ln K^0.$$

Finally, we get

$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} = K^0.$$

This is the condition of chemical equilibrium for the reaction considered.

Exercises of Chapter 11

11.1 In the case of the first reaction, we have 4 components, that is, we neglect dissociation of water and assume that activity of water $a_{\text{H}_2\text{O}} = 1$. Ammonia is treated as an ideal gas, thus,

$$\mu_{\text{NH}_3}(g) = \mu_{\text{NH}_3}^0 + RT \ln \frac{p_{\text{NH}_3}}{p^0},$$

where p_{NH_3} is the partial pressure of ammonia above the solution. The chemical potentials of the ions are expressed in terms of their activities:

$$\mu_{\text{NH}_4^+} = \mu_{\text{NH}_4^+}^0 + RT \ln a_{\text{NH}_4^+}, \qquad \mu_{\text{OH}^-} = \mu_{\text{OH}^-}^0 + RT \ln a_{\text{OH}^-}.$$

Therefore, the condition of chemical equilibrium adopts the following form:

$$\frac{(a_{\text{NH}_4^+})(a_{\text{OH}^-})p^0}{p_{\text{NH}_3}} = K^0.$$

The second reaction concerns a saturated solution of slightly soluble salt, which means that we have coexistence of practically pure crystalline salt with aqueous solution of that salt. It can be assumed that the activity of the solid is equal to unity, hence, only the activities of the ions appear in the condition of chemical equilibrium, i.e.,

$$(a_{\text{Ba}^{2+}})(a_{\text{SO}_4^{2-}}) = K^0.$$

Since the salt is slightly soluble, its concentration in the solution is small. In the case of electrolytes, such as aqueous solutions of salt for instance, the solute whose concentration in the solution is small is practically completely dissociated. Thus, the equilibrium constant K^0 is a measure of solubility of the salt in water. For this

reason, it is called the solubility constant or solubility product of the salt, and is denoted by K_s. It can be easily understood if we replace the activity with the molar concentration, which is justified in the case of strong dilution. Then we have

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = K_s,$$

and because $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}]$, the molar concentration of each ion amounts to $K_s^{1/2}$. Thus, the constant K_s provides information about solubility of the salt in water.

11.2 Expressing the chemical potential in terms of the activity, we write the condition of chemical equilibrium as follows:

$$\mu_{A_x B_y}^0 + RT \ln a_{A_x B_y} - x \left(\mu_A^0 + RT \ln a_A \right) - y \left(\mu_B^0 + RT \ln a_B \right) = 0.$$

Assuming that the activity of the pure solid $a_{A_x B_y} = 1$, we obtain the following form of the equilibrium condition:

$$a_A^x a_B^y = K_s,$$

where K_s denotes the equilibrium constant of the reaction considered. It is a generalization of the solubility product considered in Exercise 11.1. Applying this formula to aqueous solution of the salt Ag_2CO_3, which dissociates according to the equation

$$\text{Ag}_2\text{CO}_3(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{CO}_3^{2-}(aq),$$
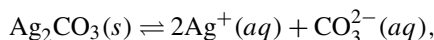
we get

$$K_s = (a_{\text{Ag}^+})^2 (a_{\text{CO}_3^{2-}}) \approx \left[\text{Ag}^+ \right]^2 \left[\text{CO}_3^{2-} \right].$$

For each CO_3^{2-} ion, there are two Ag^+ ions, hence, $[\text{Ag}^+] = 2[\text{CO}_3^{2-}]$ and we get

$$4 \left[\text{CO}_3^{2-} \right]^3 = K_s = 6.2 \times 10^{-12},$$

i.e., $[\text{CO}_3^{2-}] = 1.16 \times 10^{-4} \text{ mol L}^{-1}$ and $[\text{Ag}^+] = 2.32 \times 10^{-4} \text{ mol L}^{-1}$.

11.3 We use relation (11.84) between the standard potential and equilibrium constant:

$$E^0 = \frac{RT}{nF} \ln K^0,$$

where $F = 9.6485 \times 10^4 \text{ C mol}^{-1}$, and $n = 2$. The standard potential $E^0 = 0.339 - (-0.763) \text{ V} = 1.102 \text{ V}$, and the coefficient RT/nF amounts to

$$\frac{RT}{nF} = \frac{8.314 \times 298}{2 \times 9.6485} \times 10^{-4} \text{ J C}^{-1} = 1.284 \times 10^{-2} \text{ V},$$

hence

$$K^0 = e^{E^0 nF/RT} = e^{85.8} = 1.8 \times 10^{37}.$$

Thus, the equilibrium constant of this reaction is very big.

This exercise can also be solved in a different way. We have $E^0 = E_R^0 - E_L^0$, where $E_R^0 = 0.339$ V, $E_L^0 = -0.763$ V and

$$E_R^0 = \frac{RT}{nF} \ln K_R^0, \qquad E_L^0 = \frac{RT}{nF} \ln K_L^0.$$

K_R^0 and K_L^0 denote the standard equilibrium constants for the reactions in cells consisting of the copper and zinc electrode, respectively, in one half-cell and the standard hydrogen electrode. Thus, we have

$$\frac{RT}{nF} \ln K^0 = \frac{RT}{nF} \ln K_R^0 - \frac{RT}{nF} \ln K_L^0,$$

hence, $K^0 = K_R^0/K_L^0$. Substituting the data, we get

$$K_R^0 = e^{E_R^0 nF/RT} = e^{26.4} = 2.9 \times 10^{11},$$
$$K_L^0 = e^{E_L^0 nF/RT} = e^{-59.4} = 1.6 \times 10^{-26},$$

which gives $K^0 = 1.8 \times 10^{37}$.

11.4 46 g of Na correspond to 2 mol, thus, to obtain this amount of sodium at the cathode, an electric charge of 2 mol of electrons (according to the reaction $2Na^+ + 2e^- \to 2Na$) must flow through the salt, i.e.,

$$F \times 2 \text{ mol} = 1.9297 \times 10^5 \text{ C}.$$

Since $1 \text{ A} = 1 \text{ C s}^{-1}$, the current of 10 A must flow during

$$1.9297 \times 10^4 \text{ C A}^{-1} = 19297 \text{ s} \approx 5.36 \text{ h}.$$

During this time 1 mol of gaseous chlorine is produced at the anode, because each Cl_2 molecule provides 2 electrons, donated by 2 Cl^- ions, and the charge $F \times 2$ mol has flowed. Therefore, we obtain 70.9 g of chlorine at the anode.

11.5 To solve this problem, the relation between the enthalpy of reaction and the potential difference of the cell is to be found. To do this, we use the equality (see (11.77))

$$\Delta G = -EnF\Delta\xi,$$

which holds if E does not change during the cell reaction. The change in the enthalpy is obtained from the relation

$$G = H - TS = H + T\frac{\partial G}{\partial T},$$

hence, for $T = const$, we get

$$\Delta H = \Delta G - T\frac{\partial \Delta G}{\partial T},$$

where we differentiate at constant p and ξ. Substituting the expression for ΔG, we get

$$\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_p - E\right]\Delta\xi.$$

The same relation must hold for the differentials, i.e.,

$$\mathrm{d}H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_p - E\right]\mathrm{d}\xi.$$

The enthalpy of reaction at constant pressure is equal to the change in the enthalpy per mole of reaction, i.e., $(\partial H/\partial \xi)_{T,p}$. Thus, the relation between the enthalpy of reaction and the potential difference of the cell has the following form:

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,p} = nF\left[T\left(\frac{\partial E}{\partial T}\right)_p - E\right].$$

Now we can substitute the data for the temperature of 0 °C ($T = 273.15$ K), which gives

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,p} = -2 \times 96485 \left(273.15 \times 4.02 \times 10^{-4} + 1.015\right) \mathrm{C\,V\,mol^{-1}}$$

$$= -217.05 \mathrm{\ kJ\,mol^{-1}}.$$

The maximum work (not related to a change in volume) which can be obtained from a reversible cell at constant temperature and pressure is equal to ΔG. The part of the enthalpy of reaction which cannot be changed into work is equal to the difference

$$\Delta H - \Delta G = T\Delta S = -T\frac{\partial \Delta G}{\partial T} = nFT\left(\frac{\partial E}{\partial T}\right)_p \Delta \xi.$$

Taking the limit of infinitesimal changes, we get, per 1 mol of reaction,

$$T\left(\frac{\partial S}{\partial \xi}\right)_{T,p} = nFT\left(\frac{\partial E}{\partial T}\right)_p = -21.19 \mathrm{\ kJ\,mol^{-1}}.$$

It is about 10 % of the enthalpy of reaction. The remaining 90 % can be used to perform work, for instance, by an electric engine. This is the maximum value, which cannot be exceeded because of limitations resulting from the laws of thermodynamics. Note, however, that the electric current obtained from the cell can be used in an electric heater, instead of performing work. Then, 100 % of the energy obtained from the chemical reaction can be changed into heat, and 10 % of that heat comes from the change in the entropy of the system, which decreases (the system gives off heat). The remaining part is the heat produced during the flow of electric current through the heater.

11.6 In the reaction, gaseous hydrogen at the pressure p_{H_2} and hydrogen ions of the activity a_{H^+} take part. The expression for the potential of the half-cell can be derived in a similar way as for a metal electrode in equilibrium with its ions (see (11.89) and (11.90)). We only have to take into account different stoichiometric coefficients and replace the activity with the ratio p_{H_2}/p^0 in the case of gaseous hydrogen, which is treated as an ideal gas. For the reaction

$$\mathrm{H}^+(aq) + e^- \rightleftharpoons \frac{1}{2}\mathrm{H}_2(g)$$
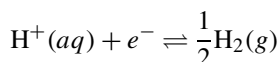
the coefficient at gaseous hydrogen amounts to $1/2$, hence

$$E_{H_2} = E_{H_2}^0 - \frac{RT}{nF} \ln \frac{(p_{H_2}/p^0)^{1/2}}{a_{H^+}},$$

where $n = 1$. In accord with the definition of the standard hydrogen electrode, we assume that $E_{H_2}^0 = 0$, hence

$$E_{H_2} = -\frac{RT}{F} \ln \frac{(p_{H_2}/p^0)^{1/2}}{a_{H^+}}.$$

If the activity of hydrogen ions is fixed, and the pressure of gaseous hydrogen changes from $p_{H_2} = p_1$ to $p_{H_2} = p_2$, then the change in E_{H_2} amounts to

$$\Delta E_{H_2} = E_{H_2}(p_2) - E_{H_2}(p_1) = \frac{RT}{2F} \ln \frac{p_1}{p_2}.$$

If the pressure is fixed, and the activity of hydrogen ions changes from $a_{H^+} = a_1$ to $a_{H^+} = a_2$, then

$$\Delta E_{H_2} = E_{H_2}(a_2) - E_{H_2}(a_1) = \frac{RT}{F} \ln \frac{a_2}{a_1}.$$

At the temperature $T = 298.15$ K, we have $RT/F = 0.0257$ V. In case (1), we get $p_1/p_2 = 9 = 3^2$, and in case (2), we get $a_2/a_1 = 3$. Thus, in both cases, we have

$$\Delta E_{H_2} = \frac{RT}{F} \ln 3 = 0.0282 \text{ V}.$$

11.7 We use expression (11.94) for the redox potential. Since the reduced form corresponds to pure zinc in the solid phase, we have $a_{Red} = a_{Zn} = 1$, hence

$$E_{Zn} = E_{Zn}^0 + \frac{RT}{2F} \ln a_{Zn^{2+}} = \left(-0.763 + \frac{1}{2} 0.0257 \times \ln 0.1 \right) \text{ V}$$
$$= -(0.763 + 0.0296) \text{ V} = -0.7926 \text{ V}.$$

11.8 Adding the reactions in the half-cells, we obtain the total cell reaction

$$\frac{1}{2} H_2(g) + AgCl(s) \rightleftharpoons Ag(s) + H^+(aq) + Cl^-(aq).$$
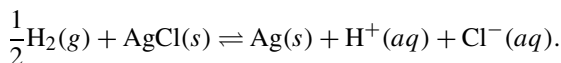
The potentials of the half-cells are given by the following expressions (see Exercise 11.6):

$$E_{H_2} = -\frac{RT}{F} \ln \frac{(p_{H_2}/p^0)^{1/2}}{a_{H^+}}$$

and

$$E_{Ag|AgCl} = E_{Ag|AgCl}^0 - \frac{RT}{F} \ln \left(\frac{a_{Ag} a_{Cl^-}}{a_{AgCl}} \right).$$

Since the activities of pure solids, a_{Ag} and a_{AgCl}, can be omitted as equal to 1, the potential of the cell amounts to

$$E = E_{Ag|AgCl}^0 - \frac{RT}{F} \ln \frac{(a_{H^+})(a_{Cl^-})}{(p_{H_2}/p^0)^{1/2}}.$$

We know that the activities of anions and cations cannot be measured separately, but only their product can be determined (see Sect. 11.1.2). Using the molality as a measure of concentration, we have $a_{H+} = \gamma_+ m_+ / m^0$, $a_{Cl-} = \gamma_- m_- / m^0$, hence

$$(a_{H+})(a_{Cl-}) = a_{HCl} = \gamma_\pm^2 (m/m^0)^2,$$

where $\gamma_\pm^2 = \gamma_+ \gamma_-$, and $m = m_+ = m_-$, as the molality of both ions is the same. For the pressure $p_{H_2} = p^0$, we can write

$$E + \frac{2RT}{F} \ln \frac{m}{m^0} = E^0_{Ag|AgCl} - \frac{2RT}{F} \ln \gamma_\pm.$$

The left-hand side of this equation contains quantities which are determined experimentally: the cell potential E and the molality m. It means that we can calculate the average activity coefficient of ions for the electrolyte, $\gamma_\pm$, provided that we know the standard potential $E^0_{Ag|AgCl}$. On the other hand, the standard potential can be determined from the measurement of the cell potential for dilute solutions. Since $\gamma_\pm \to 1$ when $m/m^0 \to 0$, the left-hand side of the equation must tend to the constant $E^0_{Ag|AgCl}$ if we extrapolate to $m = 0$.

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