INTRODUCTION

This textbook is a reference material for laboratory course in General and Inorganic Chemistry for the study program Biological Chemistry. It contains manuals for the experiments performed in the course. Each manual is composed of a brief introductory part written in an easily understandable way aimed at background essential for the experiment, instructions for experiments and questions. Further theoretical details are discussed in seminars and lectures on General and Inorganic Chemistry. Each manual contains one or two experimental tasks (one manual correspond to one laboratory course). Questions at the end of each experiment have to be addressed in the laboratory protocol and are a subject of valuation. Finally, the last chapter is dedicated to chemical calculations. It contains basic theory, mathematical equations and instructions for common calculations. The calculations are done continuously during the term.

The goal of this course is to familiarize students with basic English terms for laboratory equipment and operations and to gain experience with them. Early experiments fall in laboratory technique and general chemistry (determination of density, solubility, making solutions, purification by recrystallization, hydrolysis). Syntheses cover different approaches towards preparation of inorganic compounds, such as redox reactions, precipitation, neutralization, heterogeneous reactions and ligand substitution. Determination of acid concentration by neutralization is also included as titration is one of the most important methods of analytical chemistry in inorganic laboratory.

MANUALS

1. Density

INTRODUCTION

Density (ρ, sometimes d) of a substance is defined as its mass (m) divided by volume (V):

$$\rho = \frac{m}{V}$$

It means that density depends on pressure and temperature (compression, expansion). The density of homogeneous materials is normally determined in two steps: the mass is measured with a weighing scale, the volume is measured either directly (using volumetric flask, cylinder, or pycnometer) or by the displacement of a fluid (solid samples). Determination of the density of heterogeneous and non-compact materials is complicated as their density varies between different regions of the object. Density is usually given in kilograms per cubic meter [$kg \cdot m^{-3}$], grams per cubic centimeter [$g \cdot cm^{-3}$], kilograms per liter [$kg \cdot L^{-1}$] or grams per milliliter [$g \cdot mL^{-1}$].

Table 1 Densities of different materials at 25°C

Material	Density [$kg \cdot m^{-3}$]	Material	Density [$kg \cdot m^{-3}$]
H_2O	997.0479	**Air**	1.184
Ice (at 0°C)	916.7	**He**	0.179
Be	1850	**NaCl**	2165
V	6090	**H_2SO_4 (98%)**	1840
Fe	7874	**Ethanol**	789
U	19160	**Acetone**	784.5
Ir*	22650	**Silica nanofoam****	≈ 1
Os	22610	**Aerogel****	≈ 100

* Element with the highest density.
** The lowest density materials.

Pycnometric determination of density is based on accurate determination of the mass and volume of an analyte. The mass is determined directly (by weighing), the volume indirectly: by weighing the volume of the liquid in the filled pycnometer (solutions) or by weighing the volume of the liquid that is displaced from the pycnometer by a solid (in the case of density determination of solid samples, e.g. metals). The volume of the pycnometer is calibrated at certain temperature (mostly 25 °C) therefore the measured liquid should be allowed to reach this temperature. When handling the pycnometer we touch it only with fingers at the neck to prevent increasing the temperature of the liquid.

EXPERIMENT PYCNOMETRIC DETERMINATION OF DENSITY

Volume of the pycnometer

Use analytical scales for determination of the mass of the clean and dry pycnometer. Then, fill it with distilled water (beware of bubbles). Use filtration paper to dry the pycnometer (the capillary of the pycnometer must be filled completely by water). Weigh the pycnometer and calculate the mass of the water. Use Table 2 for the calculation of the volume of the pycnometer.

Table 2 Density of water at various temperatures

t [°C]	ρ [g·cm^{-3}]	t [°C]	ρ [g·cm^{-3}]
14	0.99927	**18**	0.99862
15	0.99912	**19**	0.99843
16	0.99897	**20**	0.99823
17	0.99880	**21**	0.99802

Density of NaCl solution

Rinse the pycnometer with the solution of NaCl, fill it with this solution and dry it with filtration paper. Determine the mass of the pycnometer with the solution of NaCl and calculate the density of the solution. Do this experiment three times for higher accuracy (use the average value when calculating the density). When you are finished, rinse the pycnometer with distilled water, ethanol and place it in the drying plant. Use chemical tables to determine the mass fraction of NaCl (w) in the solution.

Density of an unknown metal

Weigh the clean, dry and empty pycnometer (m_p). Use tweezers and fill it with pieces of a metal. Find the mass of the filled pycnometer ($m_{p+metal}$), and then calculate the mass of the metal pieces (m_{metal}). Fill the pycnometer with distilled water and weight it ($m_{p+metal+water}$). Finally, weigh the pycnometer filled with water only ($m_{p+water}$). Calculate the volume of the pycnometer using the mass of water ($m_{p+water}$ - m_p). Pycnometer with metal and water contained the decreased volume of water. This decreased volume corresponds to the volume of the metal. Repeat the measurement three times with different pieces of the metal. Calculate the density of the unknown metal and use chemical tables to find out which metal did you use.

(Note: we assume here that 1 g of water has the volume of exactly 1 cm^3)

$$\rho_{metal} = \frac{m_{p+metal} - m_p}{(m_{p+water} - m_p) - (m_{p+metal+water} - m_{p+metal})}$$

QUESTIONS

1. Why is it necessary to first rinse a pycnometer with a solution prior to its actual measurement?
2. Give an example of a metal whose density cannot be determined by the method you used today and explain why.

2. Solubility

INTRODUCTION

Solubility is very important phenomenon in chemistry. Knowing the solubility of a substance is of utmost importance when preparing solutions (dissolving) and crystallizing compounds (concentrating solutions followed by exceeding the solubility product and subsequent formation of crystals, eventually precipitates). Dissolving proceeds in two steps. First, the crystal structure of a solid substance is disintegrated by the molecules of the solvent and then the molecules/ions of the dissolved substance are being surrounded by the solvent molecules – *solvation* (if the solvent is water we use the term *hydration*). The first process requires energy, during the second one is energy released. Thus, the difference in these two energies determines the solubility product. Dissolution is sometimes followed by *solvolysis* – reaction of the dissolved species with solvent molecules. In inorganic chemistry *hydrolysis* of salts occurs relatively often (Manual 5).

EXPERIMENT 1 DEPENDENCE OF SOLUBILITY ON TEMPERATURE

Fix a large test tube with a clamp to a stander and fill it with a saturated solution prepared by dissolving the unknown salt in 50 mL of distilled water. Add a small excess of the salt in the test tube. Take one portion of the solution with a spoon and place it in a weighed porcelain dish (note the temperature). Find the mass of the dish with the solution. Then, evaporate the solution to dryness on a water bath. Let the dish cool down and weigh it to determine the mass of the residue.

Dip the test tube with the solution in a large beaker. The beaker should contain sufficient water so that the entire volume of the solution of the unknown salt is immersed in a water bath. Heat this apparatus until the temperature in the test tube reaches 80 °C (the temperature is measured with a mercury thermometer). Take one portion of the solution with a spoon and place it in a weighed porcelain dish. Find the mass of the dish with the solution. Then, evaporate the solution to dryness on a water bath. Let the dish cool down and weigh it.
Let the solution in the test tube cool down to 40 °C and repeat the measurement of the mass of a residue from one portion of an evaporated solution.
Cool the solution to room temperature; suck the crystallized salt on a Buchner funnel, mark it and put in a dryer.
If you are unable to evaporate a sample to dryness, you can use the dryer.

QUESTIONS

1. Calculate the solubility of the unknown salt in grams per 100 grams of water, in grams per 100 grams of solution and calculate the mass fraction (in %).
2. Describe the influence of the temperature on the solubility of the salt.
3. Draw the solubility curve for the sample.
4. Compare your results with data from your teacher.
5. Solubility is a function of temperature. Find few examples of salts which are more or less soluble in conjunction with rising temperature.

EXPERIMENT 2 PREPARATION OF INSOLUBLE COMPOUNDS

Weigh approximately 1 g of unknown calcium salt on a watch glass (use analytical scales). Transfer the sample quantitatively into a beaker and add distilled water to the final volume of about 100 mL. Stir the mixture with a glass rod until it completely dissolves. Boil the solution and then precipitate it with 0.1 M solution of sulfuric acid:

$$Ca^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightarrow CaSO_4\,(s)$$

Drop the solution of H_2SO_4 with a pipette until the precipitate is forming. When the precipitation is complete boil the suspension to convert the fine precipitate to a more bulky one. Let the precipitate settle, decant it three times with 30 – 40 mL of hot water and filter it on a Buchner funnel (weigh the filtration paper before filtration). Dry the precipitate on air bath. Find the mass of the calcium sulfate and calculate the mass percentage of the calcium salt in the unknown sample.

QUESTIONS

1. Based on your result, can you propose the composition of the unknown calcium salt?
2. Give five examples of insoluble salts having different anions.
3. Describe shortly how would you prepare a solution of HNO_3 if you had at disposal a solution of $Ba(NO_3)_2$ and mineral acids. Which acid would be the best choice and why?

3. Solutions

INTRODUCTION

Solutions are usually prepared by dissolving weighted solid compounds in solvents (mostly in water) or by diluting stock solutions. When preparing solution from solid samples, we must ensure full transfer of the solid in the solution. Thus, we dissolve the compound in small volume of water, pour it in the flask, then rinse the beaker with distilled water and pour the washing water in the flask. Only then we fill the flask with water to the given volume (to the mark). When preparing solutions by mixing or diluting from stock solutions, we use usually volumetric pipettes. Graduated pipettes and cylinders are less frequently used because by using them we lost the accuracy achieved in preparation of the stock solution using volumetric flasks and analytical scales.

EXPERIMENT PREPARATION OF SOLUTIONS

Solution I

Prepare the stock solution I in the 250 mL volumetric flask. Weigh 10.2 g of NaH_2PO_4 and dissolve it in a beaker in approx. 30 mL of distilled water. Pour the solution quantitatively in the volumetric flask (rinse the beaker several times with distilled water and pour the solution in the flask). Fill the flask with distilled water 1–2 cm below the mark. Then complete the filling with a wash bottle so that the lower meniscus of the liquid is exactly on the mark. Close the flask with stopper and shake it.

Solution II

Prepare the stock solution II in the 250 mL volumetric flask. Weigh 0.17 g of NaH_2PO_4 and follow the procedure as above.

Solution A

Fill a 100 mL volumetric flask with 33.3 mL of stock solution I and add distilled water to the mark.

Solution B

Fill a 250 mL volumetric flak with 25 mL of stock solution II and add distilled water to the mark.

Solution C

Fill a 100 mL volumetric flask with 33 mL of stock solution I and 20 mL of stock solution II and add distilled water to the mark.

Solution D

Fill a 500 mL volumetric flask with 0.5 mL of stock solution I and 20 mL of stock solution II and add distilled water to the mark.

Prepare four test tubes and fill them with 15 mL of solutions A to D. Add 3–5 mL of the indicator methyl red, close the test tubes with stoppers and shake them. Notice the color changes.

QUESTIONS

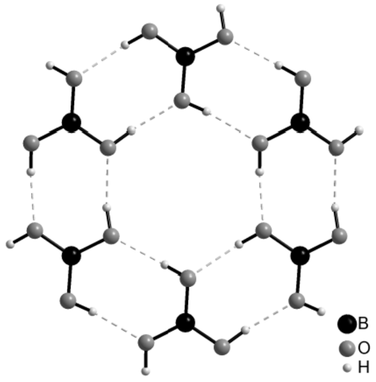
1. Calculate the concentration of NaH_2PO_4 in stock solutions I and II and in solutions A, B, C, D.
2. Compare and explain the color of solutions A + C and B + D. Confront the colors with calculated concentrations.

4. Crystallization, affecting chemical reactions

INTRODUCTION

Crystallization is a process in which atoms, molecules or ions form highly organized solids – crystals. During nucleation molecules of solute start forming clusters (aggregates) and the concentration of solute in that region of solution significantly exceeds the average concentration of the solute. If the clusters are stable enough (this is influenced by many factors, such as temperature, chemical properties, and thermodynamics) nuclei are formed. In the next process – crystal growth, the size of the nuclei increases in all directions.

H_3BO_3 forms a pearly white flaky crystals; in Nature it occurs as mineral sassolite crystallizing in triclinic system; t_t =171 °C, ρ = 1.43 g·cm^{-3}, M = 61.83 g·mol^{-1}. In crystal structure the molecules of H_3BO_3 are almost planar connected by hydrogen bonding forming hexagonal clusters arranged in layers; therefore the crystals are soft and easily cleavable:



Its solubility in water depends on temperature: $w(10\ °C) = 3.52\%$, $w(20\ °C) = 4.64\%$, $w(80\ °C) = 19.05\%$. It dissolves easily in ethanol, diethyl ether and glycerol. The aqueous solution containing 3% of H_3BO_3 is used in health care as a mild antiseptic. Boric acid is very weak monobasic acid ionized in water in an unusual way:

$$H_3BO_3 + 2H_2O \rightarrow H_3O^+ + [B(OH)_4]^-$$

The addition of some organic compounds (e.g. glycerol, certain carbohydrates) to a solution of H_3BO_3 results in formation of chelates which act as strong acids. Boric acid is prepared in laboratory by the reaction of borax with hydrochloric acid giving the by-product sodium chloride. Therefore, it is usually contaminated with sodium chloride. NaCl is removed from the obtained product by recrystallization, because boric acid is about 5 times less soluble in water than NaCl (by weight) at room temperature.

EXPERIMENT 1 PURIFICATION OF H_3BO_3

Weigh 10.0 grams of contaminated H_3BO_3. Pulverize the substance in a mortar to fine powder and pour it into a beaker (250 ml). Measure calculated amount of distilled water with graduated cylinder and pour it into a beaker with H_3BO_3. The concentration of H_3BO_3 in the solution should be 9.1%. Put the beaker with the mixture on a tripod, burn the burner (moderate heat) and stir the mixture with a glass rod. At the first signs of boiling switch off the burner.

Next, prepare the apparatus for filtration at atmospheric pressure. Use gloves to remove the hot beaker from the tripod. Carefully pour the solution in the funnel along the glass rod. Mark the beaker. Let the solution cool down to room temperature and then cool it in an ice bath until the temperature reaches approx. 10 °C. While the crystals of H_3BO_3 are forming prepare the apparatus for the filtration under reduced pressure. Suck the grown crystals on a Buchner funnel and wash it with 10 mL of cold distilled water. Dry the crystals in the flow of air in fume hood. Finally, weigh the product and calculate the yield in %.

QUESTIONS

1. Calculate the theoretical mass of boric acid you should have obtained by cooling its saturated solution to 10 °C (use chemical tables).
2. Why should you crush and grind the substance prior to dissolving?
3. What is the advantage of heating the mixture while dissolving?
4. How do you build the apparatus for filtering at atmospheric pressure and under reduced pressure? Make a schematic drawing.
5. Name all seven lattice systems and describe them by lengths (a, b, c) and angles (α, β, γ) of the lattice.
6. Which methods of crystallization do you know?

EXPERIMENT 2 THE COURSE OF A CHEMICAL REACTION

Do all experiments in the fume hood.

Influence of concentration:

Throw one piece of zinc in test tubes containing 2 mL of hydrochloric acid diluted by water to 1:1 and 2 mL of hydrochloric acid diluted by water to 1:100.

$$2\ HCl + Zn \rightarrow H_2 + ZnCl_2$$

Influence of temperature:

Throw one piece of zinc in a test tube containing 2 mL of hydrochloric acid diluted to 1:20 and watch the reaction. Put the test tube in boiling water bath and monitor the speed of hydrogen evolving. Finally, cool the mixture in stream of water and notice the change in the speed of hydrogen evolving.

Influence of catalyst:

Pour 2 mL of 0.02 M solution of $KMnO_4$ and 2mL of HCl (diluted to 1:1) in three test tubes. The first test tube is a blank. Throw a piece of zinc into the remaining two. When the hydrogen starts to evolve add 0.5 mL of 1 M solution of HNO_3 in one test tube. Compare the speed of decolorization of the samples.

$$Zn + 2HCl \rightarrow 2\ H + ZnCl_2$$
$$2\ KMnO_4 + 10\ H + 6\ HCl \rightarrow 2\ MnCl_2 + 2KCl + 8\ H_2O$$

The catalytic effect of the nitrate anion causes:

$$5\ KNO_3 + 10\ H \rightarrow 5\ KNO_2 + 5\ H_2O$$
$$5\ KNO_2 + 2\ KMnO_4 + 6\ HCl \rightarrow 5\ KNO_3 + 2MnCl_2 + 2KCl + 3\ H_2O$$

Thermal effects:

Fill two small beakers to about 1/3 of the volume with distilled water. To the first one add a teaspoon of ammonium chloride; to the second one add few flakes of sodium hydroxide. Observe a change in temperature of both beakers (the temperature change may be recorded using a thermometer).

QUESTIONS

1. Describe and explain all observations.
2. Name the factors which can influence the kinetics of a chemical reaction.
3. Define a catalyst and an inhibitor. Give at least two examples of catalysts used in industry.
4. Define endothermic and exothermic reaction.

5. Hydrolysis

INTRODUCTION

Hydrolysis in general is any reaction with the participation of water. Regarding aqueous solutions the term *hydrolysis of salts* refers to the chemical reactions of solute ions with water. One has to always consider possible chemical reactions which may proceed when dissolving compounds. For example, upon dissolving Na_3PO_4 in water all phosphorus is present as $H_2PO_4^-$ and HPO_4^{2-} (the concentration of the individual species depends on phosphorus concentration and pH). The PO_4^{3-} anion is entirely missing in the solution. Different example is $Bi(NO_3)_3$. The compound is soluble in water; however, it hydrolyses immediately forming precipitate of $Bi(OH)_3$ and $BiO(OH)$. Thus, hydrolysis affects the composition and pH of solutions of some compounds.

EXPERIMENT 1 SYNTHESIS OF $KHSO_4$

$$\underset{\text{50\% sol.}}{KOH(aq)} + \underset{\substack{\text{50\% sol.}\\ \text{1.5 excess}}}{H_2SO_4(aq)} \rightarrow \underset{\text{7 g}}{KHSO_4(aq)} + H_2O(l)$$

Pour 50% solution of potassium hydroxide in small portions into the solution of 1.5 excess of 50% sulfuric acid by constant stirring. The solution gets hot. When the reaction is complete the solution has to be acidic (check it with a pH paper).

Evaporate the solution of potassium hydrogensulfate on a water bath until crystals of the salt start forming. Cool the solution, suck the crystals on a Buchner funnel and wash them with 10 mL of ice–cooled water. Release the vacuum, pour 10 mL of ethanol on the crystals and suck the solution. Dry the product at laboratory temperature.

QUESTIONS

1. Write the chemical equation describing reaction of aqueous solution of potassium carbonate with the excess of sulfuric acid (1:2).
2. Write the chemical equation describing reaction of aqueous solution of potassium hydroxide with equimolar amount of sulfuric acid (stochiometric neutralization).
3. Why must be the solution acidic?
4. Explain how would you distinguish $KHSO_4$ and K_2SO_4 and perform the test on your sample.

EXPERIMENT 2 HYDROLYSIS OF SALTS

Pour ≈ 5 mL of water in nine test tubes. The first test tube is a blank. Add small amounts of following salts into the remaining test tubes: potassium acetate, ammonium acetate, aluminum chloride, potassium chloride, sodium hydrogensulfite, sodium sulfite, sodium hydrogencarbonate, sodium carbonate. After dissolution check the pH of the solutions with a pH paper.

Next, add a drop of phenolphthalein in the solutions of sodium hydrogencarbonate and sodium carbonate. Note the color. Boil both solutions very carefully and watch the color change.

QUESTIONS

1. Write the chemical equations describing hydrolysis of all salts you used in this experiment.
2. Explain the color change after heating solutions of sodium hydrogencarbonate and sodium carbonate.
3. Write the chemical equations describing hydrolysis of NH_4Cl, KF, $FeSO_4$, $Cu(ClO_4)_2$ and AgCN.