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# 56 Chemistry Olympiad

## Final competitions (27<sup>th</sup> Mar 2010)

### *Theoretical tasks and solutions*

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#### TASK 1:

##### **Rust removal**

A substance enabling removal of corrosion traces or its results (e.g. enabling opening rusty padlocks) is phosphoric acid. Its efficiency results from both low pH value of its solutions, stimulating oxides / hydroxides dissolution and complexation of iron(III) ions by phosphate anions. Corrosion products have complex composition, it can be assumed for simplicity that they contain entirely ferric hydroxide,  $\text{Fe}(\text{OH})_3$ .

##### **Problems:**

- Calculate pH of 0.1 M phosphoric acid solution. Determine degree of dissociation of this acid and calculate concentrations of all phosphate forms in this solution:  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ .
- Iron(III) nitrate was added to 0.1 M  $\text{H}_3\text{PO}_4$  solution, to obtain total iron(III) concentration equal to  $10^{-4}$  M. Calculate mol.% amount (in relation to total amount of iron(III) in solution) of complexes  $\text{Fe}(\text{HPO}_4)^+$ ,  $\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$  and hydrated ions  $\text{Fe}^{3+}$ .
- Calculate molar solubility of  $\text{Fe}(\text{OH})_3$  in pure water and pH value of saturated  $\text{Fe}(\text{OH})_3$  solution.
- Derive equation enabling calculation of molar solubility of  $\text{Fe}(\text{OH})_3$  in 0.1 M  $\text{H}_3\text{PO}_4$  solution (assuming for simplicity that neither pH nor concentration of any phosphate form changes as result of  $\text{Fe}(\text{OH})_3$  dissolution).
- Check by calculation, whether a 0.10 g sample of  $\text{Fe}(\text{OH})_3$  can be completely dissolved in 1 L of 0.1 M  $\text{H}_3\text{PO}_4$  solution.
- Compare molar solubility of  $\text{Fe}(\text{OH})_3$  in 0.1 M  $\text{H}_3\text{PO}_4$  solution and in solution of the same pH but in the absence of complexing agents (in relation to  $\text{Fe}^{3+}$  ions)

Solubility product of  $\text{Fe}(\text{OH})_3$ :  $K_{s0} = 2 \cdot 10^{-39}$

Dissociation constants of  $\text{H}_3\text{PO}_4$ :  $K_{a1} = 6 \cdot 10^{-3}$ ;  $K_{a2} = 6 \cdot 10^{-8}$ ;  $K_{a3} = 5 \cdot 10^{-13}$

Stability constants of  $\text{Fe}^{3+}$ : with one  $\text{HPO}_4^{2-}$  ion  $\beta_1 = 2 \cdot 10^8$ , with one  $\text{H}_2\text{PO}_4^-$  ion  $\beta_1^* = 3 \cdot 10^3$

Molar masses: Fe: 55.85 g/mol; O: 16.00 g/mol; H: 1.01 g/mol.

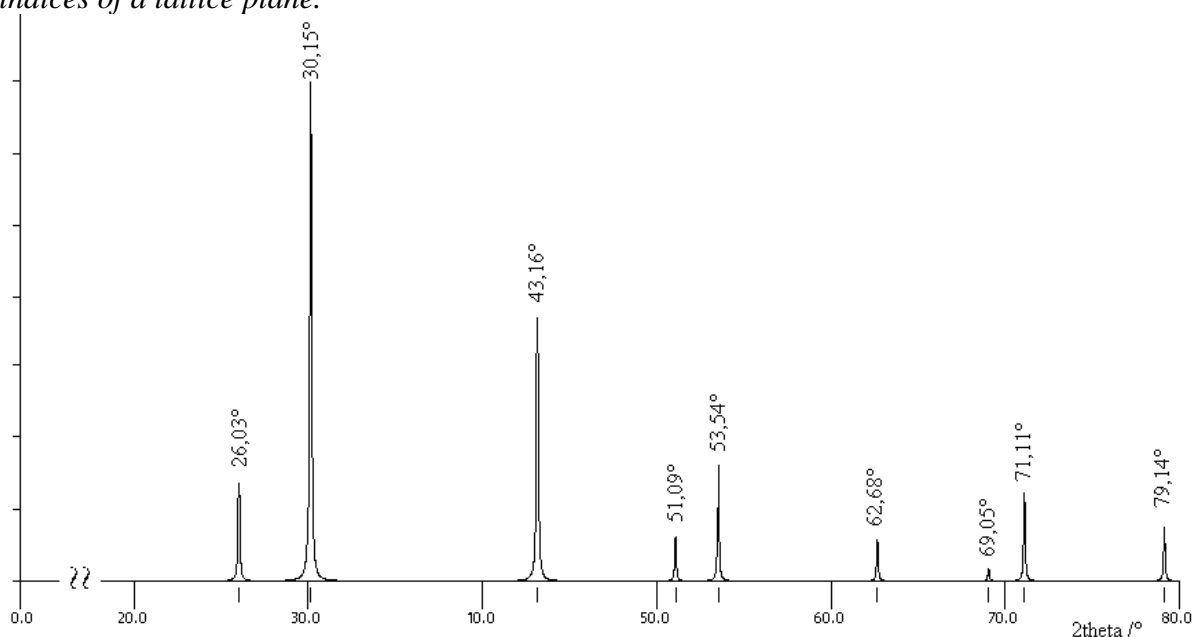
#### TASK 2

##### **X-ray Structure Analysis**

A solution of strontium nitrate(V) was added in a 1:1 molar ratio to a solution, obtained by dissolving 3.44g of selenium(IV) dioxide in water. The resulting solution was neutralized with ammonia and the formed precipitate of salt **A** was washed with water several times, dried at the temperature of 200°C and weighed. Subsequently, the produced salt **A** was put into a quartz boat and heated in a flow of dried ammonia for around 3 hours at 860°C in a pipe furnace. The loss of mass was determined to amount to 22.4%. The resulting product was examined with the help of the X-ray diffraction method. The picture below shows the powder diffractogram of the investigated sample (the  $\text{CuK}\alpha_1$  radiation with the wavelength  $\lambda = 1.5406\text{\AA}$  was used). After the analysis of the obtained diffraction pattern, it was concluded that the sample contains one crystalline phase – a salt of hydracid **B**, that is isostructural with NaCl.

*Sodium chloride crystallizes in the cubic system (space group  $Fm\bar{3}m$ ). In case of the translational lattice of type F, only those reflexes whose Miller indices are all even or all odd are allowed (zero*

is considered to be even). For the cubic system the equation for the interplanar distance is as follows:  $\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$ , where:  $a$  – lattice constant,  $d_{hkl}$  – interplanar distance;  $h, k, l$  – Miller indices of a lattice plane.



### **Problems:**

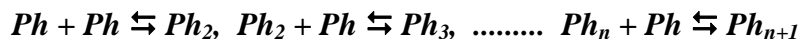
- (3 points) Write the chemical equations in molecular form (reagent form) of all the reactions leading to the formation of salt **B**.
- (2 points) Confirm the empirical formulae of compounds **A** and **B** with the appropriate calculations.
- (3 points) Using the scheme of a unit cell given in the answer sheet, calculate the number of cations and the number of anions of compound **B** in the unit cell.
- (5 points) Assign Miller indices to every reflex that is present in the diffraction pattern.
- (3 points) Determine the lattice constants and the unit cell volume of the compound **B**.
- (4 points) Calculate the density of the unit cell of compound **B**.

In your calculations use the following value of the Avogadro's number:  $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$  and the following values of molar masses: N – 14.01 g/mol, O – 16.00 g/mol, Se – 78.96 g/mol, Sr – 87.62 g/mol, H – 1.01 g/mol

### **TASK 3**

#### ***Association and phase equilibrium***

Phenol (**Ph**), when dissolved in carbon tetrachloride, is strongly associated. It means that molecules are grouped in associates, probably, in a form of simple chains **Ph<sub>2</sub>**, **Ph<sub>3</sub>** and in general **Ph<sub>n</sub>**, where **n** is a degree of association. In practise, a degree of association, **n**, may reach very high values, let's say, "goes to infinity". The measurements of light absorption at the wavelength of 2968 nm (absorption band of hydroxyl group in infrared) can be explained assuming that the following reactions occur in the solution:



and all of them are characterized by the same equilibrium constant, **K**.

The situation is completely different in aqueous solutions, where phenol exists in a form of single molecules (monomers) only, because it creates the hydrogen bond water-phenol, much stronger than the bond phenol-phenol.

In two independent experiments carried out at temperature 298 K the three component system: phenol/water/carbon tetrachloride, containing different amounts of phenol, was brought to equilibrium and the two-phase systems were obtained. Next, each system was separated into aqueous and organic phases. The equilibrium concentrations of phenol in particular phases were determined and the results are shown in the table below (the concentrations of phenol in aqueous phase and in organic phase are denoted as  $a$  and  $c$ , respectively). An assumption that water and carbon tetrachloride are completely immiscible has to be made.

	experiment 1	experiment 2
$c/(\text{mol}/\text{dm}^3)$	1,536	2,903
$a/(\text{mol}/\text{dm}^3)$	0,137	0,158

The following symbols for denoting the concentrations of particular associates of phenol in carbon tetrachloride solutions are proposed: monomer  $-\text{[Ph]}$ , dimer  $-\text{[Ph}_2\text{]}$ , trimer  $-\text{[Ph}_3\text{]}$  and  $n$ -mer  $-\text{[Ph}_n\text{]}$ .

**Problems:**

- Derive the dependence of total concentration of phenol ( $c$ ) on: concentration of phenol in aqueous phase ( $a$ ), equilibrium constant of reaction of association ( $K$ ), and distribution coefficient of phenol between the organic and aqueous phases ( $k$ ).
- Calculate the value of equilibrium constant of reaction of association ( $K$ ), common for all reactions, and the value of distribution coefficient of phenol between the organic and aqueous phases ( $k$ ).
- Derive the dependence of average number ( $\bar{n}$ ) of phenol molecules in associates  $\text{Ph}_{\bar{n}}$  on: concentration of phenol in aqueous phase ( $a$ ), equilibrium constant of reaction of association ( $K$ ), and distribution coefficient of phenol between the organic and aqueous phases ( $k$ ).
- Calculate the values of average number ( $\bar{n}$ ) of phenol molecules in associates  $\text{Ph}_n$  occurring in both experiments.

**Hint:**

According to general rules, the thermodynamic equilibrium constant is dimensionless, so in calculations the concentrations divided by standard concentrations equal to unity must be used. Solving the problem it would be necessary to introduce the standard concentrations, e.g.  $c_1^0 = 1 \text{ mol}/\text{dm}^3$  for monomers and similarly,  $c_n^0 = 1 \text{ mol}/\text{dm}^3$  for all associates. It would cause an unnecessary complication in writing the equations. For that reason the usage of "dimensional" equilibrium constant having the same numerical value is suggested. This change will not affect the way of solving the problem nor change the result.

In a solution of the problem the sums of numerical sequences, that is the numerical series, will appear. Both of them are infinite and convergent, which means that the quotient of subsequent terms  $x$  is less than 1.

The formula for geometric series with  $x = \text{constant}$  and  $x < 1$  is:

$$1 + x + x^2 + x^3 + \dots + x^n + \dots = (1-x)^{-1}. \tag{I}$$

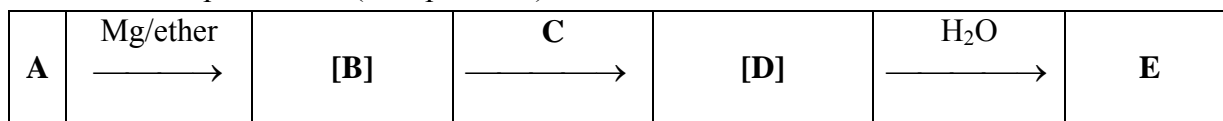
Differentiation of both sides of the above gives another series (with variable quotient, but convergent) useful for a solution of the problem:

$$1 + 2x + 3x^2 + \dots + nx^{n-1} + \dots = (1-x)^{-2}. \tag{II}$$

### TASK 4

#### Something for arachnophobes

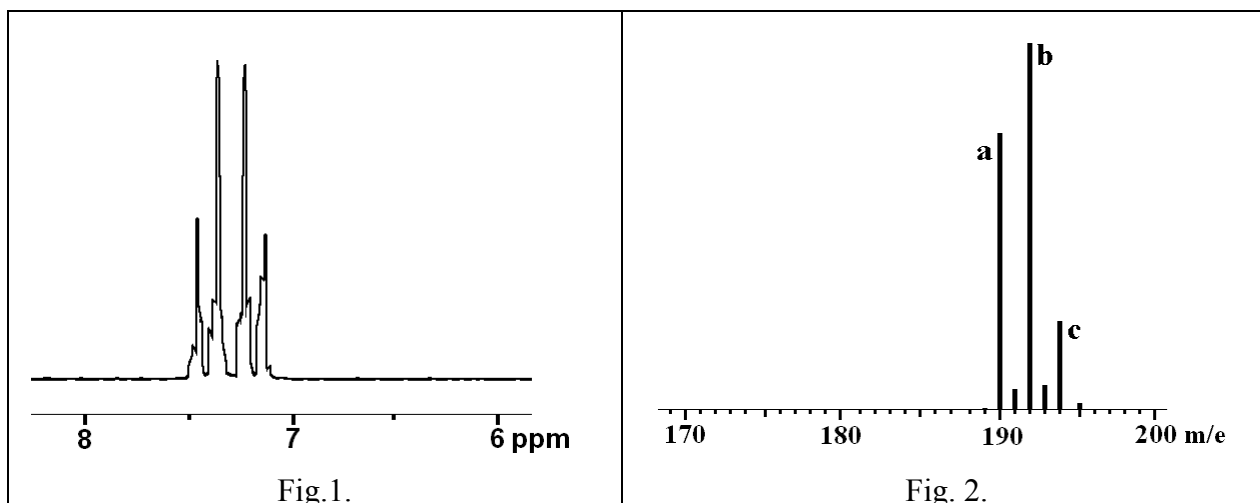
A mite and spider killer (Compound **E**) can be obtained as follows:



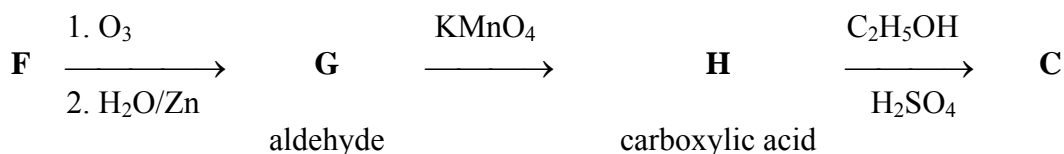
slow addition of twofold molar excess of Compound **B** in ether into Compound **C**

Intermediates **B** and **D** are not isolated. The final product **E** contains 21,85 % of chlorine (by mass) and also carbon, hydrogen and oxygen.

Molecular weight of Compound **A** is 191.5 g/mol.  $^1\text{H}$  NMR (100 MHz) spectrum of **A** shows two signals only with the following chemical shifts:  $\delta = 7,21$  and  $7,39$  p.p.m. (Fig. 1.). Fig. 2 shows a fragment of MS spectrum of Compound **A** with isotopic peaks pattern for molecular ion region.



Compound **C** could be prepared by ozonolysis of cyclobutadiene (Compound **F**) according to the following scheme:



#### Problems:

- Give chemical structures of **G**, **H** and **C**.
- Identify the isotopic composition of peaks **a**, **b** and **c** (Fig. 2.). Hint: Notice that not only chlorine is a mixture of isotopes, which mass numbers differs of two units.
- Explain the intensity pattern of peaks **a**, **b** and **c** (Fig. 2.).
- Give chemical structures of **A** and **E**.
- Give the few-step scheme for the synthesis of Compound **A** starting from nitrobenzene. The following reagents can be used: acetic anhydride,  $\text{Br}_2$ ,  $\text{CuCl}$ ,  $\text{Fe}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ , acetic acid,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaNO}_2$  and  $\text{NaOH}$ .
- Answer the following questions concerning  $^1\text{H}$  NMR spectrum (Fig. 1):
  - are protons of  $\delta = 7,21$  and  $7,39$  p.p.m. coupled each other?
  - why the peaks of the splitted signals are of different intensity?
  - why the peaks of the splitted signals are significantly broadened?

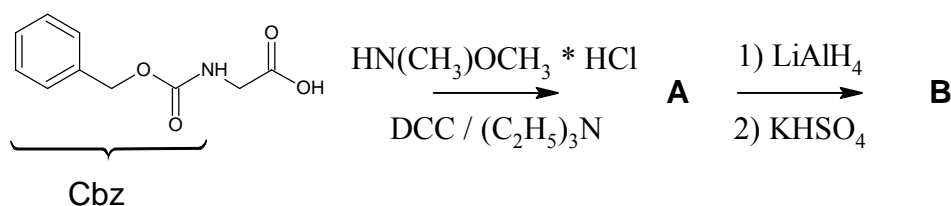
## TASK 5

### Cyclic analogs of aromatic amino acids

Constrained analogs of aromatic amino acids (with restricted rotation of side chains) have been used for many years in the investigation of bioactive structure of peptides.

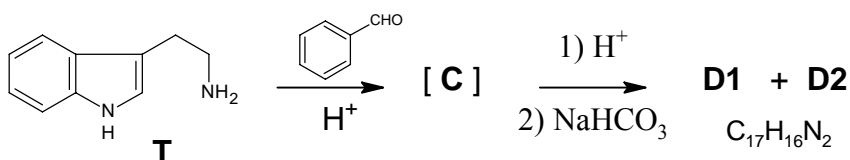
Last year during the Third Stage of our Olympiad we got to know one method of constraining the side chain of amino acid. In this task we will learn how to obtain another type of constrained analogs.

Amino aldehydes **B**, obtained from amino acids with protected amino group, are very often used as building blocks in organic synthesis. It is not possible to obtain those compounds by direct reduction of amino acids with protected amino group. They are prepared by reduction of Weinreb amides **A** (Scheme 1, DCC – coupling reagent).



Scheme I

The analogs of tryptamine **T** were synthesized according to the protocol presented on Scheme II. Compound **C** is an intermediate product. In the presence of acid compound **C** is transformed into its isomers. It is an electrophilic substitution reaction and the new C-C bond is formed (the stable ring is created). As a result of isomerisation the mixture of enantiomers **D1** and **D2** is obtained. It is easy to differ tryptamine from products **D1** and **D2** in the ninhydrine test: tryptamine gives violet colour, whereas compounds **D1** and **D2** give yellow one.



Scheme II

In the reactions presented on the scheme II methyl ester of tryptophan (instead of tryptamine) and amino aldehyde **B** (instead of benzaldehyde) may be used. The mixture of isomers **E1** and **E2** is formed as a result.

### Problems:

- Draw the structural formulas of compounds **A**, **B**. It is not possible to prepare amino aldehyde with protected amino group by direct reduction of amino acids. Explain it.
- Draw the structural formulas of compounds **C**, **D1**, **D2**, knowing that absolute configuration of **D1** is R and absolute configuration of **D2** is S.
- Draw the structural formula of a product of reaction between **D1** and acetyl chloride in the presence of triethylamine.
- Draw the structural formulas of compounds **E1**, **E2**. The absolute configuration of methyl ester of tryptophan is S. What type of isomers are compounds **E1** and **E2**?

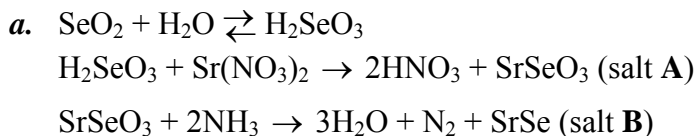
## SOLUTIONS

### SOLUTION OF TASK 1

- a.** Basing on the values of dissociation constants it can be assumed that solution pH is determined by the first dissociation step:  $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$  described by dissociation constant  $K_{a1}$ . Assuming total acid concentration,  $c$ , concentration of  $\text{H}_3\text{PO}_4$  is  $c - [\text{H}^+]$ , and  $[\text{H}_2\text{PO}_4^-] = [\text{H}^+]$ . Thus,  $K_a = [\text{H}^+]^2 / (c - [\text{H}^+])$ . Taking  $c = 0.1$  M, after solving the quadratic equation one obtains  $[\text{H}^+] = 0.022$  M, i.e.  $\text{pH} = 1.66$ . Hence,  $[\text{H}_2\text{PO}_4^-] = [\text{H}^+] = 0.022$  M.  $[\text{H}_3\text{PO}_4] = (0.10 - 0.022)$  M = 0.078 M. Degree of dissociation =  $[\text{H}^+] / c = 0.022 / 0.10 = 0.22$  (22 %)
- Using the constant  $K_{a2} = [\text{H}^+][\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-]$  and assuming  $[\text{H}_2\text{PO}_4^-] = [\text{H}^+]$ , one obtains  $[\text{HPO}_4^{2-}] = K_{a2} = 6 \cdot 10^{-8}$  M. This denotes that  $\text{H}^+$  ions from the second dissociation step ( $6 \cdot 10^{-8}$  M) can be neglected, compared to ions from the first step (0.022 M).
- Using dissociation constant  $K_{a3} = [\text{H}^+][\text{PO}_4^{3-}] / [\text{HPO}_4^{2-}]$ , after rearrangement one obtains:  $[\text{PO}_4^{3-}] = K_{a3} [\text{HPO}_4^{2-}] / [\text{H}^+]$ . By taking into account  $[\text{HPO}_4^{2-}] = 6 \cdot 10^{-8}$  M,  $[\text{H}^+] = 0.022$  M, one obtains  $[\text{PO}_4^{3-}] = 1 \cdot 10^{-18}$  M.
- b.** Total concentration of iron(III),  $c_{\text{Fe}} = [\text{Fe}^{3+}] + [\text{Fe}(\text{HPO}_4)^+] + [\text{Fe}(\text{H}_2\text{PO}_4)^{2+}] = [\text{Fe}^{3+}](1 + \beta_1[\text{HPO}_4^{2-}] + \beta_1^*[\text{H}_2\text{PO}_4^-])$ . Mole fractions of various forms (in relation to  $c_{\text{Fe}}$ ) are: for  $\text{Fe}^{3+}$ , mole fraction =  $[\text{Fe}^{3+}] / c_{\text{Fe}} = 1 / (1 + \beta_1[\text{HPO}_4^{2-}] + \beta_1^*[\text{H}_2\text{PO}_4^-])$ ; for  $\text{Fe}(\text{HPO}_4)^+$ , mole fraction =  $[\text{Fe}(\text{HPO}_4)^+] / c_{\text{Fe}} = \beta_1[\text{HPO}_4^{2-}] / (1 + \beta_1[\text{HPO}_4^{2-}] + \beta_1^*[\text{H}_2\text{PO}_4^-])$ ; for  $\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$ , mole fraction =  $[\text{Fe}(\text{H}_2\text{PO}_4)^{2+}] / c_{\text{Fe}} = \beta_1^*[\text{H}_2\text{PO}_4^-] / (1 + \beta_1[\text{HPO}_4^{2-}] + \beta_1^*[\text{H}_2\text{PO}_4^-])$ ;
- Using concentration values of  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  determined in point **a**, one obtains mole fractions: for  $\text{Fe}^{3+}$ : 0.01, for  $\text{Fe}(\text{HPO}_4)^+$ : 0.15, for  $\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$ : 0.84 and % amounts, for  $\text{Fe}^{3+}$ : 1 %, for  $\text{Fe}(\text{HPO}_4)^+$ : 15 %, for  $\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$ : 84 %
- c.** Dissolution equilibrium of  $\text{Fe}(\text{OH})_3$ ;  $\text{Fe}(\text{OH})_3 \rightleftharpoons \text{Fe}^{3+} + 3 \text{OH}^-$ , is described by solubility product:  $K_{s0} = [\text{Fe}^{3+}][\text{OH}^-]^3$ . Owing to low solubility of  $\text{Fe}(\text{OH})_3$  one can assume that  $[\text{OH}^-]$  is the same as in pure water, i.e.  $10^{-7}$  M. Assuming then that molar solubility,  $S = [\text{Fe}^{3+}]$ ,  $S = K_{s0} / [\text{OH}^-]^3 = 2 \cdot 10^{-39} / (10^{-7})^3 = 2 \cdot 10^{-18}$  M. This means that concentration of  $\text{OH}^-$  originating from hydroxide dissolution is  $6 \cdot 10^{-18}$  M, i.e. much lower than concentration of  $\text{OH}^-$  from water dissociation. Thus, for saturated  $\text{Fe}(\text{OH})_3$  solution  $\text{pH} = 7$ .
- d.** Solubility product equation can be used:  $K_{s0} = [\text{Fe}^{3+}][\text{OH}^-]^3$ . It can be assumed that molar solubility  $S = c_{\text{Fe}} = [\text{Fe}^{3+}](1 + \beta_1[\text{HPO}_4^{2-}] + \beta_1^*[\text{H}_2\text{PO}_4^-])$ , i.e.  $[\text{Fe}^{3+}] = S / (1 + \beta_1[\text{HPO}_4^{2-}] + \beta_1^*[\text{H}_2\text{PO}_4^-])$ ;  $[\text{OH}^-] = 10^{-14} / 0.022 = 4.5 \cdot 10^{-13}$  M.  $K_{s0} = \{S / (1 + \beta_1[\text{HPO}_4^{2-}] + \beta_1^*[\text{H}_2\text{PO}_4^-])\} [\text{OH}^-]^3$ . After rearrangement;  $S = K_{s0} (1 + \beta_1[\text{HPO}_4^{2-}] + \beta_1^*[\text{H}_2\text{PO}_4^-]) / [\text{OH}^-]^3$  or  $S = K_{s0} [\text{H}^+]^3 (1 + \beta_1[\text{HPO}_4^{2-}] + \beta_1^*[\text{H}_2\text{PO}_4^-]) / (10^{-14})^3$
- e.** Molar mass of  $\text{Fe}(\text{OH})_3$  is 106.88 g/mol. Dissolving 0.10 g in 1 L water corresponds to concentration  $c_{\text{Fe}} = 9.4 \cdot 10^{-4}$  M. Since, after inserting this value into equation describing solubility (point **d**), formally calculated value  $S = 1.7$  M, denoting that the  $\text{Fe}(\text{OH})_3$  sample will be dissolved. This conclusion can be also obtained by using mole fraction of  $\text{Fe}^{3+}$  determined in point **b**,  $[\text{Fe}^{3+}] = 9.4 \cdot 10^{-4} \cdot 0.01 = 9.4 \cdot 10^{-6}$  M. Taking into account  $[\text{OH}^-] = 4.5 \cdot 10^{-13}$  M (determined in point **d**), the product  $[\text{Fe}^{3+}][\text{OH}^-]^3$  is  $9 \cdot 10^{-43}$ , i.e. lower than  $K_{s0}$ ; the deposit dissolves completely.

In the absence of complexation the expression derived in point **d** can be written in a simpler form:  $S = K_{s0} [\text{H}^+]^3 / (10^{-14})^3$ . Thus, the ratio of solubility in the absence and presence of complexation is:  $1 + \beta_1[\text{HPO}_4^{2-}] + \beta_1^*[\text{H}_2\text{PO}_4^-]$ . After inserting the concentration data, this ratio will be 79.

**SOLUTION OF TASK 2**

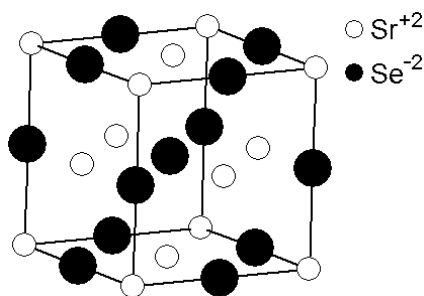


b. It follows from the equation of the  $\text{SrSeO}_3$  reduction reaction with ammonia that one obtains 1 mole of  $\text{SrSe}$  from 1 mole of  $\text{SrSeO}_3$ . The theoretical loss of mass accompanying the reaction equals:

$$\Delta m = [(214.58\text{g} - 166.58\text{g})/214.58\text{g}] \cdot 100\% = 22.4\%.$$

The agreement between this result and the value given in the problem confirms the fact that salt **A** is strontium selenate(IV) –  $\text{SrSeO}_3$  and that salt **B** is strontium selenide, having the formula  $\text{SrSe}$ .

c.



The number of cations  $\text{Sr}^{2+}$ :  $8 \times 1/8 + 6 \times 1/2 = 4$ ,

The number of anions  $\text{Se}^{2-}$ :  $12 \times 1/4 + 1 = 4$ , so  $Z = 4$ .

d.

No.	2theta	(h k l)	$h^2 + k^2 + l^2$
1	26.03°	1 1 1	3
2	30.15°	2 0 0	4
3	43.16°	2 2 0	8
4	51.09°	3 1 1	11
5	53.54°	2 2 2	12
6	62.68°	4 0 0	16
7	69.05°	3 3 1	19
8	71.11°	4 2 0	20
9	79.14°	4 2 2	24

e. Using the Bragg's law, we calculate the distance between lattice planes for any reflex, e.g.

$$(1\ 1\ 1): d_{(111)} = \frac{1 \cdot 1.54056 \text{ \AA}}{2 \cdot \sin(26.03/2)} = 3.420 \text{ \AA}.$$

Then using the equation for the interplanar distance, we calculate the lattice constant:

$$\frac{1}{3.420^2} = \frac{1^2 + 1^2 + 1^2}{a^2} \Rightarrow a = 5.924 \text{ \AA}$$

We calculate the unit cell volume for cubic system from the equation:  $V = a^3 = 207.9 \text{ \AA}^3$ .

f. We may calculate the density of a unit cell, keeping in mind that the mass of one unit cell amounts to  $m = \frac{M_m \cdot Z}{N_A}$ , so the formula for density is:  $\rho_r = \frac{M_m \cdot Z}{V \cdot N_A}$ .

For SrSe the density of its unit cell equals:

$$\rho_r = \frac{166.58 \cdot 4}{207.9 \cdot 10^{-24} \cdot 6.022 \cdot 10^{23}} = 5.32 \text{g/cm}^3.$$

**Comments to the solution of task 2**

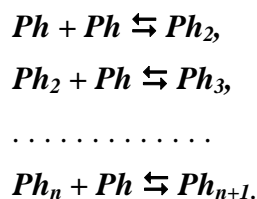
- b. The confirmation of the fact, that **B** is a compound in which the ratio of the cations' number to the anions' number equals 1:1, is the information that it is isostructural with sodium chloride which eliminates compounds such as strontium nitride from among the products of the SrSeO<sub>3</sub> reduction reaction with ammonia.
- c. Using the scheme of the strontium selenide's unit cell, we may calculate the number of cations and anions (Z) of the compound **B** in the cell. One has to keep in mind that 1/8 of an ion situated in the corner of a cell belongs to it, only 1/4 of the ion situated in the edge, a half of the ion situated on the wall and only the ion situated inside a cell belongs wholly to this cell.

**SOLUTION OF THE TASK 3**

a. The distribution coefficient of a substance between two phases is a ratio of the concentrations of the same chemical individual (the same form of the substance). In a context of this problem the only chemical individual present simultaneously in organic (CCl<sub>4</sub>) and aqueous phases is a monomer of phenol. Thus, the distribution coefficient of phenol between carbon tetrachloride and water is:

$$k = \frac{[Ph]}{a} \tag{1}$$

In organic phase the following simultaneous reactions of association occur:



The reactions are described by corresponding equilibrium constants, numerically equal to **K**. To simplify notation of the equations let's introduce the informal equilibrium constants (**K<sub>i</sub>**) calculated without relating the concentrations to proper standard concentration (these constants have the proper units). From the equations of equilibrium constants the concentrations of all associates can be calculated:

$$K_1 = \frac{[Ph_2]}{[Ph]^2} = K \quad \Rightarrow \quad [Ph_2] = K \cdot [Ph]^2$$

$$K_2 = \frac{[Ph_3]}{[Ph] \cdot [Ph_2]} = \frac{[Ph_3]}{K \cdot [Ph]^3} = K \quad \Rightarrow \quad [Ph_3] = K^2 \cdot [Ph]^3$$

$$K_3 = \frac{[Ph_4]}{[Ph] \cdot [Ph_3]} = \frac{[Ph_4]}{K^2 \cdot [Ph]^4} = K \quad \Rightarrow \quad [Ph_4] = K^3 \cdot [Ph]^4 \tag{2}$$

.....

$$K_n = \frac{[Ph_{n+1}]}{[Ph] \cdot [Ph_n]} = \frac{[Ph_{n+1}]}{K^{n-1} \cdot [Ph]^{n+1}} = K \quad \Rightarrow \quad [Ph_{n+1}] = K^n \cdot [Ph]^{n+1}$$

In the system all chemical equilibria occur in coexistence with each other and simultaneously with the equilibrium between two-phases described by the distribution coefficient. Additionally, the mass balance equation for organic phase must be fulfilled:

$$[Ph] + 2[Ph_2] + 3[Ph_3] + \dots + n[Ph_n] + (n+1)[Ph_{n+1}] + \dots = c. \quad (3)$$

Substituting the concentrations of particular associates  $[Ph_i]$  in Eq. 3 with the expressions from Eqs. 2 and replacing  $[Ph]$  by  $a \cdot k$  according to Eq. 1, we get:

$$a \cdot k + 2a^2 \cdot k^2 \cdot K + 3a^3 \cdot k^3 \cdot K^2 + \dots + (n+1)a^{n+1} \cdot k^{n+1} \cdot K^n + \dots = c.$$

Removing the common factor of each term of above expression and placing it outside the parentheses (curly brackets have to be used for clarity), we obtain:

$$a \cdot k \cdot \{1 + 2a \cdot k \cdot K + 3a^2 \cdot k^2 \cdot K^2 + \dots + (n+1)a^n \cdot k^n \cdot K^n\} + \dots = c. \quad (4)$$

It has to be noted that the series inside the curly brackets  $\{...\}$  in Eq. 4 is equivalent to the series in Eq. II of the hint (given in the text of the problem). Thus, Eq. 4 can be simplified to:

$$c = a \cdot k \cdot (1 - a \cdot k \cdot K)^{-2}. \quad (5)$$

b. The equilibrium constant can be calculated from Eq. 5 as equal to:

$$K = (a \cdot k)^{-1} - (a \cdot c \cdot k)^{-1/2} \quad (6)$$

The constant described with Eq. 6 must be equal in both experiments with the results given in the table. Thus the right hand sides of Eq. 6 must be equal when written for two experiments (the concentrations found in experiments 1 and 2 are marked with corresponding subscripts):

$$\frac{1}{a_1 \cdot k} - \frac{1}{\sqrt{k} \cdot \sqrt{a_1 \cdot c_1}} = \frac{1}{a_2 \cdot k} - \frac{1}{\sqrt{k} \cdot \sqrt{a_2 \cdot c_2}}$$

The distribution coefficient  $k$  can be calculated from above equation as follows:

$$\begin{aligned} \frac{1}{a_1} - \frac{1}{a_2} &= \frac{k}{\sqrt{k}} \cdot \left( \frac{1}{\sqrt{a_1 \cdot c_1}} - \frac{1}{\sqrt{a_2 \cdot c_2}} \right) \\ \sqrt{k} &= \frac{\frac{1}{a_1} - \frac{1}{a_2}}{\frac{1}{\sqrt{a_1 \cdot c_1}} - \frac{1}{\sqrt{a_2 \cdot c_2}}} \\ k &= \left( \frac{\frac{1}{a_1} - \frac{1}{a_2}}{\frac{1}{\sqrt{a_1 \cdot c_1}} - \frac{1}{\sqrt{a_2 \cdot c_2}}} \right)^2. \end{aligned}$$

Substituting the proper concentrations in above equation with values from the table (in mol/dm<sup>3</sup>) the distribution coefficient  $k = 1.90$  is calculated. Putting this value into Eq. 6 together with any pair of concentrations from the table, we obtain the value for equilibrium constant  $K = 2.26$  (mole/dm<sup>3</sup>)<sup>-1</sup>.

c. Average number of phenol molecules in associates ( $\bar{n}$ ) is equal to a quotient: a total number of molecules (monomers) ( $m$ ) in unit volume divided by a number of associates ( $p$ ) in the same volume of solution,  $\bar{n} = m/p$ . A number of phenol molecules in the solution in CCl<sub>4</sub> is proportional

to the total concentration of phenol in organic phase ( $c$ ). This concentration corresponds to the number of moles of monomers, which means that each associate  $Ph_i$  is treated as a number of single molecules equal to  $i$ .

Eq. 3 exhibits exactly the sum of concentrations of all molecules (monomers) present in different associates, so the number of monomers ( $m$ ) can be calculated from Eq. 3 converted to the form of Eq. 5:

$$m = A \cdot \{ a \cdot k + 2 \cdot a^2 \cdot k^2 \cdot K + 3 \cdot a^3 \cdot k^3 \cdot K^2 + \dots + (n+1) \cdot a^{n+1} \cdot k^{n+1} \cdot K^n + \dots \} = A \cdot a \cdot k \cdot (1 - a \cdot k \cdot K)^{-2}, \quad (7)$$

where:  $A$  is the Avogadro number, however, a multiplication by Avogadro number is not necessary because the number of molecules can be expressed in moles, as well.

The number of all associates ( $p$ ) we calculate as the sum: number of monomers + number of dimers + number of trimers + ..... and so on. It can be expressed as:

$$p = A \cdot \{ a \cdot k + a^2 \cdot k^2 \cdot K + a^3 \cdot k^3 \cdot K^2 + \dots + a^{n+1} \cdot k^{n+1} \cdot K^n + \dots \} = A \cdot a \cdot k \cdot \{ 1 + a \cdot k \cdot K + a^2 \cdot k^2 \cdot K^2 + \dots + a^n \cdot k^n \cdot K^n + \dots \}. \quad (8)$$

The expression inside the curly brackets  $\{...\}$  is equivalent to geometrical series with a quotient of subsequent terms  $q = a \cdot k \cdot K < 1$ , so its sum (according to Eq. 1 in the hint) is equal to:

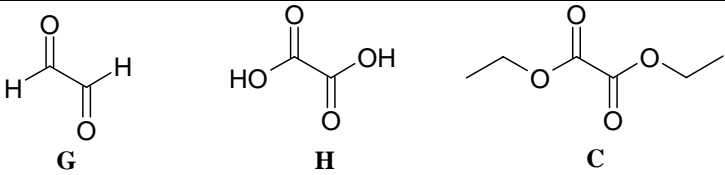
$$p = A \cdot a \cdot k \cdot (1 - a \cdot k \cdot K)^{-1}. \quad (9)$$

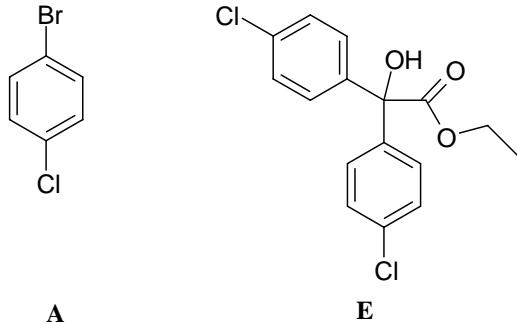
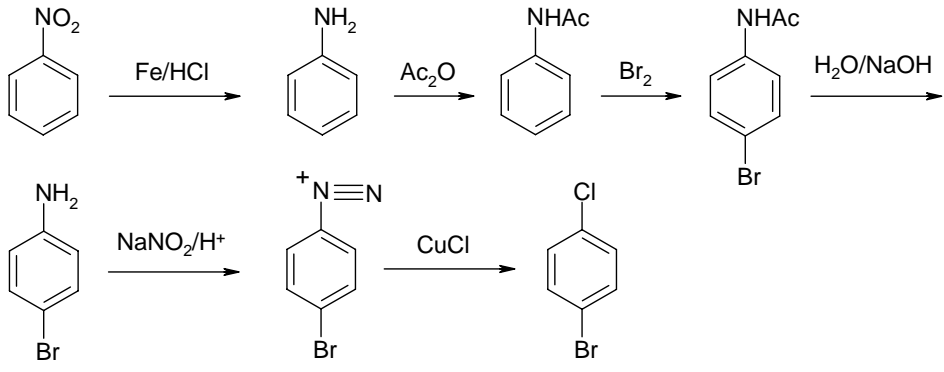
Thus, the average number of molecules (monomers) in average associate ( $\bar{n}$ -mer) is equal to:

$$\bar{n} = m/p = (1 - a \cdot k \cdot K)^{-1}.$$

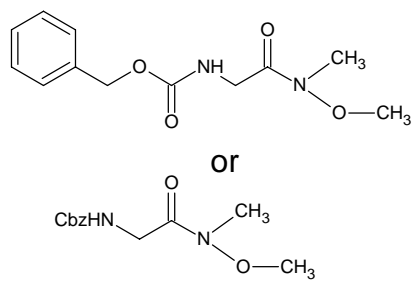
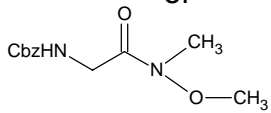
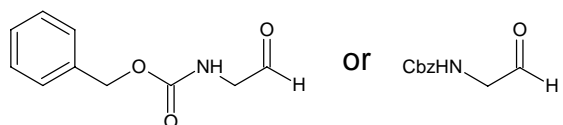
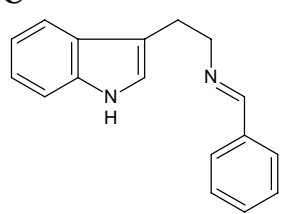
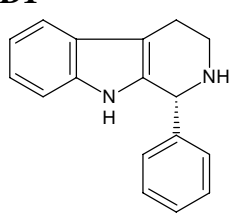
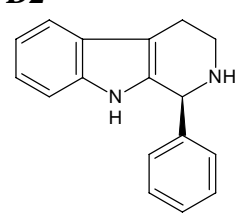
As can be seen from above equation the average number of molecules in associates ( $\bar{n}$ ) depends on concentration of phenol, so in each of two experiments it is equal to:  $\bar{n}_1 = 2.4$  and  $\bar{n}_2 = 3.1$ , respectively.

#### SOLUTION OF TASK 4

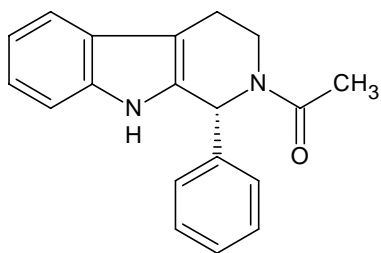
<b>a.</b>	 <p style="text-align: center;"> <span style="margin-right: 100px;"><b>G</b></span> <span style="margin-right: 100px;"><b>H</b></span> <span><b>C</b></span> </p>
<b>b.</b>	<p><b>a</b> = <math>6 \times 12</math> (<math>^{12}\text{C}</math>) + <math>4 \times 1</math> (<math>^1\text{H}</math>) + <math>35</math> (<math>^{35}\text{Cl}</math>) + <math>79</math> (<math>^{79}\text{Br}</math>) = 190</p> <p><b>b</b> = <math>6 \times 12</math> (<math>^{12}\text{C}</math>) + <math>4 \times 1</math> (<math>^1\text{H}</math>) + <math>37</math> (<math>^{37}\text{Cl}</math>) + <math>79</math> (<math>^{79}\text{Br}</math>) = 192</p> <p style="padding-left: 20px;">and <math>6 \times 12</math> (<math>^{12}\text{C}</math>) + <math>4 \times 1</math> (<math>^1\text{H}</math>) + <math>35</math> (<math>^{35}\text{Cl}</math>) + <math>81</math> (<math>^{81}\text{Br}</math>) = 192</p> <p><b>c</b> = <math>6 \times 12</math> (<math>^{12}\text{C}</math>) + <math>4 \times 1</math> (<math>^1\text{H}</math>) + <math>37</math> (<math>^{37}\text{Cl}</math>) + <math>81</math> (<math>^{81}\text{Br}</math>) = 194</p>
<b>c.</b>	<p>Bromine is a mixture of <math>^{79}\text{Br}</math> and <math>^{81}\text{Br}</math> isotopes with almost equal populations. Chlorine is a mixture of <math>^{35}\text{Cl}</math> and <math>^{37}\text{Cl}</math> isotopes with populations of about 3 : 1, respectively.</p> <p>So peak containing the combination of <math>^{79}\text{Br}/^{37}\text{Cl}</math> + <math>^{81}\text{Br}/^{35}\text{Cl}</math> (peak <b>b</b>) is the biggest one (about 130 %) of basic peak (peak <b>a</b>, which is the combination of <math>^{79}\text{Br}/^{35}\text{Cl}</math>), and intensity of peak <math>^{81}\text{Br}/^{37}\text{Cl}</math> (<b>c</b>) is the lowest one (about 30 % of the basic peak).</p>

<p><b>d.</b></p>	 <p><b>A</b> <b>E</b></p>
<p><b>e.</b></p>	
<p><b>f.</b></p>	<p>Protons are coupled. Intensity of splitted peaks differs because of roof effect. (AM system, in which the difference in chemical shifts – 18 Hz is only two-fold bigger than the coupling constant – 9 Hz). Peaks of the splitted signals are broadened because of far range coupling with <i>meta</i> and <i>para</i> protons (which are magnetically not equal).</p>

### SOLUTION OF TASK 5

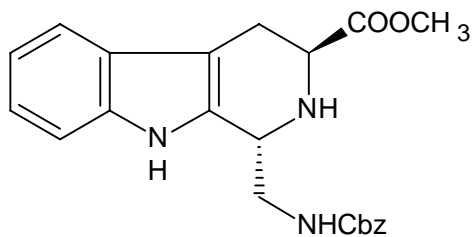
<p><b>a) Structural formulas</b></p>		
<p><b>A</b></p>  <p><b>OR</b></p> 	<p><b>B</b></p>  <p><b>OR</b> <chem>CbzHNCH2CHO</chem></p>	
<p><b>Answer:</b> Direct reduction of amino acids gives aminoalcohols with protected amino group</p>		
<p><b>b) Structural formulas</b></p>		
<p><b>C</b></p> 	<p><b>D1</b></p> 	<p><b>D2</b></p> 

**c) Structural formulas**

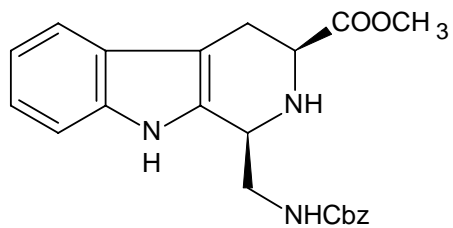


**d) Structural formulas**

**E1**



**E2**



**or vice versa**

**Answer:** Compounds **E1** and **E2** are diastereomers or *cis/trans* isomers.



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# 56 Chemistry Olympiad

## Final competitions (26<sup>th</sup> Mar 2010)

### *Practical tasks and solutions*

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#### TASK I:

##### *Determination of anions*

There is a mixture of **sodium sulphate(VI)** and **potassium dichromate(VI)** in a 200 mL volumetric flask marked with the letter **P**. The mixture was acidified with **hydrochloric acid**, 100 mL of 0,050 mol·L<sup>-1</sup> **barium chloride** solution were added to the flask and it was filled up to a volume of 200.0 mL. Less than 0.005 moles of sodium sulphate(VI) and at least 0.025 moles of potassium dichromate(VI) were used for preparing the mixture. The hydrochloric acid concentration in flask **P** is not greater than 0.2 mol·L<sup>-1</sup>. The precipitate volume in the flask can be neglected.

#### **Apparatus and reagents at your disposal:**

<b>on a stand for each participant:</b>		<b>on a stand for two participants:</b>
burette	two Erlenmeyer flasks with ST	0,1000 mol·L <sup>-1</sup> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution
three beakers	three pieces of filter paper	2 mol·L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> solution
two glass rods	25 mL volumetric pipette	1 mol·L <sup>-1</sup> NH <sub>3</sub> solution
analytical funnel	pisette with distilled water	20% KI solution
graduated cylinder	two pH indicator papers	1% starch solution

#### **Problems:**

- (4 points) Propose an analysis plan to determine the number of moles of sulphate(VI) and dichromate(VI) anions in the mixture, using the procedure given below.
- (3,5 points) Write the chemical reactions taking place during the analysis.
- (4 points) Derive the formulae to calculate the number of moles of the determined anions that incorporate appropriate volumes of titrant used during the titration.
- (6 points) Find the mass of potassium dichromate(VI) used for preparing the solution in flask **P**.
- (6 points) Give the mass of sodium sulphate(VI) in the mixture.
- (2,5 points) Give the amplification coefficient of the dichromate(VI) and sulphate(VI) ions determination method according to the given procedure. Justify your answer.

#### **Procedure**

##### *Indirect determination of sulphates*

Add hydrochloric acid to the sample containing sulphate(VI) ions, heat it up and add a known amount of barium chromate(VI) [in a molar excess with respect to sulphate(VI) ions] in a form of a solution obtained by dissolving a weighed amount of BaCrO<sub>4</sub> in hydrochloric acid. Alkalize the resulting suspension with an ammonia solution. Filter the formed precipitate, collecting the filtrate into an Erlenmeyer flask with ST. **When planning your work consider the fact that the filtration takes around 30 minutes.** Wash the precipitate with a few portions of water with a drop of ammonia, collecting the filtrates into the flask. Add 10 mL of potassium iodide solution and 15 mL of sulphuric(VI) acid solution. Close the flask and leave it standing for 5 minutes. Titrate the produced iodine with a sodium thiosulphate solution of a known concentration. At the end of titration, when the solution turns olive-green, add the starch solution and continue titration until the solution turns colourless.

**CAUTION!** The remaining solutions from flask **P** and the solutions after titration have to be disposed to special containers for waste. The same applies to the filter paper containing precipitate.

## TASK 2

### ***Electrolysis in qualitative analysis***

There are solutions of the substances presented in the table below in the test tubes labelled with numbers **1-8** and letters **A-D**:

<b>Test tubes 1-8</b>	Sodium nitrate(V)	<b>Test tubes A-D</b>	Ferroun
	Zinc nitrate(V)		Methyl red
	Potassium chloride		Bromothymol blue
	Magnesium sulphate(VI)		Phenolphthalein
	Manganese(II) sulphate(VI)		
	Cadmium chloride		
	Potassium iodide		
	Sodium bromide		

The concentration of salt solutions equals  $0.1 \text{ mol}\cdot\text{L}^{-1}$  and the concentration of remaining substances around 0.1%.

#### **The following apparatus is at your disposal:**

battery with graphite electrodes  
two white, china vessels  
six polyethylene Pasteur pipettes

6 empty test tubes  
pissette with distilled water  
tissue paper for drying the electrodes

You may use the solutions for problem 1.

#### **Problems:**

- a. (12 points)* Identify the substances in the test tubes **1-8** and **A-D** using the given procedure.
- b. (12 points)* Give unambiguous justification of every substance's identification based only on the observations made during or after the electrolysis.
- c. (4 points)* Explain the differences in the course of manganese(II) sulphate(VI) and sodium bromide electrolysis without the addition of an acid and after acidification.
- d. (6 points)* Write the equations of the chemical reactions that took place during the electrolysis of salts taking into account your observations.

#### **Procedure of electrolysis:**

Transfer ca. 2 mL of a salt solution into the china vessel and dip electrodes in the solution. Watch changes taking place during approximately 30 seconds of electrolysis. Repeat the electrolysis adding a few drops of indicators from test tubes **A-D** and acidifying the solution, if needed. After the electrolysis mix the solution in the vessel. If necessary, transfer the solution to a test tube and use for further investigation. Clean the electrodes with paper or tissue after every electrolysis.

USE YOUR SOLUTIONS ECONOMICALLY. DO NOT USE GREATER AMOUNTS OF YOUR SOLUTIONS THAN 2 mL FOR THE TESTS.

**Important! The answers for the questions have to be placed in the right fields in the table on the answer sheet. Anything placed beyond those fields will not be marked!**

**Write your answers neatly and legibly. Illegible answers may be the reason for lower marks and will not be considered in the appeals**

**Remember to work safely when carrying out analysis**



<p><b>Problem f.</b> Looking at the reactions one can notice that 1 mole of dichromate(VI) ions reacts with 6 moles of thiosulphate ions, so the amplification coefficient of the iodometric determination of dichromate(VI) ions equals 6. When determining sulphate(VI) ions according to the method given in the procedure, the filtrate contains an amount of chromate(VI) ions that is the same as the amount of sulphate(VI) ions in the sample (after filtering the precipitate containing both barium sulphate(VI) and barium chromate(VI))</p> $n_{\text{sulph}} = n_{\text{chrom, filtrate}}$ <p>Thus, the amplification coefficient of iodometric determination of sulphate(VI) ions equals</p>	<b>2,5</b>
<b>SUM OF POINTS FOR TASK 1</b>	
<b>26</b>	

### SOLUTION OF TASK 2

Exemplary arrangement of substances for analysis:

Test tube	Substance	Test tube	Substance
<b>1</b>	Sodium nitrate(V)	<b>A</b>	Ferroin
<b>2</b>	Zinc nitrate(V)	<b>B</b>	Methyl red
<b>3</b>	Potassium chloride	<b>C</b>	Bromothymol blue
<b>4</b>	Magnesium sulphate(VI)	<b>D</b>	Phenolphthalein
<b>5</b>	Manganese(II) sulphate(VI)		
<b>6</b>	Cadmium chloride		
<b>7</b>	Potassium iodide		
<b>8</b>	Sodium bromide		

The participant can make notes in the rough paper in such a way (this is just an example):

Test tube	Area	Without indicator	Description of a test tube with an indicator			
			<b>A</b> ferroin	<b>B</b> methyl red	<b>C</b> bromoth. blue	<b>D</b> phenolphth.
<b>1</b> NaNO <sub>3</sub>	anode	gas, nc	gas, red, nc	gas, red	gas, yel, nc	gas, nclr
	cathode	gas, nc	gas, red, nc	gas, yel, nc	gas, blue	gas, rsp
	mixed	nclr, nc	red, nc	yel, nc	yel, nc	nclr
<b>2</b> Zn(NO <sub>3</sub> ) <sub>2</sub>	anode	gas, nc	gas, red, nc	gas, red	gas, yel-gr, nc	gas, nclr
	cathode	mt, gas, nc	gas, red, nc	gas, yellow, nc	gas, yel-gr, nc	gas, nclr
	mixed	nclr, nc	red, nc	red	yel-gr, nc	nclr, nc
<b>3</b> KCl	anode	gas, nc	gas, red, nc	gas, red, clrl	gas, yel, nc	gas, nclr
	cathode	gas, nc	gas, red, nc	gas, yel, nc	gas, blue	gas, rsp
	mixed	nclr, nc	red, nc	nclr	yel, nc	nclr,
<b>4</b>	anode	gas, nc	gas, red, nc	gas, red,	gas, yel, nc	gas, nclr, nc

MgSO <sub>4</sub>	cathode	mt, gas, nc	gas, red, nc	gas, yel, nc	gas, yel-gr, nc	gas, pink
	mixed	nclr, nc	red, nc	Orange	yel, nc	nclr, nc
<b>5</b> MnSO <sub>4</sub>	anode	↓br	red, clrl	gas, red, nc	gas, yel, nc	gas, nclr, nc
	cathode	mt, gas nc	gas, red, nc	gas, red, nc	gas, yel, nc	gas, nclr, nc
	mixed	br zaw	clrl after acidif	red, nc	yel, nc	nclr, nc
<b>6</b> CdCl <sub>2</sub>	anode	gas, nc	gas, red, nc	gas, red, clrl	gas, yel	gas, nclr
	cathode	mt, nc	red, nc	yel, nc	yel-gr, nc	nclr, nc
	mixed	nclr, nc	red, nc	nclr	yel, p. clrl	nclr, nc
<b>7</b> KI	anode	yel	br	red	gas, yellow	gas, yellow
	cathode	gas, nc	gas, red, nc	gas, yel, nc	gas, blue	gas, rsp
	mixed	yel	red br	orn	blue	rsp
<b>8</b> NaBr	anode	yel	orn	red, clrl	gas, orn	gas, yel
	cathode	gas, nc	gas, red, nc	gas, yel, nc	gas, blue	gas, rsp
	mixed	yellowish	red, nc	clrl	yel, p. clrl	clrl

**Abbreviations used in tables:** smpl- sample, nc – no changes, → state after electrolysis, ↓ precipitate, br – brown, red – red, blue - blue, yel – yellow, rsp – raspberry, orn – orange, gr – green, nclr – colourless, acidif – after acidification, clrl – turns colourless, p. clrl – partially turns colourless, stir – after stirring, hazy – haziness, mt – metal, C – cathode(-), A – anode(+)

### Comments to the solution of problem 2

During electrolysis of the salt solutions, one can notice brown precipitate being formed around anode in the solution from the test tube **5**. It can suggest that it contains MnSO<sub>4</sub>. There is yellow colour appearing around anode for test tubes **7** and **8** which could suggest that iodine or bromine are produced there. Upon addition of starch (from problem 1) blue colour appears only in the test tube **7**, which indicates KI. One can assume NaBr is in the test tube **8**.

Electrolysis of acidified solutions from test tubes **5** and **8** proceeds more vigorously and additionally in the test tube **5** there is violet colour appearing around anode. This is the only solution that makes the solution from the test tube **A** colourless, where probably ferroin is. It points unambiguously to manganese(II) sulphate(VI) in the test tube **5** and ferroin in the test tube **A**. The solution from the test tube **8** is more intensely yellow than after electrolysis without acid. This solution reacts with the contents of the test tube **7** giving iodine (reaction with starch). It also reacts with the indicator from the test tube **B**, which at first changes its colour from yellow to red and afterwards turns colourless. The test tube **B** probably contains methyl red.

Electrolysis of salts with the indicator from the test tube **B** causes the colour of the indicator to turn yellow from red around anode for the solutions from all the test tubes. This confirms presence of methyl red in the test tube **B** and points to the fact that H<sub>3</sub>O<sup>+</sup> cations are produced on anode during electrolysis. At the same time one can notice that the solutions from test tubes **3,6** and **8** turn colourless which points to the formation of chlorine or bromine that destroy the dye's structure. For

test tubes **2** and **4** mixing of the solution causes the whole solution to turn red and for the test tube **5** the red colour of the solution before the electrolysis remains unchanged upon stirring. Test tubes **2** and **4** contain salts whose solutions are acidified during the course of electrolysis as a result of the formation of metal on the cathode. These can be zinc nitrate(V) or magnesium sulphate(VI). The solution from the test tube **1** was the only one not to change its colour, which may point to sodium nitrate(V).

The indicator from the test tube **C** changes its colour from yellow to blue around cathode for test tubes **1, 3, 7** and **8**, whereas for test tubes **4** and **6** from yellow to yellow-green. It indicates that test tubes **1, 3, 7** and **8** contain salts of sodium and potassium and the test tube **C** contains bromothymol blue. After mixing the yellow colour comes back only for the solutions from test tubes **1** and **4** and the blue colour appears for the solution from the test tube **7**. This shows that test tubes **1** and **4** contain salts of oxygen-containing acids and that the test tube **7** contains halides. Thus, it confirms the presence of sodium nitrate(V) in the test tube **1** and potassium iodide in the test tube **7**.

The indicator loses its properties for test tubes **3, 6** and **8** – the appearing yellow colour does not change during further electrolysis. It confirms the presence of potassium chloride in the test tube **3**, cadmium chloride in the test tube **6** and sodium bromide in the test tube **8**.

The fact that no change of colour was observed for solutions from test tubes **2** and **5** [where manganese(II) sulphate(VI) was found] indicates that the test tube **2** contains zinc nitrate(V).

Electrolysis of salt solutions in the presence of the indicator from the test tube **D** causes raspberry colour to appear around cathode of the samples **1, 3, 7** and **8**, and a pink colour for the test tube **4**. This points unambiguously to phenolphthalein in the test tube **D**, salts of sodium or potassium in **1, 3, 7** and **8** and magnesium sulphate(VI) in the test tube **4** (the distinction from cadmium and zinc, where the formation of the metal on the cathode is not accompanied by the production of hydrogen nor the alkalization of solution).

<b>Problems a., b.</b>			
T. tube	Found	Justification	Points
<b>1</b>	NaNO <sub>3</sub>	Electrolysis without indicators – formation of nclr gazu on C and A C: C yel→blue, stir - yellow; D nclr→rsp, stir - nclr A;; B yel→red, stir - yellow	<b>id. 1,0</b> <b>j. 1,0</b>
<b>2</b>	Zn(NO <sub>3</sub> ) <sub>2</sub>	Electr. Without indicators –formation of mt and gas on C, A nclr gas C: C yel→nc, stir - yel; D nclr→nc, stir - nclr A;; B yel→red, stir - red	<b>id. 1,0</b> <b>j. 1,0</b>
<b>3</b>	KCl	Electrolysis without indicators – formation of gas on C and A C: C yel→blue, stir - yel, clrl; D nclr→rsp, stir - nclr, clrl A;; B yel→red, clrl, stir - clrl	<b>id. 1,0</b> <b>j. 1,0</b>
<b>4</b>	MgSO <sub>4</sub>	Electr without indicators formation of mt and gas on C, A nclr gas C: C yel→yel-gr, stir - yel; D nclr→pink, stir - nclr A: B yel→red, stir - red	<b>id. 1,0</b> <b>j. 1,0</b>
<b>5</b>	MnSO <sub>4</sub>	Electr without indicat – formation of mt and gas on C, on A br prec. C: C yel→nc, stir yel; D nclr→nc, stir nclr A: B red→nc, stir - nc; A red, stir i acidif – clrl or pale blue	<b>id. 1,0</b> <b>j. 1,0</b>

<b>6</b>	CdCl <sub>2</sub>	Electrolysis without indicators – formation of mt on C, A gas C: <b>C</b> yel→yel-gr, stir yel, clrl; <b>D</b> nclr→nc, stir - clrl A:; <b>B</b> yel→red, clrl, stir - clrl	<b>id. 1,0</b> <b>j. 1,0</b>
<b>7</b>	KI	El without ind. – gas on C , on A yel, stir yel +starch navy blue C: <b>C</b> yel→blue, stir blue; <b>D</b> nclr→ rsp, stir - pink A: <b>B</b> yel→orn, stir yel; <b>A</b> red→red haziness	<b>id. 1,0</b> <b>j. 1,0</b>
<b>8</b>	NaBr	Electr without indicat – formation of gas on C , A yel, stir nclr. C: <b>C</b> yel→blue, stir yel, clrl; <b>D</b> nclr→ rsp, stir clrl A: <b>B</b> yel→red, clrl, stir clrl; <b>A</b> red→nc	<b>id. 1,0</b> <b>j. 1,0</b>
<b>A</b>	Ferrouin	C: all the sm red→nc, A: all the sm red→nc except for: 5 - clrl, 7 – red haziness stir: acidif sm <b>5</b> clrl or pale blue, sm <b>7</b> - red haziness	<b>id. 1,0</b> <b>j. 1,0</b>
<b>B</b>	Methyl red	C: all the sm except for <b>5</b> yel→nc, sm <b>5</b> red→nc A: all the sm yel→red, stir: - clrl for sm <b>3, 6</b> and <b>8</b> , red for sm <b>2</b> and <b>4</b>	<b>id. 1,0</b> <b>j. 1,0</b>
<b>C</b>	Bromo-thymol blue	C: all the sm yel→blue for sm <b>1, 3,7</b> and <b>8</b> , pozost nc A: all the sm yel→nc, stir - clrl for sm <b>3, 6</b> and <b>8</b>	<b>id. 1,0</b> <b>j. 1,0</b>
<b>D</b>	Phenolphthalein	C: all sm nclr→ rsp for sm <b>1, 3, 7</b> and <b>8</b> , pink <b>4</b> , the rest nc A: all sm nclr→nc, stir - clrl for sm <b>3, 6</b> and <b>8</b> , rsp for sm <b>7</b>	<b>id. 1,0</b> <b>j. 1,0</b>
<b>Sum</b>			<b>24,0</b>

<b>Problem c.</b>			
Test tube	Found	Justification	Points
5	MnSO <sub>4</sub>	Electr without indicat – vigorous formation of gas on C, on A violet colour and a little farther away from the electrode brown precipitate C: <b>C</b> red→nc, stir red; <b>D</b> nclr→nc, stir nclr A: <b>B</b> red→nc, stir red; sm <b>A</b> red→clrl After stirring the solution and adding a few drops from solution <b>A</b> , they loose their colour and the solution turns slightly blue	<b>2,0</b>
8	NaBr	Electr without indicat – vigorous formation of gas on C, on A yel colour, after mixing still yellow C: <b>C</b> red→blue, stir yel, clrl; <b>D</b> nclr→pink, stir clrl A: <b>B</b> red→clrl, sm <b>A</b> red→nc After stirring the solution after electrolysis the smell of bromine can be felt, adding a few drops of the solution <b>B</b> causes them to be nclr	<b>2,0</b>
<b>Problem d.</b>			
test tube	Cathode	Anode	

<b>1</b>	$4\text{H}_2\text{O} + 4\text{e} \rightarrow 2\text{H}_2\uparrow + 4\text{OH}^-$	$2\text{H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2\uparrow + 4\text{H}^+$	<b>1,0</b>
<b>2</b>	$2\text{Zn}^{2+} + 4\text{e} \rightarrow 2\text{Zn}$ $\text{NO}_3^- + 10\text{H}^+ + 8\text{e} \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O}$	$2\text{H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2\uparrow + 4\text{H}^+$ $4\text{H}_2\text{O} - 8\text{e} \rightarrow 2\text{O}_2\uparrow + 8\text{H}^+$	<b>1,0</b>
<b>3</b>	$2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2\uparrow + 2\text{OH}^-$ $4\text{H}_2\text{O} + 4\text{e} \rightarrow 2\text{H}_2\uparrow + 4\text{OH}^-$	$2\text{Cl}^- - 2\text{e} \rightarrow \text{Cl}_2\uparrow$ $2\text{H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2\uparrow + 4\text{H}^+$	<b>0,5</b>
<b>4</b>	$2\text{Mg}^{2+} + 4\text{e} \rightarrow 2\text{Mg}$ $4\text{H}_2\text{O} + 4\text{e} \rightarrow 2\text{H}_2\uparrow + 4\text{OH}^-$	$2\text{H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2\uparrow + 4\text{H}^+$ $2\text{H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2\uparrow + 4\text{H}^+$	<b>0,5</b>
<b>5</b>	$5\text{Mn}^{2+} + 10\text{e} \rightarrow 5\text{Mn}$	$2\text{Mn}^{2+} + 8\text{H}_2\text{O} - 10\text{e} \rightarrow 2\text{MnO}_4^- + 16\text{H}^+$ *) $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$	<b>1,5</b>
<b>6</b>	$\text{Cd}^{2+} + 2\text{e} \rightarrow \text{Cd}$ $2\text{Cd}^{2+} + 4\text{e} \rightarrow 2\text{Cd}$	$2\text{Cl}^- - 2\text{e} \rightarrow \text{Cl}_2\uparrow$ $2\text{H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2\uparrow + 4\text{H}^+$	<b>0,5</b>
<b>7</b>	$2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2\uparrow + 2\text{OH}^-$ $4\text{H}_2\text{O} + 4\text{e} \rightarrow 2\text{H}_2\uparrow + 4\text{OH}^-$	$2\text{I}^- - 2\text{e} \rightarrow \text{I}_2\uparrow$ $2\text{H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2\uparrow + 4\text{H}^+$	<b>0,5</b>
<b>8</b>	$2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2\uparrow + 2\text{OH}^-$ $4\text{H}_2\text{O} + 4\text{e} \rightarrow 2\text{H}_2\uparrow + 4\text{OH}^-$	$2\text{Br}^- - 2\text{e} \rightarrow \text{Br}_2\uparrow$ $2\text{H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2\uparrow + 4\text{H}^+$	<b>0,5</b>
<b>Sum</b>			<b>10,0</b>
<b>SUM OF POINTS FOR TASK 2</b>			<b>34</b>

\*) reaction taking place in the solution and not on the electrode