

## 6. Oxidation and reduction I

### INTRODUCTION

Many of the aspects of chemistry derive from changes in oxidation state. Electron gain is called reduction and electron loss is called oxidation; the joint process is called a redox reaction. The species that supplies electrons is the reducing agent (reductant) and the species that removes electrons is the oxidizing agent (oxidant). It is essential to understand that oxidation number of an element is a human-made formal term and its importance is in rationalizing redox reactions. It does not represent a real electric charge of the element ( $B^{3+}$  does not exist, but  $B^{III}$  does). Redox character of an individual species is always relative and depends on the reaction partner. Redox reaction can be expressed as the difference of two reduction half-reactions. The standard reduction potential,  $E^\circ$ , of a couple  $M^+/M$  describes its redox properties. If  $E^\circ$  is positive and large, the oxidized member of the couple is a strong oxidizing agent. If  $E^\circ$  is negative and large, the reduced member of the couple is a strong reducing agent. For example:

$E^\circ = +1.76 \text{ V}$  for  $Ce^{4+}/Ce^{3+}$        $Ce^{4+}$  is strong oxidizing agent

$E^\circ = +0.77 \text{ V}$  for  $Fe^{3+}/Fe^{2+}$        $Fe^{3+}$  is moderate oxidizing agent

$E^\circ = -3.04 \text{ V}$  for  $Li^+/Li$        $Li$  is very strong reducing agent

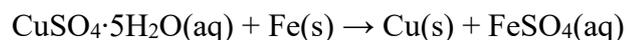
However, the values of  $E^\circ$  have been taken under strict conditions (25 °C, 1 atm,  $c = 1 \text{ mol}\cdot\text{dm}^{-3}$  in aqueous solution). Under different conditions (other solvent, pH, presence of ligands etc.) the redox properties may change dramatically. Thus, when comparing  $E^\circ$  for different half-reactions one should keep in mind that the tabulated standard redox potentials are rather orientational.

Based on  $E^\circ$  the elements and their oxidized/reduced forms are listed in electrochemical series. The most negative  $E^\circ$  values are placed at the beginning of the electrochemical series, and the most positive at the end. Thus, elements on the left in the list are good reductants and their ions are unwillingly reduced to the elemental form. On the other hand, the elements on the right are rather noble and reluctant to be oxidized.

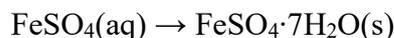
Li, Cs, Rb, K, Ba, Fr, Sr, Ca, Ra, Na, La, Y, Mg, most lanthanoids & actinoids, Be, Al, Mn, Zn, Cr, Fe, Cd, Co, Ni, Sn, Pb, H, Ge, Re, Bi, Cu, Ag, Hg, Au, Pd, Pt (Xe, Kr\*).

\*  $KrF_2$  is the strongest oxidizing agent,  $E^\circ = +3.27 \text{ V}$  ( $E^\circ Xe^{2+}/Xe = 2.32 \text{ V}$ ). It oxidizes Br to  $BrF_6^+$  and Au to  $AuF_5$ .

## EXPERIMENT 1      SYNTHESIS OF Cu AND FeSO<sub>4</sub>·7H<sub>2</sub>O.



$$\begin{array}{c} 5 \text{ g} \\ w = 15\% \end{array}$$



Prepare a water bath. Prepare the solution of CuSO<sub>4</sub>·5H<sub>2</sub>O in water and add two drops of concentrated sulfuric acid. Transfer the solution in an evaporating dish and add some excess of iron rods. Stir the reaction mixture with a glass rod during the reaction to remove the copper from the iron rods. Simultaneously keep the volume of the solution at the initial state. When the color of the solution turns from blue to green the reaction is complete.

Filter the hot solution carefully but leave the copper and iron in the evaporating dish. Pour the filtrate (solution of iron(II) sulfate) in another evaporating dish, add three drops of concentrated sulfuric acid, place it on a water bath and evaporate it to ½ of the initial volume. The solution has to be green. If it is yellow or brown, add one iron rod to reduce the Fe(III) to Fe(II). Transfer the solution in an ice bath. Suck the crystals on a Buchner funnel and dry it in air flow of the fume hood. Find the mass of the compound.

While evaporating the solution of iron(II) sulfate use tweezers to remove the iron rods from the copper, wash it with water and place them in a flask. Use 20.0 mL of 10% sulfuric acid to rinse the copper from the evaporating dish to a beaker, cover it with a watch glass and boil it for about 2 minutes to dissolve the residual iron (copper does not react with diluted sulfuric acid). Decant the copper several times with 50.0 mL of distilled water, filter it and dry in a dryer.

### QUESTIONS

1. Why iron reduces copper(II) cations?
2. Why is it necessary to keep the solution acidic during the synthesis?
3. Why is the solution light-green at the end of the reaction?
4. Define noble metals and non-noble metals.

## EXPERIMENT 2      PREPARATION OF SIMPLE SUBSTANCES AND OXIDES

### O<sub>2</sub>

Pour 1 mL of 0.02 M KMnO<sub>4</sub> in a test tube, acidify the solution with few drops of 2 M H<sub>2</sub>SO<sub>4</sub> and add two drops of 5% H<sub>2</sub>O<sub>2</sub>. The violet solution decolorizes immediately and bubbles of oxygen appear.

### H<sub>2</sub>

Pour 2 mL of 36% HCl in two test tubes. Add a piece of aluminum in the first one and a piece of copper in the other one. Watch the reactions.

### Cl<sub>2</sub>

Pour 1 mL of 0.02 M KMnO<sub>4</sub> in a test tube. Add few drops of concentrated HCl.

### SO<sub>2</sub>

Take a piece of sulfur with an iron rod and place it in flame. Sulfur burns with a blue flame.

Use the pH paper to check the pH of the fumes.

### Ag<sub>2</sub>O

Pour 1 mL of 0.01 M AgNO<sub>3</sub> and 1 mL of 2 M NaOH in a test tube.

### NO<sub>2</sub>

Prepare a test tube with 1 mL of concentrated nitric acid and a beaker with 50 mL of distilled water. Add a piece of copper in the test tube. You will see orange–brown gas – NO<sub>2</sub>. Cease the reaction by pouring distilled water into the test tube.

### CO<sub>2</sub>

Add approx. 0.5 g of Na<sub>2</sub>CO<sub>3</sub> in a test tube. Add dropwise 2 mL of 1 M HCl.

### CuO

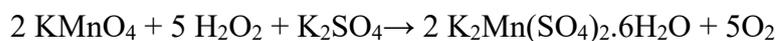
Pour approx. 3 mL of 0.2 M solution of Cu(NO<sub>3</sub>)<sub>2</sub> in a test tube and add 1 mL of 2 M NaOH. Blue precipitate of Cu(OH)<sub>2</sub> is formed. Heat the test tube in a flame to prepare CuO.

## QUESTIONS

1. Explain different observations when trying to prepare H<sub>2</sub>.
2. Three of the reactions are not redox reactions. Name them and write reaction equations describing synthesis of those oxides by redox reactions.

## 7. Oxidation and reduction II

### EXPERIMENT 1 SYNTHESIS OF MANGANESE DIPOTASSIUM SULFATE



Fill 100 mL Erlenmeyer flask with 17.0 mL of water, add 1.00 mL of 96 %  $\text{H}_2\text{SO}_4$  with a pipette and in the prepared solution dissolve 1.01 g of  $\text{K}_2\text{SO}_4$ . Cool the solution, add 6.00 mL of given solution of  $\text{H}_2\text{O}_2$  and mix the solution.

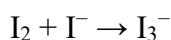
Weigh 1.82 g of  $\text{KMnO}_4$  on a filtration paper and add it in portions in the solution. Mix the reaction mixture thoroughly (not with a glass rod). The reaction is accompanied by the release of oxygen. The reaction is complete when the sparkling stops and the solution is colorless. Evaporate the solution in an evaporating dish to about 2/3 of the initial volume (approximately 15 mL). Cool the solution to room temperature, add 3 mL of ethanol and place the dish in an ice bath. Suck the crystals on a Buchner funnel and dry in air flow (in fume hood).

### QUESTIONS

1. Calculate the theoretical yield of the double salt and the expected volume of released oxygen (at normal conditions).
2. Why do we cool the solution prior to the addition of hydrogen peroxide?
3. What are Tutton's salts?

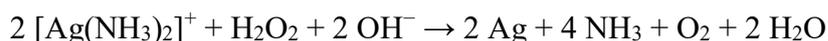
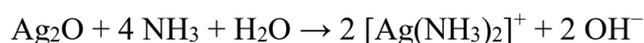
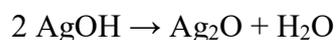
### EXPERIMENT 2 REDOX PROPERTIES OF HYDROGEN PEROXIDE

1. Pour 1 mL of 0.2 M KI in a test tube, acidify the solution with few drops of 2 M  $\text{H}_2\text{SO}_4$  and add two drops of 5%  $\text{H}_2\text{O}_2$ . The iodide anion is oxidized to iodine in acidic solution. The iodine is dissolved immediately thanks to the reaction with iodide anions and brown solution is formed:



2. Pour 1 mL of 0.1 M  $\text{AgNO}_3$  and 1 mL of 2 M NaOH in a test tube. To the brown precipitate of  $\text{Ag}_2\text{O}$  add slowly 2 M  $\text{NH}_3$  until the precipitate dissolves. Then, add very carefully drop by

drop 5 % H<sub>2</sub>O<sub>2</sub>. You can gently heat the test tube. You can watch oxygen bubbles and silver metal of grey color. In some cases the formation of a silver mirror on the wall of the test tube can be observed.



3. Place small amount of MnO<sub>2</sub> in a test tube and add 2 mL of distilled water. Shake the mixture and acidify the solution with 1–2 drops of 65% HNO<sub>3</sub>. Add 2 mL of 5 % H<sub>2</sub>O<sub>2</sub>. Colorless solution is formed.



## QUESTIONS

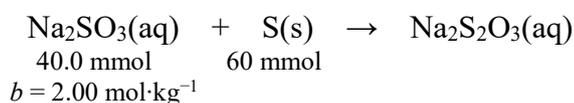
1. Based on your observations describe redox properties of hydrogen peroxide. What are the products of its oxidation and reduction?

## 8. Heterogeneous reactions, proof reactions of inorganic cations and anions

### INTRODUCTION

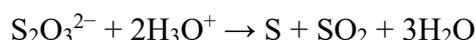
Heterogeneous reaction is any type of chemical reaction, in which the reacting components are in different phases, for example: solid + liquid (Na(s) + H<sub>2</sub>O(l)), solid + gas (NaOH(s) + CO<sub>2</sub>(g)), liquid + gas (NaCl(aq) + CO<sub>2</sub>(g)), two immiscible liquids etc. The chemical change undergoes at the interface of the two phases. Heterogeneous reactions have huge practical applications in catalysis. For example, the catalytic oxidation of side products of combustion engines takes place on the surface of a metal catalysts.

### EXPERIMENT 1 PREPARATION OF A SOLUTION OF SODIUM THIOSULFATE



Prepare the solution of Na<sub>2</sub>SO<sub>3</sub>. Crush sulfur in a mortar and add the solution of sodium thiosulfate. Mix both components thoroughly. Transfer the suspension using a funnel into a boiling flask and mount the reflux (do not forget to secure the water cooling). Let the teacher check your apparatus. Put a triangle with a net below the flask and start heating it for 1.5 hours. Then, turn off the burner and keep cooling the apparatus for about 10 minutes. Meanwhile, prepare the apparatus for filtration. Filter the solution into a beaker and use it in the following experiments:

a) Fill a test tube with cca 1 cm<sup>3</sup> of the prepared solution and 3 cm<sup>3</sup> of 2 M sulfuric acid. You can see formation of yellow sulfur and bubbles of sulfur dioxide:



b) Add cca 2 cm<sup>3</sup> of water in a test tube and add few drops of Lugol's solution. Then, add cca 1 cm<sup>3</sup> of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution:



## QUESTIONS

1. State the oxidation numbers of all atoms of reactants and products.
2. Does the name of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> truly represent the structure? Explain.
3. Did you use stoichiometric amounts of reactants? If not, which reactant was in excess?

## EXPERIMENT 2      PROOF REACTIONS OF INORGANIC CATIONS AND ANIONS

### I. Flame tests.

Flame tests are suitable for proving inorganic cations in simple matrices (the solution must not contain other species which undergoes atomization in flame accompanied by a color effect).

First, clean the platinum rod: Wash it with distilled water, dip it in a solution of HCl (1:1) and anneal it in the colorless region of the flame. Repeat the procedure until the flame is colorless during annealing.

Then, dip the annealed platinum rod into the solution of LiCl, insert it in the flame and notice the color change. Clean the rod as above and repeat the flame test with solutions of KCl, CaCl<sub>2</sub>, SrCl<sub>2</sub>, CuCl<sub>2</sub> and NaCl.

## II. Proving cations

| Cation                            | Test  | Result   |
|-----------------------------------|---|--|
| <b>NH<sub>4</sub><sup>+</sup></b> | add solution of an alkaline hydroxide, check pH of the vapors | gaseous ammonia is released which can be detected on wet pH paper                          |
|                                   | add Nessler solution: $K_2[HgI_4] \cdot H_2O + KOH$           | yellow or brown precipitate is formed, the intensity of color depends on the concentration |
| <b>K<sup>+</sup></b>              | $Na_3[Co(NO_2)_6]$  | yellow precipitate   |
| <b>Ca<sup>2+</sup></b>            | oxalic acid   | white precipitate insoluble in acetic acid and soluble in mineral acids                    |
| <b>Mg<sup>2+</sup></b>            | $Na_2HPO_4$   | white precipitate  |
|                                   | alkaline hydroxide + azo violet                               | white precipitate gets blue thanks to azo violet   |
| <b>Fe<sup>3+</sup></b>            | $K_4[Fe(CN)_6]$   | blue precipitate (Prussian blue)   |
|                                   | KSCN  | red solution   |
| <b>Cu<sup>2+</sup></b>            | diluted alkaline hydroxide                                    | blue precipitate, soluble in excess of hydroxide   |
|                                   | diluted ammonia solution                                      | blue precipitate soluble in excess of ammonia forming violet solution                      |
| <b>Zn<sup>2+</sup></b>            | diluted alkaline hydroxide                                    | white precipitate soluble in excess of hydroxide   |
|                                   | $Na_2S$   | white precipitate  |
| <b>Pb<sup>2+</sup></b>            | diluted alkaline hydroxide                                    | white precipitate soluble in excess of hydroxide   |
|                                   | $Na_2S$   | black precipitate  |

### III. Proving anions

| Anion                | Test  | Result   |
|----------------------|---|--|
| $\text{CO}_3^{2-}$ * | mineral acid, dip a glass rod with a drop of $\text{Ba}(\text{OH})_2$ solution in the vapor                                       | carbonate is decomposed in $\text{CO}_2$ which reacts with $\text{Ba}(\text{OH})_2$ forming white precipitate                                |
| $\text{Cl}^-$        | $\text{AgNO}_3$   | white precipitate insoluble in diluted $\text{HNO}_3$ and soluble in ammonia   |
| $\text{NO}_3^-$      | fresh saturated solution of $\text{FeSO}_4$ , carefully add conc. $\text{H}_2\text{SO}_4$ on the wall of the test tube            | brown ring on the interface of the two phases ( $\text{H}_2\text{SO}_4$ below + $\text{FeSO}_4/\text{NO}_3^-$ up)                            |
| $\text{SO}_4^{2-}$ * | $\text{Ba}(\text{II})$ salt   | white precipitate insoluble in mineral acids   |
| $\text{PO}_4^{3-}$ * | acidify with diluted $\text{HNO}_3$ , add excess of saturated solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and heat      | ostentatiously yellow precipitate  |
| $\text{S}^{2-}$ *    | Do this experiment in fume hood.<br>diluted mineral acid, dip filtration paper soaked with solution of lead nitrate in the vapors | very toxic and horribly smelling gas is released ( $\text{H}_2\text{S}$ ) which reacts with $\text{Pb}(\text{II})$ forming black precipitate |

\* The proofs are also valid for hydrogen salts.

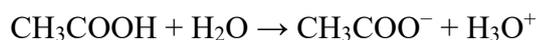
### QUESTIONS

1. Write chemical equations describing all experiments and reactions.
2. Find formula and systematic name of azo violet.
3. Chose one cation and one anion different from the lists and find proof reactions for them.

## 9. Acids and bases, neutralization, amphoterism

### INTRODUCTION

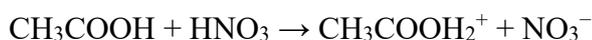
Reactions of acids with bases are called acid–base reactions (or neutralization if equimolar amounts of acid and base are considered). The term “protolytic reaction” is not used in English; however, the deprotonation of acids is called protolysis. In an acid–base reaction we always consider transfer of a single hydron:



$\text{CH}_3\text{COOH}$  is acid and  $\text{CH}_3\text{COO}^-$  is its conjugated base,

$\text{H}_2\text{O}$  is base and  $\text{H}_3\text{O}^+$  is its conjugated acid.

The distribution of compounds into acids and bases is relative. It always depends on the individual reaction partner:

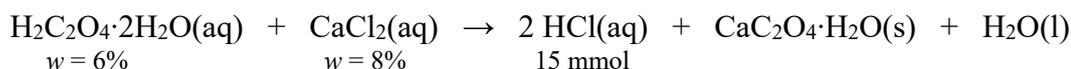


$\text{CH}_3\text{COOH}$  is base and  $\text{CH}_3\text{COOH}_2^+$  is its conjugated acid,

$\text{HNO}_3$  is acid and  $\text{NO}_3^-$  is its conjugated base.

Remember the difference:  $\text{H}^+$  *hydron* (any atom of hydrogen in oxidation state +I),  $^1\text{H}^+$  *proton* (atoms of protium in oxidation state +I),  $^2\text{H}^+$  or  $\text{D}^+$  *deuteron*,  $^3\text{H}^+$  or  $\text{T}^+$  *triton*. Thus, the term *hydron* is preferred.

## EXPERIMENT 1    SYNTHESIS    OF    HCl    AND    DETERMINATION    OF    ITS CONCENTRATION

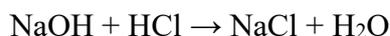


Prepare the solutions of oxalic acid and calcium chloride and mix them in a beaker with the volume  $100 \text{ cm}^3$ . White precipitate of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  is forming while hydrochloric acid remains in the solution. Stir the reaction mixture thoroughly and wait 15 minutes. The precipitate settles on the bottom of the beaker. Filter the solution at atmospheric pressure using two filtration papers (the precipitate is very fine). Capture the filtrate in a 50 mL cylinder. Note the volume of the filtrate.

Keep the precipitate and decant it three times with hot water while you will do the next task. Then, filter it on a Buchner funnel using weighted filtration paper, dry it in fume hood and find its the mass.

Rinse a burette twice with distilled water, and then fill it with water and check if it is sealed properly. Fill the burette with a solution of NaOH (the teacher will tell you its concentration). The lower meniscus of the liquid has to reach zero and the burette has to be filled completely from this point to the tap. Use a volumetric pipette to transfer 10 mL of the filtrate to a 100 mL volumetric flask, fill it with distilled water to the mark, close it with a stopper and shake the solution. Use a 25 mL volumetric pipette to transfer 25 mL of the diluted solution to a titration

(conical) flask, add three drops of bromthymol blue and titrate it with the solution of NaOH until yellow solutions turns to blue:



Make the titration three times. The values of consummated NaOH solution should not differ by more than 0.1 mL. Calculate the average value and use it for the calculation of:

- the molar concentration of HCl in the volumetric flask,
- the molar concentration of HCl in the filtrate,
- the amount of HCl in the filtrate.

Rinse the burette and other glassware with water (twice) and with distilled water (once).

## QUESTIONS

1. What is the difference in hydrochloric acid and hydrogen chloride?
2. Draw the electron structural formula of oxalic acid and state the oxidation numbers of all atoms.
3. What is bromthymol blue? Give few other examples.
4. Why did you use volumetric pipettes instead of graduated pipettes?

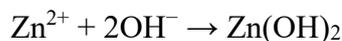
## EXPERIMENT 2 AMPHOTERISM

### Preparation of NaOH

Work in a fume hood. Fill a large beaker with 250 mL of water, add few drops of phenolphthalein. Use tweezers to drop a piece of sodium in the solution.

### Amphoteric hydroxides

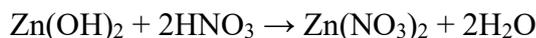
Fill two test tubes with 1 mL of 0.2 M solution of  $\text{ZnSO}_4$  and 0.5 mL of 2 M NaOH. The precipitate of  $\text{Zn(OH)}_2$  is formed.



- a) Add few drops of the NaOH solution to the first test tube until it dissolves:



- b) Add few drops of diluted nitric acid (1:1) to the second test tube until it dissolves:



Repeat the same procedure with solutions of  $\text{Cr(NO}_3)_3$ ,  $\text{Mg(NO}_3)_2$ ,  $\text{Al(NO}_3)_3$  and  $\text{Cu(NO}_3)_2$ .



Ensure yourself that beakers and glassware you are going to use are clean and dry. Do not pour the acetone and its solutions washbasin. Use a collecting container. Under no circumstances light the burners. Keep the beakers with solutions in acetone covered with watching glasses to minimize its evaporation in laboratory.

Prepare the starting solutions in acetone ( $\rho = 0.7606 \text{ g}\cdot\text{cm}^{-3}$ ).  $\text{LiCl}\cdot\text{H}_2\text{O}$  must be grinded in a mortar prior to dissolving.  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  forms blue solution,  $\text{LiCl}\cdot\text{H}_2\text{O}$  dissolves very slowly forming colorless or pale yellow solution.

After 10 minutes you can mix both solutions, although  $\text{LiCl}\cdot\text{H}_2\text{O}$  is not entirely dissolved. You should obtain orange or brown solution of lithium tetrachloridocuprate. Stir the solution until all  $\text{LiCl}\cdot\text{H}_2\text{O}$  is dissolved. Use the apparatus for preparation of gaseous ammonia in the fume hood to introduce ammonia in the solution. You will watch formation of blue precipitate while the solution above the precipitate decolorizes. If you add more ammonia, the solution will turn deep violet and you will not get the desired product. Suck the precipitate on the Buchner funnel quickly using filtration paper with known mass. The filtration paper must fit the funnel perfectly. Wash the precipitate with few milliliters of acetone, dry it on air and weigh. If you work properly, the filtrate will be colorless.

## QUESTIONS

1. Why is it necessary to use acetone as solvent instead of water? Imagine you do the synthesis in aqueous solutions. Try to propose the reaction products.
2. Describe and explain the method for preparation of ammonia.

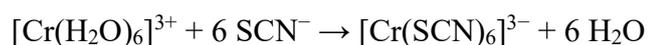
## EXPERIMENT 2 INFLUENCE OF LIGAND CHANGE ON THE COLOR OF COORDINATION COMPOUNDS

You will use solutions with the concentration  $0.2 \text{ mol}\cdot\text{dm}^{-3}$ . Do the experiments in test tubes.

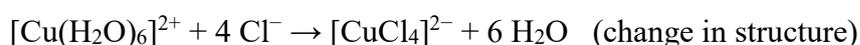
- a) Add  $1 \text{ cm}^3$  of  $\text{NH}_3(\text{aq})$  to  $1 \text{ cm}^3$  solution of  $\text{Cu}(\text{NO}_3)_2$ . Watch the color change.



- b) Add solid  $\text{KSCN}$  to  $1 \text{ cm}^3$  of solution of  $\text{Cr}(\text{NO}_3)_3$ . Watch the color change.



- c) Add  $2 \text{ cm}^3$  of 36%  $\text{HCl}$  to  $1 \text{ cm}^3$  of solution of  $\text{Cu}(\text{NO}_3)_2$ . Watch the color change.



- d) Add few crystals of  $\text{Cr}(\text{NO}_3)_3$  and  $\text{CrCl}_3$  in two test tubes. Fill the test tubes with water to the half and shake them to dissolve the salts. Watch the color difference.

## QUESTIONS

1. Explain the changes in color in a) and b). Think about the spectrochemical series and frequency of absorbed/transmitted light.
2. Explain different color of solutions in d).