3.1 Preparation of a saturated sodium chloride solution

To 100 mL of water add 50 g of ground sodium chloride until no more salt dissolves. Determine the added mass by weighing back the remaining portion. How much salt does a liter of saturated sodium chloride solution contain? The dissolved mass of NaCl in 100 mL of water and the calculated mass concentration (in g / L) of the resulting solution will be checked.

3.2 Dummy chapter

3.3 Separation of three precipitates from the solution

First, prepare the precipitations. Fill 3 beakers with 100 mL of water. Add 5 mL each of the following salts to the water.

Beaker 1: Calcium chloride ($CaCl_2$) und sodium carbonate (Na_2CO_3)

Beaker 2: Barium chloride ($BaCl_2$) und Pottassium chromate (K_2CrO_4)

Beaker 3: Ferric chloride ($FeCl_3$) und sodium hydroxide (NaOH)

The solutions can be prepared by adding a spatula tip of the corresponding salt to 5 mL of water in a test tube.

When carrying out this experiment, ensure that no chromatic waste is poured into the drain! Those must be placed in the container for poisonous aqueous liquids.

Characterize the resulting precipitates. Try to separate the corresponding precipitate from the solvent by decantation, filtration, centrifugation and suction filtration. To do this, divide the three solutions into four equal parts. Please compare the separation procedures for their suitability for the individual precipitate. Display your results in the form of a table. Divide the results into suitable (+), conditionally suitable (O) and not suitable (-). Explain the classification. Give the reaction equations for the precipitation reactions.

Decanting

Allow the liquid to stand in a quiet place with the precipitate for some time. By tilting the vessel, the liquid above the sediment is then discharged (decanted). With some practice, this can be done with ordinary beakers or by Erlenmeyer flasks which have been previously placed tilted. A simple pouring tool for decanting without liquid loss, especially for quantitative purposes, is a glass stirring rod, which is held on the vessel edge, where the liquid can flow off.

Filtration

When doing a filtration, the precipitate quantity, the liquid volume and the assignment must be taken into account.

When small amounts of solid substance have to be isolated from a large quantity of liquid or when separation is quantitative, a filter of as small as possible size should be used in order to concentrate a precipitate on a small space.

However, if small amounts of solid substances are to be removed from a solution in which only the liquid is to be further processed, the filter will be adapted to the liquid volume, i.e. if the liquid volume is large, a filter with a large surface area should be used, For example, fluted filters, in order to be able to filter as quickly as possible.

In the laboratory a glass funnel with inserted paper filter is used. The customary filter papers are produced in various sizes and with different pore size (2 bis 6 μm). These round filters are folded and inserted into the funnel so that the inner edge of the funnel remains uncovered (s. Fig. 3.2). Before filtering, moisten the paper filter and press it to the funnel wall.

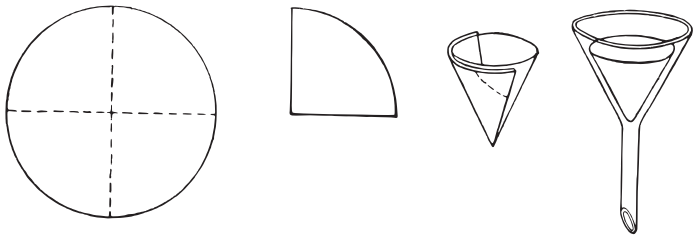

Abb. 3.2: Folding of paper filters

The suction effect of the filtrate can be increased by the lengthening of the liquid column under the filter. This is the case with Jena analytical funnels specially designed for rapid filtration. In this case, the funnel angle is also exactly 60°, so that the round filter paper can fit tightly on the top. Their lower part is mostly free, because of a cavity inside the glass funnel, through which the filtrate can flow quickly.

Zentrifugation

An electrical laboratory centrifuge is available in the lab. It is an angular centrifuge. Glasses are arranged rigidly at a fixed angle with respect to the rotor axis. The precipitate does not accumulate exactly in the tip, which is a disadvantage at small amount of precipitate.

Handle the electric centrifuges carefully. As a counterbalance use another centrifuge glass filled with water. The weight has to be exactly the same and has to be set by weighing. The same filling height is not sufficient, since the contents can have different densities.

Allow the centrifuge to run out: the precipitate is stirred up by too fast deceleration. The mixture is centrifuged for about one to two minutes. If the precipitate settles well, the liquid is carefully sucked off with a long dripping pipette.

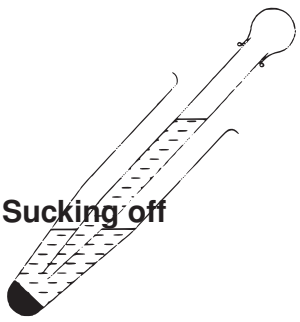

Abb. 3.3: Pipetting the supernatant

Sucking off is a filtration with a Büchner funnel. This porcelain nutsch filter is placed with a with rubber cone onto a feeding bottle, which can be evacuated by a water jet pump. The vacuum created by the suction of the air below the filter accelerates the filtration. For filtration, place a suitable paper filter (located in the shelf with chemicals) flat on the perforated base plate of the Büchner funnel. The filter is moistened and sucked in by switching on the water jet pump, before the filtered liquid with the precipitate is poured in.

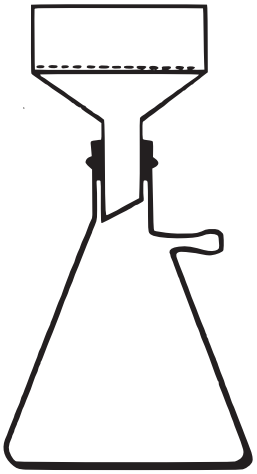

Abb. 3.4: sucking flask with suction strainer

3.4 Distillation of two binary mixtures (T)

Equipment to be supplied: Distillation apparatus, Oilbath, Heating plate, elevating platform.

You should study the boiling behavior of two mixtures:

a) Unknown mixture of 2 substances (please give a 500 mL round-bottomed flask with cork ring labeled with name, place and experiment number to G105 the day before the distillation)

b) A mixture of 80 g of cyclohexane and 20 g of 1-propanol. This mixture you produce you yourself.

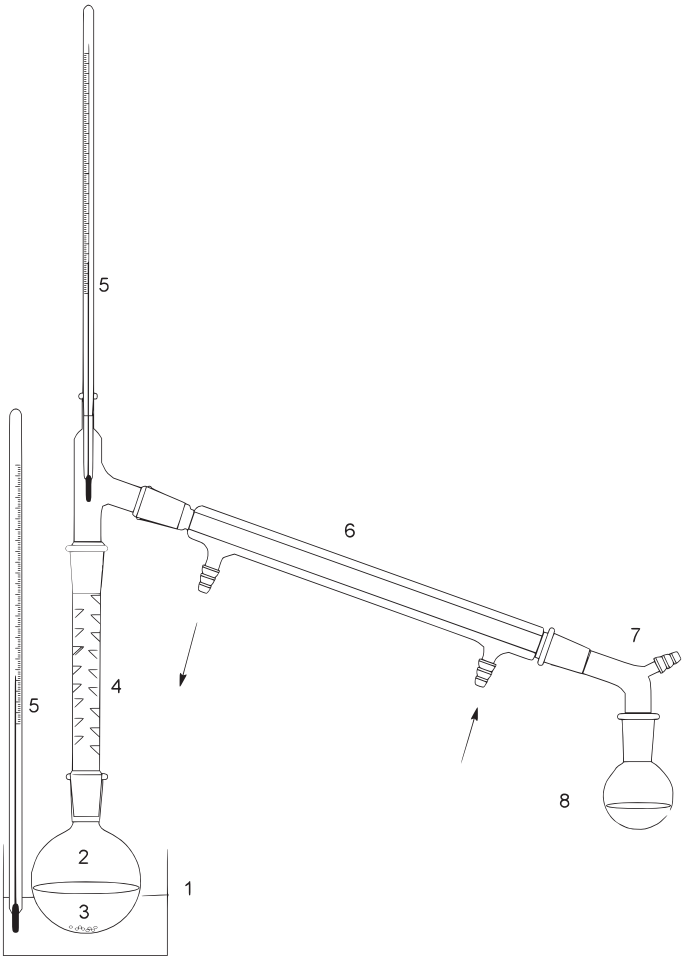

Abb. 3.5: Die aufzubauende Destillationsapparatur: 1: heating bath, 2: Distillation flask, 3: boiling chips, 4: Vigreux column, 5: Thermometer, 6: Liebig cooler, 7: Vakuum feed, 8: receiver

First, install the distillation apparatus. Put only very little grease on the ground joints. The grease dissolves in many organic solvents and can contaminate the distillate. The parts not included in your equipment can be found in the equipment output (G105). The cooling water hoses are connected to the Liebig cooler so that the water flows from the bottom to the top.

To measure the boiling temperature, a thermometer is installed in the distillation bridge. Its mercury tip is to be completely washed by the vapors of the passing substances. In order to avoid boiling retardations, some boiling stones are placed in the distillation flask before heating the distillation. These work only once: after cooling the mixture below the boiling point, new stones have to be added.

Before start of the distillation apparatus up, it must be checked by an assistant and launch must be authorized! The authorization is signed on the front plate of the fume hood.

Distill slowly, write down the temperatures and times

Fill the mixture to be distilled into the distillation flask and heat it with an oil bath (aluminum pan, hot plate) for weak boiling (2 to 4 drops of distillate per second, carefully

control the heating power). From the beginning of the experiment, the temperatures of steam and oil bath are read and recorded at regular intervals6. The distillation is continued until about three quarters of the liquid has passed.

change receiver

You should collect the substances separately: If about one third of the liquid is distilled, remove the receiver (Fig. 3.5, part 8) and fill the collected liquid in a beaker. Then reload the receiver and continue distilling. When the 2nd liquid arrives, recognizable by the changed steam temperature, wait a few more minutes and change the receiver again, in order to catch the second fraction.

What can be said about the boiling behavior of the mixtures? What boiling points do you observe? Can the substances be separated by distillation? Use the boiling points to determine the two components of the unknown mixture (see table7, consider the pressure dependency of the boiling point). You can use other characteristic properties of the components such as miscibility, smell, density and color. Compare with the possible pure substances.

What is your observation at b)? Record the measured temperatures of steam and oil bath in a plot against the time.

3.5 Adsorption on activated carbon

Add 3 to 4 drops of a solution of methylene blue (on the solution rack) to about 3 mL water in a test tube. Look for the color. Then add 2 spatula tips of activated charcoal and shake. After approximately half a minute, use a round filter in the glass funnel to filter of the solids. Did the look of the liquid change?

3.6 Adsorption chromatography (column chromatography)

A chromatography tube is first clogged with some glass wool at the lower end. In this case, the glass wool layer should have a surface which is as flat as possible, without threads extending upwards. The column is then filled with alumina for chromatography. The following method has proved successful:

1. Fill the column so far with ethanol that the liquid ends just below the tube of the funnel.
2. Slowly pour alumina through a (dry!) funnel into the ethanol until a layer about 2 - 3 cm thickness is formed. Gently tap the tube from the side to reach a tight pack and avoid air bubbles.
3. Place some sea sand in the column until a few millimeters high sand layer on the Alumina is produced.
4. Drain the ethanol until the upper limit of the liquid has sunk into the sand.

Place 10 drops of alcoholic mixed-indicator solution (provided on the solution rack) on the top of the filling. Then, carefully add ethanol and open the tap at the bottom of the column so that the differently colored zones will pass through the alumina column and continue to separate. When the first approx. 5 mL have passed through, you can fill the column up to the top, then the ethanol runs somewhat faster by the hydrostatic pressure. After separating and collecting the first fraction (blue zone), acidified ethanol with 1% by volume of acetic acid is used as the solvent. In this way, the yellow zone can also be eluted.

Check whether the color of the separated dyes changes with the pH in aqueous solution.

3.7 Shaking iodine with an organic solvent

Add 20 mL H_2O, about 20 drops of iodine-potassium iodide solution and 5 mL of chloroform in a separation funnel. After a short shake (hold stopper), the diverting funnel is held up with the tap and the overpressure caused by shaking is drained by carefully opening the tap. Then the separation funnel is placed in a ring, which is attached to a rod, and then the chloroform layer (bottom) passes through the stop cock into a test tube. The shaking is repeated several times with fresh chloroform (about 5 mL). A few drops of the aqueous layer are taken off between the shaking and the solution is checked for iodine with a starch solution. Does the color of the collected chloroform change?

3.8 partition chromatography (paper chromatography)

Equipment to be supplied: Capillary tubes (consumables)

In paper chromatography, the distribution of the components of a mixture between a mobile phase and the water (stationary phase) adsorbed on the cellulose fibers of the paper is utilized. The eluent (solvent) you make by yourself. For this purpose, 5 volumes of n-butanol are shaken with 1 volume fraction of 12% hydrochloric acid. If 2 phases are formed in the separating funnel, drain the lower (aqueous) one and use the upper butanol phase. The 12% hydrochloric acid is obtained by diluting a small amount of the concentrated hydrochloric acid (36%) with twice the amount of water (in the fume hood!).

Draw around the center of a round filter a circle of1,5 cm in diameter. Using a capillary, add 1 drop of 3 solutions to the circumference of this circle at an angular distance of 120° (i. e. uniformly distributed): a 3% solution of mercury (II) chloride, a 6% copper (II) chloride solution (the solutions are located on the small shelf) and a mixture (1:1) of the two solutions. Mark the three application points with pencil12 and carefully dry the drip points with a blow dryer without heating the paper too much.

Punch a hole in the middle of the filter and insert a filter paper roll (wick) through the hole. Place the whole unit on a porcelain dish with the solvent so that the wick immerses in the solvent. Cover the upper side of the paper with a matching watch glass. Just before the solvent front reaches the periphery edge of the paper filter14, remove it and dry again with the blow dryer. Then spray the filter paper with a small amount of the sodium sulfide solution (also in the fume hood!).

If you have done everything right, you should see that two spots have arisen from the spot of the mixture. The other two spots allow their identification15. Which compound goes faster? Sketch what you see after the chromatography on the filter.

3.9 Separation of ions using an ion exchanger

Equipment to be supplied: Granulated ion exchanger

One method for separating ions from aqueous solution is the fixing of ions on the ion exchangers. As such, strongly crosslinked organic resins are used which contain acid or basic groups in their chains. On the acidic groups, cations can be fixed, for which H^+ ions enter into the solution. Anions can be exchanged for OH^- ions at the basic groups. The ion exchangers can be regenerated with strong acids or bases, since the strong excess of H^+ or OH^- ions again replaces the foreign ions. .

For this experiment, a detection method for Ca^{2+} ions in aqueous solution is required. This is done with ammonium oxalate, ($(NH_4)_2C_2O_4$) which forms a white precipitate with Ca^{2+} ions in an alkaline environment. Therefore, the pH of the solution must be checked before the testing and, if necessary, ammonium hydroxide solution (ammonia water) should be added until the pH value exceeds 7.

Fill the chromatography tube with approx. 1 cm of glass wool16 and then the ion exchanger with enough distilled water so that the resin is completely covered with water. The ion exchanger is stored under water and given to you in a beaker (bring the beaker to the equipment output!) and can be poured into the chromatography column, if you fill it in advance. You can then drain the excess water at the stop cock.

Understand this experiment completely before performing it! The individual steps are:

1. Carry out the detection reaction (blank test)
2. Check the ion exchanger for Ca^{2+} ions
3. Remove the Ca^{2+} ions from the solution using the ion exchanger
4. Test whether the ions have been removed from the solution.
5. Regenerate the ion exchanger (release of the Ca^{2+} ions)
6. Detect the ions in the regeneration liquid

Prepare approximately 20 mL of $CaCl_2$ solution from a small spatula tip $CaCl_2$ and water and check, in a small sample of it, for the Ca^{2+} ions with a previously prepared solution of $(NH_4)_2C_2O_4$. (This is called blank test.)

Add approximately 10 mL of half-concentrated hydrochloric acid (18%) to the ion exchanger and rinse with distilled water. You should rinse until the pH value of the eluate is higher than 5.

Capture the eluate18 and make a small sample of it alkaline by adding sufficient ammonia water (pH > 7). Then test it for Ca^{2+} ions.

Add 10 mL of the $CaCl_2$ solution to the column filled with an ion exchanger and rinse with about twice the amount of distilled water. The eluates are collected. Check the small samples of the eluates for $CaCl_2$ ions.

Finally, regenerate the ion exchanger with half-concentrated hydrochloric acid, trap the eluate and test again for Ca^{2+} ions. Finally, the ion exchanger is rinsed with distilled water until the neutral reaction of the indicator paper (pH $\geq$ 6 is sufficient).

Explain your observations in your lab journal.

3.10 Sublimation

Heat a spatula tip of NH_4Cl or I_2 carefully in an Erlenmeyer flask over a Bunsen burner and ceramic net (in the fume hood!). Mount a test tube filled with ice water in the Erlenmeyer flask so that it is shortly above the substance to be sublimed in the Erlenmeyer flask.

What happens on the outside of the test tube?

3.11 Purification of an unknown substance by recrystallization (T)

Equipment to be supplied: Thiele apparatus with the melting point determination tubes

Give a small glass beaker labeled with the name, experiment number, and place number in G105 to obtain a sample of unknown substance.

Determine the melting point of the presumed contaminated substance with the Thiele apparatus. To do this, fill some substance (about 1 cm) in a melting point tube and place in one of the lateral openings of the Thiele apparatus so that the closed end of the substance is immersed in the oil. Then crystallize the substance. For this purpose, a part of the given sample is heated to boiling with so much solvent in the beaker that the substance is completely dissolved. Start with little solvent! On cooling, the solute precipitates again if you have not taken too much solvent. The solid is then separated from the solvent by filtration or suction. The substance is then completely dried by drying in a drying cabinet, and the melting point is determined again.

Identify the substance on the basis of the melting point found and the outgoing table. If you are unsure, check your guess by a mixed melting point.

You will get an certificate for the identified unknown substance and the measured melting points.

4 Properties of atoms and molecules

The spatial structure of matter can be determined by complicated instruments for measuring the scattering of X-rays, neutrons or electrons. With extensive investigations of this type the size and shape of many molecules have been determined very precisely. It is also possible to determine the size of molecules by very simple methods, which can be carried out as part of a beginners' course. (Experiment 4.1)

The absolute energy content of an atom or molecule is of little interest to the chemist. Much more interesting is the question of which energy quantities (energy quanta) can absorb or release such a particle. In addition to the kinetic energy of the particle as a whole, atoms and molecules can occur only in very definite,

discrete states. see Fig. 4.1.

The state of lowest energy is called the ground state E_0. Above this are the excited states E_i mit $i = 1, 2, 3, \ldots$ The corresponding energy level scheme is characteristic for each atomic or molecular species and is therefore a unique recognition feature. The relative position of the energy levels of an atom or molecule is obtained quantitatively by measuring the corresponding energy differences ΔE_{ij} between the energey levels i und j This can be done in two ways:

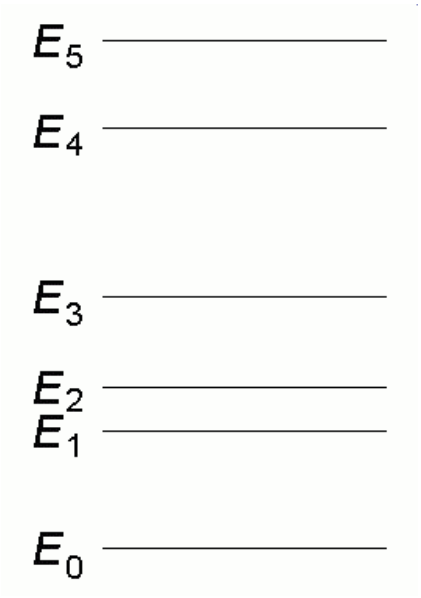

Abb. 4.1: Possible energetic states of a molecule

(a) The particles to be investigated are, for example by collisions, at elevated temperatures brought in excited states. The return to lower states then occurs with the emission of light quanta (photons) whose energy content E_{Photon} is exactly equal to ΔE_{ij}. This energy difference is emitted as light (light emission spectroscopy). The emitted light colors are called spectral lines.

(b) Photons of known energy are used as a measuring probe when the particles to be examined are irradiated with them. If the energy E_{Photon} of the photons coincide exactly with a difference ΔE_{ij}, they are absorbed with a certain probability, depending from the atoms or molecules. The incident light intensity will thus reduced at certain wavelengths (absorption spectroscopy).

The energy of the photons is calculated from the frequency ν and the wavelength λ of the light via the Einstein relation

$$E_{\text{Photon}} = h\nu = \frac{hc}{\lambda} \quad , \tag{4.1}$$

where h is is the Planck constant and c the speed of light in vacuum. The determination of the relative energy emitted by an atomic or molecular species is thus attributed to the experimental determination of the wavelength of light. It is carried out with spectroscopes or spectrophotometers, the schematic diagram of which is shown in Fig. 4.2.

The light of a light source Q illuminates the entry slit S, which lies in the focal plane of a lens L1. The light beam made parallel by this lens followed by refraction by a prism P, the stronger the shorter the wavelength of the light.

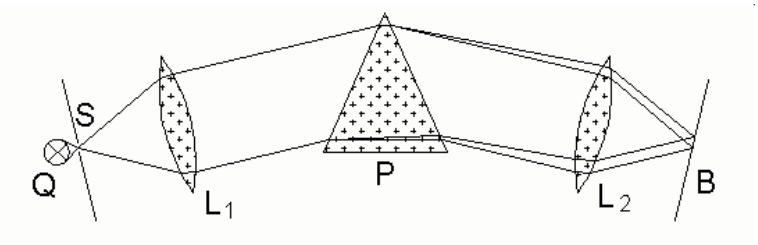

Abb. 4.2: Beam path in the spectroscope

A next lens L2 finally focuses the light beams of different wavelengths spatially separated from one another. The colored images of the entrance slit formed in the focal plane B of the lens L2 can then be observed in two ways:

In the spectroscope a ground glass screen and behind a magnifying glass sitting in the focal plane B of the lens L2 (eyepiece), with which the various slit images on the ground glass are observed as lines. They are the sharper the narrower the entrance slit, but, on the other hand, the wider the slit has been set, the brighter lines are. The slit width should be optimized so that closely spaced lines can be distinguishable even and the faintest lines are still visible. The wavelength of the light can be read on a mirrored scale. The scale, which can be shifted with an adjusting screw, is calibrated with light of known wavelength. In the hand-held spectroscope used here, the sodium D line is marked at 589 nm.

In the spectrophotometer, an exit slit located in the focal plane B of the lens L2 has a shape of the slit image. The prism P is arranged turnable about an axis perpendicular to the drawing plane. For each angle the slit image of only the certain wavelength is imaged on the exit slit. The intensity I_0 of the transmitted light can thus be measured as a function of the wavelength λ with a suitable detector behind the exit slit. The wavelength calibration is already carried out by the equipment manufacturer.

If, in addition to the intensity I_0 without a sample in the beam path, the light intensity I when the sample to be examined is located between the light source and the entrance slit or between the output gap and the detector, the following relationship known as Lambert-Beer's law is valid:

$$E = \lg \frac{I_0}{I} = \epsilon c l \tag{4.2}$$

Where E is the absorbance (optical density), c is the concentration of the sample, l is the path length, and ϵ is the decadic extinction coefficient. Since E is unit-free, ϵ must have the units of $c^{-1} \cdot l^{-1}$, that is, L mol^{-1} cm^{-1}. The quantities E, I_0, I und ϵ depend on the wavelength. Value ϵ is the probability that an atom or molecule will transfer from a lower energy state to an excited state when a „matching" photon ($E_{\text{Photon}} = \Delta E_{ij}$) is offered. If E is measured for a sample of known concentration, an unknown concentration of the same sample can be determined by measuring the corresponding absorbance value by keeping λ constant.

4.1 Size of stearic acid molecules

Equipment to be supplied: 10-mL-Burette, plastic tub, stearic acid solution

The area F_S of a single molecule in the film and the length d (= thickness of the stearic acid film) are determined from the area F_G and the mass m of a monomolecular stearic acid film.

A monomolecular film is formed when a suitable volume V of a stearic acid solution having a well-known mass concentration c_m is dropped onto a water surface and the solvent evaporates. The stearic acid molecules remaining on the water surface have a polar (hydrophilic, water-attractive) end on a long non-polar hydrocarbon chain (hydrophobic, water-repellent). One can say it is amphiphilic. The molecules dip into the water surface with their polar carboxyl groups; the non-polar hydrocarbon chains are forced out of the water.

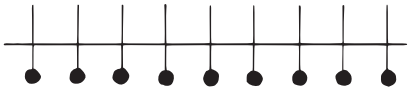

Abb. 4.3: The molecules of stearic acid on water surface

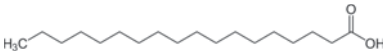

Abb. 4.4: Stearic acid molecule

The burette is mounted on a stand with a burette holder so that there is enough room below it for the plastic wall. The stearic acid solution must be treated with a jar in the burette should be filled with the stearic acid solution by wash bottle so that the concentration change due to evaporation of heptane remains as low as possible.

The volume of stearic acid solution required for monomolecular coverage is added dropwise to the water surface via a 10 mL burette, counting the number of drops.5 The volume of a single drop can be determined by adding a sufficient number of drops (about 50 - 100) of the stearic acid solution into a vessel and read off the corresponding volume change at the burette. This measurement should be repeated three times; the result is arithmetically averaged.

The well-cleaned tub is filled up to the mark with dist. Water and placed under the burette so that the drops drop to the center of the water surface. Die gut gereinigte Wanne wird bis zur Markierung mit dest. Wasser gefüllt und so unter die Bürette gestellt, dass die Tropfen etwa auf die Mitte der Wasseroberfläche fallen.

Keep the beaker under the burette and adjust the dripping rate to approximately 10 drops per minute. Then pull the beaker between 2 drops. Now count the drops spreading on the water surface. If the solution no longer spreads well on the surface of the water in the bath, only single drops should be added. The surface is completely covered when a round droplet is left on the place where the droplets touch the water for at least one minute.

The „area“ of a stearic acid molecule, that is, the space occupied by a molecule on the water surface, and the thickness of the film, which is equivalent to the length of a stearic acid molecule as shown in 4.3.

In the calculation of the area, it is assumed that the stearic acid molecules lie densely packed on the surface, that is, there are no gaps between the individual molecules. The molecules on the surface share the total area F_G of the bath. The area F_S of a molecule is the ratio of the total area F_G and the number of the stearic acid molecules N_S.

$$F_S = \frac{F_G}{N_S} \tag{4.3}$$

N_S is obtained from the molar amount n and the Avogadro's number N_A

$$N_S = n \cdot N_A \tag{4.4}$$

After substituting Eq. 4.4 in Eq. 4.3 one gets

$$F_S = \frac{F_G}{nN_A} \tag{4.5}$$

The molar amount of stearic acid n is still not calculated. The volume V_L of the dripped solution is known. The relationship $m = V_L \cdot c_m$between the dropped mass of the stearic acid m, the mass concentration c_m of the solution and the dripped volume V_L, mass m, molar amount n and molar mass M of the stearic acid are related in the proportion $m = n \cdot M$,

$$F_S = \frac{F_G}{n \cdot N_A} = \frac{MF_G}{mN_A} = \frac{MF_G}{V_L c_m N_A} \tag{4.6}$$

The thickness of the film is obtained by dividing ts volume V_F by the area

$$d = \frac{V_F}{F_G} \tag{4.7}$$

V_F can be obtained from the mass and density of the film

$$V_F = \frac{m}{\rho} \tag{4.8}$$

When Eq. 4.8 is substituted in Gl. 4.7 the thickness of the film is obtained

$$d = \frac{V_F}{F_G} = \frac{m}{\rho F_G} \tag{4.9}$$

Density $\rho = 0,838\,\mathrm{g/mL}$ and molar Mass $M = 284,5\,\mathrm{g/mol}$ of the Stearic acid are also required for the calculation.

Calculate the length and the „area requirement" of a stearic acid molecule! Then you will receive the Testat.

4.2 A simple spectral analysis (T)

Supplied equipment: Hand-held spectroscope, possibly Jander-Blasius

Using the hand-held spectroscope, determine which of the elements Li, Na, K, Ca, Sr and Ba are present in the test sample (maximum three are present). For this purpose, you first examine the above mentioned salts of the pure alkali and alkaline earth metals (Use chlorides or nitrates) , learn to use the hand-held spectroscope, and compare your observations with literature values from tables in textbooks (e.g. in the Jander-Blasius, appendix, available in the device output). In order to be able to investigate really pure substances, place the sample in the flame of the Bunsen burner, where individual atoms or ions are separated and excited by an addition of the thermal energy to salt crystals. Of course, you will not only see the emission of the sample in the spectroscope, but also that of the flame itself: a continuous spectrum, such as you can observe in a rainbow.

In detail, you should proceed as follows:

- To carry out the experiment, you should select a dark fume hood away from the windows as far as possible and switch off the lighting of the fume hood.
- A magnesia rod is carefully annealed in the colourless flame of a Bunsen burner. For this purpose, the magnesia rod is dipped from time to time into a small beaker containing concentrated hydrochloric acid until the glowing magnesia rod no longer colors the flame.
- The still hot, annealed magnesia rod is pressed into a part of the sample to peak up some granules.
- The rod thus prepared is held in the hottest part of the burner flame, which is watched by the hand-held spectroscope.

Sodium salts is present as an impurity in all samples, in the hydrochloric acid solution and in the burner. Therefore, the sodium detection is only positive if the yellow coloring of the flame remains long and it is very intensively visible. With its very intensive emission, sodium contamination brings another problem: sometimes it outshines in the hand-held spectroscope the emission of other elements, especially the very weak one of potassium. Here, a cobalt glass filter serves to solve it by absorbing yellow light and lets red one passes through. In general, it is recommended to direct the spectroscope with a stand to the flame, since some flame colours occur only for one second.

Write your assumption which substances are contained in the sample, in your laboratory book and ask an assistant to check it.

4.3 The Lambert-Beer Law(T)

Supplied equipment: optical cuvette

The spectrophotometer must be switched on 30 minutes before use. At the initial setting, proceed as follows:

- Adjust the measuring wavelength to 525 nm (absorption maximum of the permanganate ion) with the arrow keys and keep it unchanged during the whole experiment
- A carefully cleaned cuvette (several times rinsed with water) is filled with water and introduced into the cell holder. The liquid must be free of bubbles.
- The reading is set to is zero with the ZERO button.

Potassium permanganate

To check the Lambert-Beerschen law (Equation 4.2), a freshly prepared aqueous solution of potassium permanganate is required. For this purpose about 8 to 10 mg KMnO4 are weighed in (at analytical balance in Room G105) and dissolved in about 150 ml of water in an Erlenmeyer flask. This is the so-called stock solution with the concentration c_0

For the measurements use the same cell, which used during calibration. You are intended to measure solutions with the concentrations given in Table 4.1.

You prepare them by dilution from the stock solution with the concentration c_0. You can obtain good results you use a burette to measure the volume of stock solution. Put it into a volumetric flask and then fill up the flask to the calibration mark.

c (as fraction)	c (Decimal)
c_0	$1.00 \cdot c_0$
$3c_0/4$	$0.750 \cdot c_0$
$2c_0/3$	$0.667 \cdot c_0$
$c_0/2$	$0.500 \cdot c_0$
$c_0/3$	$0.333 \cdot c_0$
$c_0/4$	$0.250 \cdot c_0$
$c_0/6$	$0.167 \cdot c_0$
$c_0/8$	$0.125 \cdot c_0$
$c_0/10$	$0.100 \cdot c_0$

Tab. 4.1: Concentrations of $KMnO_4$,

The nine solutions are measured successively, starting with the smallest concentration. After the cuvette has been inserted (note the marking), the optical density can be read directly on the device. After each measurement clean the cuvette and dry. Rinse the dry cuvette twice with the solution to be measured before measuring.

Write down a table of measured values of optical density and concentration. Draw plot of optical density against the concentration. You will get the Testat for a table of measured values of optical density and concentration.

Unknown dye solution

Determine the concentration of the dye solution. The wave length to be set and the extinction coefficient are given for the solution. (Methylene blue, $\epsilon_{665\text{nm}} = 7,15 \cdot 10^4\,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$). Set the specified wavelength at the spectrophotometer. Further, you need the pathlength l of the cell: this is 1 cm.

Prepare two dye solutions with concentrations by diluting the stock solution with the defined solvent:

a) $3,5 \cdot 10^{-6}$ mol/L

b) $1,5 \cdot 10^{-6}$ mol/L

Check the concentrations with the spectrometer. Determine the optical density of the dilute solutions and calculate the concentration using the Lambert-Beer law. If you have worked carefully, the calculated concentrations correspond to those in the assignment.

You will get the Testat for the calculated concentration of the unknown solution and the measured extinctions of the dilute solutions.

5.1 Behavior of an aqueous solution of antimony trichloride

In a test tube add water dropwise to a pea-sized amount of $SbCl_3$. When a white precipitate has formed, add concentrated hydrochloric acid and then, more water again. Shake the contents over and over again by shaking the Test tube. Discuss your observations in the protocol regarding the present equilibrium

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2\,HCl\,,$$

between antimony trichloride and water on the one side and antimony oxychloride and hydrochloric acid on the other side. Write down the mass balance equation for the reaction.

$SbCl_3$ is soluble, SbOCl forms a poorly soluble white precipitate.

5.2 Dissociation equilibrium of ferric thiocyanate

To 2 mL solution of ferric chloride ($FeCl_3$), add 2 mL solution of ammonium thiocyanate[2] (NH_4SCN) and 5 mL dilute Hydrochloric acid and 100 mL Water in a suitable Beaker.

Fill four test tubes about 5 mL of this prepared solution. Place in a test tube Add an additional 1 mL of the ammonium thiocyanate stock solution, in a further addition 1 mLof the iron (III) chloride stock solution. The third remains without addition. How does that change? Color intensity of the solutions?

Lastly, slowly pour water into the fourth test tube with a squirt bottle while looking in the test tube from the top and mixing the contents by shaking. Does the color intensity change? Would you get the same result when diluting a potassium permanganate solution? (See Lambert-Beer's Law, Eq.4.2 on page 67.)

In the solution, the complex compound iron thiocyanate forms according to the reaction equation

$$Fe^{3+} + 3\,SCN^- \rightleftharpoons Fe(SCN)_3\,.$$

Fe^{3+}-ions are pale yellow, thiocyanate ions are colorless and ferric thiocyanate is deep red. Discuss the observations in the protocol using the reaction equation and equation of mass balance for the reaction.

5.3 No experiment

[2] Both availiable in G105. Pick them up in two test tubes.

5.4 Coupling of two solution equilibria

All solutions for this experiment are provided in G105. Do not use the solutions in the laboratory shelves whose concentrations are insufficient.

To 25 mL of a 0.01 M NaCl solution, add 0.5 mL of a K_2CrO_4 solution containing 5 g of K_2CrO_4 in 100 mL of water. Then use a burette to add 0.1 M $AgNO_3$.

Add a few milliliters while stirring. Do not waste the $AgNO_3$ solution, it is expensive.

Fetch about 10 mL $AgNO_3$ solution in a suitable Beaker and bring excess, not contaminated remains back to the stock solution in G105 after you finished the experiment.

Pay attention to color changes at the place of drip. How much silver nitrate solution is added when the color at the point of dripping no longer disappears? Which salt precipitates first?

Calculate the theoretical order of the precipitations in the evaluation of the experiment with the help of the solubility products and compare them with your observations. The solubility products are about 10^{-10} mol^2/L^2 for AgCl and 10^{-12} mol^3/L^3 for Ag_2CrO_4.

Nernstscher Verteilungssatz

Wegen der unterschiedlichen Wechselwirkungen einer gelösten Substanz mit verschiedenen Lösungsmitteln wird sich eine gelöste Substanz ungleich auf zwei nicht oder nur teilweise mischbare Lösungsmittel verteilen. Im Gleichgewicht gilt der nernstsche Verteilungssatz

$$\frac{c_1}{c_2} = k \quad , \tag{7.3}$$

wobei c_1 und c_2 die Konzentrationen des Gelösten im Lösungsmittel 1 bzw. 2 sind und k eine Konstante ist, die von der Temperatur abhängt. Voraussetzung für die Gültigkeit von Gl.(7.3) ist, dass der gelöste Stoff in beiden Lösungsmitteln weder assoziiert noch dissoziiert und dass die Konzentrationen c_1 und c_2 klein sind. Eine große praktische Bedeutung hat der nernstsche Verteilungssatz beim Ausschütteln (siehe Versuch 7.9 und auch 3.7).

7.1 Miscibility of alcohols with water and n-hexane

Try to mix 1 mL each of methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol with 1 mL each H_2O and 1 mL n-hexane. Use test tubes for the experiments. Write down your observations.

7.2 Miscibility of carboxylic acids with water

Add glacial acetic acid (anhydrous acetic acid), benzoic acid and stearic acid in three test tubes (1 mL or a spatula tip) gradually with water (up to about5 mL).

See if heating promotes the dissolution process, and watch the solution as it cools. Check the pH of the solution with universal indicator paper and make a note of your observations.

7.3 Volume and temperature changes when mixing liquids

Supplied equipment: Thermometer with 1/10 °C-Graduation

Mix equal amounts (exactly 50 mL each) of the following substances and determine the temperature change ΔT and the volume change ΔV (after reaching the original temperature):

a) Acetone / Water

b) Acetone / Cyclohexane

c) Cyclohexane / Ethanol [1]

- First check the calibration of the 25-mL-volumetric pipette and the 100-mL-volumetric flask with acetone. To do this, fill four times 25 mL of acetone with the volumetric

[1] Use destilled Ethanol. If you use normal Ethanol, the experiment will not work. The dest. Ethanol is provided in a small bottle in the solvents shelf)

pipette into the 100-mL-volumetric flask (not measuring cylinder!) and compare the read volume with the expected. Do the volumes match?

- Determination of volume change: The neck of the volumetric flask is covered with a strip of provided graph paper. To convert the observed height difference to the volume change, fill the dried volumetric flask with water up to the calibration line. Add a known amount of water to the volumetric flask and measure the change in height of the surface of the water in the neck.
- Determine the temperature of the two components to be mixed (these should be at room temperature), and pipette 50 mL each into the volumetric flask. Measure the temperature immediately after mixing (shaking briefly but thoroughly.
- Allow the mixture to return to the starting temperature. Then determine the volume change.

You can get the thermometer with 1/10 °C-graduation required for temperature measurement in G105.

The measured temperature changes ΔT and the measured volume changes ΔV will be signed, when correct.

7.4 Solubility curve of a compound (T)

You will get the salt in G105.

Prepare 120 mL of a solution of the salt saturated at about 80 °C. While the solution is cooling down, decant approximately 20 mL at 60 °C, 50 °C, 40 °C, 30 °C und 20 °C into a 400-mL-Beaker

Determine the mass of the decanted solution and then reduce this with the Bunsen burner on the wire mesh. Make sure that nothing spills out of the beaker! The remaining moisture is removed in the drying cabinet at 100 °C to 110 °C until the weight does not go down any more.

Determine the mass of solute from the weight of the empty beaker and the weight of the beaker after evaporation.

Prepare a table with the solubility of the substance in grams per 100 g of solvent at the measured temperatures. In the report, prepare a graph of the natural logarithm of the dissolved mass of the substance in grams per 100 g of solvent as a function of the reciprocal absolute temperature. Calculate the heat of solution ΔH_L by multiplication of the determined slope with the negative general gas constant R.

7.5 Heat of solution of calcium chloride and calcium chloride hexahydrate

Fill two 25 mL graduated cylinders with 10 mL water each and measure the water temperature. In one graduated cylinder, dissolve 5 g of anhydrous calcium chloride ($CaCl_2$), in the other the

same molar amount (not mass!) of Calcium chloride hexahydrate ($CaCl_2 \cdot 6\ H_2O$). Measure the temperature change, and later, when the solutions return to the starting temperature, the volume change. The observed temperature and volume changes as well as the mass of Calcium chloride hexahydrate, which you have calculated, are signed.

7.6 Heat capacity of a simple calorimeter

Supplied equipment: calorimeter, magnetic stirrer with fish, thermometer with 1/10 °C-graduation

The heat capacity C of a calorimeter is the amount of energy that a calorimeter must be supplied to heat the calorimeter and its content by 1 K. It is therefore given in Joules per Kelvin.

Borrow a calorimeter in G105[2]. The mixing of the calorimeter content is ensured by a magnetic stirrer. Put the appropriate stirrer into the calorimeter, which is clean and dry and has room temperature T_0. Heat about 0.3 kg of water[3] to about 50 °C; the exact same amount of water must used in experiment 7.7 in the determination of an unknown heat of solution, So you have to write down the exact value. Then one determines the temperature T_2 of this Water and pour it immediately afterwards (the pouring time is $t = 0$) into the calorimeter and start the stopwatch. During cooling, the temperature is measured every half a minute and logged in a table. Measure the temperature for about 10 min. For temperature measurement, a thermometer with 1/10 °C-graduation is used.

Plot temperature against time and detect by extrapolation of the curve part with slow slop to $t = 0$ the Temperature T_1 which is the temperature the entire calorimeter (vessel plus water) at infinitely fast heat exchange would take.

The heat capacity C then results to

$$C = \frac{m_{H_2O} \cdot c_{H_2O} \cdot (T_2 - T_0)}{(T_1 - T_0)} \quad , \qquad (7.4)$$

where $c_{H_2O} = 4184\,J\,K^{-1}\,kg^{-1}$ is the specific heat of water.

The calculated value of C (with unit) will be signed.

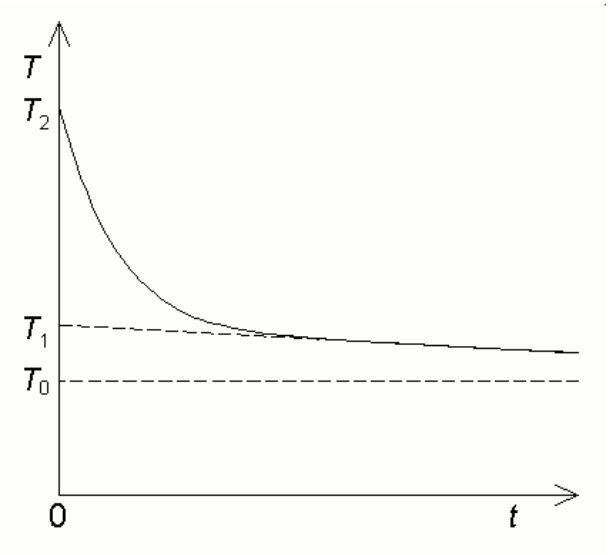

Abb. 7.1: Temperature change when determining the heat capacity

[2]The calorimeters are numbered. Make a note of the number, you will need the same calorimeter in Exp. 7.7.
[3]It is not important how much water you use, but you need to know the exact mass.

7.7 Specific heat of solution of an unknown salt (T)

Supplied equipment: calorimeter, magnetic stirrer with fish, thermometer with 1/10 °C-graduation

Put exactly the same amount of water in the same calorimeter as you did in Exp. 7.6.

A well known amount m_S of the salt to be examined (about 5 g) in a closed test tube is hanged through the corresponding opening in the lid of the Calorimeter. With constant stirring, write down every 30 s the temperature until you gained enough measurement points for extrapolation. Then the tempered salt is poured into the water rapidly, the test tube put away. Subsequently read the temperature again every 30 s until at least five minutes after the complete dissolution of the salt.

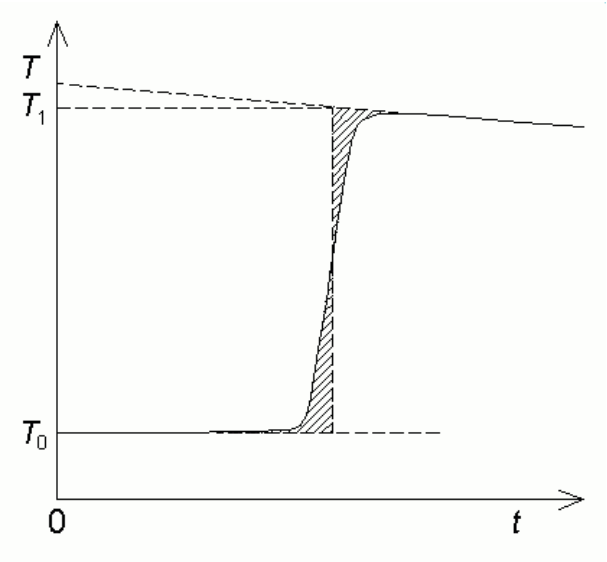

Abb. 7.2: Temperature profile when determining the heat of solution

Create from your measurement data a Temperature-time diagram, and from this determine the temperature difference $T_1 - T_0 = \Delta T$, as shown in Fig. 7.2.

With this method, the idealized curve is determined, which would be observed if the dissolution process and the corresponding heat exchange would happen infinitly quick. This is obtained by drawing in the area of the strong temperature change a parallel to the T-axis such that the hatched areas the same size. The specific heat of solution L then results to

$$L = -\frac{C\Delta T}{m_S} \quad , \tag{7.5}$$

where C is the heat capacity of the calorimeter as measured in Exp. 7.6. All temperature measurements are carried out with a thermometer with with 1/10 °C-graduation.

Calculate the specific solution heat in J/g from your measurements. This value will be signed.

7.8 Molality of two salt solutions (T)

Supplied equipment: magnetic stirrer with fish, thermometer with 1/10 °C-graduation

The aim is to determine the molality of two aqueous salt solutions (Type AB $\rightarrow$ A^+ + B^-). You will receive these two solutions if you hand in two small beakers in G105.

First, water, and then the unknown solutions are measured.

Put a stirring rod into the beaker and a magnetic stirrer under the beaker. Use a thermometer with 1/10 °C-graduation to measure the temperature of the liquid. Record the temperature of

the solution regularly at intervals of 30 s. The Freezing point is indicated by a temperature that remains almost constant for a few minutes and the precipitation of fine ice crystals[4]. It may come to a supercooling of the solution. In this case, you still need to cool down until ice crystals are forming.

Calculate in your report from the temperature difference ΔT between the freezing point of pure water, to be determined by the same procedure, and that of solution then according to Eq. (7.2) the molality of the solution for non-dissociating (!) solutes. The molar freezing point depression of water is $k_f = 1,86\,\mathrm{K\,kg\,mol^{-1}}$.

Perform *each* measurement three times, giving the average of the individual measurements. The measured freezing point depressions ΔT are signed.

7.9 Partition coefficient of iodine in chloroform and water

Supplied equipment: Separating funnels with ring, magnetic stirrer with stirring rod

Determine the distribution of iodine on the two solvents H_2O and $CHCl_3$ at room temperature for two different iodine concentrations. Calculate the concentrations in the two phases, and from this the distribution coefficients k from Eq. (7.3).

In this experiment the concentrations of the iodine in the two liquid phases are measured. It is done after the separation of the phases in the separating funnel by titration with a solution of sodium thiosulphate ($Na_2S_2O_3$) of known concentration. For this purpose, the aqueous phase is mixed with a small amount of starch solution, which colours the iodine solution in deep dark blue. Thus, the presence of iodine is clearly visible. The connection between iodine molecule and starch does not interfere with the reaction of the iodine with the thiosulfate ions.

$$I_2 + 2\,S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \tag{7.6}$$

The iodine-starch complex is blue, all other compounds are colorless. The reverse reaction is practically impossible because the equilibrium is almost completely on the right side.

According to Eq. (7.6) the amount of thiosulfate is just twice as large as the amount of iodine at the time of discoloration. If the determined amount of substance is divided by the volume of the sample of the solution, you get the concentration of I_2.

In the determination of the I_2 concentration in the chloroform phase the procedure is similar, but water is added to the chloroform before the titration. Once again there is a distribution equilibrium between water and chloroform phase, but the equilibrium is constantly disturbed during titration. The iodine in the aqueous phase reacts to iodid-ions by adding the thiosulfate solution. Iodine is consumed and more is redeemed from the chloroform phase, as long as there is iodine in the chloroform phase. Therefore, the transition point is time lagged. So titrate slowly.

In detail, proceed as follows:

1. Pour 250 mL demineralised water into a separatory funnel.

[4] Too much ice leads to false (too deep) values, because the ice crystals are mainly pure water, so the concentration of the remaining liquid goes up

2. The iodine (0.1 g and 0.25 g) is dissolved in 50 mL chloroform (heat up if necessary). When all the iodine has dissolved, add the solution to the separating funnel as well.

3. Shake the contents of the funnel vigorously. (Do not forget to ventilate!). Subsequently put the funnel in its ring and wait until the two liquid phases (iodine-water solution and iodine-chloroform solution) have completely separated.

4. Drain the $CHCl_3$ phase into a large Erlenmeyer flask.

5. Transfer 200 mL of the aqueous phase 200mL and of the chloroform phase 5 mL in a large Erlenmeyer flask each.

   Add 100 mL water to the chloroform solution and stirr. Add a few mL of starch solution.

6. The solutions thus obtained are most easily titrated on a magnetic stirrer with 0.01 M $Na_2S_2O_3$-solution. Color changes are easier recognize against a white background. (underlay a white paper)

The titrated volumes are signed.