Physical-chemical practicals

T10 Dissolved oxygen

Task

1. Experimental determination of the oxygen content in water in the temperature range of $5\,^0\mathrm{C}$ until $40\,^0\mathrm{C}$.
2. Determination of Henry's constant K_{px}^{H} of the system $\mathrm{O_2\,(g)/O_2\,(aq)}$ at the measured temperatures.
3. Determination of temperature-dependent heat of solution ΔH_L of oxygen in water.

Basics

1. Oxygen is soluble in water to a small extent, the order of magnitude is 10 mg/L (what *concentration* in mol/L does this correspond to?). In thermodynamic equilibrium, the amount of dissolved oxygen in the aqueous phase depends on the partial pressure of oxygen *above* the phase and on the temperature, among other things. If the water contains salts, salinity also plays an important role (all other things being equal, sea water contains less oxygen than fresh water). In the environment, the amount of dissolved oxygen can be either lower or higher than the thermodynamic limit, since both photosynthesis and respiration play a role, albeit in opposite directions.

2. The equilibrium between the oxygen above the aqueous phase and the dissolved oxygen is described by Henry's law:

$$K_{px}^{H} = \frac{p_{O_2,\,\text{Gasphase}}}{x_{O_2,\,\text{flüssige Phase}}}. \tag{1}$$

Herein is $p_{O_2,\,\text{Gasphase}}$ the partial pressure of oxygen above the liquid phase, and $x_{O_2,\,\text{flüssige Phase}}$ is the mole fraction of oxygen in the solution. Strictly speaking, the fugacity should be used instead of the partial pressure, but the difference is negligible for oxygen. The constant K_{px}^{H} refers to the *outgassing* , not the *dissolving* of O_2. The index "px" in the constant K_{px}^{H} refers to the fact that the equilibrium pressure p above the aqueous phase and the mole fraction x of the dissolved gas in the aqueous phase (there are also other formulation options for K^{H}). In Eq.1 the pressure is usually used in the unit atm (atmosphere);
$1\,\text{atm} = 101325\,\text{Pa} = 1013,25\,\text{hPa} = 1013,25\,\text{mbar}$;
however, other pressure units can also be used.

The relative proportion of oxygen in *dry* air is 20.95%. Since the humidity fluctuates (order of magnitude 1%), the actual oxygen content of the air is lower and depends on the weather.

3. Because of the very low solubility of oxygen in water, the following applies to a very good approximation:

$$n_{H_2O} + n_{O_2} \approx n_{H_2O},$$

so that

$$x = \frac{n_{O_2}}{n_{H_2O}} = \frac{c_{O_2}}{c_{H_2O}}.$$

4. *Temperature dependence of the solution equilibrium.—* The equilibrium constant K_{px}^{H} depends on the temperature according to the van't Hoff equation as follows:

$$\frac{\mathrm{d}\ln K_{px}^{H}}{\mathrm{d}\,(1/T)} = -\frac{\Delta H_T}{R}. \tag{2}$$

Herein is ΔH_T the reaction enthalpy of the chemical reaction described by the equilibrium (according to the formulation of K_{px}^H This is the reaction enthalpy of outgassing). ΔH_T generally depends more or less on the temperature. If ΔH is practically independent of temperature, the application of $\ln K^H$ above $1/T$ a straight line with the slope $-\frac{\Delta H}{R}$, from which the reaction enthalpy can be determined. However, if ΔH from T *depends on the temperature, a curved* curve is obtained . The reaction enthalpy at a *certain* temperature is then obtained from the *tangent slope* of the curve at this temperature. Experimentally, a slightly curved curve is actually obtained for the dissolution of oxygen in water.

5. There are numerous works in the literature on the determination of the curve $\ln K_{px}^H = f(1/T)$ which are summarized in Ref. [1] and the literature cited therein. It was shown that a second degree polynomial in $1/T$ is well suited to describe the dependence of Henry's constant on the reciprocal Kelvin temperature:

$$\ln K_{px}^H = a_0 + a_1 \cdot \frac{1}{T} + a_2 \cdot \left(\frac{1}{T}\right)^2. \qquad (3)$$

The constants a_0 etc. are empirical constants; they have no theoretical significance. They are known to an accuracy of approximately 1 ppm (relative error 10^{-6}) and in Ref. [1]. The tangent slope, from which according to Eq. 2 The heat of solution can be determined from equation 3 by deriving $1/T$:

$$\frac{\mathrm{d} \ln K_{px}^H}{\mathrm{d} (1/T)} = a_1 + 2a_2 \cdot \frac{1}{T}. \qquad (4)$$

The summary of Eq. 2 and 4 results in:

$$-\frac{\Delta H_T}{R} = a_1 + 2a_2 \cdot \frac{1}{T}, \qquad (5)$$

which for each temperature within the measuring range by simply changing the corresponding size ΔH_T So if you want a certain Kelvin temperature T If you want to deter-

mine the corresponding heat of solution, you only need to T in Eq.5 and after ΔH

Please note that according to the formulation of Henry's constant K_{px}^H itself ΔH refers to the outgassing, not to the dissolution of oxygen. If you want to determine the heat of solution ΔH_L according to the first law of thermodynamics, the sign of ΔH around.

Experimental setup

The experimental setup has the following components:

1. a temperature-controlled beaker filled with distilled water with a lid provided with three openings;
2. an optical dissolved oxygen sensor (3510 IDS);
3. a thermostat to set the temperature in range 1 ^{0}C to 40 ^{0}C;
4. an electrically operated aquarium air pump (EHEIM air100, 3.5 watts, 100L/h);
5. a diffuser to disperse the air in the water;

Proceed roughly as follows:

1. The thermostat will have a starting temperature of approx. $40\,^0\mathrm{C}$ set. Heating takes about 10—15 minutes. The temperature of the thermostatted beaker is read using the oxygen sensor.
2. The protective cap of the sensor is unscrewed and the sensor is inserted through one of the two side openings of the lid until the sensor head is positioned approximately halfway up the beaker. The measuring head of the sensor should be located close to the diffuser.
3. The beaker is filled with distilled water until the metal part of the oxygen sensor is completely below the water surface.
4. The sensor measuring device is switched on. After "booting up", the device displays the temperature and the oxygen content in mg/L.
5. First, wait until thermal and chemical equilibrium has been established and the numerical value read for the oxygen content no longer changes.

6. Now the actual measurement begins. The thermostat is set to a target temperature of $5\,^0\mathrm{C}$ set. The final temperature is reached after approx. 2 hours. During this time, the following measurement data is read from the measuring device at intervals of 1—2 minutes and tabulated: temperature and oxygen concentration in mg/L.

Evaluation

1. Set the measured oxygen concentration in the unit mg/L above the temperature in the unit $^0\mathrm{C}$ graphically in a correctly labeled figure.

2. For each measured oxygen concentration, calculate the value of the logarithmic Henry's constant $K_{p,x}^H$ and the reciprocal Kelvin temperature. In the usual environmental chemistry textbooks and monographs, the external pressure is given in the unit atm (atmosphere); 1 atm = 101 325 Pa. Present this in a table. To determine K_{px}^H you need the partial pressure of oxygen in the gas phase. You noted this during the measurement. To determine the mole fraction (amount of O_2 in the amount of H_2O per liter of water - how many moles of H_2O are contained in one liter of water?) you need the density ϱ of water. This is slightly temperature dependent. In the range of $5\,^0\mathrm{C}$ until $40\,^0\mathrm{C}$ you can use the following polynomial [2] :

$$\varrho(\vartheta) = 1001.1 - 0.0867 \cdot \vartheta - 0.0035 \cdot \vartheta^2. \qquad (6)$$

In this numerical equation, the temperature ϑ in $^0\mathrm{C}$ is used, the density is given in $\mathrm{kg/m}^3 = \frac{\mathrm{g}}{\mathrm{L}}$.

3. Set the values for $\ln K_{px}^H$ graphically as a function of the reciprocal Kelvin temperature.

4. Using a quadratic polynomial fit and a suitable software (e.g. Igor Pro; MS Excel also works), determine the coefficients a_0, a_1 and a_2 from the equation 3. Attention: here the reciprocal temperature $\frac{1}{T}$, and not T, the independent variable (the variable x, so to speak).

5. Write the equations 3 and 4 with the coefficients you determined.

6. Plot the enthalpy of solution for oxygen in water in the measured temperature interval as a function of the Celsius temperature.

7. What is the heat of solution of oxygen in pure water at 25 ^{0}C? Compare the value you obtained with literature references and cite the literature correctly in your report.

8. What could be the reasons why the oxygen content in an environmental body of water deviates from the thermodynamic equilibrium value? Can supersaturation also occur?

9. **Oxygen content of Berlin waters** :

   ○ Find out about the oxygen content in mg/L of a body of water in Berlin that you have chosen and the corresponding temperature, and assign the body of water to a water quality class. Cite your sources correctly.

   ○ Calculate the thermodynamic oxygen saturation of the water. To do this, first use Eq.3 $\ln K$ for the temperature of the water body, determine the thermodynamic target value of the oxygen concentration in mg/L, and calculate from this what percentage of the target value is reached in the water body.

So you should create **three** graphics:

1. the raw data (mg(O2) vs Celsius temperature,
2. ln(K) vs 1/T
3. ΔH vs Celsius temperature.

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literature

1. BB Benson, D. Krause, Jr., MA Peterson: *The Solubility and Isotopic Fractionation of Gases in Dilute Aqueous Solution. I. Oxygen* , J SOLUTION CHEM 8 (1979), 655-690.

2. Syeilendra Pramuditya, *Water Thermodynamic Properties* , ITB Physics Department – Technical Document, [Please click here](#)

Attachment

Raw data from test measurements on November 25, 2019 are shown graphically below (Fig. 1). The oxygen saturation was between 99.5% and 99.9%. The logarithms of the Henry's constant determined from the data K_{px}^{H} are shown graphically in Figure 2.
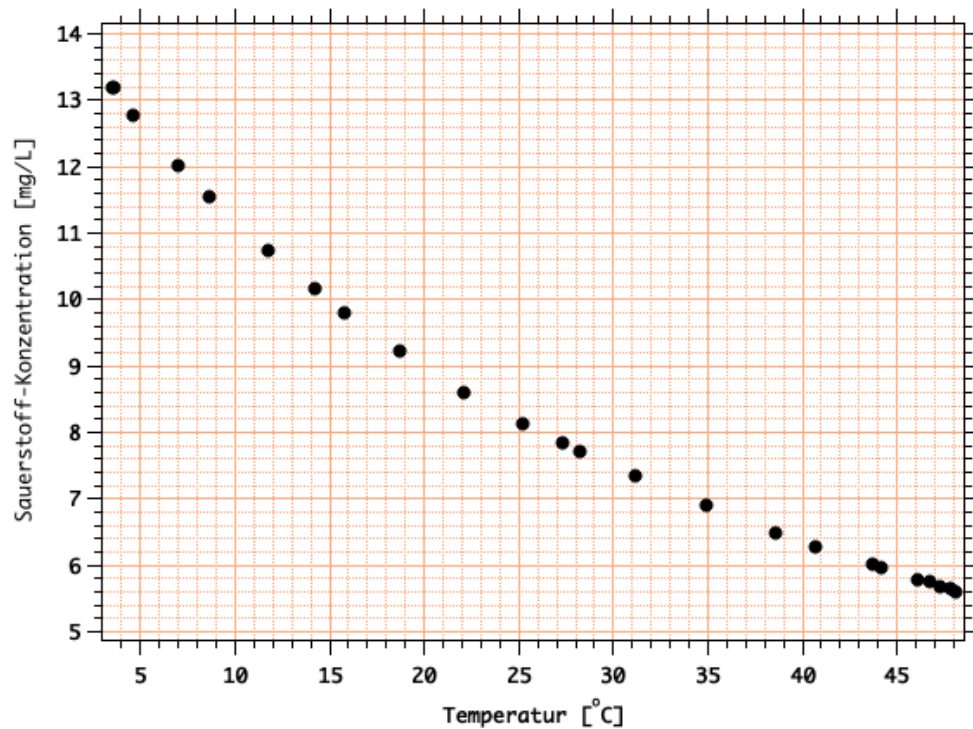

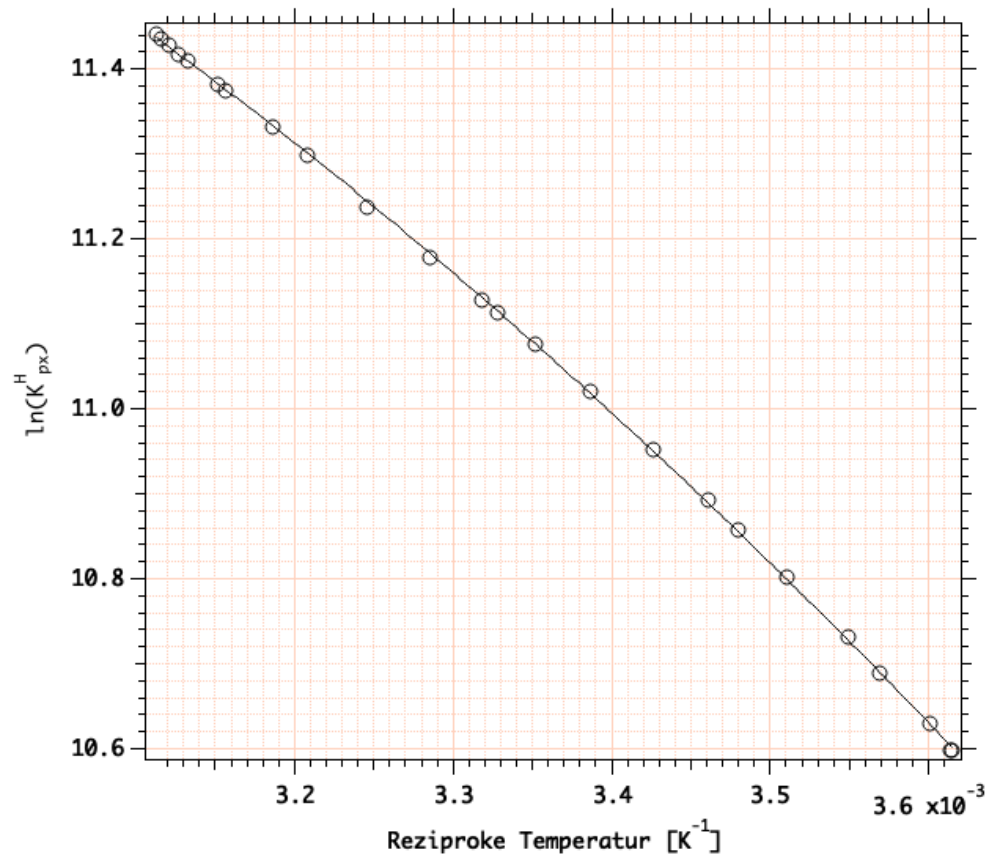**Fig. 1:** Oxygen concentration in mg/L in demineralized water as a function of temperature.

Fig. 2: Representation of the logarithmic Henry's constant K_{px}^H over the reciprocal Kelvin temperature with the data from Fig. 1. Please note the curvature of the best fit curve, which is obtained by a polynomial fit according to Eq.3was generated.

Note: the heat of solution ΔH_L is on the order of –10 to –20 kJ/mol.

Notes on error calculation: We are interested in the error in $\ln K$ and in ΔH, i.e. for $\Delta \ln K$ and $\Delta \Delta H$.

The experimentally determined $\ln K$-Values scatter around the mathematical compensation function3. Random measurement errors are the cause of this scatter. As a result, the values given in Eq.3occurring coefficients$a_0$etc. are subject to inaccuracy. Your data analysis software will give you this inaccuracy (usually as standard deviationσThis allows you to $\ln K$ an error$\Delta \ln K$indicate:

$$\Delta \ln K = \frac{\partial \ln K}{\partial a_0} \cdot \Delta a_0 + \frac{\partial \ln K}{\partial a_1} \cdot \Delta a_1 + \frac{\partial \ln K}{\partial a_2} \cdot \Delta a_2.$$

You have to calculate the partial derivatives yourself (treat the coefficients$a_i$formally like variables that you can derive from; for example, $\frac{\partial \ln K}{\partial a_1} = 1/T$), the$\Delta a_i$The analysis software provides you with this information. The error can also

beΔHcalculated from the standard deviations of the coefficients:

$$\Delta\Delta H = \frac{\partial \Delta H}{\partial a_1} \cdot \Delta a_1 + \frac{\partial \Delta H}{\partial a_2} \cdot \Delta a_2.$$

A systematic analysis of the errors in the <u>measured</u> variables is therefore not necessary.

Notes on taking logarithms: For data analysis, the Henry's constant must be taken as a logarithm. If a quantity that$n$ significant digits, the logarithm of the size must be placed <u>after</u> the decimal separator (point or comma)$n$digits. The digits *before* the decimal separator only correspond to the order of magnitude of the original numerical value and have nothing to do with the accuracy.

Example:

$Z = 1,723 \rightarrow \log Z = 0,2363$

$Z = 17,23 \rightarrow \log Z = 1,2363$

$Z = 172,3 \rightarrow \log Z = 2,2363$

$Z = 1723\ \ \rightarrow \log Z = 3,2363$

For the natural logarithm ($\ln$) the same applies as for the decimal logarithm ($\log$).

Authors and revisions:

1. Bunkowski (01/2020): Bachelor thesis, preliminary version of the scripts
2. Flesch (01/2020): LaTeX version
3. Demirkaya (01/2021): Migration from LaTeX to html/MathJax
4. Flesch (12.03.2021): Addition of Fig. 2; reference to units ofK_{px}^{H}; minor corrections and additions.
5. Flesch (31.03.2021): Corrections and additions.
6. Flesch (17.08.2021): Corrections, notes on error calculation.
7. Flesch (07.03.2022): Changes in the experimental part (pump)