INFORMATION REGARDING LABORATORY SESSIONS

1 Laboratory regulations and dealing with chemicals

1. Students are obliged to come on time and properly prepared.
2. Students must wear laboratory slippers and protective clothing and they should use safety accessories (e.g. safety glasses).
3. Students may only work in the laboratory under supervision of the lecturer in the dedicated area and with the specified accessories. Students must obey instructions and are not allowed to alter them on their own initiative.
4. Eating, drinking, smoking or using laboratory glassware for eating and drinking is strictly prohibited in the laboratory.
5. Keep the working area tidy. Do not leave bags or other items which are not necessary for the performance of experiments on or below the laboratory desk. Bottles with reagents should be closed immediately after the use and put back in the correct place.
6. Picking up solid chemicals using one's hands is prohibited. Use a laboratory spoon instead. Any chemical spillages must be reported to the lecturer.
7. If the skin is affected it is necessary to rinse it with a large amount of water. Any injuries, headaches or sickness must be reported to the lecturer.
8. Unused chemicals should never be put back into storage vessels due to their possible contamination.
9. Waste chemicals are to be poured into discharge funnels with an open water supply so as not to cause any damage to the waste facilities. Solutions of heavy metals, organic solvents, waste oil and other substances that do not mix with water must not be discharged directly into funnels but should be collected in separate vessels designated for this purpose.
10. The working desk must not be stained with caustics, as these substances corrode textiles, paper etc. even when diluted to a great extent.
11. Broken glass is to be collected separately in special waste boxes.
12. If fire breaks out, shout **FIRE!** and keep away from the source of fire. Close the main gas valve (in the corridor) and try to extinguish the flame, if this is possible.
13. After finishing work, turn off the gas taps and water supply, switch off all electrical appliances and tidy up the working desk. Check to ensure all bottles containing chemicals are closed with stoppers.
14. Pregnant women are excluded from working in the chemical lab, as are mothers until the 9th month after childbirth.

2 General guidelines for experiments

Amounts of chemicals used in experiments

If it is not prescribed directly in the text the experiments require us to use approximately 0.1−0.2 g of solid chemicals (half a small spoonful) and approx. 1 mL of liquid reagents. For easier estimation, 1 mL of liquid in a test tube corresponds to a column of 1 cm in height (Fig. 1). You should allow for the successive addition of several reagents in some experiments, and therefore it is necessary to plan the amount of chemicals so that they fill the test tube to a maximum of ¾ of its volume.

Heating of liquids

Liquids are heated in glassware (test tube, beaker) above the flame of a burner. Only test tubes filled to one third of their volume can be heated directly above the flame, other glass or ceramic vessels can only be heated using tripod with a protective plate. Before you light the burner, close the air supply. You can then slowly open the air supply to obtain a dark flame. The burner has to stand on a fireproof underlay and it should not be used near inflammable subjects or substances. **Safety glasses must be always worn while heating**. It is necessary to shake the test tube during heating in order to avoid the danger the substance will suddenly start boiling. You should also make sure that the test tube mouth does not point towards your or anybody else's face or body.

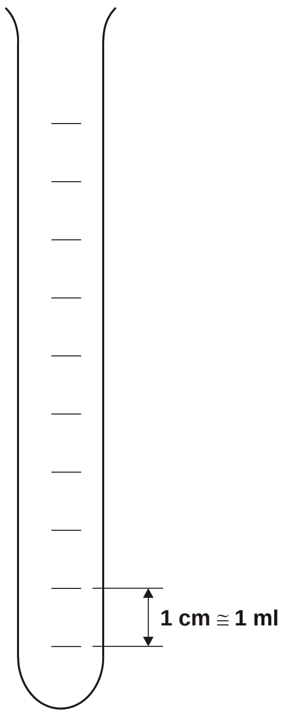


Fig. 1

Working with caustics

Strong acids and bases are caustics. Even small droplets can cause burns or they injure eyes badly. **When diluting acid or a base always add the acid or base into water − never vice versa!**

Spilled caustics should be flushed away with water or wiped up with wet cloth.

First aid. If the skin is affected it is necessary to rinse it with a lot of water. If it is sulphuric acid, wipe it with filter paper and rinse it with a lot of water. The rest of it is neutralised with 2% sodium hydrogen carbonate in solution. Skin affected by lyes is to be rinsed with a lot of water and then neutralised by 2% boric acid. Any affected clothes must be taken off immediately. Eyes affected by caustics must be rinsed thoroughly with a stream of water for several minutes, and then - in the case of acid - neutralised with 2% borax in solution. In the case of lye use 2% boric acid in solution. Nevertheless, immediate rinsing with water is much more efficient than the application of neutralising agents. See a doctor immediately.

Filtration

Filtration is used for the separation of two phases by means of a permeable material that allows only one phase to pass through it. It is generally considered as the separation of solids from liquids or gases. The basic labware for filtration is a funnel with inserted filtration paper. The filter is made from a circular piece of paper that is folded into same-sized quarters and then opened to form a cone (Fig. 2). The suspension on the filter must not be stirred − filtration cannot be accelerated but the filter might be torn by accident.

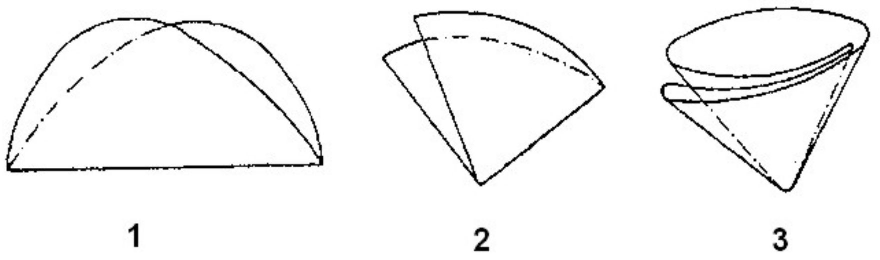


Fig. 2 Folding of filtration paper

Titration

Titration is a volumetric method for the quantitative analysis of solutions. It is based on a chemical reaction between the analysed substance and a volumetric reagent. This reaction must proceed quantitatively, quickly and unambiguously according to defined stoichiometry. Reagent is gradually added in the form of a solution with a known concentration until the equivalence point is reached, i.e. the point when the mole of analysed substance is equal to the mole of volumetric reagent. The equivalence point is observed visually when the volumetric indicator changes colour.

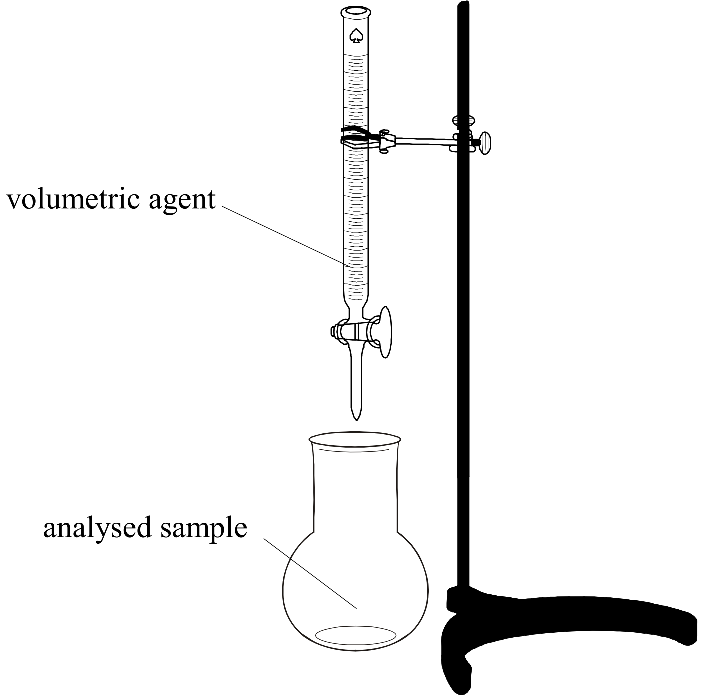


Fig. 3 Titration apparatus

First, using a small funnel, fill the burette with volumetric reagent to above the zero point. After that, pull out the funnel and set the meniscus of the liquid to zero by carefully discharging the necessary amount of liquid using the stopcock (Fig. 4). Put an admeasured amount of the analysed solution into a titration flask and add 2 – 3 drops of indicator. Then, add the volumetric reagent into the titration flask dropwise and stir the solution via a gyral movement of the hand. Near the equivalence point, when the colour starts to change more markedly but after stirring the former colour returns, it is necessary to add reagent **drop by drop**. The first drop that causes a permanent colour change determines the equivalence point. Read the volume of added reagent from the scale on the burette with an accuracy of 0.1 mL and calculate the molar concentration of the analysed solution.

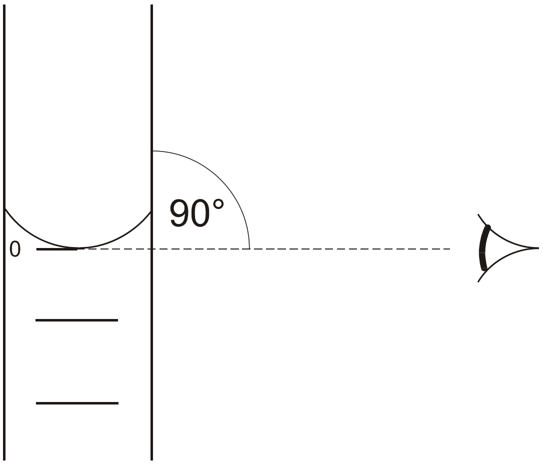
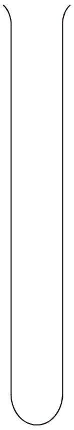
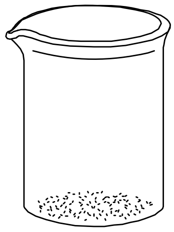


Fig. 4 Reading volumes

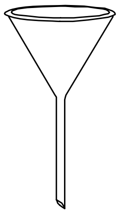
3 Selected chemistry glassware



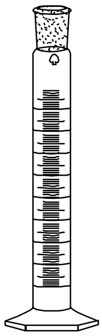
test tube



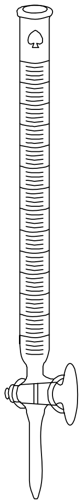
beaker



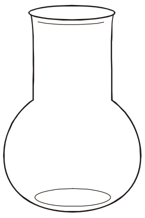
funnel



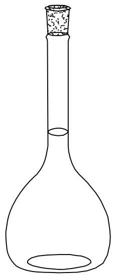
graduated cylinder



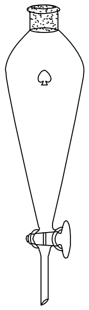
burette



titration flask



volumetric flask



separatory funnel

2 ACIDS

Very polar substances in an aqueous solution split into positively charged particles, **cations**, and negatively charged particles, **anions**. The number of positive charges carried by cations is equal to the number of negative charges carried by anions. This process is generally called **dissociation**.

Acids are (according to the Arrhenius concept) compounds containing hydrogen atoms that can be split like H^+ ions. The residual part of the acid gains a negative charge and becomes an anion, which is called a **conjugate base**. According to the number of hydrogen atoms that can be split by dissociation we distinguish between monoprotic (e.g. HCl), diprotic (e.g. H_2SO_4), triprotic (e.g. H_3PO_4), and even polyprotic. This dissociation is described by the following equations:

$$HCl \rightleftharpoons H^+ + Cl^-$$
$$H_2SO_4 \rightleftharpoons 2\ H^+ + SO_4^{2-}$$
$$H_3PO_4 \rightleftharpoons 3\ H^+ + PO_4^{3-}$$

Hydrogen ions do not exist separately in an aqueous solution – they bind to molecules of water to form hydronium (H_3O^+):

$$H^+ + H_2O \longrightarrow H_3O^+$$

Strong acids are totally dissociated, i.e. practically all molecules are split into ions. In contrast, **weak acids** dissociate only partially – only a particular, relatively small number of molecules are split into ions.

Caution! The strength of acids is not associated with the concentration of molecules in the solution. Even the solution of a strong acid can be poorly acidic as long as the concentration of such acid is very low. However, this does not mean that strong acid becomes weak via multiple dilutions. The same principle is valid for bases as well.

2.1 Sulphuric acid (H_2SO_4)

Concentrated sulphuric acid contains approx. 98% H_2SO_4. It is a colourless dense liquid that readily absorbs water, i.e. it is a hygroscopic substance. It dehydrates organic matter (cellulose, glucose) to form elementary carbon (carbonisation effect). It is miscible with water in any ratio and this process is followed by the liberation of strong dilution heat. Therefore, if preparing dilute sulphuric acid **we always put concentrated acid slowly into water,** never vice versa, in order to avoid overheating of the liquid, as this often causes acid droplets to spew out of the vessel in all directions. Sulphuric acid is a very strong diprotic acid that forms two series of salts – sulphates (e.g. Na_2SO_4, $CaSO_4$) and hydrogensulphates (e.g. $NaHSO_4$).

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$
$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

Experiment 2.1 H_2SO_4 properties

Carbonisation of organic matter

Put approx. 2 mL of concentrated sulphuric acid into a test tube, immerse a piece of a wooden skewer inside it for a couple of seconds and observe the changes.

Dilution heat

Pour the concentrated sulphuric acid from the previous experiment (after pulling out the skewer) carefully into another test tube filled with the same volume of water. Observe the change in temperature by touching the test tube.

Questions:

1. What happens when sulphuric acid comes into contact with cellulose and what is the product of this action?
2. What kind of effect do we observe during the dilution of acids?

2.2 Hydrochloric acid (HCl)

Hydrochloric acid is formed by the dissolution of gaseous hydrogen chloride in water. It is a strong volatile monoprotic acid that easily liberates acrid gaseous HCl. The maximum concentration of hydrochloric acid is approx. 38% HCl. Its salts are called chlorides.

Experiment 2.2 Preparation and reactions of HCl

Put about half of a small spoonful of solid sodium chloride into a test tube. Then, very carefully add ca 1 mL of concentrated sulphuric acid. This is an example of the reaction in which one acid (HCl) is pulled out of its salt by another strong acid (H_2SO_4) that is less volatile.[1] The reaction with dilute sulphuric acid only proceeds at an elevated temperature. **Caution!** If larger amounts are mixed the mixture can bubble out of the test tube. Therefore it is necessary to use a reasonable amount of NaCl, to add the sulphuric acid carefully, and to carry out the experiment above the laboratory sink.

Gaseous hydrogen chloride that is liberated can be identified by the following means:

- careful smelling;
- putting a wet pH test strip over the test tube mouth and comparing the observed colour change with a colour scale;
- holding the test tube mouth near the neck of a bottle with concentrated ammonium hydroxide, from which gaseous ammonia, NH_3, is liberated. The ammonia reacts with the gaseous hydrogen chloride and the solid fumes of ammonium chloride arise.

Questions:

1. Express the formation of hydrogen chloride via a chemical equation.
2. What was the measured pH value and what conclusion arises from this observation?
3. Write the chemical equation for the reaction of hydrogen chloride with ammonia.

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[1] Sulphuric acid reacts with sodium chloride to form HCl and $NaHSO_4$.

2.3 Carbonic acid

Carbonic acid is produced by the reaction of carbon dioxide with water:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

However, only a small part of dissolved carbon dioxide reacts in this way because the equilibrium is shifted to the left in favour of carbon dioxide. Carbonic acid is a very weak diprotic acid from which two series of salts can be derived – hydrogen carbonates (e.g. $NaHCO_3$) and carbonates (e.g. $CaCO_3$).

In an aqueous solution, there is an equilibrium among carbon dioxide (CO_2), carbonic acid (H_2CO_3) and its dissociated forms HCO_3^- and CO_3^{2-} that determines the pH of natural water resources.

Carbon dioxide is only partially soluble in water, therefore an increase in CO_2 or H_2CO_3 concentration results in the liberation of carbon dioxide bubbles from the solution.

Experiment 2.3 Formation of H_2CO_3 and CO_2, and their properties

Formation of CO_2

Prepare two clean test tubes. Put a max. of 2 mL of distilled water into the first test tube and heat it until it boils in order to remove dissolved CO_2. Then, let it cool under cold tap water and measure its pH. Put 2 – 3 pieces of marble ($CaCO_3$) into the other test tube and add 1 mL of water and 2 mL of conc. HCl (**Caution!!** The chemicals react immediately when they come into contact with each other). Close the test tube with a stopper equipped with a bent glass pipe and lead the liberated carbon dioxide[2] through the pipe into the distilled water in the first test tube for several minutes (Fig. 2.1). Then, measure the pH of the distilled water in test tube no. 1 again. Keep the test tube no. 2 for the next experiment.

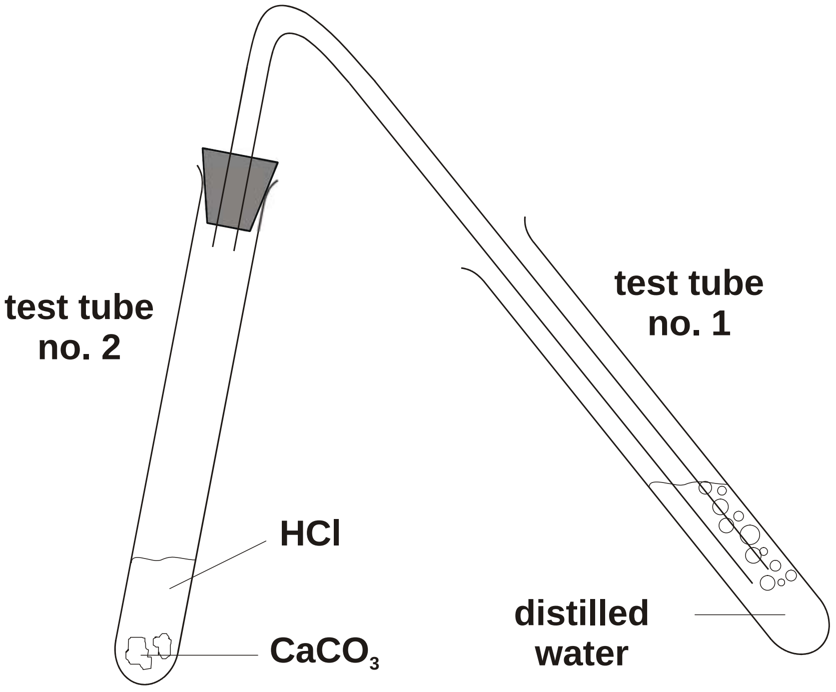

Fig. 2.1

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[2] Gaseous CO_2 is prepared in test tube no. 2 according to the following reaction:
$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + \mathbf{CO_2}\uparrow$

Properties of CO_2
Carbon dioxide is a colourless and odourless gas which is heavier than air. It is non-flammable with fire extinguishing properties and that is the reason why it is used in fire extinguishers. Put a burning match into the mouth of test tube no. 2.

Questions:

1. Based on the observed pH values, describe what happens when CO_2 passes though distilled water. What kind of chemical results from the reaction of carbon dioxide with water?
2. Why does carbon dioxide extinguish the flame?

2.4 Action of strong and weak acids

Strong acids dissociate completely or almost completely whereas weak acids dissociate only partially. The acidity of the solution, which is determined by the concentration of hydrogen ions, is influenced by the concentration of the acid and its dissociation degree. The acidity of the solution is usually expressed by its pH value and can be indirectly assessed from the rate of calcium carbonate decomposition:

$$2\ H^+ + CaCO_3 \longrightarrow Ca^{2+} + H_2O + CO_2$$

Carbonic acid originating from this reaction decomposes immediately to form water and carbon dioxide, which is liberated from the solution. The intensity of bubbles is proportional to the acidity of the inspected solution.

The content of Ca^{2+} ions can be proved by the addition of ammonium oxalate $(NH_4)_2C_2O_4$. When Ca^{2+} is present, a white precipitate of calcium oxalate (CaC_2O_4) occurs. The amount of the precipitate is proportional to the amount of Ca^{2+} ions in the solution.

$$(NH_4)_2C_2O_4 + Ca^{2+} \longrightarrow CaC_2O_4 + 2\ NH_4^+$$

Experiment 2.4 Comparison of strong and weak acids

Put 3 mL of dilute hydrochloric and acetic acid separately into two test tubes and add a piece of limestone or marble (of similar size) to both test tubes. You will observe bubbles more or less intensively exiting the reaction mixture. After a couple of minutes, pour part of the clear solution into the other two test tubes and add 1 mL of ammonium oxalate solution. Let the originated precipitates settle and compare their amounts, which are proportional to the Ca^{2+} content in the solution.

Acid	HCl	CH_3COOH
dilution	1+3	1+3
c(mol/l)	3	4.3
pH	0.40	2.07

Questions:

1. Based on the results of the experiment, deduce which acid is strong and which one is weak. Explain your opinion!

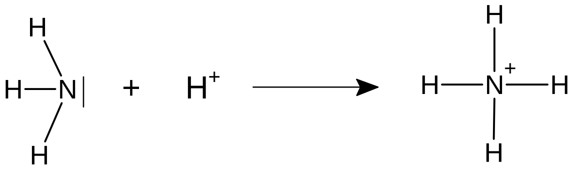
3 BASES

According to the Arrhenius definition, a **base** is a compound that produces hydroxide ions OH^- in an aqueous solution. Dissociation of bases can be expressed by the following equations:

$$NaOH \rightleftharpoons Na^+ + OH^-$$
$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2\ OH^-$$

Strong bases dissociate totally. That means (by analogy to acids) that practically all molecules dissolved in an aqueous solution are split into ions. In contrast, weak bases are dissociated only partially, i.e. a relatively small proportion of molecules are split into ions.

The Arrhenius concept is, however, limited because it allows for only one kind of base – which produces hydroxide ions. A more general definition is suggested in the Brønstedt-Lowry model. According to this, an acid is a proton (H^+) donor and a base is a proton acceptor, i.e. there is an unshared electron pair in the molecule that can form a covalent bond with an H^+ ion. An example of such a base is ammonia.



3.1 Strong bases

Hydroxides derived from alkali metals (e.g. NaOH, KOH) and alkaline earth metals (e.g. $Ca(OH)_2$) belong to the group of strong bases. These hydroxides are solids at standard temperature and pressure. NaOH and KOH are easily soluble in water (ca 110 g in 100 ml of water at 20 °C), whereas $Mg(OH)_2$ and $Ca(OH)_2$ are only partially soluble. The solubility of $Ca(OH)_2$ decreases with rising temperature, which can be considered anomalous (the solubility of $Ca(OH)_2$ in 100 ml of water is 0.166 g at 20 °C, 0.129 g at 50 °C and 0.079 g at 100 °C).

The aqueous solution of $Ca(OH)_2$ is called **lime water** and can be prepared by filtering a suspension of $Ca(OH)_2$, so-called ‘milk of lime’.

Experiment 3.1 Solubility of $Ca(OH)_2$ in water

Put a small spoonful of solid $Ca(OH)_2$ into a small beaker and stir the mixture. Filter part of the suspension through a paper filter into another test tube. Heat the rest of the mixture up to near boiling point and filter approximately the same amount of the solution into another test tube. Then add 1 mL of 5% ammonium oxalate to both test tubes. The resulting precipitates indicate Ca^{2+} content in the solution. Let them settle and then compare the amount of precipitate in both test tubes.[1]

Questions:

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[1] The amount of originated precipitate is proportional to the Ca^{2+} content in the solution, i.e. the amount of dissolved $Ca(OH)_2$.

1. Based on the amount of produced precipitate decide whether the solubility of $Ca(OH)_2$ in water is higher at an ambient temperature or after heating.

3.2 Weak bases

Ammonia, NH_3, is a typical example of a Brønstedt weak base. Gaseous ammonia easily dissolves in water and reacts with water molecules to form ammonium hydroxide.

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

However, this reaction does not proceed quantitatively. Ammonia is liberated from its concentrated solution (25% wt.) as an acrid colourless gas, the reactivity of which has already been proved in experiment 2.1.

Experiment 3.2 Reaction of NH_3

Hold a wet pH test strip just above the opened mouth of a bottle containing concentrated ammonia and assess the pH value via comparison with the colour scale.

Questions:

1. What pH have you observed and what can be concluded from this observation?

3.3 Heavy metal hydroxides

Heavy metals are practically all metals excluding alkalis and alkali earth metals. The hydroxides derived from these metals are insoluble in water, and therefore if we add soluble hydroxide to a solution of heavy metal, the corresponding metal hydroxide will precipitate.

$$M^{n+} + n\,NaOH \longrightarrow M(OH)_n + n\,Na^+ \qquad (M = \text{heavy metal})$$

Precipitated hydroxides can be redissolved trough a reaction with strong acid, e.g. HCl, under the formation of corresponding chlorides and water.

$$M(OH)_n + n\,HCl \longrightarrow MCl_n + n\,H_2O$$

Hydroxides derived from some metals that are called **amphoteric** ($Al(OH)_3$, $Zn(OH)_2$, $Cr(OH)_3$), can be dissolved not only in acids but also in strong bases, e.g. in an NaOH solution. In arising soluble hydroxy complexes the metal acts as a central atom surrounded by hydroxy groups.

$$M(OH)_n + NaOH \longrightarrow Na[M(OH)_{n+1}]$$

These complexes decompose through the addition of acid and reprecipitation of hydroxide occurs.

$$Na[M(OH)_{n+1}] + HCl \longrightarrow M(OH)_n + NaCl + H_2O$$

Experiment 3.3 Heavy metal hydroxides

Prepare 3 test tubes add 2 mL of just one of the following solutions to each test tube: a) copper(II) sulphate, b) iron(III) chloride, c) aluminum sulphate. Then, add a dilute solution of NaOH **dropwise** to each test tube until a precipitate appears. Then, continue adding NaOH to test tube c) and observe the changes. After that, add dilute HCl drop by drop and describe your observation.

Questions:

1. What is the colour of the precipitate?
2. What happened after further addition of NaOH to test tube c) and what is the reason for such behaviour?
3. Write all chemical equations that describe the observed chemical processes of precipitation and dissolution (8 equations)!

4 NEUTRALISATION AND HYDROLYSIS OF SALTS

4.1 Dissociation of water

Similarly to acids and bases, water also dissociates to produce H^+ and OH^- ions. However, the number of dissociated molecules is negligible.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (4.1)$$

The relation between concentrations of these ions is expressed by the equation:

$$c(H^+) \cdot c(OH^-) = K_w = 10^{-14} \qquad (4.2)$$

K_w is the **ion product of water**. Since it is a constant the concentrations of H^+ and OH^- can be considered to be "balanced" against each other and cannot change independently. In pure water, the following equilibrium results according to equation *(4.1)*:

$$c(H^+) = c(OH^-) \qquad (4.3)$$

because 1 mol of H_2O splits into 1 mol of H^+ and 1 mol of OH^-. It can be derived from equation *(4.2)* that in pure water:

$$c(H^+)^2 = 10^{-14}\ \text{mol}\cdot\text{l}^{-1} \longrightarrow c(H^+) = 10^{-7}\ \text{mol}\cdot\text{l}^{-1}.$$

Nevertheless, in 1 litre of water (1 L = 1 $dm^3 \approx$ 1 kg = 1000 g) there are:

$$n = \frac{m}{M} = \frac{1000}{18{,}01} = 55{,}52\ mol\ H_2O.$$

Definition of pH

The concentration of hydrogen ions in a solution is expressed by the pH value, defined as the negative logarithm of hydrogen ions concentration.

$$pH = -\log c(H^+) \qquad (4.4)$$

This definition of pH is valid only for dilute solutions of strong acids. For concentrated solutions activity should be applied instead of concentration ($a = c \cdot \gamma$, where γ is an activity coefficient and tends to 1 for common solutions).

According to equation *(4.2)*, the pH of the solution can vary from 0 to 14. Values below 7 indicate that the number of H^+ ions outweighs the number of OH^- and concentration of H^+ is the higher the lower the pH is – the solution is **acidic**. At a pH of above 7, OH^- ions exceed H^+ and with the increasing concentration of OH^- the pH increases as well – the solution is **basic**. Finally, a **neutral** solution is the one in which the concentration of H^+ is equal to the concentration of OH^- and the pH is exactly 7.00.

Acidobasic indicators

Accurate measuring of pH is carried out using a special device, a pH-meter. However, we usually manage with a simple assessment of acidity or basicity using acidobasic indicators. These are organic dyes that change their colour at a specified pH. According to the colour we can decide whether the pH of the solution is higher or lower than the pH at which the colour changes. These indicators are also used to determine the end of acidobasic titration, a method for quantitative analysis of acid and base concentration in an aqueous solution. The exact pH at which the colour changes depends on the temperature and concentration of the indicator.

Common acidobasic indicators are:

Acidobasic indicator	pH of colour change	Colouration	
		acidic	basic
methyl orange	3.1 – 4.4	pale red	yellow
methyl red	4.4 – 6.2	red	yellow
Tashiro	4.2 – 6.2	purple	green
phenolphthalein	8.2 – 10.0	colourless	violet

Universal indicators (e.g. pH test strips) are mixtures of several acidobasic indicators. Colour changes fluently with pH in a specified pH range. Comparing the colour with the colour scale gives the approximate pH value of the solution.

Experiment 4.1 Differentiation between acids and bases using acidobasic indicators

Put ca 1–2 mL of sample no. 1 into 3 test tubes and then add 2–3 drops of just one of the following indicators (methyl orange, phenolphthalein, Tashiro) and observe the changes in colour. Then, also carry out this experiment similarly in a similar way with sample no. 2.

Questions:

1. Based on the colour changes decide which of the two samples is HCl and which one is NaOH.

4.2 Neutralisation

Neutralisation is a chemical reaction in which an acid reacts with a base to form water and corresponding salt. Salt is composed of an anion derived from the acid and a cation derived from the base. Free H^+ (from the acid) and OH^- (from the base) ions react immediately with each other and form non-dissociated water molecules.

$$\mathbf{2\,K}OH + H_2\mathbf{SO_4} \longrightarrow 2\,H_2O + \mathbf{K_2SO_4}$$

$$\mathbf{Na}OH + H\mathbf{Cl} \longrightarrow H_2O + \mathbf{NaCl}$$

According to the previous equations the following equality relation holds for the state of reaching the equivalence point (the point at which equal quantities of H^+ and OH^- exist to cancel each other out) during the titration of NaOH with HCl:

$$n(\mathrm{NaOH}) = n(\mathrm{HCl})$$

$$c(\mathrm{NaOH}) \cdot V(\mathrm{NaOH}) = c(\mathrm{HCl}) \cdot V(\mathrm{HCl}) \quad \Longrightarrow \quad c(NaOH) = \frac{c(HCl) \cdot V(HCl)}{V(NaOH)}$$

n ... mole [mol]
c ... concentration of the solution [$\mathrm{mol \cdot l^{-1}}$]
V ... volume of the solution [l]

Experiment 4.2 Titration of NaOH with hydrochloric acid

Measure out 50 mL of the examined 1% NaOH using a graduated cylinder, put it into a titration flask and add 2–3 drops of Tashiro indicator. Then, add HCl (1 mol/L) dropwise from the burette while stirring the solution with a gyral movement of the hand. The first drop that permanently changes the colour of the solution indicates the equivalence point (the end of titration). The volume of added HCl can be read from the scale on the burette with an accuracy of 0.1 mL. After noting down the consumption value you can add several more drops of HCl and see what happens.

Questions:

1. Calculate the concentration of the examined NaOH solution.
2. Describe the colour changes during the titration and determine which chemical is responsible for the colour of the solution.

4.3 Formation of salts – reaction of acids with metal oxides

Salts can be formed not only by the reaction of hydroxides and acids, but also by the reaction of metal oxides with acids, non-metal oxides with bases (*see Chap. 6 – Lime, gypsum*), and by the dissolution of metals in acids (*see Chap. 12 – Metals*).
Metal oxides react with acids similarly to hydroxides to form water and corresponding salt.

Experiment 4.3 Formation of zinc(II) chloride from ZnO and HCl

Make a suspension of a small amount of zinc oxide[1] in ca 3 mL of distilled water. Then add 1 mL of concentrated hydrochloric acid, shake the mixture and observe the changes.

Questions:

1. Describe the changes during the reaction.
2. Write a chemical equation for the observed reaction.

4.4 Hydrolysis of salts

Salts dissociate into ions in a water solution similarly to acids and bases.
Sodium carbonate, salt derived from a strong base (NaOH) and a weak acid (H_2CO_3), dissociates according to the following equation. Water is also partly dissociated according to the second equation:

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[1] Zinc oxide is insoluble in water, whereas zinc chloride dissolves to a colourless solution.

$$\begin{aligned} Na_2CO_3 &\rightleftharpoons \mathbf{2\,Na^+} + CO_3^{2-} \\ 2\,H_2O &\rightleftharpoons \mathit{2}\,H^+ + \mathbf{2\,OH^-} \end{aligned}$$

Thus, ions Na^+, OH^-, H^+ and CO_3^{2-} (HCO_3^- is avoided for simplicity) ions are present in the solution. The first two ions imaginarily form a **strong base NaOH**, which dissociates completely; hence, these ions do not tend to combine into molecules. In contrast, the other two ions form a **weak acid H_2CO_3**, which is only partly dissociated in the solution. Therefore, part of CO_3^{2-} combines with H^+ to form non-dissociated H_2CO_3 molecules. The excess OH^- anions cause the ***basic*** reaction of the solution. This process, called hydrolysis, is summarised in the following equation:

$$Na_2CO_3 + 2\,H_2O \rightleftharpoons \mathbf{2\,Na^+ + 2\,OH^-} + H_2CO_3$$

Another example is ***aluminum chloride***, which is derived from a strong acid (HCl) and a weak base ($Al(OH)_3$). Dissociation follows the equations:

$$\begin{aligned} AlCl_3 &\rightleftharpoons Al^{3+} + \mathbf{3\,Cl^-} \\ 3\,H_2O &\rightleftharpoons \mathbf{3\,H^+} + 3\,OH^- \end{aligned}$$

Analogically to the former example, H^+ and Cl^- ions do not tend to combine into molecules, whereas Al^{3+} and OH^- ions combine with each other to form non-dissociated molecules of $Al(OH)_3$. When this occurs the number of H^+ ions exceeds the number of OH^- and the solution becomes ***acidic***. The hydrolysis of $AlCl_3$ is summarised in the following equation:

$$AlCl_3 + 3\,H_2O \rightleftharpoons Al(OH)_3 + \mathbf{3\,H^+ + 3\,Cl^-}$$

Ions that come from a dissociation of salts derived from both **strong acids and strong bases** (e.g. NaCl) have no tendency to combine with H^+ and OH^- ions. Such salts do not hydrolyse and the solution remains ***neutral***.

$$\begin{aligned} NaCl + H_2O &\rightleftharpoons Na^+ + Cl^- + H^+ + OH^- \\ H^+ + OH^- &\rightleftharpoons H_2O \end{aligned}$$

To sum up the above mentioned explanation we can say that the hydrolysis of salts derived from strong acids (HCl, H_2SO_4) and weak bases ($Al(OH)_3$, $Fe(OH)_3$, NH_3) results in an acidic solution, the hydrolysis of salts derived from weak acids (H_2CO_3) and strong bases (NaOH, KOH) results in basic solution, and the hydrolysis of salts derived from strong acids as well as strong bases results in a neutral solution.

Experiment 4.4 Hydrolysis of salts

Put a drop of 5% Na_2CO_3 and 1% $FeCl_3$ on a pH test strip and read the pH value of the solutions. Finally, prepare a solution of sodium chloride by dissolving solid NaCl in distilled water in test tube. Measure the pH value of this solution using a pH test strip.

Questions:

1. According to measured pH decide whether the solution is acidic, neutral or basic.
2. Specify from which acid and base these salts are derived (strong or weak).

5 OXIDATION AND REDUCTION

Redox reactions are processes consisting of two antagonistic reactions – oxidation and reduction. This process is connected with the exchange of electrons between the reacting agents and the change in their oxidation states. **Oxidation** is a process in which a substance loses electrons *(donor)* while the oxidation state increases. **Reduction** is a process in which a substance gains electrons *(acceptor)* while the oxidation state decreases. These reactions always run simultaneously because something cannot lose electrons unless something else gains them. The redox process can be depicted as follows:

$$\mathrm{Ox} + e^- \quad \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} \quad \mathrm{Red}$$

E.g. $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

Substances are divided into reducing or oxidizing agents according to whether they lose or gain electrons.

Reducing agent – a substance that loses electrons and provides them to another substance. It oxidises itself. (e.g. Na_2SO_3, KI).

Oxidizing agent – a substance that gains electrons from another substance. It reduces itself. (e.g. $KMnO_4$, H_2O_2).

A common example of a redox reaction is the ***reduction of Fe^{3+} to Fe^{2+} by iodide***, which oxidises itself to iodine[1]:

Equations:

$$\begin{array}{ll} \text{reduction} & Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad /\cdot 2 \\ \text{oxidation} & 2\,I^- \rightleftharpoons I_2^{\,0} + 2\,e^- \\ \hline \end{array}$$

$$2\,Fe^{3+} + 2\,I^- \rightleftharpoons 2\,Fe^{2+} + I_2^{\,0}$$

In both half-reactions we have to obey the rule that the number of ions (atoms) and the charge on both sides of the equation must be equal. Since the number of interchanging electrons has to be the same in both reactions, the reduction reaction is to be multiplied by two. The overall reaction is then gained by summing both half-reactions.

Multi-atomic ions or molecules can also take part in redox reactions. An example of such particles is violet coloured permanganate ions which can be reduced to colourless Mn^{2+} ions in an acidic solution. In this case, Mn(VII) reduces to Mn(II). ***Oxidation of Fe^{2+} to Fe^{3+} by permanganate*** can be schematically described as follows:

$$\begin{array}{rl} MnO_4^- + 8\,H^+ + 5\,e^- \rightleftharpoons & Mn^{2+} + 4\,H_2O \\ Fe^{2+} \rightleftharpoons & Fe^{3+} + e^- \quad /\cdot 5 \\ \hline \end{array}$$

$$MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \rightleftharpoons Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$$

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[1] Aqueous solution of iodine is yellow. After the addition of colloidal starch to a solution of iodine the colour turns deep blue, or in the case of higher concentrations of iodine, a black precipitate appears.

5.1 Redox system Fe(II) – Fe(III)

Iron usually occurs in two oxidation states, +II (ferrous salts) and +III (ferric salts). Fe^{2+} and Fe^{3+} ions show different chemical properties and reactivity. In insufficiently acidic solutions, both ions hydrolyse and precipitate in the form of hydroxides. $Fe(OH)_2$ is green and oxidises to rusty $Fe(OH)_3$ via the action of oxygen from the air.

Proof of Fe^{3+} can be obtained by thiocyanate SCN^- (e.g. KSCN). Fe^{3+} ions form a blood-red complex $[Fe(SCN)]^{2+}$ with SCN^- ions in an acidic medium. Fe^{2+} ions do not undergo this reaction and the solution remains colourless. In contrast, potassium hexacyanoferrate(III) $K_3[Fe(CN)_6]$ proves the presence of Fe^{2+} ions in the form of a blue complex (Prussian blue).

Experiment 5.1.1 Oxidation of ferrous salt by permanganate

Add several drops of dilute H_2SO_4 to 1 mL of Fe^{2+} solution. Then, add a dilute solution of potassium permanganate dropwise (from a burette), shake it well and observe the colour change. As soon as the solution stops decolorizing, add 0.5 mL of KSCN solution and observe the colour change again.

Questions:

1. Can you explain the colour changes during the reaction?
2. Express the reaction of ferrous salt with permanganate using a chemical equation.

Experiment 5.1.2 Oxidation of ferrous salt by hydrogen peroxide

Add several drops of KSCN into a solution of ferrous salt. Then add several drops of hydrogen peroxide and observe the change in colour.

Questions:

1. Can you explain the colour change during the reaction?

Experiment 5.1.3 Reduction of ferric salt by iodide

Add several drops of KSCN into a solution of ferric salt. Then, add a small amount of solid potassium iodide and observe the colour change. Split the solution into two identical parts. Mix one part with several drops of colloidal solution of starch, and the other part with a few drops of potassium hexacyanoferrate(III) solution (ferricyanide $K_3[Fe(CN)_6]$) and observe the colour changes.

Questions:

1. What results from the reaction of ferric salt with iodide? Write a chemical equation.
2. What substances have you proved by the addition of colloidal starch and potassium hexacyanoferrate(III), respectively, to the reaction mixture?

5.2 Redox system of manganese compounds

Manganese occurs in its compounds in different oxidation states, usually II, III, IV, VI, and VII. Mn^{2+} solutions are only stable in an acidic medium. Mn(VI) and Mn(VII) compounds are very strong oxidizing agents and therefore they cannot be found in nature

Permanganates can be reduced, for example, by sodium sulphite, Na_2SO_3, which is oxidised to sulphate:

$$SO_3^{2-} + H_2O \rightleftharpoons SO_4^{2-} + 2\,H^+ + 2\,e^-$$

The oxidation number of sulphur in sulphites is +IV and in sulphates +VI. This difference corresponds to two electrons that are released from sulphur in SO_3^{2-}. It is interesting to mention that the total ion charge does not change.
The way at which of MnO_4^- (Mn^{VII}) is reduced depends on the concentration of hydrogen ions (pH) in the solution. It reduces either to colourless Mn^{2+}salt (Mn^{II}), brown precipitate of MnO_2 (Mn^{IV}), or green solution of manganate, MnO_4^{2-} (Mn^{VI}). The reactions occur according to the following equations:

$$MnO_4^- + 8\,H^+ + 5\,e^- \rightleftharpoons Mn^{2+} + 4\,H_2O$$
$$MnO_4^- + 4\,H^+ + 3\,e^- \rightleftharpoons MnO_2 + 2\,H_2O$$
$$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$$

Experiment 5.2 Reduction of permanganate by sulphite

Take three test tubes with a solution of potassium permanganate and put just one of the following solutions into each of them:

- 1 mL of dilute sulphuric acid (acidic medium),
- 1 ml of water (neutral medium),
- 1 mL of sodium hydroxide solution (basic medium).

Then, put half a small spoonful of sodium sulphite into each test tube and observe the changes.

Questions:

1. Based on your observations decide what kind of solution (acidic, neutral or basic) is necessary for the reduction of Mn^{VII} to Mn^{VI}, Mn^{IV} or Mn^{II}, respectively.

5.3 Redox system Cr(VI) – Cr(III)

Chromium usually forms compounds with oxidation number III and VI. It is very important to distinguish between these two oxidation states because unlike Cr^{III} salts, compounds containing Cr^{VI} are particularly toxic.

Chromium is amphoteric, hence it can form both cations and anions in ***oxidation state III***.[2] When Cr^{3+} salts react with strong hydroxide (e.g. NaOH) insoluble chromium hydroxide, $Cr(OH)_3$, precipitates. However, in excess NaOH it dissolves to form green solution of hexahydroxochromate(III), $[Cr(OH)_6]^{3-}$. ***Oxidation of chromium(III) salts*** only proceeds in a basic medium. The reaction follows the equation:

$$Cr^{3+} + 8\,OH^- \rightleftharpoons CrO_4^{2-} + 4\,H_2O + 3\,e^-$$

Chromium with ***oxidation number VI*** occurs in two species, chromate CrO_4^{2-} and dichromate $Cr_2O_7^{2-}$, which can be formed by the merging of two chromate molecules in an acidic medium:

$$2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + 2\,H_2O$$

The reaction is reversible – in a basic medium, dichromate ions split back into pairs of chromate ions. The transformation of one form into the other one is connected with a colour

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[2] Chromium(III) salts have a green colour.

change because chromates are yellow whereas dichromates are orange. Proof of the presence of Cr^{VI} compound can be given by the reaction with hydrogen peroxide in an acidic medium during which unstable blue peroxochromic acid is formed.

Chromates as well as dichromates behave as oxidizing agents, reducing themselves to chromium (III) salts. The ***reduction of dichromates*** proceeds only in an acidic medium for which ferrous salt or sulphite can be used:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O$$

Experiment 5.3.1 Reduction of dichromate by sulphite

Put a small amount of 1% potassium dichromate into a test tube. Add several drops of dilute sulphuric acid and half a small spoonful of sodium sulphite. Observe the changes.

Questions:

1. What happens when sulphite is added to dichromate solution?
2. Why do we add sulphuric acid to the reaction mixture?

Experiment 5.3.2 Oxidation of Cr^{3+} salt by hydrogen peroxide

Prepare a solution of Cr^{3+} salt by dissolving half a spoonful of $KCr(SO_4)_2 \cdot 12H_2O$ (purple) in 2 mL of water. Add a dilute solution of sodium hydroxide dropwise until the mixture remains perfectly clear. Then add hydrogen peroxide, shake well and observe the colour change. Pour off 3 mL of the solution into a clean test tube and add a few drops of dilute sulphuric acid. The colour will change for a couple of seconds.

Questions:

1. What happens with the Cr^{3+} ions during the reaction with hydrogen peroxide?
2. Why do we add sodium hydroxide to the reaction mixture?
3. What colour appeared after the addition of sulphuric acid to the solution? What kind of specie does it prove?

6 LIME, PLASTER OF PARIS

6.1 Lime

Lime is a technical name for calcium oxide (CaO) with a different level of purity. It is produced by the thermal decomposition of natural limestone at temperatures at which the originated product is able to react quickly with water to form $Ca(OH)_2$, a main component of lime binders.

Generally, there are two types of lime used in civil engineering:

- **Air lime**, which consists mainly of CaO with a minor amount of MgO. High quality lime contains more than 90 % of main components (CaO + MgO) but only MgO < 5 %. Lime that contains more than 5 % MgO is referred to as dolomitic lime.
- **Hydraulic lime**, which is produced from less pure limestone containing more than 10 % of hydraulic components, i.e. SiO_2, Al_2O_3, Fe_2O_3.

According to the terminology, air lime only sets and hardens in air, while hydraulic lime also sets and hardens under water.

Air lime is produced from natural limestone by its annealing at temperatures above 950 °C. Calcium oxide is formed according to the reaction:

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad \Delta H = 178{,}4\ kJ\cdot mol^{-1}$$

The smaller the grains of limestone and the higher the temperature the faster is the rate of $CaCO_3$ decomposition. However, at temperatures above 1340 °C so-called *overburnt lime* is formed. Unfortunately, it hydrates very slowly due to shrinkage of the surface layer and the closure of pores caused by sintering.
The reaction of calcium oxide with water according to the following reaction is called ***lime slaking***:

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad \Delta H = -65{,}2\ \ kJ\cdot mol^{-1}$$

It is an example of a hydration reaction with the release of a rather large amount of heat. In order to avoid problems with slaking, the producers provide slaked lime in the form of *lime hydrate*. It is a quite pure calcium hydroxide that contains less than 3 wt% of free water. Aqueous solution of calcium hydroxide is called *lime water*, whereas its suspension (containing fine grains of calcium hydroxide) is called *milk of lime*, or *paste of lime*.[1]
Calcium hydroxide is a strong base and the pH of its saturated solution is 12.45 at 25 °C. Compared with $CaCO_3$, it decomposes at a much lower temperature (about 500 °C) to form calcium oxide and water.

$$Ca(OH)_2 \longrightarrow CaO + H_2O$$

Carbonation – the reaction of $Ca(OH)_2$ with CO_2 from the air plays a significant role in the hardening of lime mortars

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[1] Burnt or air lime can be expressed by the chemical formula CaO; slaked lime, lime hydrate, paste of lime, milk of lime or lime water can be expressed as $Ca(OH)_2$.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \qquad \Delta H = -112{,}9\ kJ{\cdot}mol^{-1}$$

The hardening of lime mortars results in the formation of $CaCO_3$, which is chemically identical to the raw material that is used for the production of lime. The heat that is needed for the annealing process is released back during slaking and carbonation.

The natural content of CO_2 in the air is about 0.038 vol.%, which is why carbonation of mortars proceeds so slowly. However, carbonation can be accelerated by the intensive desiccation of moisture that is formed during the reaction.

The action of water containing carbon dioxide (aggressive) leads to the decomposition of *insoluble* limestone and the formation of *soluble* hydrogencarbonate:

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$$

The reaction is reversible and can be influenced for example by the concentration of CO_2 dissolved in water. Continuous addition of CO_2 favours the formation of $Ca(HCO_3)_2$. If CO_2 is removed (e.g. by deaeration or boiling) the equilibrium shifts towards the formation of insoluble $CaCO_3$ (limescale).

This reaction is the principle behind karst effects in areas with limestone bedrock. Water with CO_2 slowly dissolves a limestone massif, but when it gets into a cavern, CO_2 is released and $CaCO_3$ precipitates in the form of stalactites as a result of the reverse reaction. The action of CO_2 also causes the degradation of concrete.

Experiment 6.1.1 Proof of calcium carbonate[2]

Put a small piece of marble ($CaCO_3$) into a solution of dilute hydrochloric acid and watch the reaction.

Questions:

4. Describe the reaction using a chemical equation.

Experiment 6.1.2 Preparation of slaked lime

Take a small piece of marble using forceps and anneal it in the dark flame of burner for about 3 minutes until a red glow appears. Then, drop the annealed piece into ca 5 mL of water in a porcelain dish and measure the pH of the resulted suspension using a test strip. The basic reaction is a proof of calcium hydroxide formation.

Repeat this experiment but without annealing the marble and compare your results.

Questions:

1. Write chemical equations describing this experiment.
2. Compare and explain the obtained pH values.

Experiment 6.1.3 Carbonation of lime mortars and the influence of aggressive CO_2 on lime based building materials

Prepare a suspension of calcium hydroxide in water (half a small spoonful in 10 mL of distilled water) and filter the suspension to prepare lime water. Then, lead gaseous carbon dioxide from the Kipp's apparatus into the solution. The clear solution becomes turbid due to carbonation. Further addition of carbon dioxide then leads to the dissolution of the precipitate

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[2] Carbonates can be proved by the reaction with hydrochloric acid. When calcium carbonate reacts with HCl, calcium chloride, water and gaseous CO_2 arise.

and the clarifying of the solution.

Questions:

1. Explain your observations and describe the experiment using suitable chemical equations.
2. Where can you observe such an effect in nature?

6.2 Plaster of Paris

Plaster of Paris is prepared by the partial dehydration of gypsum $CaSO_4 \cdot 2H_2O$, which can be found in nature or is produced as a by-product in the chemical and power supply industry. Power plants often use fossil fuel, which contain sulphur, and power plant gypsum is produced during the desulfurisation of stack gases using a limestone suspension.

Dehydration of gypsum proceeds in two steps:

- in the first step (up to 170 °C), hemihydrate ($CaSO_4 \cdot 1/2H_2O$) is produced. It is the main component of *quick-setting plaster*,
- in the second step (800 – 1000 °C) anhydrous $CaSO_4$ (anhydrite) is formed. It is the main component of *slow-setting plaster* and *anhydrite binder*.

$$\underset{\textit{gypsum}}{CaSO_4 \cdot 2H_2O} \longrightarrow \underset{\textit{hemihydrate}}{CaSO_4 \cdot 1/2H_2O} \longrightarrow \underset{\textit{anhydrite}}{CaSO_4}$$

Due to the high temperature of production, anhydrite partially decomposes:

$$CaSO_4 \longrightarrow CaO + SO_2 + ½\ O_2$$

to form calcium oxide (max. 3%), which causes the basic reaction in the water suspension of slow-setting plaster.

Experiment 6.2 Distinguishing between types of plaster

Put about 10 mL of distilled water into two porcelain dishes. Add half a spoonful of quick-setting plaster to one of the dishes and slow-setting plaster to the other one. Then, stir the mixtures (beware of mutual contamination of the solutions) and add 3 drops of phenolphthalein[3] solution.

Questions:

1. Explain the colour change after the addition of phenolphthalein.

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[3] Phenolphthalein turns violet in a basic medium.

7 CEMENT

Cement is a pulverised hydraulic binder that sets and hardens after mixing with water. It usually consists of ground silicate or aluminate clinker and other admixtures.
The most common cement is ***Portland cement*** (abbreviated as p–cement or PC), which is produced by the annealing of limestone and aluminosilicate minerals (clays, marl, schist, shale) above clinkering temperature (1350 °C) to form Portland clinker. It consists of four main clinker minerals: $3CaO{\cdot}SiO_2$ (C_3S) – tricalcium silicate (*alite*), β-$2CaO{\cdot}SiO_2$ (C_2S) – dicalcium silicate (*belite*), $3CaO{\cdot}Al_2O_3$ (C_3A) – tricalcium aluminate, and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ (C_4AF) – tetracalcium aluminnoferrite. The clinker is then finely ground with 3 – 5% of gypsum ($CaSO_4{\cdot}2H_2O$), which acts as a setting retarder.

Blended cements are prepared by replacing 6 to 95% of Portland cement with admixtures having latent hydraulic or pozzolanic properties (blast furnace slag, fly ash, natural pozzolanas).

Setting and hardening of cements is based on the reaction of clinker minerals with water:

$$2[3CaO{\cdot}SiO_2] + 6\,H_2O \longrightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + 3Ca(OH)_2$$

$$2[2CaO{\cdot}SiO_2] + 4\,H_2O \longrightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + Ca(OH)_2$$

$$3CaO{\cdot}Al_2O_3 + 6\,H_2O \longrightarrow 3CaO{\cdot}Al_2O_3{\cdot}6H_2O$$

The first two reactions proceed quite slowly, whereas the last one is very fast, and therefore it must be retarded by the addition of $CaSO_4{\cdot}2H_2O$. The originated products are ettringite, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$, and subsequently calcium aluminate monosulphate phase, $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$. However, these mechanisms are considerably simplified.

Originated calcium silicate hydrate, $3CaO{\cdot}2SiO_2{\cdot}3H_2O$, is the main binding phase in cement mortars and concretes. Since it has a xerogel character and its composition varies, it is usually described by the general formula "CaO-SiO_2-H_2O gel" (shortly "CSH gel"). The second hydration product, $Ca(OH)_2$ (*portlandite*), reacts directly with admixtures in blended cements forming extra CSH gel that fills in the voids left by evaporated mixing water.

7.1 Composition of Portland cement

Portland cement belongs to the group of silicate cements. It consists of Portland clinker (95 – 97 %) and gypsum $CaSO_4{\cdot}2H_2O$ (3 – 5 %).
The chemical composition of clinker is listed in the following table:

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O
62 – 65 %	18 – 24 %	4 – 8 %	1.5 – 4.5 %	0.5 – 4 %	1 – 1.15 %	0.1 – 1 %

The content of sulphate and magnesium ions must be particularly controlled. A higher content than allowed by standards can cause sulphate or magnesium corrosion, which leads to crack formation and finally the complete disintegration of concrete.

Chemical proofs for selected ions

Sufficient proof of silicates is the formation of a white insoluble gel of polysilicic acid (partially dyed due to insoluble substances) during heating of the analysed material (e.g. cement) with nitric acid.

A presence of $\boldsymbol{Ca^{2+}}$ can be proved by the addition of ammonium oxalate. A white precipitate of calcium oxalate is formed when Ca^{2+} is present.

$\boldsymbol{Al^{3+}}$ and $\boldsymbol{Fe^{3+}}$ can be proved by the addition of dilute ammonium hydroxide (1 + 2). Aluminum forms a white precipitate of aluminum hydroxide whereas iron forms a rusty precipitate of ferric hydroxide.

$\boldsymbol{Fe^{3+}}$ ions can also be proved by direct reaction with potassium thiocyanate solution (KSCN). Fe^{3+} forms a blood-red complex with SCN^-.

A presence of $\boldsymbol{Mg^{2+}}$ can be proved by the addition of sodium hydroxide until a dense precipitate occurs, and several drops of 0.05% titanium yellow solution in ethanol. When magnesium is present a pink colour appears. According to the EN standard the maximum content of MgO must not exceed 6%.

$\boldsymbol{SO_4^{2-}}$ can be proved by the addition of $BaCl_2$ solution. White $BaSO_4$ precipitates when sulphate ions are present.

Experiment 7.1 Proof of major components in Portland cement

Put a small amount of PC into a test tube, add about 1 – 2 mL of water and shake. Using a glass rod, place a small drop of the suspension on the pH test strip. Note down the observed pH value. Keep the suspension for further analysis.

Portland cement, in contrast to natural silicates, easily decomposes in solutions of strong acids (HCl, HNO_3). About 0.2 g of the sample is enough for the whole analysis.
Add 2 – 3 mL of conc. HNO_3 to the suspension and heat it in a moderate flame while shaking until the colour of the mixture turns yellow (max. 2 min.). You can stop heating after the grey cement powder has completely disappeared. Then, add about 8 ml of distilled water, **shake** the mixture and let the solid parts settle. If necessary, filter the suspension to obtain a clear solution. Divide the clear solution (if this is not possible, you will have to filter it) into five test tubes for separate analyses. Test for the presence of Ca^{2+}, Al^{3+}, Fe^{3+}, Mg^{2+}, and SO_4^{2-} ions in the solution according to the above mentioned methods.

Questions:

1. Explain the pH value of a cement suspension in water.
2. Describe the changes occurring during the reaction of cement with nitric acid. Which cement component does it give a proof of?
3. Which of the given ions have you proved in the solution obtained after the decomposition of cement in nitric acid? Explain your results.

7.2 Differentiation between ordinary Portland cement and slag cements

Cements blended with blast furnace slag can be easily recognised due to the content of sulphides, which are notably present only in slag. If a water suspension of a sample containing sulphides (usually CaS) is acidified with several drops of conc. HCl, a bad smell of hydrogen sulphide arises:

$$\mathrm{CaS} + 2\ \mathrm{HCl} \longrightarrow \mathrm{H_2S} + \mathrm{CaCl_2}$$

A positive reaction proves that the cement is blended. This method is, however, not applicable for hydrated cement and concrete.

Experiment 7.2 Determination of cement type

There are two unknown samples of cement. Make a water suspension of both samples (half a spoonful) and add 1–2 mL of dilute hydrochloric acid into each suspension. Decide, which of the samples is ordinary Portland cement and which one is blended.

Questions:

1. Give reasons for your conclusions.

8 OTHER BUILDING MATERIALS

Except for common materials, which were already mentioned in chapters 6 and 7, there are also other less used materials such as water glass, porous concretes and secondary raw materials. The latter are basically waste or by-product from other industrial branches that can partially replace or supplement binder or filler in concrete. Blast furnace slag and fly ash are among the most commonly used secondary raw materials.

8.1 Water glass

Water glass is a colloidal aqueous solution of sodium or potassium silicate. The important parameter of water glass is its silicate modulus – a molar SiO_2 to $Na_2O(K_2O)$ ratio that commonly ranges between 2.0 and 3.3. Sodium water glass is used more often, for example as a resistant or waterproof coat, a fireproof impregnation or an alkali activator for geopolymers.

Setting and hardening of water glass is caused by the formation of framework of silicate hydrogel that can be supported by

- water reduction
- pH decrease (reaction with acid, e.g. carbonic acid)

$$Na_2Si_2O_5 + H_2CO_3 \longrightarrow Na_2CO_3 + H_2Si_2O_5$$

In most cases it concerns decrease in the concentration of OH^- ions and this results in polymerisation (the formation of chains or a framework of repeating atomic groups) of silicic acid[1].

Re-dissolution of gel to a colloidal solution is performed by warming it with strong hydroxide, e.g. sodium hydroxide.

Experiment 8.1 Precipitation of silicic acid gel

Put max. 1 mL of water glass in to a test tube and dilute it with 5 mL of water. Use a pH test strip to measure the pH value of the solution. Then add dilute HCl dropwise until the gel starts to precipitate.
Caution! If too much acid is added the gel will precipitate throughout the whole volume and it will be impossible to pour it out of the test tube.

After the gelation of the water glass, pour out the residual liquid and add 3 mL of NaOH. Stir the mixture with a glass rod and warm it very carefully above a burner. Observe the changes.

Questions:

1. Explain the measured pH value of water glass solution[2] (*see chap. 4 – hydrolysis of salts*).
2. Express the gelation of water glass using a chemical equation.
3. What happens during the warming of silicic acid gel with hydroxide solution?

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[1] H_2SiO_3 is a weak acid.

[2] A solution of water glass can be considered a solution of sodium silicate.

8.2 Porous concrete

Structural elements based on porous concrete exhibit low bulk density and excellent noise and thermal insulating properties. Large pores can be created in concrete in two different ways: mechanically (foam concrete), when the voids are filled with entrained air, or chemically (gas concrete), when the gas released by a chemical reaction forms bubbles that remain entrapped in the concrete after hardening. This gas is usually hydrogen which is produced by the dissolution of aluminum powder in the basic solution of concrete mixture:

$$2\ Al + 2\ OH^- + 6\ H_2O \longrightarrow 2\ [Al(OH)_4]^- + 3\ H_2$$

Reaction products are rapidly removed from the surface of the aluminum powder. Thus the surface remains available for further reaction with a high reaction rate and a high yield of up to 100%. The reaction can even be accelerated by mild warming.

Experiment 8.2 Determination of the reactivity of aluminum powder

Put the following components into a small porcelain dish: cement, lime hydrate and aluminum powder. Stir the mixture and add several drop of water to prepare a viscous paste. Put the dish on a central heating body for 10 – 15 minutes. Then observe what has happened.

Questions:

1. What is the reason for the foaming of the mixture?
2. What reaction type does it concern (redox, neutralisation, hydrolysis)?

8.3 Secondary raw materials

Many secondary raw materials are used in the building industry; of these, several types of fly ash and blast furnace slag are the most utilised.

Blast furnace slag is a by-product of pig iron production. It contains several calcium and magnesium aluminosilicates, sulphur and manganese. With respect to its lower CaO/SiO_2 ratio, slag is bit more acidic than Portland cement. Slag also contains sulphur and manganese, which are present in iron ores and become part of the slag during manufacturing. A presence of Mn^{2+} can be proved by a reaction with periodate in an acidic solution.

$$2\ Mn^{2+} + 5\ IO_4^- + 3\ H_2O \longrightarrow 2\ MnO_4^- + 5\ IO_3^- + 6\ H^+$$

Experiment 8.3 Proof of manganese in blast furnace slag

Decompose a small amount of slag by heating it with approximately 4 mL of dilute nitric acid (1+1). Decomposition is finished when the slag is completely dissolved. Pour half of the solution into another test tube. Then, add half a spoonful of potassium periodate and heat it again until the colour changes.

Questions:

1. What colour did you finally observed?
2. What happens to Mn^{2+} ions during the reaction with periodate?

9 WATER

9.1 Natural water

We distinguish between three types of natural water: rain water, surface water and ground water. Precipitation in the form of rain or snow partially flows over the ground as surface runoff and partially infiltrates deep into the ground and replenishes aquifers. Some ground water finds openings in the land surface and emerges as freshwater springs. Over time, the water returns to the ocean[1], where it evaporates again.

Rain water absorbs substances from the air – e.g. CO_2, SO_2, NO_x, while passing through the atmosphere. However, it generally contains only a small amount of such dissolved substances. In contrast, ***groundwater*** is rich in substances that have been dissolved while passing through the soil. These includes inorganic salts[2] in high concentrations, composed of Na^+, K^+, Ca^{2+}, Mg^{2+} cations and HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- anions. Groundwater contains no oxygen, but often high concentrations of carbon dioxide and sometimes also Fe^{2+} and Mn^{2+}. As there is quite intensive life in ***surface water***, dead bodies and metabolic products of living organisms supply the water with organic compounds. Water quality is often impaired by anthropogenic contaminants from agriculture, industry or domestic usage. Therefore, most water requires some type of treatment before use as drinking water (*see chapter 10*).

Proofs of selected ions in water

Calcium Ca^{2+} can be proved by the addition of ammonium oxalate. White precipitate of calcium oxalate arises if calcium is present in the solution.

Magnesium Mg^{2+} can be proved by the addition of several drops of 0.05% titanium yellow in alcohol and sodium hydroxide. A pink colour appears if magnesium is present.

Ammonium NH_4^+ can be proved by the addition of several drops of Nessler's agent (solution of $K_2[HgI_4]$ in sodium hydroxide). According to the content of NH_4^+ a yellow to orange colouration appears, at higher concentrations a brown precipitate arises.

Sulphates SO_4^{2-} can be proved by the addition of barium chloride. A white precipitate of $BaSO_4$ arises when sulphate ions are present.

Chlorides Cl^- can be proved by the addition of silver nitrate. Chlorides give a white precipitate of silver chloride AgCl with silver ions.

Hydrogencarbonate HCO_3^- can be proved by the addition of a saturated solution of $Ca(OH)_2$. If HCO_3^- is present the water turns turbid due to the formation of $CaCO_3$. This can be explained on the basis of two successive reactions. The addition of OH^- increases pH and transforms HCO_3^- into CO_3^{2-}, which reacts with Ca^{2+} to form insoluble $CaCO_3$:

$$OH^- + HCO_3^- \rightleftharpoons CO_3^{2-} + H_2O$$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$$

---

[1] ***Sea water*** has a large content of salts (30 g·l^{-1} on average).

[2] Groundwater with a high content of dissolved inorganic substances (>1000 mg·l^{-1}) is considered a ***mineral water***.

A presence of ***nitrates*** NO_3^- can be proved by the addition of diphenylamine and sulphuric acid. Put several crystals of diphenylamine into the tested water and shake it. Then carefully add concentrated sulphuric acid in order to get two liquid layers (H_2SO_4 is heavier than water and falls to the bottom of the test tube). A blue ring on the interface is a proof of NO_3^-.
Caution! The reaction only occurs with conc. H_2SO_4, and after mixing, i.e. dilution of the acid, blue colour disappears!

Experiment 9.1 Proof of selected ions in water

At first, verify the presence of NH_4^+ and NO_3^- ions in waste water. Then choose one of the following types of water (drinking, mineral, sea) and test for the presence of all selected ions: Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, Cl^-, HCO_3^-, NO_3^-.[3]

Questions:

1. Which of the ions did you prove in the selected sample, and how?

9.2 Water in civil engineering

Water is an essential part of concrete mixture because it is necessary for the cement hydration. In civil engineering we distinguish between three types of water. ***Mixing water*** is added to the fresh mixture in order to provide hydration and good workability, ***curing water*** is used for the curing of concrete during hydration, and ***impact water*** has a negative effect on the finished structure.

Water quality requirements for civil engineering are stipulated by ČSN and EN standards and depend on the quality of building material. There are limits especially for sulphates, chlorides, magnesium and organic compounds, and these are evaluated by the CHSK method, and the pH in mixing and curing water. These are substances that can prevent cement from hydrating and cause the deterioration of mechanical properties. For instance, humic compounds that occur in peaty water decrease strength due to the formation of calcium humates. Sulphates and magnesium (*see chapter 7*) have a negative effect on hardened concrete, hence they concern curing water rather than mixing water. Chlorides have a corrosive effect mainly on steel reinforcement. Aggressive CO_2 is not so harmful because it is neutralised by the $Ca(OH)_2$ that originates from the cement hydration. Aggressive CO_2 is considered to be a part of dissolved carbon dioxide which reacts with insoluble $CaCO_3$ to form soluble $Ca(HCO_3)_2$ (*see chapter 6*):

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$$

This reaction causes the decomposition of the main binder component in lime mortars – $CaCO_3$. Sulphates represent a serious problem for the durability of concrete structures. They react with hydrated tricalcium aluminate – part of the binder – to form a compound called *ettringite* (*see chapter 7*). Its voluminous molecules generate a pressure on the binder, which cracks and is finally completely destroyed. Magnesium forms $Mg(OH)_2$ with OH^- ions. It is less soluble than $Ca(OH)_2$ and has no binding properties. Ammonia in the form of NH_4^+ ions gets into water with waste water and sewage. It reacts with $Ca(OH)_2$ to form soluble or non-binding calcium salts and gaseous NH_3 is released.
According to the ČSN standard, water which affects the structures can be divided into three

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[3] If not specified directly, add 1–2 mL of reagent solutions.

classes: mildly, mediumly and highly aggressive.

Aggressivity	Aggressive CO_2 [mg·l^{-1}]	SO_4^{2-} [mg·l^{-1}]	NH_4^+ [mg·l^{-1}]	Mg^{2+}[mg·l^{-1}]	pH value
mild	15–40	200–600	15–30	300–1000	5.5–6.5
medium	40–100	600–3000	30–60	1000–3000	4.5–5.5
high	> 100	3000–6000	60–100	> 3000	4.0–4.5

Concentration of hydrogen ions in water

The concentration of hydrogen ions in water is usually expressed as a pH value, which is affected mainly by the concentration of carbon dioxide, carbonic acid and its ionic forms – HCO_3^- and CO_3^{2-}. All these species are in equilibrium. The only carbon dioxide contained in distilled water comes from the air (air contains approx. 0.038% CO_2). Since distilled water contains no salts, even little CO_2 can cause quite a large drop in pH. Natural and drinking water contain HCO_3^-, which is in equilibrium with carbonic acid. Therefore, other substances dissolved in such water have very little or no impact on pH.

Experiment 9.2.1 pH of water

Samples of distilled and drinking water with the addition of universal indicator have already been prepared in two test tubes.
Compare the colour of the solution with the provided pH scale and note down the observed values.

Questions:

1. Explain the difference in pH between distilled and drinking water.

Humic water

Humic substances in water can be proved by the addition of 30% NaOH. When humic compounds are present, the solution becomes yellowish to brown in colour. For the concrete production purposes, the following table was set up:

Degree	Water colouration	Suitability of water as mixing water
1.	colourless or pale yellow	suitable even for high strength concrete
2.	yellow	suitable
3.	brownish yellow	applicable only for weakly loaded structures
4.	dark red to dark brown	not suitable

Experiment 9.2.2 Proof of humic substances in water

Add 20 mL of 30% NaOH to 10 mL of the tested water in a beaker and mix it. Check the colouration at the end of the session (regular reaction time is 24 hours according to the ČSN standard).

Questions:

1. Based on colour of the solution, decide whether the tested water is suitable as mixing water for concrete.

Experiment 9.2.3 Corrosive effect of aggressive CO_2 on lime binders

Take two clean test tubes. Fill one of them with 5 mL of distilled water and the other one with the same amount of water saturated with CO_2. Add about one small spoonful of $CaCO_3$ into each of the test tubes, shake them well and filter both suspensions into clean test tubes. Then, add 0.5 mL of ammonium oxalate to the clear filtrates.[4] After sedimentation compare the amounts of precipitate in both test tubes.

Questions:

1. Which test tube contains more precipitate and why?
2. Express the action of aggressive CO_2 on lime binders using a chemical equation.

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[4] The amount of white precipitate is proportional to the content of soluble Ca^{2+} in the water.

10 WATER IN CONSUMPTION AND THE ENVIRONMENT

Water plays an incommutable role in nature and is necessary for life. The quality of water for everyday use, industry and agriculture must meet the requirements for ***drinking and supply water***. Since natural water sources mostly do not meet these standards, water must be treated prior to supplying it to the end-user. The main treatment consists of controlling the iron, manganese and aggressive carbon dioxide content. These metals can secondarily precipitate in the form of insoluble compounds that are deposited on the surface of pipelines, which can eventually become blocked. Excess carbon dioxide is corrosive to concrete and metals. If the source for drinking and supply water is surface water, it is also necessary to control the content of bacteria and organic compounds in their soluble as well as colloidal forms. Drinking water for the municipal supply must be disinfected so that no germs can contaminate water on the way from the waterworks to the end-user.

Runoff water from urban and industrial areas as well as agriculture has to be treated before discharging it into a natural water recipient. Coarse insoluble particles are removed by sedimentation in large tanks, whereas colloidal and soluble organic substances are reduced using biochemical processes. Organic compounds serve as a nutrient substrate for bacteria, which convert it through metabolic processes and with the help of air oxygen into harmless inorganic substances.
The objective of this session is to show some processes that are used in water treatment.

10.1 Iron in water

As has already been mentioned, the content of iron in drinking and supply water must be controlled. The best source of drinking water is groundwater. However, it contains iron in the form of soluble ferrous salts (due to the lack of oxygen and the increased content of CO_2). The deironing of water involves aeration, which causes a decrease in the concentration of carbonic acid as well as the oxidation of Fe^{2+} to Fe^{3+} by air oxygen. Ferric salts are unstable under such conditions and they hydrolyse to give a rusty precipitate of $Fe(OH)_3$, which can be removed by sedimentation or filtration in waterworks.

Iron belongs to those heavy metals, which form insoluble hydroxides (*see chapter 3*). In laboratory experiment, iron in the form of Fe^{2+} can be removed via the addition of a soluble hydroxide (e.g. NaOH). Iron precipitates as green $Fe(OH)_2$, which is slowly oxidised by air oxygen to rusty $Fe(OH)_3$. The originated insoluble hydroxides can then be removed by filtration.

A proof of ferrous salt Fe^{2+} consists in the oxidation of Fe^{2+} to Fe^{3+} using a suitable oxidizing agent (e.g. H_2O_2). Fe^{3+} is subsequently proved by the addition of potassium thiocyanate when the colour of the solution turns deep red (*see chapter 5*).

Experiment 10.1 Deironing of water

Pour about 3 mL of the examined water, containing Fe^{2+}, into a test tube. Give a proof of Fe^{2+} ions by addition of 1 mL of dilute HNO_3, several drops of KSCN and 1 mL of hydrogen peroxide. Then, take another test tube, pour in 3 mL of tested water and add 3 mL of NaOH solution. Shake the mixture intensively until the colour turn brownish yellow and filter out the originated precipitate. Then, test for the presence of iron in the treated water again.

Questions:

1. What happened after the addition of NaOH to the tested water?
2. To what extent did you manage to remove the iron from water? Was it completely, partially, or did the amount of iron in the water remain unchanged?

10.2. Organic compounds in water

It is difficult and very expensive to determine various organic compounds in water. In practice, a group-determination of all organic compounds is usually sufficient. The principle behind this test is the oxidation of organic compounds by $KMnO_4$ or $K_2Cr_2O_7$ and the measurement of the consumption of the oxidizing agent.

Experiment 10.2 Oxidation of organic substances using $KMnO_4$

Water containing organic compound is simulated by glucose solution. Put 5 mL of glucose solution (1 $g \cdot l^{-1}$) and 0.5 mL of dilute sulphuric acid into a test tube. Heat it up to near boiling point and then, dropwise, add a solution of $KMnO_4$ (0.05 $mol \cdot l^{-1}$). Observe how the colour changes.

Questions:

1. What reaction type does it concern (precipitation, redox, neutralisation)?
2. According to the colour change and with the help of chapter 5, decide how the oxidation state of manganese changes during the reaction.
3. Decide whether $KMnO_4$ is an oxidizing or reducing agent in this reaction.

10.3 Clarification as a water treatment process

Clarification is used for the treatment of surface water to make it save to drink. Ferric or aluminum salts (Fe^{3+}, Al^{3+}) are dosed to treated water and hydrolyse to voluminous flakes of $Fe(OH)_3$ and $Al(OH)_3$, respectively. Colloidal particles and bacteria are absorbed by the flakes and after separation of the flakes by sedimentation and filtration, the water remains clear.

Experiment 10.3 Clarification of water

Put approx. 5 mL of turbid water into a test tube. Add several drops of $FeCl_3$ and NaOH solutions and shake the mixture. Then filter the originated precipitate and compare the filtrate with the original turbid water.

Questions:

1. What happened after the addition of NaOH to the solution of water with $FeCl_3$? What chemical compound arose from the reaction?
2. Did you manage to remove the colloidal particles from the turbid water? Where did they remain?

11 METALS

Metals are elements which can release electrons and form positively charged ions (*cations*). Their typical physical properties are: electric and heat conductivity, ductility. They are usually heavier than non-metals and except for mercury they are solid under normal conditions.

Alkali metals (Li, Na, K) only occur in compounds with the oxidation number +I and alkali earth metals (Mg, Ca, Sr, Ba) just in compounds with an oxidation number of +II. Other metals can occur in several oxidation states but one of them usually predominates. The formation of ions, which have *n* positive charges from neutral metal atoms, generally termed *Me* (*metallum*), can be expressed by redox equation:

$$\mathbf{Me \rightleftharpoons Me^{n+} + n\,e^{-}}$$

$$Na \rightleftharpoons Na^{+} + e^{-}$$
$$Cu \rightleftharpoons Cu^{2+} + 2\,e^{-}$$
$$Al \rightleftharpoons Al^{3+} + 3\,e^{-}$$

11.1 Interaction in redox systems – metal and its ion

The utilisation of metals in civil engineering is closely connected with knowledge of the impact of water and water solutions on undesirable corrosion processes. Atoms of metal are released into solution as ions, each of which leaves electrons on the metal. The dissolution of metal depends on the relative ease with which electrons can be removed from metal atoms and the energy available when these ions are hydrated. The more active the metal, the greater this tendency is. In the reverse reaction ions gain electrons and are deposited on the metal as neutral atoms. When the rates of the two opposite reactions become equal, equilibrium is established. However, the solution becomes more positive and the metal is more negative since electrons are left on it. The gradient of potentials between the metal and its solution can be expressed by ***Nernst equation***, in which ion in the solution is an oxidizing agent and metal (its concentration is constant) is a reducing agent:

$$E_{Me} = E^{0}_{Me} + \frac{0.058}{n}\log c(Me^{n+})$$

where E^{0}_{Me} is the standard potential of metal, which is created between a metal electrode immersed into a solution of its ions $c(Me^{n+})$ = 1 mol·l^{-1} and a standard hydrogen electrode ($E^{0}_{H_2}$ = 0 V). Metals can be placed in the electrochemical series of potentials according to the scale of increasing standard potentials E^{0}_{Me}. Some members of the series are listed below:

Ca^{2+}/Ca	Na^{+}/Na	Zn^{2+}/Zn	Fe^{2+}/Fe	Pb^{2+}/Pb	$2\,H^{+}/H_2$	Cu^{2+}/Cu	Ag^{+}/Ag
–2.760 V	–2.715 V	–0.762 V	–0.441 V	–0.122 V	0 V	0.344 V	0.799 V
non-noble metals						***noble metals***	

The potentials determine the tendency of an element to form cations. The lower the potential the higher the tendency to release ions into a solution: such metal is a stronger reducing agent. Metal ions with a ***higher standard potential*** (more noble) can be displaced from a solution by a metal with a ***lower standard potential***.

Experiment 11.1 Precipitation of a more noble metal from the solution of its salt

1. Put an iron nail cleaned with emery paper into a blue solution of $CuSO_4$. After several minutes you can observe changes affecting the immersed part of the nail.
2. Put a granule of zinc into a colourless solution of $Pb(NO_3)_2$. After several minutes you can observe changes on the surface of the zinc.
3. At the end of the experiment rinse the iron nail and zinc granule with water and put them back into the assigned vessels.

Questions:

1. What has precipitated onto the surface of the objects immersed in the solution of more noble metal?
2. Explain the observed phenomenon on the basis of the electrochemical series of potentials.
3. Suggest other metals that can precipitate onto the surface of iron nail?

11.2 Corrosion of metals

Corrosion of metals concerns chemical or electrochemical processes that lead to the degradation of metals. The principle of electrochemical corrosion is the formation of a local galvanic cell that originates from the potential difference in the contact layer of two distinct metals or due to a gradient of concentrations in the same metal according to Nernst's equation.

These processes can be illustrated with the ***corrosion of iron***:
In the experiment 11.2 an iron wire represents a local cell. The immersed part behaves as a local anode and in the part where the solution is in contact with the air a local cathode is formed.

Anode: $Fe \longrightarrow Fe^{2+} + 2\,e^-$
The iron wire releases Fe^{2+} ions into the solution[1], which results in a gradient of potentials. The iron electrode bears a negative change due to free electrons and the solution is positively charged with Fe^{2+} ions that are attracted to the surface of wire by electrostatic force.

Cathode: $2\,H_2O + O_2 + 4\,e^- \longrightarrow 4\,OH^-$
Electrons released from the first reaction can be conducted through the metal to another point on its surface, where they reduce O_2 from the air. This reaction results in the formation of hydroxide ions.[2]

Generally, iron oxidises to Fe^{2+} and forms pits on its surface. The ferrous ions then migrate away from the pitting region to another point where the reduction of oxygen occurs. There Fe^{2+} and OH^- combine into $Fe(OH)_2$. Oxygen is also active in the second oxidation, which accomplishes $Fe(II) \rightarrow Fe(III)$ conversion. The ferric ion hydrolyses and precipitates as hydroxide $Fe(OH)_3$ and hydrated iron oxides (rust). Since this precipitate does not adhere tightly to the metal it allows further corrosion to take place. The formation of rust is a side-effect and the first evidence of iron corrosion. These processes are summarised by the following equations:

$$Fe^{2+} + 2\,OH^- \longrightarrow Fe(OH)_2$$

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[1] $K_3[Fe(CN)_6]$ forms a complex of Prussian blue with Fe^{2+} ions (see chapt. 5)

[2] Phenolphthalein is violet in a basic solution.

$$4\ Fe(OH)_2 + O_2 + 2\ H_2O \longrightarrow 4\ Fe(OH)_3$$

Experiment 11.2 Corrosion of iron

Fill about 2/3 of porcelain dish with water. Add a small spoonful of sodium chloride and several crystals of potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$. Clean an iron wire with emery paper and immerse it in the solution so that both ends extend above the water level (Fig. 11.1). After 15–20 minutes, add a drop of phenolphthalein on the wire just at the point where it makes contact with the solution. Observe the colour changes (watch carefully – they are quite indistinct!).

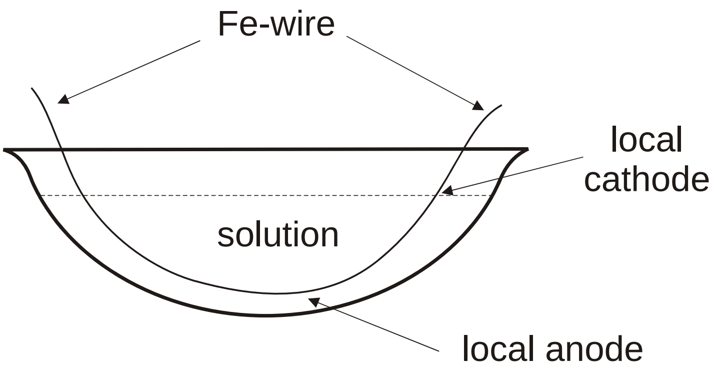

Fig. 11.1

Questions:

3. Describe the changes in colour on the local anode and cathode. What ions do these changes give a proof of?
4. What substance (except for water) is necessary for iron corrosion to proceed?

11.3 Dissolution of metals in acids

Non-noble metals ($E^0_{Me} < 0$) react with acids, in which they dissolve, to form gaseous hydrogen and corresponding salt.[3] An example of such a reaction is the dissolution of zinc in dilute hydrochloric or sulphuric acid.

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

On the other hand, ***noble metals*** ($E^0_{Me} > 0$) dissolve only in acids with a strong oxidizing effect such as concentrated nitric acid or hot concentrated sulphuric acid. An example of such a reaction is the dissolution of copper in concentrated nitric acid, which occurs according to the following reaction:

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$$
$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

The liberated gas is not hydrogen but nitrogen oxide, which is the product of HNO_3 reduction. It is a colourless gas that on exposure to air immediately oxidises to yield brown nitrogen

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[3] Hydrogen is a flammable gas that, when mixed with oxygen, explodes accompanied by the formation of water vapour.

dioxide (NO_2). Copper is oxidised to a blue copper(II) salt during its dissolution.

Experiment 11.3.1 Dissolution of zinc in hydrochloric acid

Put about 3 granules of zinc into a test tube with concentrated HCl (1/3 of test tube volume). Catch the arising gas that is given off in another **dry** test tube by holding it upside down. After 1 minute, put this test tube close to a flame of the burner. Describe what happened.

Questions:

1. What kind of gas is liberated during the reaction? Write a chemical equation and explain its formation on the basis of the electrochemical series of potentials.
2. Write a chemical equation for the combustion of the obtained gas in the flame.

Experiment 11.3.2 Dissolution of copper in nitric acid

Put a piece of copper into 0.5 mL of concentrated HCl. Note down your observation. Then, carefully add 2 mL of conc. nitric acid and observe what happens.

Questions:

1. What kind of gas is liberated during the reaction? Write chemical equations for its formation.
2. Explain why copper does not produce gaseous hydrogen during its reaction with HNO_3.

12 PROPERTIES OF SELECTED ORGANIC COMPOUNDS

Contemporary progress in the technology of building materials is connected with the use of organic materials. These materials posses a variety of physical and chemical properties that are useful for building purposes (durability, plasticity, resistance to a corrosion, low density, good workability and machinability etc.). However, their extreme flammability is the main drawback of their utilisation.

Production of these materials is based on organic synthesis, where reactants are usually basic organic compounds − hydrocarbons, alcohols, phenols etc. Some of their properties and related reactions are described in the following text.

12.1 Hydrocarbons

Hydrocarbons are compounds containing carbon and hydrogen in their molecules. The bonds between these atoms are covalent and non-polar, which implies the non-polar character of organic compounds. One of their properties is immiscibility with polar solvents, e.g. water. Examples of such non-polar compounds are benzene, toluene or benzine, which is a mixture of low-boiling hydrocarbons.

Experiment 12.1 Miscibility of benzine with water

Pour 5 mL of benzine and 10 mL of water into a 25 mL graduated cylinder. Shake the mixture and after the separation of both phases read the volumes again.

Questions:

3. How did the volumes of both liquids change after mixing and what can be concluded from this experiment?
4. Which of the liquids has a lower density?

12.2 Alcohols

Alcohols are hydroxy derivatives of hydrocarbons that contain at least one hydroxyl group –OH. In contrast to the ionic bond in inorganic hydroxides OH^-, the bond in organic alcohols is covalent. This contrast is reflected in the different behaviour of these substances in an aqueous solution. As a result of dissociation only hydroxide can affect the pH of the solution.

Experiment 12.2

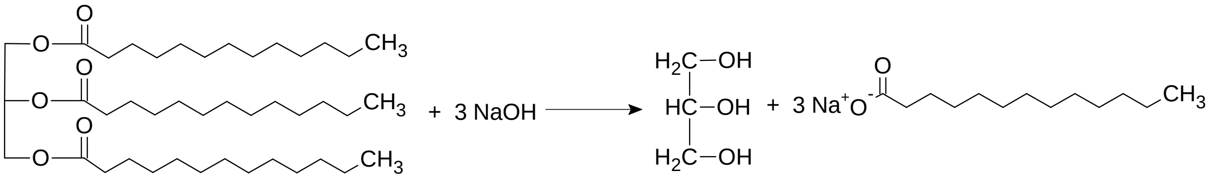
Put a drop of 8% NaOH and a drop of ethanol, res., on a pH test strip and read the value for each by comparison with the colour scale.

Questions:

1. What pH values have you measured? Explain the difference between them.

12.3 Fat, vegetable and mineral oil

Fats and vegetable oils are esters of trifunctional alcohol glycerol (propane-1,2,3-triol) with high molecular weight aliphatic acids. Alkaline saponification of fats and vegetable oils results in the formation of soap, whereas mineral oils, mixtures of high-boiling hydrocarbons, do not react. Vegetable oil transforms into a mix of alkaline salts of high molecular weight aliphatic acids (soap) and glycerol, while mineral oil does not change and remains insoluble. Soap is soluble in water and after being shaken with distilled water it forms foam.



vegetable oil *glycerol* *soap*

Experiment 12.3 Distinction between vegetable and mineral oil

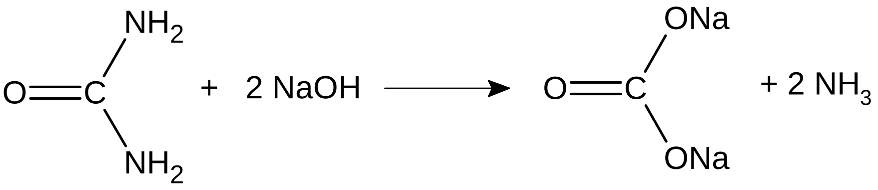
Pour 3 mL of 30% NaOH into two test tubes. Then, add several drops of just one of the oil samples to one of the test tubes and add the same amount of the other oil sample to the other. Heat both mixtures for 2 – 3 minutes above a moderate flame. After the mixture have cooled down, add about 3 mL of distilled water, shake the mixtures and describe what you observe.

Questions:

1. Based on your observation decide which sample is vegetable oil and which one is mineral oil. Explain your decision.

12.4 Urea

Urea (used as a de-icing agent) is a diamide of carbonic acid, which is unstable in an alkaline medium and releases gaseous ammonia and the corresponding carbonate (Na_2CO_3):



Experiment 12.4 Decomposition of urea

Put a small spoonful of urea into a test tube, add 3 mL of 30% NaOH and heat the mixture. Smell the liberated gas and put a wet pH test strip over the test tube mouth. Compare the observed colour with the colour scale.

Questions:

1. What pH have you measured? What gas is released in the reaction with NaOH?