

Exercises to the Textbook

“Physical Chemistry from a Different Angle”

The exercises offer in addition to the textbook the possibility to practice the different topics by working with concrete problems and help in this way to deepen the understanding.

Exercises with a higher level of difficulty are characterized by *. The exercises characterized by † are based on exercises authored by Prof. Friedrich Hermann.

In the following, exercises to the first five chapters are presented. A student manual with exercises to all chapters and detailed solutions with step-by-step explanations will be published at the end of the year.

We would be very grateful for any contributions or suggestions for corrections by the readers. Please send your comments to the following e-mail address: Regina.Rueffler@jobstiftung.de.

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1 Exercises

1.1 Introduction and First Basic Concepts

1.1.1 Molar concentration

A sample of 500 cm^3 of an aqueous solution of glucose (Glc) ($\text{C}_6\text{H}_{12}\text{O}_6$) contains 45 g of this sugar. What is the molar concentration $c(\text{Glc})$ of the solution?

Hint: The molar masses M of the considered substances are usually not given because they can be easily calculated with the help of the content formula: They correspond to the sums of the molar masses (whose numerical values are equal to the relative atomic masses) of the elements which form the compound multiplied by the corresponding content numbers. Glucose, for example, is composed of the elements carbon, hydrogen and oxygen with the molar masses of $12.0 \times 10^{-3} \text{ kg mol}^{-1}$, $1.00 \times 10^{-3} \text{ kg mol}^{-1}$ and $16.0 \times 10^{-3} \text{ kg mol}^{-1}$. The molar masses of the elements can be found in appropriate Tables or on the Internet. Finally, the molar mass of glucose results in $(6 \times 12.0 + 12 \times 1.0 + 6 \times 16.0) \times 10^{-3} \text{ kg mol}^{-1} = 180.0 \times 10^{-3} \text{ kg mol}^{-1}$.

1.1.2 Mass fraction and mole fraction

A volume of 100 mL of a saline solution (solution S) contains 15.4 g of dissolved sodium chloride at $25 \text{ }^\circ\text{C}$. Calculate the mass fraction $w(\text{NaCl})$ and the mole fraction $x(\text{NaCl})$, if the density of the saline solution is $\rho = 1.099 \text{ g mL}^{-1}$.

1.1.3 Mass fraction

Simplistically, hard liquor can be considered as a homogeneous mixture of ethanol (E) and water (W). We would like to make a “hard liquor” with a mass fraction w of 33.5 % of alcohol which corresponds to 40 percent alcohol by volume (vol%) the unit common in liquor trade. (Many varieties of vodka for example have such an alcoholic content.) For this purpose, we have 100 g of ethanol at hand. How many grams of water must be added to obtain the desired alcoholic content?

1.1.4 Composition of a gas mixture

- a) What are the molar concentration and mass concentration, $c(\text{O}_2)$ and $\beta(\text{O}_2)$, as well as the mole fraction and mass fraction, $x(\text{O}_2)$ and $w(\text{O}_2)$, of oxygen in air at standard conditions? (Air is roughly a mixture of N_2 and O_2 where 21 % of the molecules are O_2 .)

Hint: For the sake of simplicity, one should assume an amount of air of one mole and take into account that one mole of any gas, be it pure or mixed, has a volume V of approx. 24.8 L at standard conditions.

- b) How might air be expressed with the help of a content formula?

1.1.5* Converting measures of composition

In Table 1.1 in the textbook “Physical Chemistry from a Different Angle”, the relations for converting the most common measures of composition for binary mixtures of two components A and B are given. Prove that the expression

$$\frac{M_A c_B}{\rho - c_B (M_B - M_A)}$$

in the second column of the first line corresponds to x_B .

1.1.6 Description of a reaction process

The ammonia synthesis is the main industrial process for the conversion of the hardly reactive atmospheric nitrogen into usable nitrogenous compounds (such as fertilizers). We consider the formation of ammonia in a continuous-flow reactor under stationary conditions for a short while.

Conversion formula: $\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$.

Extent of conversion: $\zeta(10^{\text{h}}10^{\text{m}}) = 13 \text{ mol}$, $\zeta(10^{\text{h}}40^{\text{m}}) = 19 \text{ mol}$.

- What are the conversion numbers $\nu(\text{N}_2)$, $\nu(\text{O}_2)$ and $\nu(\text{NH}_3)$?
- Calculate the conversion $\Delta\zeta$ in the observation period.
- Calculate the changes in amount of substance and mass of all three substances in this period.

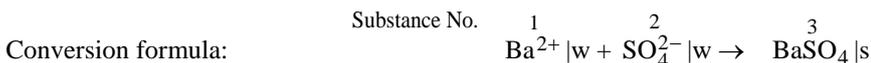
1.1.7 Application of the basic stoichiometric equation in titration

After addition of a few drops of a phenolphthalein solution to 250 mL of a sulfuric acid solution (A) of unknown concentration $c_{A,0}$, this solution is titrated with a sodium hydroxide solution (B) (concentration $c_{B,0} = 0.1 \text{ kmol m}^{-3}$) until the color of the solution changes from colorless to pink. 24.40 mL of base are required.

- Write down the conversion formula of the underlying acid-base reaction as well as the corresponding basic stoichiometric equation.
- What is the molar concentration of the sulfuric acid solution?
- Calculate the mass of H_2SO_4 (in mg) contained in the initial solution.

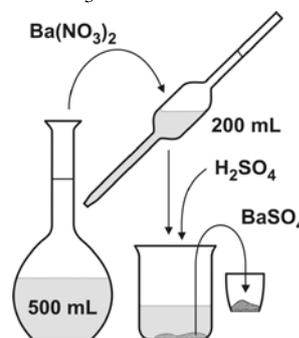
1.1.8 Application of the basic stoichiometric equation in precipitation analysis

A pipette is used to transfer a certain volume of a Ba^{2+} solution from a volumetric flask into a beaker. An excess of diluted sulfuric acid is added whereby a precipitate of slightly soluble BaSO_4 forms. This precipitate is filtered off, washed, dried and weighed; its final mass in the filter crucible is 467 mg.



Basic stoichiometric equation:
$$\Delta \zeta = \frac{\Delta n_1}{v_1} = \frac{\Delta n_2}{v_2} = \frac{\Delta n_3}{v_3}$$

- Calculate the conversion $\Delta \zeta$ in case of complete precipitation.
- Which value results for the change Δn_1 of the amount of Ba^{2+} ?
- What is the Ba^{2+} concentration c_1 of the barium nitrate solution in the volumetric flask?
- What was the amount n_1 of Ba^{2+} in the volumetric flask filled to the mark, i.e. before taking the sample?

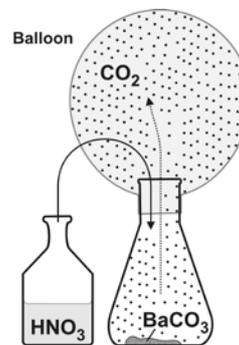


1.1.9 Basic stoichiometric equation with participation of gases

If BaCO_3 is dissolved in diluted nitric acid (to prepare, for example, the solution from Exercise 1.1.8) CO_2 is released.

- Write down the conversion formula of this process and also the basic stoichiometric equation.
- Which volume of nitric acid ($c = 2 \text{ kmol m}^{-3}$) is required at the minimum to dissolve 1 g of BaCO_3 ?
- Which volume of carbon dioxide is produced during the process (under standard conditions)?

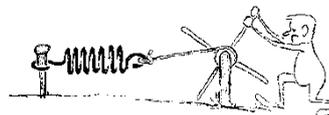
Hint: Remember that one mole of any gas has a volume of approx. 24.8 L under standard conditions.



1.2 Energy

1.2.1 Expenditure of energy for stretching a spring

A steel spring like for example the one in the picture on the right has a spring stiffness D of the order of 10^5 N m^{-1} .



- How much energy W_1 is needed to stretch the spring 10 cm from its unstretched length l_0 ?
- How much energy W_2 is needed to stretch the spring from 50 cm to 60 cm?
- A person with a mass of 50 kg hangs to the spring which is attached to the ceiling. Calculate the extension Δl of the spring.

1.2.2 Energy and change of volume (I)

The reaction between barium carbonate and diluted nitric acid mentioned in Exercise 1.1.8 takes place in an open beaker (at 25 °C and 100 kPa).

- Calculate at first the increase ΔV in volume when 20 g of carbonate are used. We imagine that the produced carbon dioxide gas drives back the air over it.

Hint: Remember that one mole of any gas, be it pure or mixed, has a volume V of approx. 24.8 L at standard conditions (25 °C, 100 kPa). Therefore, the mixing of the carbon dioxide with the air over it practically does not change the value of ΔV .

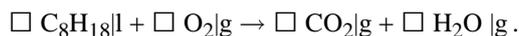
- Subsequently, determine the expenditure of energy ΔW which is necessary to make room for the produced gas. Because the stored energy decreases when the system expends energy, ΔW is negative from the point of view of the system.

Hint: Also a gas, e.g. in a cylinder with movable piston, can be considered as an elastic “body.” But there need not to be a real piston: we can imagine that the boundary between the expanding gas and the surrounding air is acting as a kind of piston.

- What could be done to make the change ΔV in volume visible?

1.2.3 Energy and change of volume (II)

Octane (C_8H_{18}), a constituent of motor fuel, is combusted under air supply and the exhaust gases are cooled down to room temperature. Calculate the energy which is exchanged between system and surroundings at standard conditions (298 K, 100 kPa) because of the change ΔV in volume. One liter of octane (density $\rho = 0.70 \text{ g cm}^{-3}$) should be used. At first, insert the conversion numbers in the following conversion formula:



Comment: For preventing the water vapor in the exhaust from condensation, the fivefold amount of (dry) air compared to that necessary for complete combustion is needed. Thereby, the volume V of the system in question changes remarkably, but not ΔV .

1.2.4 Energy of a body in motion

Starting from rest, a car with a mass of 1.5 t (1 t = 1000 kg) is accelerated on a straight road to a speed of 50 km h⁻¹.

- a) Calculate its final kinetic energy W_{kin} .
- b) How far could the car with a speed of 50 km h⁻¹ roll up a ramp without further propulsion if friction is negligible?

1.2.5 Falling without friction †

A mouse (M; $m_M = 20$ g) and an elephant (E; $m_E = 2000$ kg) jump off a bridge into water.

- a) The falling time Δt_E of the elephant is 1 s. What is its speed v_E and how much momentum h_E does it have when it reaches the water?
- b) What is the falling time Δt_M of the mouse and its speed v_M and how much momentum h_M does it have when it reaches the water?
- c) Calculate the height of the bridge (above the surface of the water).

1.2.6 Energy of a raised body †

A pumped storage hydro power station has an upper reservoir at a height h_u of 800 m and a lower reservoir at a height h_l of 400 m.

- a) The usable amount of water is 8 million cubic meters. How much energy can be stored? (The density of water is supposed to be 1 g cm⁻³.)
- b) The generators supply a power $P = W/\Delta t$ of 800 MW [1 Watt (W) = 1 J s⁻¹] at the maximum. How long will the stored energy last?

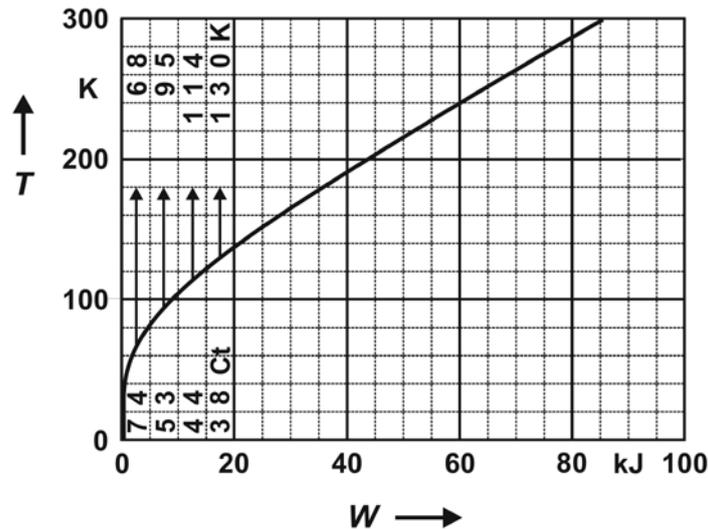
1.3 Entropy and Temperature

1.3.1 Ice calorimeter

- a) 20 g of a mixture of iron powder and sulfur powder with a mole ratio of $n_{\text{Fe}}:n_{\text{S}} = 1:1$ are placed into the test tube in the ice calorimeter of Experiment 3.5. The mixture is ignited and after the end of the reaction the produced water is collected in a graduated cylinder. The water volume V is 63 mL. (Keep in mind: A volume V_1 of 0.82 mL of melt water corresponds to an entropy S_1 of 1 Ct). Which amount of entropy S' would be generated during the reaction of $n' = 1$ mol of iron with $n' = 1$ mol of sulfur?
- b) The melting temperature of ice was determined to be 273 K with the help of the ice calorimeter (Experiment 3.6). For this purpose, the immersion heater [power $P = 1000$ W (= 1000 J s^{-1})] was turned on for a period of 27 s. Which volume V of melt water was produced?

1.3.2 Measuring the entropy content

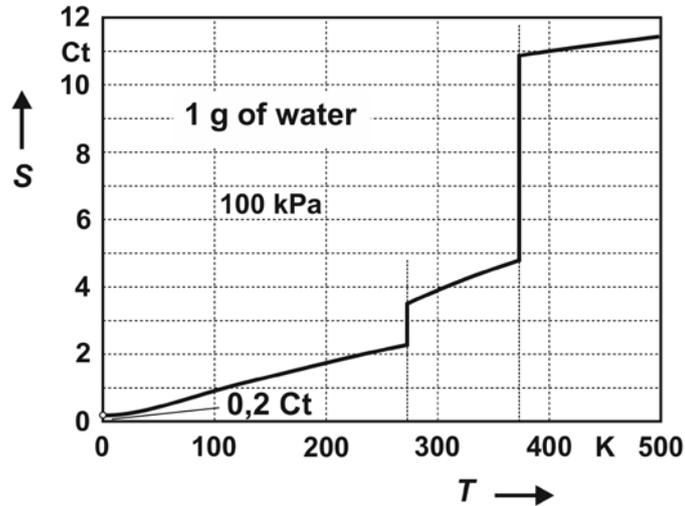
The diagram shows the heating curve for a 1 kg block of copper.



- a) As indicated, enter temperatures and entropy changes ΔS_i for every 5 kJ of energy added into the columns.
- b) How much entropy is contained in the block at 300 K in total?
- c) How much entropy is contained in it at 300 K per unit amount of substance?

1.3.3 Entropy of water

The following diagram shows the entropy of 1 g of water as a function of temperature (at constant pressure).



- What increase in entropy ΔS is needed to bring 1g of water having a temperature of 20 °C to a boil?
- What is the molar zero-point entropy $S_{0,m}$?
- What is the molar entropy of fusion $\Delta_{\text{fus}}S^\ominus$ (at standard freezing point T_{sl}^\ominus)?
- What is the molar entropy of vaporization $\Delta_{\text{vap}}S^\ominus$ (at standard boiling point T_{lg}^\ominus)?
- Explain why the values of the molar entropy of fusion and the molar entropy of vaporization differ quite strongly.

1.3.4* Entropy and entropy capacity †

The sun is shining for a period Δt of four hours on a shallow pond (p) with a surface A of 6000 m² and an average depth l of 1 m. The power density $R_{\text{in}}' = P_{\text{in}}/A$ of solar radiation, in this case referred to the pond area on which the sun is shining, is roughly 500 W m⁻².

- How much energy W_p is transferred into the pond water if only 80 % of the radiation is absorbed (efficiency $\eta_{\text{abs}} = 0.80$), while the residual is reflected?
- What is the increase in entropy of the pond water if its temperature is approximately 298 K?
- How many degrees does the temperature of the water rises? [molar entropy capacity and density of water at 298 K (and 100 kPa): $\mathcal{C}_m = 0.253 \text{ Ct mol}^{-1}\text{K}^{-1}$ and $\rho = 997 \text{ kg m}^{-3}$]

1.3.5 Heat pump †

A paddle pool is heated by a heat pump which pumps entropy from the cool ambient air ($\mathcal{G}_1 = 17^\circ\text{C}$) to the warm pool water ($\mathcal{G}_2 = 27^\circ\text{C}$). The power consumed by the heat pump is 3 kW. What is the amount of entropy S_t transferred by the heat pump in one hour from the air to the water in the ideal case?

1.3.6 Heat pump versus electrical heating †

- An (ideal) heat pump heats a house. The outdoor temperature is $\mathcal{G}_1 = 0^\circ\text{C}$ and the indoor temperature $\mathcal{G}_2 = 25^\circ\text{C}$. The heat pump transfers an amount of entropy of 30 Ct per second from outside into the house (in order to compensate the loss of entropy through the walls). What is the transferred entropy S_t and what the energy consumption W_t of the pump in one day?
- The same house is heated under otherwise identical conditions by common electric heating, i. e., the amount of entropy of 30 Ct per second necessary for compensation of entropy loss is not transferred from outside but is generated in the house. The temperature in the house should be again 25°C . How much entropy has to be generated in one day and what is the corresponding consumption of energy W_b ?

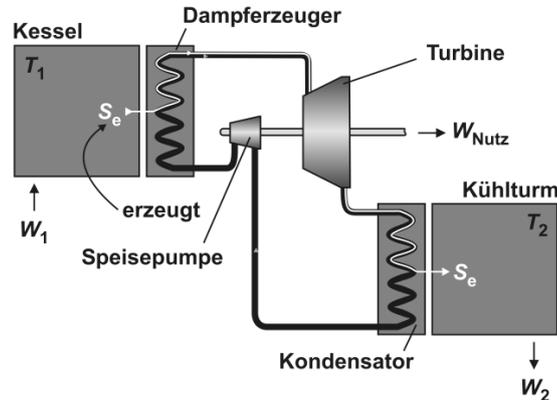
1.3.7* Thermal power plant (I)

In the common thermal power plants, the energy $W_{\text{use}} (=W_t)$ is used which can be gained during the transfer of entropy out of the steam boiler ($T_1 \approx 800\text{ K}$) into the cooling tower ($T_2 \approx 300\text{ K}$). The entropy itself is generated in the boiler by consumption of energy W_1 .

- What would be the energies W_1 and W_{use} in case of $S_g = 1\text{ Ct}$?
- Which efficiency $\eta_{\text{ideal}} = -W_{\text{use}}/W_1$ could be achieved in the ideal case?
- The actual value is $\eta_{\text{real}} \approx 40\%$.

What is the entropy S_g' which is initially generated in the firing for every kJ of gained energy? What is the entropy S_g'' which is finally released to the environment?

- From where originates the 60 % of energy losses? Which contribution is made only by the firing, which one by the rest of the plant?



1.3.8* Thermal power plant (II)

A coal-fired power plant (ambient temperature $T_a \approx 300$ K) delivers a usable energy of 1000 MJ ($W_{\text{use}} = -1000$ MJ). That is approximately the electric energy released by a big block-unit power station to the grid in one second.

- If 1 kg of hard coal (m_0) reacts with atmospheric oxygen one can gain theoretically (meaning by an efficiency of $\eta_{\text{ideal}} = 100$ %) a usable energy of approximately 35 MJ ($W_{\text{use},0} = -35$ MJ). What is the mass m_1 of coal which one has to burn in order to produce a usable energy of $W_{\text{use},0} = 1000$ MJ?
- The actual efficiency η_{real} of modern thermal power plants is approximately 40 % and the coal consumption is correspondingly higher. Calculate the mass m_2 of coal which has to be used in this case.
- Hence, 60 % of the usable energy gets already lost in the power plant for generation of entropy. Please mark the parts with a cross where the energy is mainly lost.
boiler , turbine , generator , condensor + cooling tower .
At which parts does the generated entropy leave the power plant (please mark with a cross)?
boiler , turbine , generator , condensor + cooling tower .
Through which parts is the entropy transported without an increase in its amount?
boiler , turbine , generator , condensor + cooling tower .
- How much entropy S_e is therefore finally generated (in all parts together) in the case of the supply of $W_n = 1000$ MJ?

1.3.9* Types of power plants †

A coal-fired power plant (A) and a nuclear power plant (B) release each a usable energy of 1200 MJ ($W_{\text{use}} = -1200$ MJ).

- What is the amount of entropy S_t which would need to be transferred in each case from higher temperature T_1 to lower T_2 (assuming ideal conditions)?
(Temperature T_1 at the entry of the steam turbine in the coal-fired power plant 800 K, in the nuclear power plant 550 K; Temperature T_2 , at which the entropy is released to the environment in both cases 320 K)
- How much energy W_1 would be necessary to generate this entropy in each case?
- Which efficiency $\eta_{\text{ideal}} = -W_{\text{use}}/W_1$ could ideally be achieved in a coal-fired power plant and which one in a nuclear power plant?
- What is the situation regarding generated entropy and efficiency in a hydroelectric power plant (C)?

1.3.10 Entropy generation in entropy conduction †

The heating wire of a cooking plate with a power P of 1000 W has a temperature T_1 of 1000 K.

- a) How much entropy S_e is generated in the heating wire in one second?
- b) A pot with water is placed on the cooking plate, the water temperature is $\vartheta_2 = 100$ °C. How much entropy S_e is generated along the path from the heating wire to the water?
- c) How much entropy flows in total into the water per second (assuming that no entropy is released to the environment)?

1.4 Chemical Potential

The required data are given in Table A2.1 in the Appendix of the textbook "Physical Chemistry from a Different Angle."

1.4.1 Stability of states

Using chemical potentials, decide which state of a substance is stable at standard conditions.

- a) Graphite – Diamond
- b) Rhombic sulfur – Monoclinic sulfur
- c) Solid iodine – Liquid iodine – Iodine vapor
- d) Water ice – Water – Water vapor
- e) Ethanol – Ethanol vapor

1.4.2 Predicting Reactions

Using chemical potentials, check whether the chemical drive of the following reactions is positive and if–after removal of possible inhibitions–a reaction can be expected (at standard conditions). As a first step, write the particular conversion formula down.

- a) Binding of carbon dioxide by quicklime (CaO)
- b) Combustion of ethanol vapor (while water vapor is produced)
- c) Decomposition of silver oxide into its elements
- d) Reaction of metallic silver with hydrogen sulfide

1.4.3 Dissolving Behavior

Using the chemical potentials for pure and dissolved states, estimate (in zero-order approximation) whether the following substances dissolve easily in water or not. More precise data can be obtained when mass action is taken into consideration (Chap. 6).

- | | |
|-------------------------|---------------|
| a) Cane sugar (sucrose) | b) Table salt |
| c) Limestone (calcite) | d) Oxygen |
| e) Carbon dioxide | f) Ammonia |

1.5 Influence of Temperature and Pressure on Transformations

The required data are given in Table A2.1 in the Appendix of the textbook “Physical Chemistry from a Different Angle.”

1.5.1 Temperature dependence of chemical potential and transition temperature

- Calculate the change $\Delta\mu$ in chemical potential of ethanol caused by heating it from 25 °C to 50 °C at 100 kPa.
- Which value does one obtain as a first approximation for the standard boiling temperature T_{lg}^{\ominus} of ethanol?

1.5.2 Decomposition and reaction temperatures

Calculate the decomposition temperature T_{D} or the reaction temperature T_{R} (i.e. the minimum temperature needed for the reaction) of the following processes from drive \mathcal{A}^{\ominus} and its temperature coefficient α . Formulate first the conversion formula of the corresponding process.

- Decomposition of limestone (calcite, CaCO_3) (resulting in the formation of quicklime)
- Reduction of magnetite (Fe_3O_4) with carbon (graphite) to iron thereby releasing carbon dioxide gas.

1.5.3 Pressure dependence of chemical potential

- Calculate the change in chemical potential of (liquid) water ($\beta = 18.1 \mu\text{G Pa}^{-1}$) when the pressure is increased from 100 kPa auf 200 kPa (at 298 K).
- Calculate the change in chemical potential of water vapor when the pressure is increased under the same conditions as in a). Bear in mind that water vapor has to be treated as an (ideal) gas.

1.5.4 Behavior of gases under pressure

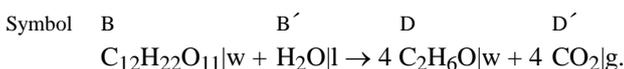
Carbon dioxide is the primary greenhouse gas emitted through human activities. Calculate the chemical of this gas at 25 °C when its pressure is decreased from 1.0 bar to 0.00039 bar, the partial pressure of CO_2 in air.

1.5.5 “Boiling pressure”

The experiments 5.3 and 5.4 demonstrate that the boiling temperature of water depends on pressure. More precisely, the lower the pressure, the lower the boiling temperature. Calculate the pressure p_{lg}^{\ominus} at which the water will already boil at room temperature (25 °C).

1.5.6 Temperature and pressure dependence of a fermentation process

Cane sugar (sucrose) can be fermented to produce alcohol (ethanol) by means of suitable yeasts (after enzymatic cleavage) and finally beverages such as rum. The conversion formula for the fermentation process in total is:



To simplify matters one uses appropriate symbols instead of the full names or formulas of the substances.

- a) Calculate first the temperature coefficient α of drive \mathcal{A}^\ominus and then the change $\Delta\mathcal{A}$ in drive when the temperature is increased from 25 °C to 50 °C. The temperature coefficient α of ethanol in aqueous solution is -148 G K^{-1} . The remaining values can be found in Table A2.1 mentioned above.
- b) Discuss the result from the point of view of matter dynamics.
- c*) If the sugar is fermented in a closed container, the pressure p will increase because of the the escape of CO_2 gas from the solution. What is the effect of an increase in pressure from 1 to 10 bar at standard temperature on the drive \mathcal{A} of the fermentation process?
- d) Discuss also this result from the point of view of matter dynamics.

1.5.7 Transition temperature and transition pressure

The chemical drive for the transition from solid rhombic sulfur (rhomb) to solid monoclinic sulfur (mono) is -75.3 G at 298 K and 100 kPa.

- a) Which modification is stable under the given conditions?
- b) The temperature coefficient α of the chemical potential of rhombic sulfur is -32.07 G K^{-1} and that of monoclinic sulfur is -33.03 G K^{-1} . Can an increase in temperature be expected to make the other modification more stable? If so, at what temperature will the phase transition occur at 100 kPa?
- c) The pressure coefficient β of the chemical potential of rhombic sulfur is $15.49 \mu\text{G Pa}^{-1}$ and that of monoclinic sulfur is $16.38 \mu\text{G Pa}^{-1}$. Can the application of pressure be expected to make the other modification more stable? If so, at what pressure will the phase transition occur at 298 K?

1.5.8* Pressure dependence of chemical potential and shift of freezing point

- a) Calculate the change in chemical potential of (liquid) water and ice (in either case at 0 °C) when the pressure is increased from 0.1 MPa to 5 MPa. In Tables we usually do not find the pressure coefficients of the substances under various conditions but their densities. The densities of water and ice at the standard melting point are 1.000 g cm^{-3} and

0.917 g cm^{-3} , respectively. Use the memory aid " $\beta = V_m = V/n$ " given in Section 5.3 for the calculation.

- b) Discuss the result from the point of view of matter dynamics.
- c) Calculate the melting point of ice under a pressure of 5 MPa. The temperature coefficient α of the chemical drive of the melting process is $+22.0 \text{ G K}^{-1}$.

1.5.9 Decomposition pressure at elevated temperature

Silver oxide (Ag_2O) is a blackish brown powder and stable under standard conditions (298 K, 100 kPa). It only decomposes completely when it is heated above the minimum temperature T_D in an *open* system (Experiment 5.2). In a *closed* (previously evacuated) glass flask, however, equilibrium is established and a specific decomposition pressure of silver oxide meaning a specific oxygen pressure $p(\text{O}_2)$ can be observed. Calculate this oxygen pressure at 400 K.