

40<sup>th</sup> International  
Chemistry Olympiad

Preparatory Problems

2008  
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Preparatory problems for the 40<sup>th</sup> International Chemistry Olympiad

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# Preface

We have developed this set of problems with the intention of making the preparation for the Olympiad easier for both students and mentors. Our intention was to shift the focus of the problems from current research topics to interesting applications of basic chemical principles that are easily accessible at the level of secondary education.

We aimed to comply with the presently valid IChO syllabus, but the Olympiad exams and the preparatory problems were prepared with a restructured syllabus in mind. We recommend the use of the version of the syllabus found at the end of this booklet during the preparations.

We restricted ourselves to the inclusion of only a few topics that are not usually covered in secondary schools. There are six such advanced topics that we expect the participants to be familiar with. These fields are listed explicitly and their application is demonstrated in the problems. In our experience each of these topics can be introduced to well-prepared students in 2-3 hours.

The official solutions are only available to the future mentors of each country at the time of publication of this set, Solutions will be published in May 2008 on the web.

We welcome any comments, corrections or questions about the problems via email at [gmagyarf@chem.elte.hu](mailto:gmagyarf@chem.elte.hu).

We have enjoyed preparing the problems and we hope that you will also enjoy solving them. See you in Budapest!

## Acknowledgement

I thank the hard and dedicated teamwork of the problem authors. They are former Olympiad participants or mentors and they will form the core of the Science Committee of the IChO. I am grateful to other members of the future SC, namely Márton Boros, Zsolt Gengelicki, Dóra Kőhalmi, Áron Kramarics, Krisztián Lőrincz, Katalin Ósz, Zsuzsanna Sánta and Zsófia Szalay for their invaluable review efforts. I also thank Miklós Riedel for his thorough review of the manuscript and Jon Baker for correcting the English of the problem set.

Budapest, 20 January 2008

Gábor Magyarfalvi  
editor

# Constants and Formulae

Avogadro constant:	$N_A = 6.022 \cdot 10^{22} \text{ mol}^{-1}$	Ideal gas equation:	$pV = nRT$
Gas constant:	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	Gibbs energy:	$G = H - TS$
Faraday constant:	$F = 96485 \text{ C mol}^{-1}$	$\Delta_r G^\circ = -RT \ln K = -nFE_{cell}^\circ$	
Planck constant:	$h = 6.626 \cdot 10^{-34} \text{ J s}$	Nernst equation:	$E = E^\circ + \frac{RT}{zF} \ln \frac{c_{ox}}{c_{red}}$
Speed of light:	$c = 3.000 \cdot 10^8 \text{ m s}^{-1}$	Arrhenius equation:	$k = A \exp\left(-\frac{E_A}{RT}\right)$
Zero of the Celsius scale:	273.15 K	Lambert-Beer law:	$A = \log \frac{I_0}{I} = \epsilon c l$

In equilibrium constant calculations all concentrations are referenced to a standard concentration of one mole per  $\text{dm}^3$ .

## Periodic table with relative atomic masses

1																	18			
1 H 1.008	2														13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18			
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95			
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80			
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc -	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29			
55 Cs 132.91	56 Ba 137.33	57-71 -	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po -	85 At -	86 Rn -			
87 Fr -	88 Ra -	89-103 -	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -										
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97						
89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -						

# Fields of Advanced Difficulty

## Theoretical

Relation between equilibrium constants, electromotive force and standard Gibbs energy;

Inorganic electrochemistry, redox titrations and redox equilibria;

Integrated rate law for first-order reactions, half-life, Arrhenius equation, determination of activation energy, analysis of moderately complex reaction mechanisms;

Solid state structures;

Stereoselective transformations (diastereoselective, enantioselective), optical purity;

Monosaccharides, equilibrium between linear and cyclic forms, pyranoses and furanoses, Haworth projection and conformational formulae, glycosides;

## Practical

Advanced inorganic qualitative analysis;

Basic synthesis techniques: filtration, drying of precipitates, thin layer chromatography;





# Theoretical problems

## Problem 1

During a new construction at 221 Baker Street, an amazing discovery was made. A small cabinet was found containing previously unknown documents. They revealed that Dr. Watson kept notes about his adventures with Mr. Sherlock Holmes into the 1950s. An interesting, but incomplete story read as follows:

....and was able to spring into a cab and drive to Baker Street, half afraid that I might be too late to assist at the *dénouement* of the little mystery. I found Sherlock Holmes alone, however, half asleep, with his long, thin form curled up in the recesses of his arm-chair. A formidable array of bottles and test-tubes, with the pungent smell of hydrochloric acid, told me that he had spent his day in the chemical work which was so dear to him. It was obvious to me that my companion had already examined the carefully closed metal box we had found in a recess behind a sliding panel just above the right bell-pull in poor Browning's sitting-room.

'No doubt the murderers were after this box,' said he. 'They searched the house from cellar to garret. I would have been at a loss myself if I had not met Irene Adler some time ago...' My attention was captured by the open box on the mantelpiece. It was empty.

'It is far better to keep the contents of the box in mineral oil,' Holmes explained and showed me a bottle. 'This will keep it safe from air but also makes it more flammable.'

The yellowish liquid in the bottle covered a few thumb-sized pellets.

'Is this a dangerous poison?' I asked.

'Not at all, Watson. Have you ever seen a poison in so big a pellet? It would hardly be healthy to swallow, but that is not the point. Now look at this.'

He took out a pellet, dried it with great care, and dropped it into a bowl of water. Instead of slowly dissolving or sinking, the pellet began a strange dance on the surface of the water, hissed ominously, gave out bubbles and some malodorous product. The acrid fumes took me by the throat and set me coughing.

'Holmes, this will kill us both,' I screamed.

'You should have seen the reaction with hydrochloric acid. Anyway, I told you it is not particularly poisonous,' said Holmes coughing. With dramatic suddenness he struck a match, and as he held the match nearer, the bubbles caught fire and gleamed with the most beautiful crimson flame I have ever seen.

'Magnificent, is it not? One ounce of this substance when reacting with water or hydrochloric acid gives more than three cubic feet of gas. To be precise, 3.068 cubic feet at 80.0 degrees and atmospheric pressure.'

'You measured this?' I cried.

'Of course I measured it,' said Holmes with an impatient gesture. He took a small bottle labelled phenolphthalein and put a few drops of its contents into the bowl of water, which turned pink immediately, its colour resembling the gleam of the flames.

'Is this why this substance is so precious?'

'Not really,' murmured Holmes. 'The Powers of Evil created these pellets, Watson, or I am very much mistaken. The murder of Browning was nothing but a trifle in this case.'

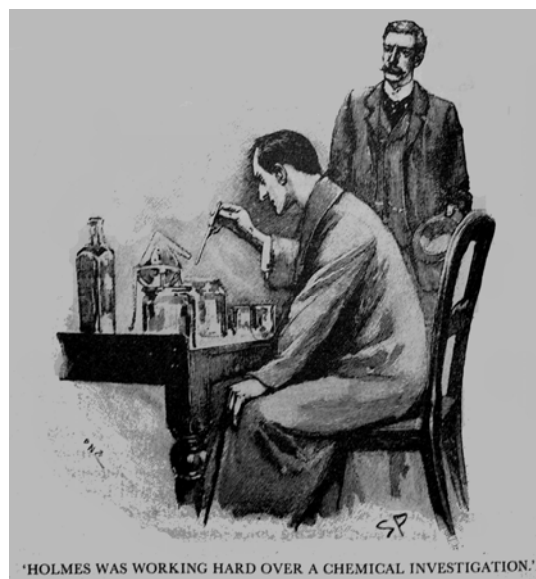
Half crazy with fear, I looked at the marble-like pellets in the bottle.

'I do not really understand, Holmes.'

'I made accurate measurements. I dissolved exactly one ounce of this substance in water, then boiled away the water. The remaining white solid I could not dry completely, so I re-dissolved it in water and added some hydrofluoric acid until the colour of phenolphthalein was gone. I boiled away the water again, and drying the white residue was not a problem this time. Its mass was precisely three and one eighth ounces. Three and one eighth. Do you see, Watson?'

'I am still in the dark,' I answered with some embarrassment.

'I do not wish to make a mystery,' said he, laughing. 'The matter is elementary; simplicity itself. You remember our little adventure with Professor Urey?'

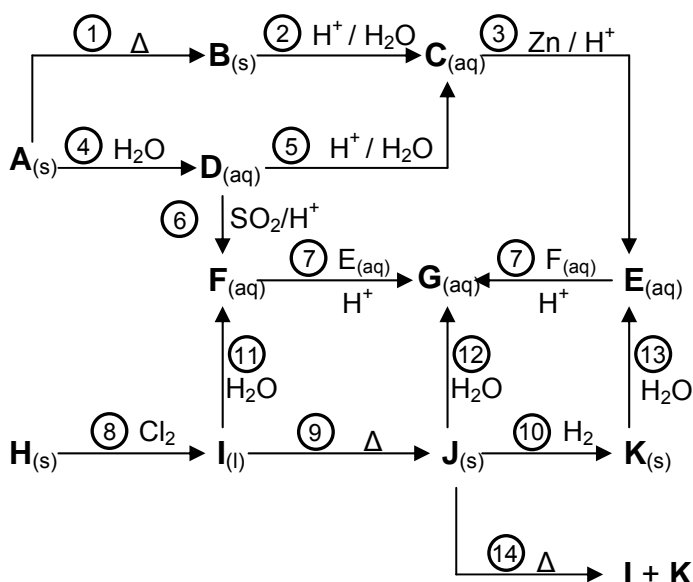


The notes end here. Sherlock Holmes uses imperial units of measurement: 1 foot equals 30.48 cm, 1 ounce is 28.350 g, the atmospheric pressure has been constant (101325 Pa) over the last few centuries. The temperature is measured in degrees Fahrenheit (°F): 0 °C equals 32 °F, whereas 100 °C is 212 °F.

Help Watson figure out what was in the box. What could it possibly have been intended for?

## Problem 2

Compound **A** is a stable salt of metal **H**. It contains 11.97 % N, 3.45 % H and 41.03 % O (mass fractions), besides the metal. The following chart describes some reactions starting from **A** and **H** ( $\Delta$  signifies heating). Above the arrows the necessary reactants are displayed. All substances tagged with a letter contain the metal, but none of the by-products do. (When a substance is labeled as dissolved in water, then it is ionic and you have to show only the ion containing the metal.)



- Identify the substances **A-K** and write down all the equations 1-14.
- Select the redox processes from the reactions.
- Select those compounds from **A-K** that are not expected to have unpaired electrons.
- On the basis of the above chart propose a reaction to obtain **G** starting from **F**, but without using **E**.
- Compound **B** is industrially very important. Show a reaction where its presence is indispensable. What role does it play?

- f) What percentage of product **I** contains  $^{35}\text{Cl}$  if chlorine gas containing 99 %  $^{37}\text{Cl}$  and 1 %  $^{35}\text{Cl}$  is used in reaction 8?
- g) What percentage of **J** produced from this sample of **I** contains  $^{35}\text{Cl}$ ?

### Problem 3

The metallic radius of chromium is estimated to be 126 pm. The density of chromium is  $7.14 \text{ g/cm}^3$ . Solid chromium belongs to the regular cubic crystal system.

- a) Determine the lattice type of chromium using only the data given above.

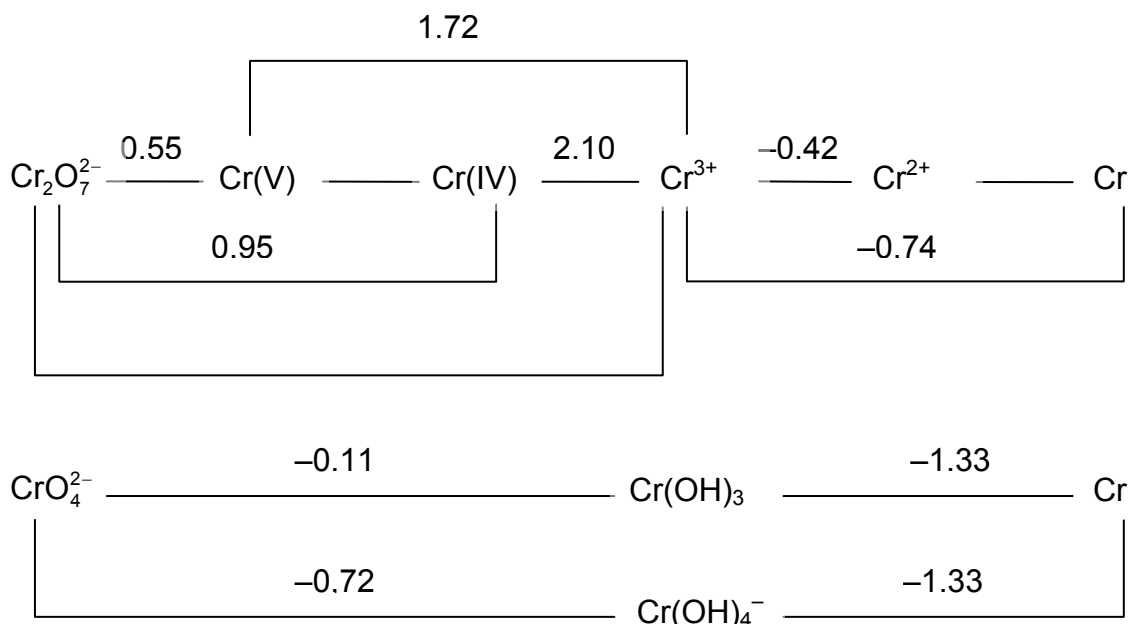
A test for the presence of  $\text{Cl}^-$  ions used to be the following: a dry mixture of the unknown material and potassium dichromate is heated with concentrated  $\text{H}_2\text{SO}_4$ . The gases produced are passed into  $\text{NaOH}$  solution, where the appearance of a yellow color indicates the presence of chlorine.

- b) What is the volatile chromium compound produced in the reaction? Draw its structure. Note that neither Cr nor Cl changes oxidation state during the reaction.

Acidifying a solution of potassium chromate gives rise to the formation of the orange dichromate ion, then the deeper red tri- and tetrachromate ions. Using concentrated sulfuric acid we obtain a red precipitate not containing potassium.

- c) Write the equations and draw the structure of the ions. Can you propose a structure for the precipitate?

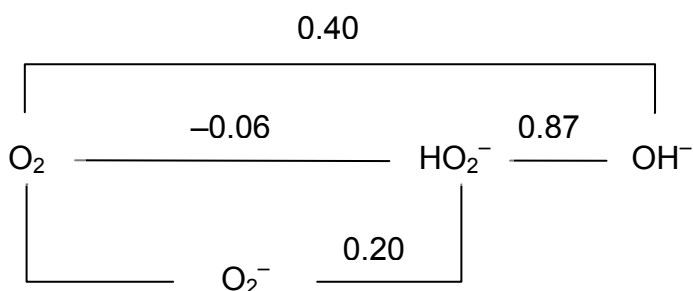
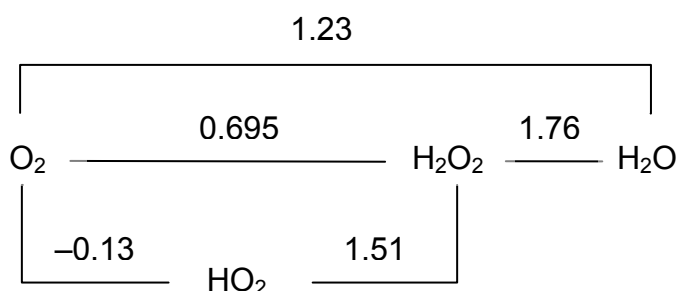
The Latimer diagrams for a series of chromium species in acidic ( $\text{pH}=0$ ) and basic ( $\text{pH}=14$ ) media is given below:



- d) Find the missing three values.

- e) Are Cr(V) and Cr(IV) stable with respect to disproportionation? Identify a simple criterion based on the Latimer diagram. What is the equilibrium constant for the disproportionation of  $\text{Cr}^{2+}$ ?
- f) Calculate the solubility constant of chromium(III) hydroxide and the overall stability constant of tetrahydroxo-chromate(III) anion.

The Latimer diagram of a series of oxygen-related species in acidic (pH=0) and basic (pH=14) media is the following:



- g) What will happen if the pH of a solution containing chromate(VI), Cr(III) and hydrogen peroxide is set to 0? What will happen if we set the pH to 14? Write down the reactions and the corresponding standard cell potential.

#### Problem 4

Silica and silica glass is held together by single covalent Si-O bonds.

- a) What is the coordination number of the Si and O atoms in the structure?

The density of silica glass is  $2.203 \text{ g/cm}^3$ .

- b) What is the average volume of a  $\text{SiO}_2$  unit? How many bonds are there on the average in such a volume?

A frequent crystal defect in silica glass is oxygen vacancy: oxygen atoms in the lattice are missing and the neighboring Si atoms of the missing oxygen stabilize by forming a Si-Si bond. An amorphous silica sample is characterized by the formula  $\text{SiO}_{1.9}$ .

- c) What percentage of the total number of the bonds are Si-Si bonds?

- d) Give an expression for the  $n_{\text{Si-Si}}/n_{\text{Si-O}}$  ratio of a  $\text{SiO}_x$  sample, as a function of  $x$ , where  $n_{\text{Si-Si}}$  is the number of Si-Si bonds and  $n_{\text{Si-O}}$  is the number of Si-O bonds. Give the value of  $x$  where, on the average, all Si atoms form one Si-Si bond.

### Problem 5

Pyrite ( $\text{FeS}_2$ ) forms NaCl-type crystals with  $\text{Fe}^{2+}$  ions occupying the positions of  $\text{Na}^+$ , and  $\text{S}_2^{2-}$  ions occupying the positions of the  $\text{Cl}^-$  ions. The directions of the S-S bonds are alternating body-diagonal.

- a) Fe is octahedrally coordinated by sulfur atoms. What is the coordination of the sulfur atoms?
- b) The density ( $\rho$ ) of an ideal pyrite crystal is  $5.011 \text{ g/cm}^3$ . Calculate the lattice constant of the smallest cubic unit cell.

It has been found that the lattice constant does not depend on the stoichiometry of the crystal, i.e., the lattice remains stable if the  $y$  in the formula  $\text{FeS}_y$  deviates slightly from 2 within a small range (1.95–2.05).

- c) Find the equation which gives the dependence of the density on  $y$ , assuming that only the iron content varies. Find a similar equation for the case when only the S content varies.
- d) Plot the two curves in the same  $y$ - $\rho$  coordinate system. Identify the following regions in the graphs: vacancies (Fe, or S deficiencies), interstitials (Fe, or S excess), perfect lattice.

In a natural pyrite sample it was found that only 99% of the iron positions are occupied, and 1 % additional sulfur atoms are in interstitial positions.

- e) Calculate the composition of the crystal. Find the corresponding point in the previously constructed  $y$ - $\rho$  diagram.

### Problem 6

Until the end of the 20<sup>th</sup> century, only two species (one molecule and one anion) were known that are composed only of nitrogen atoms.

- a) What are the empirical formulae of these two species?

The first inorganic compound containing a nitrogen-only species different from the above was synthesized by Christe and co-workers in 1999.

The starting material of the synthesis is an unstable liquid **A** that is a weak, monoprotic acid. It was liberated from its sodium salt (that contains 35.36 % sodium by mass) with a large excess of stearic acid.

- b) Determine the molecular formula of **A** and draw two resonance structures of the molecule. (Show all bonding and non-bonding valence electron pairs.)

The other starting material (**B**) was prepared from the cis-isomer of a nitrogen halogenide that contains 42.44 % nitrogen by mass.

- c) Determine the empirical formula of this halogenide. Draw the Lewis structure of the cis-isomer. Show all bonding and non-bonding valence electron pairs.

This nitrogen halogenide was reacted with  $\text{SbF}_5$  (a strong Lewis acid) in a 1:1 ratio at  $-196\text{ }^\circ\text{C}$ . The resulting ionic substance (**B**) was found to comprise three types of atoms. Elemental analysis shows that it contains 9.91 % N and 43.06 % Sb by mass; further, it contains one cation and one anion. The shape of the latter was found to be octahedral.

- d) Determine the empirical formula of the ionic substance **B**.
- e) Determine the empirical formula of the cation found in **B** and draw its Lewis structure. Show resonance structures, if there are any. Show all bonding and non-bonding electron pairs. Predict the bond angles expected in the contributing structures (approximately).

**B** reacts violently with water: 0.3223 g of the compound gave  $25.54\text{ cm}^3$  (at 101325 Pa and  $0\text{ }^\circ\text{C}$ ) of a color- and odorless nitrogen oxide that contains 63.65 % nitrogen by mass.

- f) Identify the nitrogen oxide formed in the hydrolysis reaction and draw its Lewis structure. Show resonance structures, if there are any. Show all bonding and non-bonding electron pairs.

- g) Give the chemical equation for the reaction of **B** with water.

In the experiment described by Christe and co-workers, **A** was mixed with **B** in liquid hydrogen fluoride at  $-196\text{ }^\circ\text{C}$ . The mixture was shaken for three days in a closed ampoule at  $-78\text{ }^\circ\text{C}$ , finally it was cooled down again to  $-196\text{ }^\circ\text{C}$ . A compound **C** was obtained, that contained the same octahedral anion as **B** and the expected, V-shaped cation composed only of N-atoms. **C** contained 22.90 % N by mass.

- h) Determine the empirical formula of **C**.
- i) The cation of **C** has many resonance structures. Show these structures, indicating all bonding and non-bonding electron pairs. Predict the bond angles expected in the contributing structures (approximately).
- j) Give the chemical equation for the formation of **C**. The formation of which compound makes the process thermodynamically favorable?

The cation of **C** is a very strong oxidizing agent. It oxidizes water; the reaction gives rise to the formation of two elemental gases. The resulting aqueous solution contains the same compounds as in the case of hydrolysis of **B**.

- k) Give the chemical equation for the hydrolysis of **C**.

In 2004, a further step was made. The ionic compound **E** was synthesized, whose nitrogen content was 91.24 % by mass! The first step in the synthesis of **E** was the reaction of the chloride of a main group element with an excess of the sodium salt of **A** (in acetonitrile, at  $-20\text{ }^\circ\text{C}$ ), giving rise to the formation of the compound **D** and NaCl. Gas evolution was not observed. In the second step, **D** was reacted with **C** in liquid  $\text{SO}_2$  at  $-64\text{ }^\circ\text{C}$ , giving **E** as the product. The cation : anion ratio in **E** is also 1:1 and it contains the same cation as **C**. **D** and **E** contain the same complex anion, whose central atom is octahedrally coordinated.

- l) Determine the empirical formula of **E**, given that it contains two types of atoms.

m) Determine the empirical formula of **D** and identify the main group element used.

**E** is supposed to be a potential fuel for future space travel because of its extremely high endothermic character. (It is a so-called "high energy density material"). A further advance is that the products of the decomposition of **E** are not toxic, so they do not pollute the atmosphere.

n) What are the reaction products of the decomposition of **E** in air?

### Problem 7

Calculate the analytical concentration for each of the following solutions:

- a) HCl solution, pH = 4.00 (solution A),
- b) acetic acid solution, pH = 4.00 (solution B),
- c) sulfuric acid solution, pH = 4.00 (solution C),
- d) citric acid solution, pH = 4.00 (solution D).

Calculate the pH for each of the following mixtures:

- e) equal volumes of solution A and NaOH solution (pOH = 4),
- f) equal volumes of solution B and NaOH solution (pOH = 4),
- g) equal volumes of solution C and NaOH solution (pOH = 4),
- h) equal volumes of solution D and NaOH solution (pOH = 4).
- i) equal volumes of solution A and B,
- j) equal volumes of solution A and C.

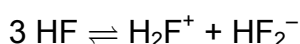
Acetic acid:  $pK_a = 4.76$

Sulfuric acid:  $pK_{a2} = 1.99$

Citric acid:  $pK_{a1} = 3.10$ ,  $pK_{a2} = 4.35$ ,  $pK_{a3} = 6.39$

### Problem 8

Numerous inorganic compounds undergo autodissociation in their liquid state. In liquid hydrogen fluoride (density,  $\rho = 1.002 \text{ g/cm}^3$ ) the following equilibrium can describe the autoprotolysis:



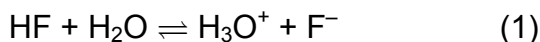
The corresponding equilibrium constant is  $8.0 \cdot 10^{-12}$ .

- a) Calculate what fraction of the fluorine is present in the cationic species in liquid HF, supposing that only these three species are present in the system.

Various reactions can take place in liquid HF.

- b) Write the equation of the reactions of liquid HF with the following substances: H<sub>2</sub>O, SiO<sub>2</sub>, acetone.

In water HF behaves as a medium-strength acid and dissociates only partially. The most important reactions determining the equilibrium properties of the solution are the following:



The equilibrium constants of the two equilibria are

$$K_1 = 1.1 \cdot 10^{-3}$$

$$K_2 = 2.6 \cdot 10^{-1}$$

- c) Calculate the analytical concentration of HF in a solution having a pH = 2.00.

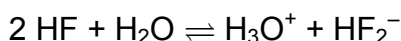
In early studies of aqueous HF, equilibrium (2) was not considered. However, pH measurements, assuming only equilibrium (1) led to contradictions.

- d) Show that, assuming only equilibrium (1), pH measurements can indeed lead to a concentration-dependent equilibrium constant for (1).

Two chemists wanted to determine the acidity constant of HF ( $K_1$ ) from one and the same solution with a known concentration. They measured the pH of the solution and then obtained a  $K_1$  value by calculation. However, the better chemist knew about equilibrium (2), while she knew that the other did not. So, she was surprised when they both obtained the same  $K_1$  value.

- e) What was the concentration of the HF solution?

- f) Calculate the equilibrium constant of the following equilibrium:



The dissociation equilibrium of a solute in a solvent can be significantly shifted by the addition of a suitable substance into the solution.

- g) Propose three different inorganic compounds for increasing the dissociation of HF in water.

Suitable compounds can also shift the autodissociation equilibrium of HF in its liquid state by orders of magnitudes. A well-known such substance is SbF<sub>5</sub>.

- h) Show how SbF<sub>5</sub> shifts the autodissociation equilibrium of liquid HF.

The shift in the autodissociation also implies an important change in the Brønsted acidity of the solvent. In fact, the degree of solvation of the proton produced from the autodissociation essentially affects the Brønsted acidity of the solvent.

- i) How is the Brønsted acidity of a given solvent determined by the extent of proton solvation?

The mixture of HF-SbF<sub>5</sub> belongs to the family of superacids, owing to their very high acidity. These acids are able to protonate very weak bases and thus have enabled the preparation of exotic protonated species. These, in turn, have opened new synthetic routes.



- j) Formulate reaction equations for the reaction of methane and neopentane with the HF-SbF<sub>5</sub> superacid. Note that in both cases there is a gaseous product.

### Problem 9

Ammonium sulfide ((NH<sub>4</sub>)<sub>2</sub>S) is a widely used reagent in qualitative analytical chemistry. To prepare the reagent, hydrogen sulfide gas is bubbled through a 4-5 mol/dm<sup>3</sup> ammonia solution, and then some water is added. The solution prepared in this way is almost never pure. It can contain either ammonia or ammonium hydrogen sulfide in excess when a lower or higher than stoichiometric amount of gas is absorbed.

- 10.00 cm<sup>3</sup> of an ammonium sulfide reagent solution was diluted to 1.000 dm<sup>3</sup>. 10.00 cm<sup>3</sup> of the resulting stock solution was transferred into a distillation flask and ~40 cm<sup>3</sup> of water was added. Then, 25.00 cm<sup>3</sup> of 0.1 mol/dm<sup>3</sup> cadmium nitrate solution was added into the collector flask (where the distilled components would condense). Moreover, 20.00 cm<sup>3</sup> of a 0.02498 mol/dm<sup>3</sup> solution of sulfuric acid was added into the distillation flask.
- Approximately one half of the solution in the distillation flask was distilled into the collector flask. (In the collector flask, the formation of a yellow precipitate could be seen.)
- The content of the distillation flask was washed completely into a titration flask. After adding a few drops of methyl red indicator it was titrated with 0.05002 mol/dm<sup>3</sup> NaOH solution. The volume of the titrant used to reach the equivalence point was 10.97 cm<sup>3</sup>.
- Bromine water was added to the solution in the collector flask (the precipitate dissolved), and the excess of bromine was removed by boiling the solution for 15 minutes. Bromine oxidizes all sulfur containing anions into sulfate ions. The hydrogen ions formed in the reactions in the collector flask were neutralized by 14.01 cm<sup>3</sup> of 0.1012 mol/dm<sup>3</sup> NaOH.

Calculate the exact composition of the reagent ammonium sulfide solution.

### Problem 10

According to the website of the Hungarian Central Bank, the silvery white Hungarian 2 forint coin is composed of an alloy containing only copper and nickel. A curious chemist (who did not know that it is illegal to destroy money in Hungary) weighed a 2-Ft coin (3.1422 g) and dissolved it completely in concentrated nitric acid in about 4 hours under a fume hood. A brown gas was produced during this process and no other gaseous products were formed.

- a) What are the chemical equations for the dissolution reactions?

Our hero diluted the solution to 100.00 cm<sup>3</sup> in a volumetric flask. To determine the composition of the coin, he devised a clever plan. First, he prepared a Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution by dissolving 6 g of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O in 1.0 dm<sup>3</sup> of water. Then he weighed 0.08590 g KIO<sub>3</sub>, dissolved it in water and prepared 100.00 cm<sup>3</sup> stock solution in a volumetric flask. He measured 10.00 cm<sup>3</sup> of this stock solution, added 5 cm<sup>3</sup> 20 % hydrochloric acid and 2 g solid KI. The solution turned brown immediately. Then he titrated this sample with the

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. In a number of parallel measurements the average for the equivalence point was 10.46 cm<sup>3</sup>.

- b) Write down the equations of all the reactions that have taken place and determine the concentration of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. What could our hero have used as an indicator?

When our hero began to wash up, he noticed that some white precipitate appeared in the first sample. He remembered clearly that he added more Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution to this sample than was necessary to reach the end point.

- c) What is the chemical equation of the process producing the precipitate?

Next, our hero returned to the greenish blue stock solution he prepared first. He measured 1.000 cm<sup>3</sup> of this solution into a titration flask, added 20 cm<sup>3</sup> of 5 % acetic acid and 2 g solid KI. He waited about 5 minutes. The solution became brown and a light-colored precipitate appeared.

- d) What is the chemical equation of the process producing the colored species and the precipitate? Why did our hero have to wait? Why would it have been a mistake to wait hours rather than minutes?

Our hero then titrated the sample with his Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. The average for the equivalence point was 16.11 cm<sup>3</sup>. Now he could calculate the composition of the 2-Ft coin.

- e) What is the mass percent composition of the coin?

As a good analytical chemist, he was not satisfied with one method and tried to determine the composition of the coin with complexometry. In this measurement he did not take into account the results obtained in the iodometric titration. First, he dissolved 3.6811 g Na<sub>2</sub>EDTA·2H<sub>2</sub>O (*M* = 372.25 g/mol) to make 1.0000 dm<sup>3</sup> solution. Then he measured 0.2000 cm<sup>3</sup> of the original greenish blue stock solution, added 20 cm<sup>3</sup> of water and 2 cm<sup>3</sup> of 25 % ammonia solution. The color of the solution became an intense violet.

- f) Which species are responsible for this color? What is the purpose of the addition of ammonia?

The equivalence point was 10.21 cm<sup>3</sup> as calculated from the average of a few parallel experiments.

- g) Did this experiment confirm the earlier conclusion about the composition of the coin?

Our hero was still not satisfied and also began to suspect that he made an error when he weighed the coin, so he turned on the old spectrophotometer in the lab. The lab he worked in was very well maintained so he found recently prepared and standardized 0.1024 mol/dm<sup>3</sup> CuCl<sub>2</sub> and 0.1192 mol/dm<sup>3</sup> NiCl<sub>2</sub> solutions in the lab. First, he measured the absorbance spectrum of the CuCl<sub>2</sub> solution using a 1.000-cm quartz cell and made notes of the absorbance values at a few wavelengths he thought suitable:

$\lambda$ / nm	260	395	720	815
<i>A</i>	0.6847	0.0110	0.9294	1.428

Then he measured the absorbances of the NiCl<sub>2</sub> solution at the same wavelengths in the same cell:

$\lambda / \text{nm}$	260	395	720	815
$A$	0.0597	0.6695	0.3000	0.1182

He diluted  $5.000 \text{ cm}^3$  of his original greenish blue stock solution to  $25.00 \text{ cm}^3$  in a volumetric flask and measured the absorbances. He obtained readings of 1.061 at 815 nm and 0.1583 at 395 nm.

- h) Why did he dilute the solution? What is the composition of the coin based on these spectrophotometric data alone?

Next, he measured the absorbance at 720 nm and obtained 0.7405.

- i) Is this value in agreement with the previous conclusions?

Finally, he tuned the instrument to 260 nm. He was surprised to see a reading of 6.000.

- j) What was his expected reading?

He decided to measure the absorbance at this wavelength in a smaller, 1.00-mm quartz cell as well. Again, he obtained a reading of 6.000.

- k) Suggest a possible explanation for this finding and a method to confirm it using chemicals and equipment that have already been used by our hero.

### Problem 11

On January 30 in 2000, a dam failure in a gold mine spilled about  $100\,000 \text{ m}^3$  of cyanide-containing waste water into the river Szamos. The pollution wave, which later reached the Central European rivers Tisza and Danube, killed massive amounts of fish. On February 15, a popular Hungarian TV news show presented a simple experiment: first a NaCN solution was prepared, the concentration of which was similar to those measured in the pollution wave. Fish were killed in this solution but survived when ferrous sulfate was also added. The TV show suggested that ferrous sulfate should have been used to lower the environmental impact of the cyanide solution. However, when the same experiment was repeated with an actual sample from the pollution wave, fish were killed even after ferrous sulfate was added. Unfortunately, this second experiment was not covered in any evening news.

To clarify the underlying chemistry, an expert designed a detailed series of experiments in which the use of a cyanide selective combination electrode was an important element. He first calibrated the electrode using 3 different concentrations at 3 different pH values. The temperature was  $25 \text{ }^\circ\text{C}$  in all experiments. The instrumental readings were as follows:

	1.00 ppm NaCN	10.0 ppm NaCN	100 ppm NaCN
0.01 mol/dm <sup>3</sup> NaOH	497.3 mV	438.2 mV	379.1 mV
0.001 mol/dm <sup>3</sup> NaOH	497.7 mV	438.6 mV	379.5 mV
pH = 7.5 buffer	598.9 mV	539.8 mV	480.7 mV

- a) Calculate the acid dissociation constant of HCN based on these measurements.

To  $100 \text{ cm}^3$  of a test solution, which contained  $49.0 \text{ mg/dm}^3$  NaCN and was buffered to pH = 7.5,  $40.0 \text{ mg}$  of solid  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  has been added. At this pH, the reaction between aqueous iron(II) and dissolved oxygen is quantitative under all conditions and gives an

iron(III) hydroxide precipitate. Ignore possible complexation reactions between the precipitate and cyanide ions.

b) Write the balanced equation for this redox reaction.

All the solutions used in the experiments initially contained  $8.00 \text{ mg/dm}^3$  dissolved oxygen. The electrode reading in this solution was  $585.9 \text{ mV}$ . Iron(II) only forms one complex with cyanide ion, which has a coordination number of 6.

c) Write the ionic equation describing the formation of this complex. Estimate the stability constant of the complex.

The following toxicity data ( $\text{LC}_{50}$ : median lethal concentration for 24-hour exposure) for fish can be found in tables:

	$\text{LC}_{50}$
cyanide ion*	$2.1 \text{ mg/dm}^3$
$\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	$6 \cdot 10^3 \text{ mg/dm}^3$

\* total noncomplexed cyanide =  $[\text{HCN}] + [\text{CN}^-]$

The loss of dissolved oxygen is not a major problem for fish in the very small volume of the experiment, but it would probably be under natural conditions.

d) Are the experimental results and the toxicity data in agreement with the result of the experiment shown on the TV news show?

A little known fact about the pollution wave was that it also contained metals, primarily copper (which is hardly surprising for a gold mine). Copper is often present in our environment as copper(II), but it was present as copper(I) in the pollution wave because of the presence of cyanide ions.

e) Write the chemical equation for the reaction between copper(II) and cyanide ion.

An actual sample from the pollution wave had a pH of 7.5, its total cyanide content (including complexed, uncomplexed and protonated cyanide ions) was determined to be 26 ppm, its total copper content 21 ppm. The cyanide selective electrode gave a reading of  $534.6 \text{ mV}$  in this solution, and an electrochemical method showed that the concentration of free copper(I) is about  $2 \cdot 10^{-15} \text{ mol/dm}^3$ . Copper(I) forms complexes with cyanide ion in a stepwise manner up to a coordination number of 3. The formation constant of  $[\text{CuCN}]$  is negligible compared to that of the other two complex ions. Dissolved oxygen, the concentration of which was  $8.00 \text{ mg/dm}^3$ , coexists with cyanocopper(I) complexes.

f) Is there any copper(I)-cyanide precipitate in the solution? ( $L_{\text{CuCN}} = 3.5 \cdot 10^{-19}$ )

g) Determine the coordination number(s) of copper(I) complex(es) dominating in the sample studied. Estimate the stability constant(s) of the cyanocopper(I) complex(es).

The toxicity of copper(I) cyano complexes is very similar to that of NaCN;  $[\text{Cu}(\text{CN})_2]^-$  has an  $\text{LC}_{50}$  value of  $4.5 \text{ mg/dm}^3$ . To  $100 \text{ cm}^3$  of the sample from the pollution wave,  $40.0 \text{ mg}$  of solid  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added. The cyanide selective electrode gave a reading of  $592.3 \text{ mV}$  in this solution.

h) Estimate the concentrations of various complexes in this sample. Is this solution expected to be toxic? Does this expectation agree with the experiment *not* shown on TV?

**Problem 12**

The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and the  $\text{H}_3\text{AsO}_4/\text{H}_3\text{AsO}_3$  systems are important redox systems in analytical chemistry, because their electrochemical equilibrium can be shifted by complex formation or by varying the pH.

a) Calculate the standard redox potential,  $E^\circ_3$  of the reaction  $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ .

The standard redox potential of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  system in 1 mol/dm<sup>3</sup> HCl is 0.710 V.

b) Give an estimate for the stability constant of the complex  $[\text{FeCl}]^{2+}$ .

Both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions form a very stable complex with  $\text{CN}^-$  ions.

c) Calculate the ratio of the cumulative stability constants for the formation of  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  ions.

d)  $\text{H}_3\text{AsO}_4$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  are dissolved in water in a stoichiometric ratio. What will the  $[\text{H}_3\text{AsO}_4]/[\text{H}_3\text{AsO}_3]$  ratio be at equilibrium if pH = 2.00 is maintained?

e) Are the following equilibrium concentrations possible in an aqueous solution? If yes, calculate the pH of the solution.

$$[\text{H}_3\text{AsO}_4] = [\text{H}_3\text{AsO}_3] = [\text{I}_3^-] = [\text{I}^-] = 0.100 \text{ mol/dm}^3.$$

$\text{Fe}^{2+}/\text{Fe}$	$E^\circ_1 = -0.440 \text{ V}$
$\text{Fe}^{3+}/\text{Fe}$	$E^\circ_2 = -0.036 \text{ V}$
$[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$	$E^\circ_4 = +0.356 \text{ V}$
$\text{H}_3\text{AsO}_4/\text{H}_3\text{AsO}_3$	$E^\circ_5 = +0.560 \text{ V}$
$\text{I}_2/2 \text{I}^-$	$E^\circ_6 = +0.540 \text{ V}$

**Problem 13**

The solubility product of silver chloride is  $2.10 \cdot 10^{-11}$  at 9.7 °C and  $1.56 \cdot 10^{-10}$  at room temperature (25 °C).

a) Estimate the solubility product and the solubility (in mg/dm<sup>3</sup>) of AgCl at 50 °C.

Although AgCl is practically insoluble in water, it dissolves in solutions containing complexing agents. For example, in the presence of a high excess of  $\text{Cl}^-$  ions, a part of the AgCl precipitate dissolves forming  $[\text{AgCl}_2]^-$  ions.

The equilibrium constant of the reaction  $\text{Ag}^+(\text{aq}) + 2 \text{Cl}^-(\text{aq}) \rightleftharpoons \text{AgCl}_2^-(\text{aq})$  is  $\beta = 2.50 \cdot 10^5$  at 25 °C.

b) Calculate the concentration of a KCl solution (at room temperature), in which the solubility of AgCl is equal to its solubility in water at 50 °C.

If a substance is present in a solution in various oxidation states, it cannot be determined directly by a redox titration. In this case, the sample has to be first reduced. For this purpose, so-called reductors are used. A reductor is a column, containing a strong reducing agent in the solid phase. An acidified sample is passed through the reductor, collected, and titrated with a strong oxidizing titrant of known concentration (for example  $\text{KMnO}_4$ ). The most common version is the so-called Jones-reductor that contains amalgamated zinc granules.

- c) What reaction would take place if the zinc was not amalgamated?
- d) Give the reactions that take place when the following solutions are passed through a Jones-reductor:  
 0.01 mol/dm<sup>3</sup> CuCl<sub>2</sub>  
 0.01 mol/dm<sup>3</sup> CrCl<sub>3</sub>  
 0.01 mol/dm<sup>3</sup> NH<sub>4</sub>VO<sub>3</sub> (pH =1)
- e) Estimate the equilibrium constants of these reactions using the redox potentials in the table.

When a milder reducing agent is required, sometimes the Ag/HCl-reductor (containing porous silver granules and aqueous HCl) is used. This might seem surprising, since Ag metal is not a good reducing agent. Considering only the standard potentials, the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> by Ag is not a spontaneous reaction.

- f) Consider a silver rod that is immersed in a 0.05 mol/dm<sup>3</sup> Fe(NO<sub>3</sub>)<sub>3</sub> solution. Calculate the equilibrium concentration of the various metal ions. What percentage of Fe<sup>3+</sup> ions has been reduced?

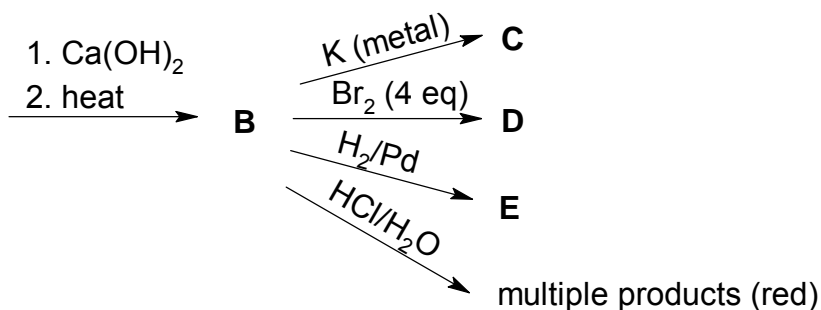
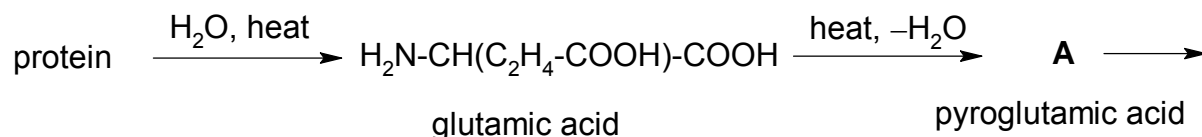
Now let us suppose that the reduction of Fe<sup>3+</sup> with Ag is carried out in a solution that also contains 1.00 mol/dm<sup>3</sup> HCl.

- g) What reaction takes place in this case? Calculate the equilibrium constant of the reaction.
- h) Calculate [Fe<sup>3+</sup>] at equilibrium if the initial concentration of Fe<sup>3+</sup> was 0.05 mol/dm<sup>3</sup>.
- i) Which of the following substances are reduced in an Ag/HCl reductor?  
 0.01 mol/dm<sup>3</sup> CrCl<sub>3</sub>  
 0.01 mol/dm<sup>3</sup> TiOSO<sub>4</sub> (c<sub>HCl</sub> = 1 mol/dm<sup>3</sup>)

	$E^{\circ} / V$		$E^{\circ} / V$
Cu <sup>2+</sup> /Cu	0.34	Cr <sup>3+</sup> /Cr	-0.74
Cu <sup>2+</sup> /Cu <sup>+</sup>	0.16	Cr <sup>2+</sup> /Cr	-0.90
VO <sub>2</sub> <sup>+</sup> /VO <sup>2+</sup>	1.00	Zn <sup>2+</sup> /Zn	-0.76
VO <sup>2+</sup> /V <sup>3+</sup>	0.36	TiO <sup>2+</sup> /Ti <sup>3+</sup>	0.10
V <sup>3+</sup> /V <sup>2+</sup>	-0.255	Ag <sup>+</sup> /Ag	0.80
V <sup>2+</sup> /V	-1.13	Fe <sup>3+</sup> /Fe <sup>2+</sup>	0.77

## Problem 14

An experience dating back to antiquity and passed on by the great alchemists is that the fumes produced when heating proteins (e.g., slaughterhouse waste) with lime stain an acid-impregnated wooden stick deep red. The compound responsible for this interesting reaction (**B**) can be produced as follows (several of its typical reactions are indicated as well):



**A-E** are all colorless (white) compounds. **B** and **E** are liquids with a characteristic odor.

- Draw the structures of **A-E**.
- Explain the stability of **B** against bases and its rapid decomposition with acids.
- Compare the basicity of **B** and **E**. Explain.
- Suggest a reaction scheme for the acidic decomposition of **B**. Explain why the products are colored.

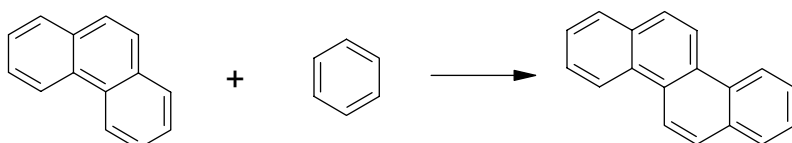
### Problem 15

Aromaticity is an important concept in organic chemistry. Compounds containing aromatic rings exhibit characteristic physico-chemical properties and reactivities. A simple rule, the Hückel rule helps us to identify aromatic structures. This rule postulates that a cyclic conjugated system is aromatic if the number of p electrons participating in the delocalized  $\pi$ -bonds is  $4n+2$ , where  $n$  is a nonnegative integer. The rule can be extended to cover polycyclic and fused ring systems.

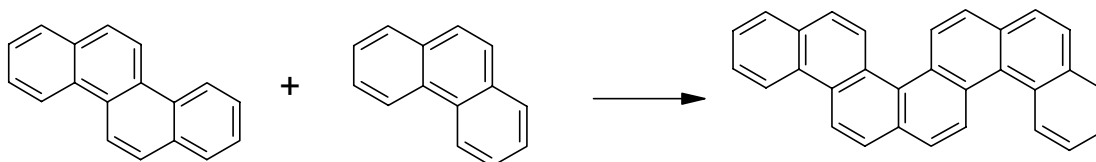
- Give examples for aromatic structures, where  $n = 0, 1, 2$ .

The Hückel rule is also applicable to fused ring systems, as a sufficient condition for their aromaticity.

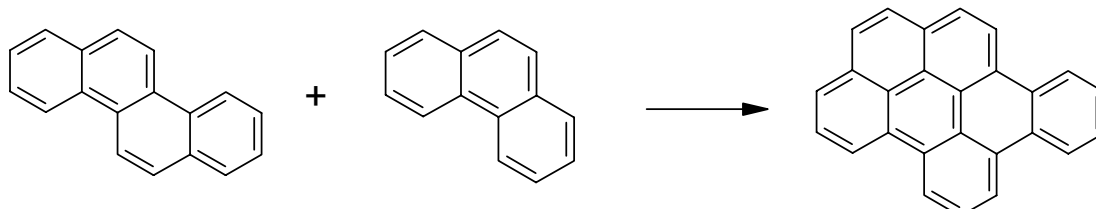
- Show that linearly fused, originally aromatic rings (where the individual rings are added stepwise to the chain via 2 carbon atoms) are Hückel aromatic. Example:



- Show that fusion of two such fused chains via 2 carbon atoms also results in Hückel aromatic structures. Example:



- d) Give a criterion for a general fusion of two aromatic hydrocarbons to yield a Hückel aromatic system. Example:

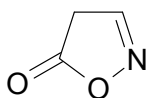


- e) Show with a counterexample that the Hückel rule is not a necessary condition for aromaticity.

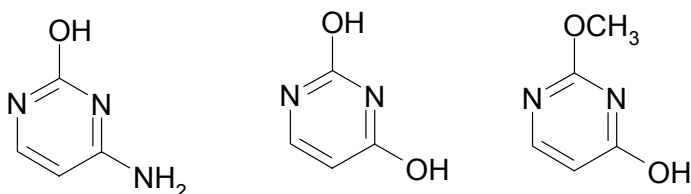
Aromaticity can be a very strong driving force in chemical processes, although not always. Let us consider the following examples:

- f) Cyclopentadiene has  $pK_a = 18$ , cyclopentene has  $pK_a = 45$ . Explain the difference!

- g) Tautomerism may also result in aromatic structures. Show how the following compound may undergo interconversion to yield an aromatic structure.



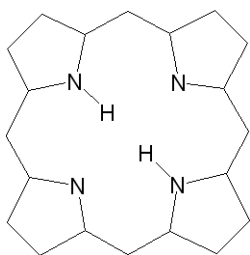
- h) However, some of the following aromatic structures prefer to rearrange into structures *not* featuring an aromatic ring. Find these structures. Where do these non-aromatic structures have essential roles? Give additional examples of tautomerism, where the molecule prefers to lose its aromatic character.



## Problem 16

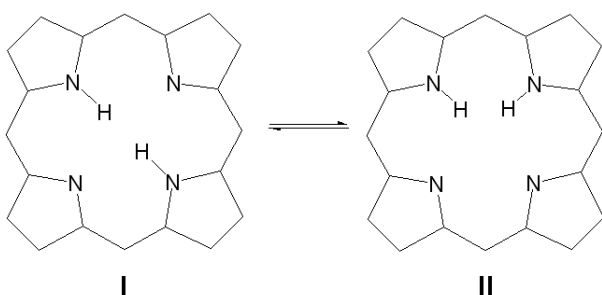
The porphin molecule is the simplest member in the family of porphyrins. Its structure, which contains four pyrrole rings, is completely planar. All its carbon and nitrogen atoms are  $sp^2$  hybridized. A conjugated double-bond system can therefore be found in the molecule. The sigma-skeleton of porphin is depicted below:





- a) How many electrons participate in the conjugated double bond system? Is the molecule aromatic? Draw a porphin structure indicating the double bonds forming the conjugated double-bond system.

Two of the central nitrogen atoms have a hydrogen substituent. These hydrogens are slightly acidic and under normal conditions, the protons can easily migrate to a neighboring N atom, as shown below:



- b) What kind of isomers are I and II? How does the migration process affect the conjugated double bond system: do less or more  $\pi$  electrons participate in isomer II than in isomer I? Draw a porphin structure for II indicating the double bonds.

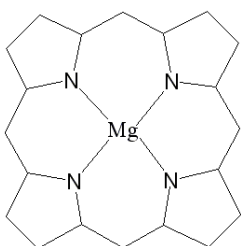
The hydrogen atoms bound to the carbon atoms of the porphin molecule can be substituted by other groups. Suppose that we introduce a methyl group onto the porphin ring. Under normal conditions, the inner-nitrogen H migration is unaffected by this substitution and takes place continuously in solvent.

- c) How many different monomethyl porphins can be produced?

We further introduce another methyl group into the porphin ring.

- d) How many isomers can be isolated in this case?

Metal complexes of porphin can be easily prepared. An important compound of this kind is the magnesium complex which is a synthetic model of chlorophyll. Its sigma-structure is displayed below:



- e) How many electrons of the organic ring system participate in the conjugated bond system in this case? What is the number of independent methyl-Mg-porphins having one methyl substituent on the organic ring?

Numerous iron-porphin derivatives (P) can be synthesized. Such salts all feature the heterocyclic macrocycle of porphin, but they contain additional substituents on the organic macrocycle as well. They are able to bind two additional ligands, coordinating them axially to the two sides of the iron atom. This complexation is a two-step process: the originally four-coordinated iron binds a ligand (L) and becomes five-coordinated (PL), and then binds a second ligand to become six-coordinated (PL<sub>2</sub>). It was found in various cases that the reaction rapidly yields the PL<sub>2</sub> complex, whereas the PL complex was very difficult to obtain. For the complexation of a given iron-porphin derivative with pyridine in inert organic solvent, scientists were able to show employing spectroscopic methods that the two steps can be characterized via the following equilibria:



- f) We see an atypical  $K_1 < K_2$  relation. Why does such a relation between two consecutive dissociation constants of a polyprotic acid never occur?

Assume that we perform this complexation reaction and reach an equilibrium concentration of 0.1 mol/dm<sup>3</sup> for ligand L.

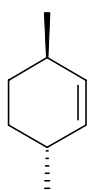
- g) Show that the five-coordinated intermediate is indeed present in negligible quantity.

Suppose we are able to generate PL *in-situ* in a solvent and due to its kinetic stability we reach a concentration of 0.1 mol/dm<sup>3</sup> PL. After a given time however the system reaches equilibrium.

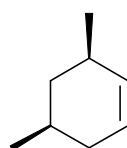
- h) How does temperature affect the kinetic stability?  
 i) What will the concentrations of P, PL, PL<sub>2</sub> and L be at equilibrium?

### Problem 17

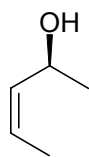
- a) How many stereoisomers do the following compounds have?



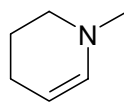
A



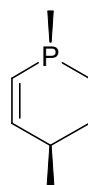
B



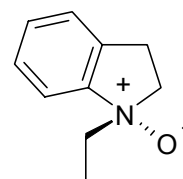
C



D

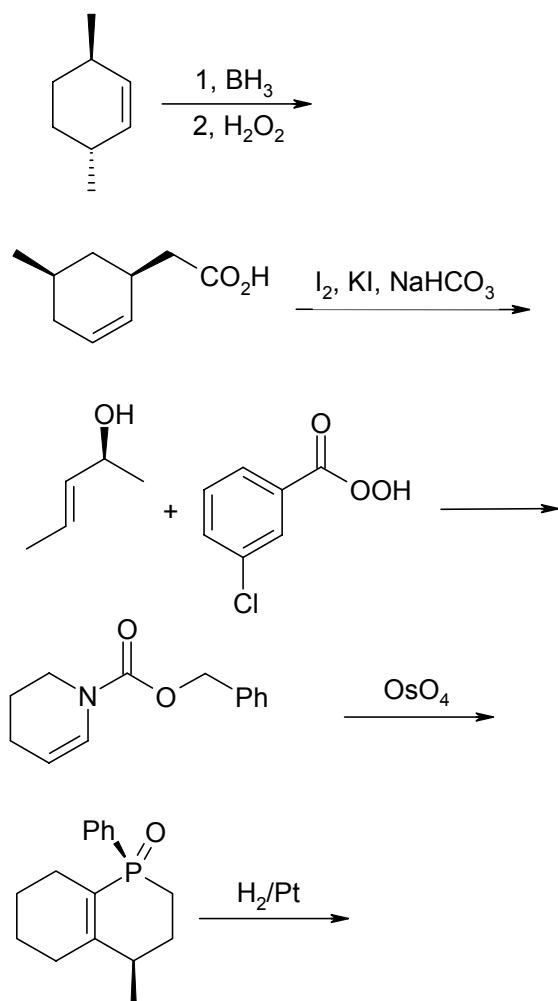


E



F

b) What is the most likely product of the following reactions following work up? How many other stereoisomers might be formed?



### Problem 18

Ascaridol (**A**) is a natural organic compound that has an exotic structure. It can be found in the volatile oil of the goosefoot (*Chenopodium album*) and many other plants. The following information is available:

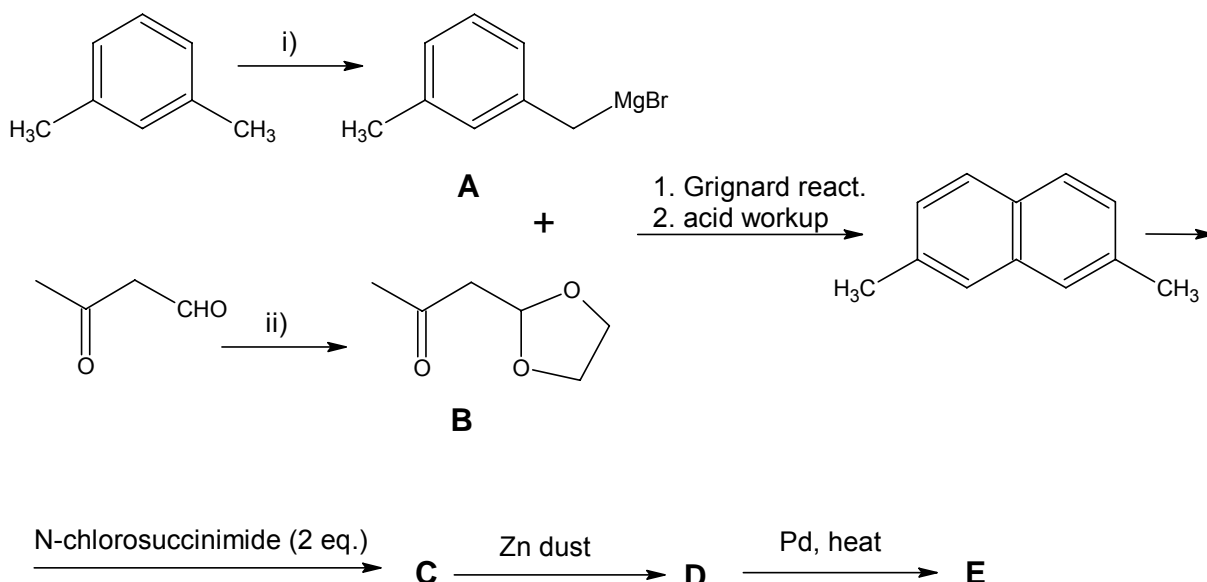
- Pure **A** can only be distilled in high vacuum because at elevated temperatures it explodes.
- The  $^{13}\text{C}$  NMR spectrum shows the presence of only one  $\text{C}=\text{C}$  double bond in **A**.
- A solution of **A** (in diethyl ether) does not react with sodium. Reduction with  $\text{LiAlH}_4$  leads to **B**.
- If **B** is reacted with  $\text{NaBH}_4$  in the presence of acetic acid, then reacted with  $\text{H}_2\text{O}_2$  in basic solution, the product is a mixture of two structural isomers.
- Reaction of **B** with one equivalent of hydrogen gas in the presence of a metal catalyst leads to **C**. **A** reacts with twice as much hydrogen as **B** in the same reaction, and also yields **C**. **C** does not react with chromic acid in acetone.

- The dehydration of **C** leads to the elimination of two equivalents of H<sub>2</sub>O and two organic compounds **D** and **E** are formed. Treatment of **D** with ozone followed by a reductive workup (Zn/H<sub>2</sub>O) leads to one equivalent of glyoxal (ethanedial) and one equivalent of 6-methyl-heptane-2,5-dione. The same reaction with **E** leads to one equivalent of 3-oxo-butanal and the same amount of 4-methyl-3-oxo-pentanal.
- It is assumed that under natural conditions **A** forms via the reaction of **D** and **F** catalyzed by chlorophyll in the presence of light.

Determine the structure of **A-F**.

### Problem 19

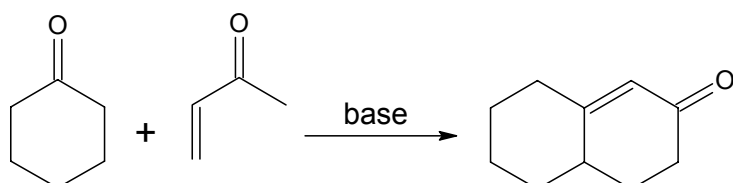
2,7-dimethylnaphtalene can be prepared by the reaction of a Grignard reagent **A** and an acetal (**B**).



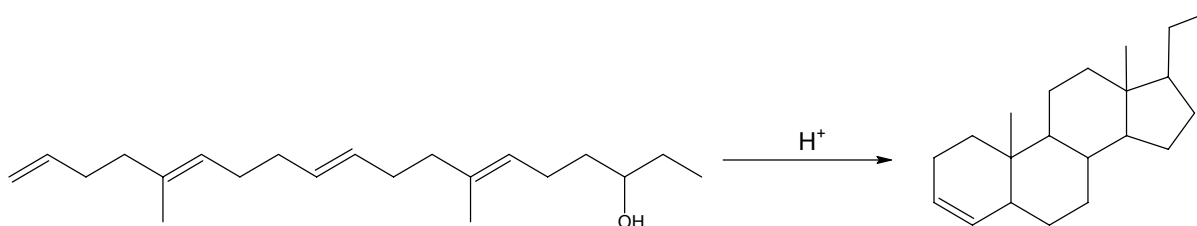
- Suggest reaction conditions for the preparation of **A** and **B**.
- Explain with a mechanism the formation of 2,7-dimethylnaphtalene.
- 2,7-dimethylnaphtalene is converted to **E** via the indicated reactions. (**E** is a fancy compound with molecular formula C<sub>24</sub>H<sub>12</sub>.) Identify **C**, **D** and **E**.

### Problem 20

- Suggest a mechanism for the following transformation (Robinson-anellation).

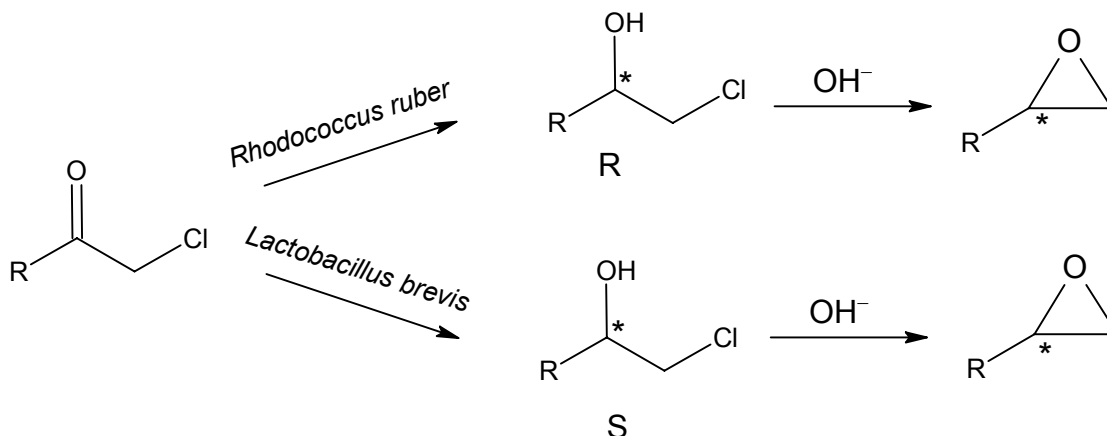


b) Rationalise the build-up of the gonane skeleton.



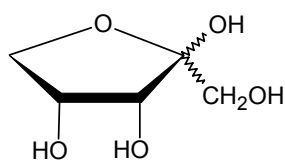
A prochiral  $\alpha$ -chloro ketone was reduced to halohydrins enzymatically (R is an alkyl group). One alcohol dehydrogenase enzyme (*Rhodococcus ruber*) produces the R isomer, and another (*Lactobacillus brevis*) gives the S isomer. Under basic conditions enantiopure epoxides were produced from the halohydrins.

c) Give the stereostructures of the halohydrin intermediates and those of the epoxides. Detail the mechanism of the ring closure reaction.

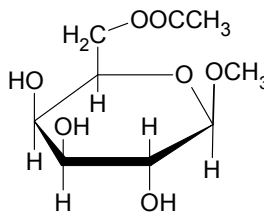


### Problem 21

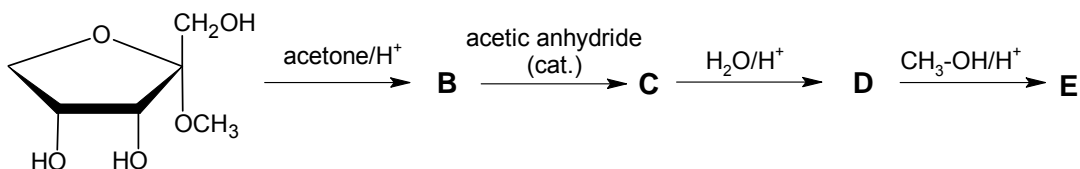
Ketoses are a special group of sugars. D-ribulose derivatives play a vital role in photosynthesis. An  $\alpha$ -methyl glycoside of D-ribulose (**A**) can be prepared from D-ribulose on treatment with methanol and an acid catalyst. Heating **A** in acetone with HCl leads to **B**, a propylidene derivative. Acetone forms acetals with vicinal diols, if the orientation of the two OH groups is suitable.



D-ribulose



F



1-O-methyl- $\alpha$ -D-ribulose<2.5>

A

- a) During the synthesis of **B** two possible products can form. Draw their structures. Which is the main product?

**B** is reacted with acetic anhydride (with catalyst) to obtain **C**. **D** is formed from **C** on heating in dilute aqueous acid. **D** reacts with methanol and acid to form **E**.

- b) Draw the structures of **C-E**.

- c) Is it possible to predict the conformation around carbon atom C1 of **E**?

Although acetonide formation is a versatile method for the temporary protection of OH groups that are close enough, in many cases it gives multiple products (or the product composition is highly dependent on the reaction conditions). In general, this is the case with sugars with 6-membered rings.

It has been shown that no acetonide can be formed when the neighbouring OH groups are both axial. However, both diequatorial and axial-equatorial vicinal diols react with acetone/HCl.

- d) Draw the two chair conformers of 1-O-methyl-6-O-acetyl- $\beta$ -D-galactose<1.5> (**F**). Designate the OH groups as axial (a) or equatorial (e). Mark the more stable conformer.

- e) How many acetonide isomers can form from this compound? How many different chair conformers of these acetonides exist?

- f) Draw the Haworth projection of L-galactose <1.5>

## Problem 22

At present, fossil fuels are the most important energy sources for humankind. Their use is generating two major concerns. First, energy production from fossil fuels releases a lot of carbon dioxide into the atmosphere, which is now understood to contribute to global warming. In addition, natural supplies of fossil fuels are expected to be exhausted at the

present rate of use in a relatively short time on a historical scale. Many experts believe that alternative sources, like hydrogen or methanol could find widespread use as environmentally friendly substitutes for fossil fuels.

Hydrogen is not a primary energy source; it would have to be produced using another source of power, e.g. nuclear or solar power. The best way would be to produce hydrogen from water, a process popularly called water splitting.

- a) Calculate how many kWh of electricity is needed to produce 1 kg hydrogen if the electrolysis operates at a voltage of 1.6 V and 90 % efficiency. Evaluate this process economically based on current industrial electricity and hydrogen prices (use average prices of 0.10 euro/kWh for electricity and 2 euro/kg for H<sub>2</sub>).

In addition to production, storage and transport of hydrogen also presents some challenges. In this respect, volumetric and gravimetric energy densities are central concepts. The volumetric energy density is the recoverable energy from a source divided by its total volume. The gravimetric energy density is the recoverable energy from a source divided by its mass.

- b) Calculate the volumetric and gravimetric energy density of hydrogen at atmospheric pressure and 298 K. (Assume that hydrogen follows the ideal gas law under these conditions.)

Hydrogen is often transported in cylinders which are normally filled to 200 bar. A typical big gas cylinder, made of steel (density 7.8 g/cm<sup>3</sup>) has a useful volume of 50 dm<sup>3</sup> and weighs 93 kg when empty. At this high pressure, hydrogen no longer follows the ideal gas law. A better description can be obtained from the van der Waals equation:

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

where  $p$  is the pressure,  $V_m$  is the molar volume,  $R$  is the gas constant,  $T$  is the thermodynamic temperature,  $a$  and  $b$  are gas-specific constants. For hydrogen,  $a = 2.48 \cdot 10^{-2} \text{ Pa m}^6 \text{ mol}^{-2}$  and  $b = 2.66 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ . Compressed hydrogen cannot be transported without a cylinder.

- c) Estimate the volumetric and gravimetric energy density of compressed hydrogen.

Hydrogen can also be transported in the form of metal hydrides. NaBH<sub>4</sub> is a promising substance in this respect, as it reacts with water in the presence of a catalyst to give hydrogen.

- d) How many moles of hydrogen can be produced from 1 mol of NaBH<sub>4</sub>?

As water is a ubiquitous substance, it does not have to be transported together with the metal hydride.

- e) Estimate the volumetric and gravimetric energy density of NaBH<sub>4</sub> as a hydrogen source. Its density is 1.07 g/cm<sup>3</sup>.

It is also important to compare these data with those of more conventional energy sources.

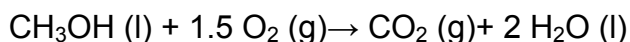
- f) To put the previously calculated energy densities in perspective, determine the volumetric and gravimetric energy densities of the following energy sources:
- Graphite as a model of coal. Calculate the density based on the fact that the bond length in graphite is 145.6 pm and the interlayer distance is 335.4 pm.

- ii. n-Octane (C<sub>8</sub>H<sub>18</sub>) as a model of gasoline. Its density is 0.70 g/cm<sup>3</sup>.
- iii. Methanol, the use of which instead of hydrogen was proposed by the 1994 Nobel laureate György Oláh. Its density is 0.79 g/cm<sup>3</sup>.
- iv. A Ni-MH rechargeable AA battery with a capacity of 1900 mAh and voltage of 1.3 V, which is shaped like a cylinder (diameter: 14.1 mm, height: 47.3 mm, weight: 26.58 g).
- v. Water as a source of hydrogen in an imaginary fusion reactor simply converting <sup>1</sup>H into <sup>4</sup>He. The relative atomic masses are: A<sub>r</sub>(<sup>1</sup>H) = 1.00782, A<sub>r</sub>(<sup>4</sup>He) = 4.00260

Hydrogen could also be stored as a cryogenic liquid at very low temperatures. The density of liquid hydrogen at its boiling point (−253 °C) is 0.071 g/cm<sup>3</sup>.

- g) Estimate the volumetric and gravimetric energy density of liquid hydrogen.
- h) What is the advantage of using liquid methanol instead of hydrogen in a hypothetical future economy?

Methanol can also be used in methanol fuel cells. The net reaction of the fuel cell is:



- i) Write down the cathode and the anode reactions.
- j) Calculate the maximum voltage of the methanol fuel cell at 25 °C.
- k) The methanol fuel cell operates best at 120 °C. At this temperature, the cell reaction potential is 1.214 V. Compare this number with your calculated data.

Thermodynamic parameters at 298 K:

H <sub>2</sub> O(l)	$\Delta_f H^\circ = -286 \text{ kJ/mol}$	O <sub>2</sub> (g)	$S^\circ = 205 \text{ J mol}^{-1} \text{ K}^{-1}$
H <sub>2</sub> O(g)	$\Delta_f H^\circ = -242 \text{ kJ/mol}$	CO <sub>2</sub> (g)	$\Delta_f G^\circ = -394.4 \text{ kJ/mol}$
H <sub>2</sub> O(l)	$S^\circ = 70 \text{ J mol}^{-1} \text{ K}^{-1}$	C <sub>8</sub> H <sub>18</sub> (l)	$\Delta_f G^\circ = 6.4 \text{ kJ/mol}$
H <sub>2</sub> O(g)	$S^\circ = 189 \text{ J mol}^{-1} \text{ K}^{-1}$	CH <sub>3</sub> OH(l)	$\Delta_f G^\circ = -166.3 \text{ kJ/mol}$
H <sub>2</sub> (g)	$S^\circ = 131 \text{ J mol}^{-1} \text{ K}^{-1}$		

### Problem 23

Most elements react with oxygen to form oxides in which the oxidation number of O is −2. At first sight it seems a striking contradiction that some alkali metals, the strongest reducing agents themselves, burn in air to give peroxides or superoxides with fairly strong oxidizing properties. Why is the oxygen only partially reduced in these reactions? To find out, we must start from some basic properties of the elements.

Alkali metals	Li	Na	K
$\Delta_{\text{vap}}H$	148 kJ/mol	99 kJ/mol	79 kJ/mol
Ionization energy	520 kJ/mol	496 kJ/mol	419 kJ/mol
Ionic radius for M <sup>+</sup>	76 pm	102 pm	138 pm



- a) Explain the trend in the ionization energies of the metals.

Oxygen anions	O <sup>2-</sup>	O <sub>2</sub> <sup>2-</sup>	O <sub>2</sub> <sup>-</sup>
$\Delta_f H$	904 kJ/mol	553 kJ/mol	-43 kJ/mol
ionic radius	140 pm	173 pm	158 pm

- b) The enthalpy of formation of the free ions dramatically increases in the sequence superoxide  $\rightarrow$  peroxide  $\rightarrow$  oxide. Why?

We know the energy required to convert the elements into separated ions. How much energy is released when these ions combine to form ionic crystals? The lattice energy of an ionic solid can be estimated by the Kapustinskii equation. In its simplest form,

$$\Delta U(\text{lattice}) = -107000 \frac{\nu |z_+| |z_-|}{r_+ + r_-}$$

where  $\nu$  is the total number of ions in the empirical formula,  $z_+$  and  $z_-$  are the charges of the individual ions,  $r_+$  and  $r_-$  are the ionic radii in pm, and the result is given in kJ/mol.

- c) Calculate the molar lattice energies of the oxides, peroxides, and superoxides of the three lightest alkali metals.  
Calculate the amount of energy released in each of the nine possible reactions leading to the oxides, peroxides, or superoxides of the elements. Always assume that 2 mols of a solid alkali metal react with oxygen to form a single product.

This simplified approach is by no means expected to give accurate estimates of the enthalpy of formation. It does, however, correctly reflect the main factors influencing the course of these reactions even without considering entropy changes. If your calculations were error-free, your conclusions will be in line with the experimental observations.

- d) For the reaction of each alkali metal with an excess of oxygen, which is the energetically most favoured product?
- e) Rationalize your results and try to explain, in terms of basic factors, why the composition of the most favoured product changes as we move down Group IA. What products do you expect from the reaction of Rb and Cs with oxygen?
- f) Does this mean that peroxides and superoxides, which are powerful oxidizers, cannot be reduced by one of the most powerful reducing agents, metallic potassium?

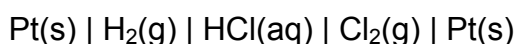
Let's now turn to the rest of the periodic system. Most other elements that form ionic oxides have multiply charged cations of relatively smaller size – properties that are generously rewarded in lattice energies.

- g) The alkali metals do not have this option. Why?
- h) Consider a metal that forms a cation M<sup>2+</sup> with a radius of 100 pm (the cations of most metals are smaller than this). Compare the lattice energies of its oxide and peroxide. What products do you expect from the reaction of such metals with oxygen?

- i) Only one of the non-radioactive Group IIA metals can form a peroxide when heated in air at atmospheric pressure. Which one? Estimate a limit for the size of its cation on the basis of our model.
- j) In conclusion, you can see that the extremely strong reducing ability of the alkali metals and the fact that some do not completely reduce oxygen when they burn in air have a common underlying reason. What is this?

### Problem 24

Let us examine three galvanic cells:



- a) Write down the equation for the cell reactions.
- b) Estimate the standard cell reaction potential of the galvanic cells at 25 °C based on thermochemical data.
- c) Write down the cathode and the anode reactions in the galvanic cells if the measured electromotive force equals the standard cell reaction potential.
- d) Calculate the equilibrium constant for the cell reactions.
- e) How do the electromotive forces change with temperature?

Let us define a 'thermal efficiency' parameter as the theoretical maximum of the ratio between the electrical work and the enthalpy change in the cell.

- f) What are the values of this parameter for these cells? What can we conclude from these numbers?

Thermochemical data at 25 °C:

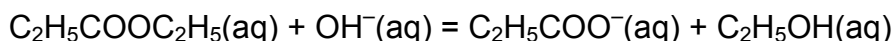
	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
$\text{Cl}_2(\text{g})$	0.0	223.1
$\text{H}_2(\text{g})$	0.0	130.7
$\text{HCl(aq)}$	-167.2	56.5
$\text{K}_2\text{SO}_4(\text{aq})$	-1414.0	225.1
$\text{KCl(aq)}$	-419.5	159.0
$\text{Pb(s)}$	0.0	26.4
$\text{PbCl}_2(\text{s})$	-359.4	136.0
$\text{PbSO}_4(\text{s})$	-920.0	148.5

**Problem 25**

You lead an interstellar expedition to a remote planet, inhabited by aliens. Unfortunately, the arrival of your spaceship initiates a reaction causing the atmosphere to decompose by a first-order rate law with a half-life of 13 hours. Everyone will have to leave by the time when only 13 % of the original atmosphere remains.

a) How much time do you have until then?

Ethyl-propionate hydrolyzes in aqueous alkaline solution:



Initial rate data were collected for different concentrations, as shown in the Table:

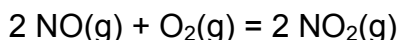
$[\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5]$	$[\text{OH}^-]$	Initial rate ( $\text{mmol dm}^{-3} \text{s}^{-1}$ )
0.045	0.300	1.09
0.090	0.300	2.15
0.090	0.150	1.11

b) Determine the partial orders of reaction, its kinetic equation and rate coefficient.

The initial rate of the reaction above doubles when the temperature is raised from 25 °C to 42 °C, with the same initial concentrations.

c) What is the Arrhenius activation energy?

The reaction



obeys the following kinetic equation:

$$r = k [\text{NO}]^2 [\text{O}_2]$$

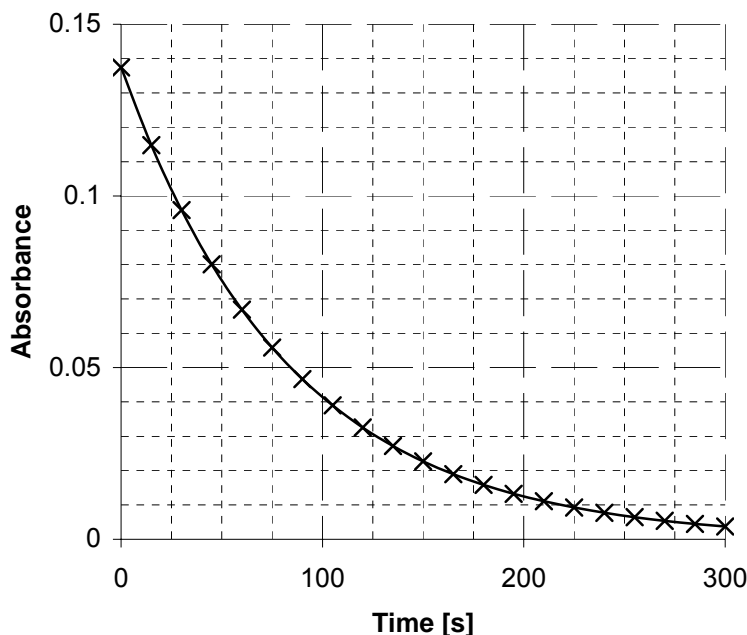
d) Explain how the rate of the reaction changes when the following concentration changes are made:

- i.  $[\text{O}_2]$  is quadrupled
- ii.  $[\text{NO}]$  is quadrupled
- iii.  $[\text{NO}]$  is halved
- iv.  $[\text{O}_2]$  is halved and  $[\text{NO}]$  is quadrupled
- v.  $[\text{NO}]$  is halved and  $[\text{O}_2]$  is quadrupled

The initial rate of the above reaction remains the same when the temperature is raised from 460 °C to 600 °C, with all the initial concentrations halved.

e) What is the Arrhenius activation energy?

The first-order decay of a compound was followed spectrophotometrically. After loading a solution with an initial concentration  $0.015 \text{ mol/dm}^3$  into a cuvette with a path-length of 0.99 cm, its absorbance (at a wavelength where only this species absorbs light) was recorded as a function of time.



- f) From this plot:
- i. Estimate the molar absorption coefficient.
  - ii. Estimate the initial rate and the rate constant.
  - iii. Estimate the half-life from the rate constant.
  - iv. Discuss whether the estimated half-life is consistent with the plot.
  - v. Calculate the time required to consume 99 % and 99.99 % of the compound.

### Problem 26

Upper atmospheric (stratospheric) ozone protects us from harmful ultraviolet radiation coming from the Sun. On the other hand, ozone in the lower atmosphere (troposphere) damages the human respiratory system as well as crops and other plants, since ozone is a strong oxidizing agent.

Ozone formation in urban areas can be attributed mainly to the two-step reaction mechanism:



The first step is the photolysis of  $\text{NO}_2$ , which is a common air pollutant in cities. (N.B.:  $k_1$  includes the intensity of the solar radiation on an average sunny day.) The second step is the reaction of the O atom formed with atmospheric oxygen. Under atmospheric conditions reaction (2) is orders of magnitudes faster than reaction (1).

Let us suppose that a small amount of  $\text{NO}_2$  (e.g.  $10^{-7}$  mole fraction of air) is introduced into the atmosphere and only reactions (1) and (2) take place.

- a) Which species is going to be in a quasi steady-state? Write down the algebraic equation to calculate its concentration after an initial (so-called induction) period.
- b) Write down the differential and integral rate equations describing ozone formation.

The rate coefficient of reaction (1) is  $0.0070 \text{ s}^{-1}$ . The initial  $\text{NO}_2$  concentration is  $2.5 \cdot 10^{12} \text{ molecule cm}^{-3}$ .

- c) What is the ozone concentration after 1 minute?  
 d) What is the half-life of  $\text{NO}_2$ ?  
 e) What effect does temperature have on the rate of ozone formation? Why?

Ozone is not only formed but also removed from the troposphere, mainly by its reaction with NO:



Assuming reactions (1-3),  $\text{O}_3$ , NO and  $\text{NO}_2$  will be in equilibrium.

$$k_3 = 1.8 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

- f) What is the  $[\text{NO}]/[\text{NO}_2]$  ratio, if the equilibrium ozone concentration is  $9 \cdot 10^{11} \text{ molecule cm}^{-3}$ ?  
 g) Assuming the same equilibrium ozone concentration, how does the above ratio change if we raise the temperature from  $10 \text{ }^\circ\text{C}$  to  $25 \text{ }^\circ\text{C}$ ? The activation energy of reaction (3) is  $10.8 \text{ kJ/mol}$ .

### Problem 27

The reaction of acetone with bromine produces bromoacetone.

- a) Give the chemical equation of the reaction assuming that acetone is in excess.

In a mechanistic study, the reaction was followed in several kinetic experiments at  $25 \text{ }^\circ\text{C}$  in aqueous solution by measuring the concentration of  $\text{Br}_2$  using a spectrophotometric method. The following kinetic curve was recorded when the initial concentrations were  $[\text{Br}_2]_0 = 0.520 \text{ mmol/dm}^3$ ,  $[\text{C}_3\text{H}_6\text{O}]_0 = 0.300 \text{ mol/dm}^3$ , and  $[\text{HClO}_4]_0 = 0.050 \text{ mol/dm}^3$ .

$t$ (min)	0	2	4	6	8	10	12	14
$[\text{Br}_2]$ ( $\mu\text{mol/dm}^3$ )	520	471	415	377	322	269	223	173

$t$ (min)	16	18	20	22	24	26	28	30
$[\text{Br}_2]$ ( $\mu\text{mol/dm}^3$ )	124	69	20	0	0	0	0	0

- b) Which is the limiting reagent in this experiment?  
 c) What is the order of reaction with respect to the limiting reagent?

The time where the characteristic break point occurs on the kinetic curve is called the reaction time and was determined in aqueous solution at  $25 \text{ }^\circ\text{C}$ . The following table gives the reaction time in several different experiments ( ' denotes minutes, " denotes seconds):

$\frac{[\text{Br}_2]_0}{\text{mmol/dm}^3}$	$\frac{[\text{C}_3\text{H}_6\text{O}]_0}{\text{mmol/dm}^3}$	$\frac{[\text{HClO}_4]_0}{\text{mmol/dm}^3}$	reaction time
0.151	300	50	5'56"
0.138	300	100	2'44"
0.395	300	100	7'32"
0.520	100	100	30'37"
0.520	200	100	15'13"
0.520	500	100	6'09"
0.520	300	200	4'55"
0.520	300	400	2'28"

- d) Determine the orders of reaction with respect to all three components.
- e) What is the rate equation of the process?
- f) What is the value and unit of the rate constant?

A different, electrochemical method allowed detection of much smaller concentrations of  $\text{Br}_2$ . A kinetic curve, the initial concentrations for which were  $[\text{Br}_2]_0 = 1.80 \mu\text{mol/dm}^3$ ,  $[\text{C}_3\text{H}_6\text{O}]_0 = 1.30 \text{ mmol/dm}^3$ , and  $[\text{HClO}_4]_0 = 0.100 \text{ mol/dm}^3$ , is given in the following table:

$t$ (s)	0	10	20	30	40	50	60	70
$[\text{Br}_2]$ ( $\mu\text{mol/dm}^3$ )	1.80	1.57	1.39	1.27	1.06	0.97	0.82	0.73

$t$ (s)	80	90	100	110	120	130	140	150
$[\text{Br}_2]$ ( $\mu\text{mol/dm}^3$ )	0.66	0.58	0.49	0.45	0.39	0.34	0.30	0.26

- g) Which is the limiting reagent in this experiment?
- h) What is the order of reaction with respect to the limiting reagent?

The half life of the limiting reagent was determined in a few experiments, and is independent of the concentration of the limiting reagent:

$[\text{Br}_2]_0$ ( $\mu\text{mol/dm}^3$ )	$[\text{C}_3\text{H}_6\text{O}]_0$ ( $\text{mmol/dm}^3$ )	$[\text{HClO}_4]_0$ ( $\text{mol/dm}^3$ )	$t_{1/2}$ (s)
1.20	3.0	0.100	24
1.50	3.0	0.100	23
1.50	1.0	0.100	71
1.50	0.4	0.100	177
1.50	3.0	0.030	23
1.50	3.0	0.400	24

- i) Determine the order of reaction with respect to all three components.
- j) What is the rate equation of the process?
- k) What is the value and unit of the rate constant?
- l) Suggest a detailed mechanism to interpret the experimental findings.

**Problem 28**

Chlorine dioxide is a somewhat exceptional molecule because it contains an unpaired electron.

- a) Draw the Lewis structure of chlorine dioxide.
- b) Name at least two other stable molecules which do not contain metals but have an odd number of electrons.

Chlorine dioxide is increasingly used in water treatment. In one study, the reaction of chlorine dioxide with iodine was studied in aqueous solution. Light accelerated the process greatly. Chloride and iodate ions were detected as final products.

- c) Write the expected balanced equation for the process.

The ratio of the decreases in chlorine dioxide and iodine concentration was experimentally determined to be 2.3.

- d) What side reactions can cause this deviation from the expected stoichiometry?
- e) Suggest a method to detect the possible side reactions.

Quantitative measurements on the photochemical reaction were carried out using a very intense halogen lamp. Between the lamp and the photoreactor, an interference filter was also used, which excluded all light with the exception of the 455–465 nm wavelength region. This wavelength band is sufficiently narrow to consider the light beam as monochromatic 460 nm light. Iodine has a molar absorption of  $\epsilon = 740 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 460 nm, whereas the molar absorption of chlorine dioxide is immeasurably low at this wavelength. A  $25.00 \text{ cm}^3$  photoreactor with a 5.00 cm long light path length was used in all of the experiments. The reaction was studied in an acidic solution with initial concentrations  $[\text{I}_2]_0 = 5.1 \cdot 10^{-4} \text{ mol/dm}^3$  and  $[\text{ClO}_2]_0 = 4.0 \cdot 10^{-4} \text{ mol/dm}^3$ . Reference experiments were also carried out in the absence of selected reagents. When the solution contained chlorine dioxide but no iodine, no change was observable.

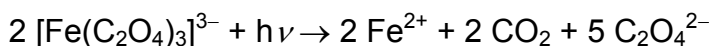
- f) Does this prove that chlorine dioxide does not photodecompose?

When the solution contained iodine but no chlorine dioxide, a very slow decay of iodine was observed, but it was orders of magnitude smaller than in the presence of chlorine dioxide. In the remaining experiments, the solution contained both reagents. In each experiment, the initial rate of the loss of chlorine dioxide ( $v_0$ ) was determined. The first experiment was carried out using the described experimental setup. In later experiments, a grey filter was inserted into the light beam before the photoreactor. The absorbance of this grey filter at 460 nm was measured in an independent experiment. In the final experiment, a steel sheet was inserted into the light beam that did not let any light through. The initial rates were determined in all of these experiments:

	no filter	filter 1 $A_{460} = 0.125$	filter 2 $A_{460} = 0.316$	filter 3 $A_{460} = 0.582$	steel sheet
$v_0 \text{ (nmol dm}^{-3} \text{ s}^{-1}\text{)}$	2.51	1.97	1.40	0.93	0.37

- g) Why doesn't the rate fall to 0 in the experiment with the metal sheet?

The intensity of the light beam was determined by ferrioxalate actinometry. A 0.00600 mol/dm<sup>3</sup> solution of K<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] was prepared in 0.05 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>. 25.00 cm<sup>3</sup> of this solution was measured into the photoreactor. Previously, the absorbance of this solution was measured to be 1.41 at 460 nm in a 1.000 cm quartz cell. The sample was illuminated for 30.00 minutes. The following process takes place in the solution:



The quantum yield for the formation of iron(II) is 1.12.

After illumination, a 1.000 cm<sup>3</sup> sample from the solution was measured into a 5.000 cm<sup>3</sup> volumetric flask, which was then filled with a solution that contained 0.0100 mol/dm<sup>3</sup> 1,10-phenanthroline and 0.50 mol/dm<sup>3</sup> 1:1 acetate/acetic acid buffer. The absorbance of this solution at 510 nm was measured in a 1.000-cm cell, the absorbance reading was 0.3823. The molar absorption coefficient of the complex Fe(phen)<sub>3</sub><sup>2+</sup> is  $\epsilon = 1.10 \cdot 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 510 nm and nothing else absorbs light in this solution at this wavelength.

- h) What is the concentration of the iron(II) complex in the cell?
- i) How much iron(II) formed during the illumination?
- j) What is the intensity of the 460 nm light in mol photon/s and W units?
- k) Determine the quantum yield in the reaction of chlorine dioxide with iodine for both the loss of chlorine dioxide and iodine.

### Problem 29

The following table displays energy data for selected atoms and diatomics in kJ/mol:

	1 <sup>st</sup> excitation ( $E_{\text{ex}}$ )	1 <sup>st</sup> ionization ( $E_{\text{I}}$ )	2 <sup>nd</sup> ionization ( $E_{\text{II}}$ )	Electronaffinity (EA)
Na	51.1	496	4564	53.1
Hu*	100.0	200	500	250.0
Cl	29.0	1251	1148	348.0
NaCl		860		70.1

\*hypothetical atom

The interaction energy of two point charges ( $q_1$  and  $q_2$ ) separated by a distance  $R$  is

$$E = -\frac{kq_1q_2}{R}$$

where  $k = 8.99 \cdot 10^9 \text{ m/F}$ . The charge of the electron ( $e$ ) is  $1.602 \cdot 10^{-19} \text{ C}$ .

- a) Na and Cl atoms are approaching each other in the gas phase. Find the minimal distance at which they still do not react.
- b) Is this distance smaller or larger if the Na atom is in its first excited state? Show your calculations.



Considering all the elements, the electron affinities vary between 4.6–348 kJ/mol, and the ionization energies vary between 375–2374 kJ/mol.

- c)** Is it possible to make a diatomic molecule dissociate into a stable state containing two ions? Show your calculation.
- d)** A neutral  $\text{Hu}$  atom and a  $\text{Hu}^+$  ion are approaching each other in the gas phase. Will they react? Prove it with calculations.

# Practical Problems

The participants of the Olympiad must be prepared to work in a chemical laboratory aware of necessary rules and safety procedures. The organizers will enforce the safety rules given in the Appendix A of the IChO Regulations during the Olympiad.

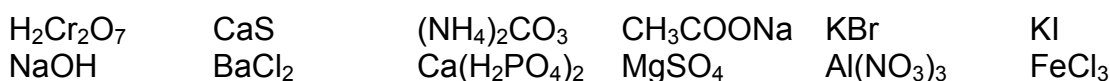
The Preparatory Problems are designed to be carried out only in properly equipped chemical laboratories under competent supervision. We did not include specific and detailed safety and disposal instructions as regulations are different in each country. Mentors must carefully adapt the problems accordingly.

The safety (S) and risk (R) phrases associated with the materials used are indicated in the problems. See the Appendix B of the Regulations for the meaning of the phrases. The Regulations are available from <http://www.icho.sk>.

Materials marked with a dagger, † will not be used at the Olympiad.

## Problem 30

You have twelve unknown aqueous solutions, each containing one, and only one, of the following compounds (all of which are used):



You have no additional reagents, only test tubes. Identify the compound in each solution.

Compound name	Formula	R phrases	S phrases
Aluminium nitrate	$\text{Al}(\text{NO}_3)_3$	8-36/38	17-26-36
Ammonium carbonate	$(\text{NH}_4)_2\text{CO}_3$	22-36/37/38	
Barium chloride	$\text{BaCl}_2$	20-25	1/2-45
Bichromic acid (solution)†	$\text{H}_2\text{Cr}_2\text{O}_7$	8-21-24/25-26-34-35-42/43-45-46-48/23-49-50/53-60-61-62	22-26-28-45-53-60-61
Calcium dihydrogenphosphate	$\text{Ca}(\text{H}_2\text{PO}_4)_2$	36/37/38	26-36/37
Calcium sulfide	$\text{CaS}$	31-36/37/38-50	28-61
Iron(III) chloride	$\text{FeCl}_3$	22-34	26-28
Magnesium sulfate	$\text{MgSO}_4$		22-25
Potassium bromide	$\text{KBr}$	36/37/38	26-36
Potassium iodide	$\text{KI}$	36/38-42/43-61	26-36/37/39-45
Sodium acetate	$\text{CH}_3\text{COONa}$		22-24-25
Sodium hydroxide	$\text{NaOH}$	35	26-37/39-45

**Problem 31**

You have three mixtures consisting of powdered inorganic solids on your desk. They could contain the following compounds:

- a)  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{AgNO}_3$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$
- b)  $\text{ZnO}$ ,  $\text{KI}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{BaSO}_4$ ,  $\text{MnO}_2$ ,  $\text{Mg}$
- c)  $\text{CaCO}_3$ ,  $\text{NH}_4\text{I}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

You can use distilled water,  $2 \text{ mol/dm}^3$   $\text{HCl}$ ,  $2 \text{ mol/dm}^3$   $\text{HNO}_3$ ,  $2 \text{ mol/dm}^3$   $\text{NH}_3$ ,  $2 \text{ mol/dm}^3$   $\text{NaOH}$  solution, pH paper, test tubes and a Bunsen burner.

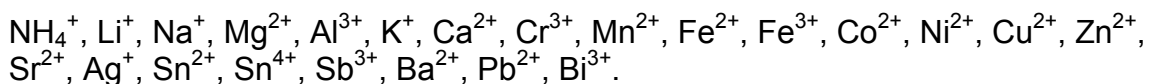
Determine which compounds are present in the mixture and which are not. Note your experimental findings in detail. Explain every conclusion (positive or negative). Include reaction equations where possible.

(not all of the compounds listed are present in the unknown samples)

Compound name	Formula	R phrases	S phrases
Ammonium carbonate	$(\text{NH}_4)_2\text{CO}_3$	22-36/37/38	
Ammonium iodide	$\text{NH}_4\text{I}$	26	
Ammonium nitrate	$\text{NH}_4\text{NO}_3$	8-36/37/38	17-26-36
Barium chloride	$\text{BaCl}_2$	20-25	1/2-45
Barium sulfate	$\text{BaSO}_4$		22-24/25
Calcium carbonate	$\text{CaCO}_3$	37/38-41	26-36/37/39
Copper(II) chloride dihydrate	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	22-36/37/38-50/53	26-60-61
Iron(II) sulfate heptahydrate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	22	
Lead(II) nitrate	$\text{Pb}(\text{NO}_3)_2$	8-20/22-33-50/53-61-62	53-45-60-61
Magnesium	$\text{Mg}$	15-17	43-7/8
Manganese(IV) oxide	$\text{MnO}_2$	20/22	25
Nickel(II) chloride dihydrate†	$\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$	23/24/25-36/37/38-42/43-45	53-26-27-28-36/37/39-45
Potassium iodide	$\text{KI}$	36/38-42/43-61	26-36/37/39-45
Silver nitrate	$\text{AgNO}_3$	34-50/53	26-45-60-61
Titanium(IV) oxide	$\text{TiO}_2$		
Zinc oxide	$\text{ZnO}$	50/53	60-61
Reagent	Concentration	R phrases	S phrases
Hydrochloric acid	$2 \text{ mol/dm}^3$	34	26-36/37/39-45
Nitric acid	$2 \text{ mol/dm}^3$	35	23-26-36-45
Sodium hydroxide	$2 \text{ mol/dm}^3$	35	26-37/39-45
Ammonia	$2 \text{ mol/dm}^3$	34-50	26-36/37/39-45-61

### Problem 32

You have moderately concentrated (5-6 % by mass) aqueous solutions containing water-soluble compounds of the following cations with one of the most common anions (chloride, sulfate or nitrate):



- Observe the color and the pH of the solutions.
- Study the reactions of these cations with the anions used in systematic qualitative analysis: chloride, sulfide, carbonate, and hydroxide. Note that some sulfides can be precipitated even from acidic solutions, others are soluble in dilute strong acids, some are soluble in water, and some would react with water. Most cations will give a precipitate with  $\text{CO}_3^{2-}$ . What happens if you use  $\text{HCO}_3^-$  instead?  
Whenever you observe no reaction at ambient temperature, try to predict whether boiling the solution would bring about a detectable change.
- Learn which cations react with some common anions: nitrate, nitrite, phosphate, sulfate, perchlorate, bromide, and iodide. Throughout this problem, use solutions in the same concentration range (approximately 5-6 % by mass).
- Which two cations in the list above cannot be distinguished from each other on the basis of their reactions with the anions mentioned so far?
- Using the reactions you have learned, identify five unknown aqueous solutions. Every solution was made from a single compound which may contain any of the cations and anions you have encountered in this problem.

### Problem 33

In this problem you will identify a metal using complexometric titrations. EDTA (the disodium salt of ethylene-diamine-tetraacetic acid) forms stable complexes with most di- and trivalent metal ions.



where M is the metal and  $\text{Y}^{4-}$  is the anion formed from EDTA.

While there is an excess of uncomplexed metal ions present, they bond to the indicator molecules. At the end of the reaction all ions form an EDTA complex and the indicator molecules will be liberated bringing about a change in color. Thus the end point of the reaction is when addition of EDTA does not change the hue of the solution. One has to titrate until a steady color is reached. A previously titrated sample can be used for comparison.

First a metal sample is dissolved in nitric acid. After setting the pH of the resulting solution to approximately 2, it is titrated with EDTA. In another measurement the oxide of the metal is dissolved and the solution is titrated again with EDTA. (The oxide was prepared previously by evaporating the nitric acid solution of the metal and calcining the residue.) Many solutions used are very acidic, treat them with due caution.

**Titration of the metal**

Weigh accurately about 150 mg of the unknown metal into a titration flask. Carefully add 3 cm<sup>3</sup> conc. nitric acid using working under the hood. Complete dissolution may take 10 minutes. Dilute the solutions to 50 cm<sup>3</sup> and then return to your desk. First add 8 cm<sup>3</sup> 5 % ammonia solution, then continue adding the ammonia solution dropwise until the contents of the flask start to opalize from the hydroxide precipitate. Add immediately 5 cm<sup>3</sup> 10 % nitric acid. Add two pinches of solid methylthymol blue indicator. Titrate with 0.0500 mol/dm<sup>3</sup> EDTA until a steady yellow color is attained. Repeat as necessary.

**Titration of the metal oxide**

Weigh accurately about 1.000 g of the oxide, dissolve it in 5 cm<sup>3</sup> conc. nitric acid and then dilute to 100 cm<sup>3</sup> in a volumetric flask. Transfer 20.00 cm<sup>3</sup> portions into a titration flask and dilute to 50 cm<sup>3</sup>. Start adding 5 % ammonia dropwise until the appearance of the precipitate. Immediately add 5 cm<sup>3</sup> 10 % nitric acid solution. Add two pinches of solid methylthymol blue indicator. Titrate with 0.0500 mol/dm<sup>3</sup> EDTA until a steady yellow color is attained. Repeat as necessary.

- Identify the metal based on calculations.
- Give the formula of the oxide.

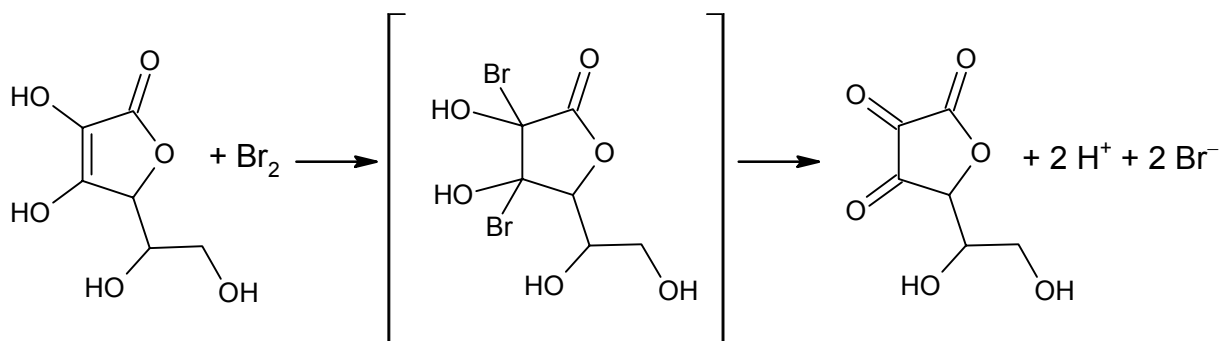
Caveat: The best marks are not necessarily awarded to results reproducing the theoretically expected values.

Reagent	Concentration	R phrases	S phrases
EDTA disodium salt	0.05 mol/dm <sup>3</sup>	36/38	26-36
Nitric acid	65 %	35	23-26-36-45
Nitric acid	10 %	35	23-26-36-45
Ammonia	5 %	34-50	26-36/37/39-45-61
Methylthymol blue			

**Problem 34**

The isolation of vitamin C was carried out by monitoring the reducing properties of green pepper extracts (1931, Szent-Györgyi). The determination of ascorbic acid can also be based on its reducing properties. This is often more convenient than titration as an acid, especially in the case of real life samples containing other acidic substances, e.g., citric acid.

A possible oxidizer is potassium bromate. Its use in direct titrations was suggested in 1872 by Györy. In strongly acidic solutions KBrO<sub>3</sub> reacts with KBr to form bromine. This will oxidize ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) to dehydroascorbic acid (C<sub>6</sub>H<sub>6</sub>O<sub>6</sub>) in this titration. The end point of the reaction can be followed by a suitable redox indicator.



Crush the vitamin C tablet with a few drops of water in a mortar. Wash the soluble parts of the mixture through a folded filter paper into a 200 cm<sup>3</sup> Erlenmeyer flask. Do not use more than 60 cm<sup>3</sup> of distilled water. Add 10 cm<sup>3</sup> of 20 % (by mass) HCl and approx. 0.2 g of KBr to the sample. Titrate it immediately with the 0.02 mol/dm<sup>3</sup> KBrO<sub>3</sub> titrant in the presence of 2 drops of p-ethoxychrysoidine indicator (0.2 % in ethanol). The red solution will change to colorless (very light yellow) at the end point.

- Write the equation for bromine formation from bromate and bromide ions.
- Give the vitamin C content of the tablet in milligrams.

Reagent	Concentration	R phrases	S phrases
Hydrochloric acid	20 %	34	26-36/37/39-45
Potassium bromate†	0.02 mol/dm <sup>3</sup>	45	45-53
Potassium bromide	solid	36/37/38	26-36
Para-ethoxychrysoidine	0.2% in ethanol		

### Problem 35

Ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) is a fairly good reducing agent ( $E^{\circ} = + 0.39 \text{ V}$ ). Due to this property, it is widely used in volumetric analysis. It can be used for the determination of various cations (e.g., Au<sup>3+</sup>, Ag<sup>+</sup>, Hg<sup>2+</sup>) and anions (e.g., ClO<sub>3</sub><sup>-</sup>, BrO<sub>3</sub><sup>-</sup>, IO<sub>3</sub><sup>-</sup>, VO<sub>4</sub><sup>3-</sup>, Fe(CN)<sub>6</sub><sup>3-</sup>). During the titration it is oxidized via loss of 2 electrons forming dehydroascorbic acid (C<sub>6</sub>H<sub>6</sub>O<sub>6</sub>) – as shown in the previous problem.

#### Preparation of 0.05 mol/dm<sup>3</sup> ascorbic acid solution

Weigh approximately 8.9 g ascorbic acid and dissolve it in a small amount of water. Do not use metal vessels or spoons. Transfer the solution to a standard volumetric flask and dilute to 1.000 dm<sup>3</sup> with freshly prepared cold distilled water.

#### Preparation of 0.00833 mol/dm<sup>3</sup> potassium hydrogen iodate solution

Weigh accurately 3.2492 g KH(IO<sub>3</sub>)<sub>2</sub> in a 50 cm<sup>3</sup> beaker and dissolve it in 50 cm<sup>3</sup> distilled water. Transfer the solution in a standard volumetric flask and dilute to 1000 cm<sup>3</sup> with freshly prepared distilled water.

#### Standardization of the 0.05 mol/dm<sup>3</sup> ascorbic acid solution

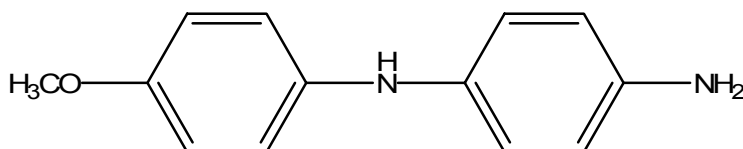
Pipette 20.00 cm<sup>3</sup> 0.00833 mol/dm<sup>3</sup> KH(IO<sub>3</sub>)<sub>2</sub> solution into a clean conical flask. Add approx. 1 g KI and 5 cm<sup>3</sup> 2 mol/dm<sup>3</sup> HCl solution. Titrate the liberated iodine with 0.05 mol/dm<sup>3</sup> ascorbic acid solution. When the colour has faded to pale yellow, add 10 drops of Variamine Blue indicator (hydrogen sulfate, 0.2 % by mass solution in water). Slowly add 20 % sodium acetate solution until the deep violet colour of the indicator

appears, then add 2 cm<sup>3</sup> more. Titrate the solution slowly until the deep violet colour disappears. Repeat the procedure as necessary.

### Determination of the silver content of the unknown

Dilute the given sample solution to 100 cm<sup>3</sup> in a volumetric flask using distilled water. Pipette 10.00 cm<sup>3</sup> of the unknown solution into a clean conical flask. Dilute the sample to 50-70 cm<sup>3</sup> with distilled water. Heat the solution to 60 °C. Add 1 cm<sup>3</sup> of Variamine Blue indicator and titrate rapidly with 0.05 mol/dm<sup>3</sup> ascorbic acid solution. The solution must be thoroughly shaken during the titration. If the temperature falls under 40 °C, reheat to 60 °C. When the blue or violet colour of the indicator has disappeared and the greyish-white colour of the precipitated silver metal has become apparent, add 20% sodium acetate solution to re-establish the colour of the indicator. Then titrate slowly adding titrant dropwise, until the colour of the indicator fades away. Repeat the procedure as necessary.

Variamine Blue has the structure shown below:

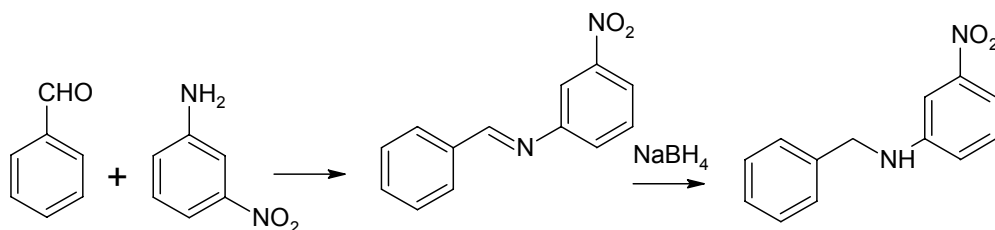


- Write a balanced equation for the formation of iodine and the titration of iodine with ascorbic acid solution in Procedure 2.
- Calculate the concentration of the ascorbic acid solution prepared.
- Variamine Blue is shown in its reduced form. Draw the structure of the oxidized form given that it is oxidized with the loss of 2 electrons. Which form is responsible for the blue-violet colour?
- Write a balanced equation of the reaction between ascorbic acid and silver ions.
- Determine the silver content of the unknown.

Reagent	Concentration	R phrases	S phrases
Unknown sample (containing Ag <sup>+</sup> ions)		34-51/53	26-36/37/39-45-61
Ascorbic acid	0.05 mol/dm <sup>3</sup>		
Potassium iodate	Solid	63-36/38-42/43	26-36/37/39-45
Potassium iodide	Solid	63-36/38-42/43	26-36/37/39-45
Hydrochloric acid	2 mol/dm <sup>3</sup>	34	26-36/37/39-45
Sodium acetate	20 %		22-24-25
Variamine Blue	0.2 % in water	23/24/25	36/37/39-45

### Problem 36

You will carry out a simple synthesis of N-benzyl-3-nitroaniline according to the reaction scheme:



Dissolve 1.1 g *meta*-nitroaniline in 10 cm<sup>3</sup> ethanol in a 25 cm<sup>3</sup> Erlenmeyer flask and add 1.5 cm<sup>3</sup> benzaldehyde to this mixture. Let the flask stand for 20 minutes with occasional shaking. Transfer the flask to an ice-water bath. On cooling a solid material precipitates. Collect it on a sintered glass funnel. You can use the filtrate to wash the solid remaining in the flask onto the filter. Since the product is moderately soluble in alcohol, do not wash it on the filter, just dry it with suction. Set aside a small sample for thin-layer chromatography (TLC).

Place the solid substance into a 100 cm<sup>3</sup> Erlenmeyer flask and dissolve it in 20 cm<sup>3</sup> of ethanol. Slowly add to this solution 0.5 g of NaBH<sub>4</sub> in small portions with constant shaking. Continue shaking the flask for an additional 15 minutes, and then pour its content into 50 cm<sup>3</sup> of ice-cold water. Collect the precipitate on a sintered glass funnel and wash with cold water. Dry the product in air and weigh it.

Compare the chromatographic properties of the starting materials, the intermediate and the product. Make a thin layer chromatogram on a silica plate with hexane/ethyl acetate = 4:1 as eluent. Suggest a method for visualization of the spots. Comment on the purity of the intermediate and the product.

		<b>R phrases</b>	<b>S phrases</b>
<i>Meta</i> -nitroaniline	solid	23/24/25-33-52/53	28-36/37-45-61
Benzaldehyde	solid	22	24
NaBH <sub>4</sub>	solid	15-24/25-34	22-26-36/37/39-43-45
Ethanol	abs.	11	7-16
Hexane		11-38-48/20-51/53-62-65-67	9-16-29-33-36/37-61-62
Ethyl acetate		11-36-66-67	16-26-33

### Problem 37

Before highly efficient methods like chromatography or genetic engineering revolutionized the elucidation of protein structure the analysis of protein hydrolyzates was very complicated. Several reagents were developed to selectively precipitate individual amino acids from mixtures often containing 20 or more different compounds. One such widely used reagent was rhodanic acid or its salts, which contain the rhodanic complex ion ([Cr(SCN)<sub>4</sub>(PhNH<sub>2</sub>)<sub>2</sub>]<sup>-</sup>). This problem demonstrates the use of this reagent.

#### Ammonium rhodanilate

In a 100 cm<sup>3</sup> flask mix 5 g hydrated chromium(III) potassium sulfate, 5.8 g potassium thiocyanate and 5 cm<sup>3</sup> water and heat it in a 80 °C water bath for 10 minutes. Under the



hood add 5 cm<sup>3</sup> aniline and continue heating for an additional 60 minutes. Dilute the product with 50 cm<sup>3</sup> water and add 10 cm<sup>3</sup> glacial acetic acid. Keep the mixture in an ice-water bath for 10 minutes with occasional scratching using a glass rod. Filter off the purple precipitate on a sintered glass filter and wash it with water.

In a flask dissolve the product in 20 cm<sup>3</sup> methanol. Filter out any insoluble impurities. To the solution add 10 cm<sup>3</sup> of concentrated ammonia solution and 50 cm<sup>3</sup> water. Collect the precipitate with filtration, wash it with water and dry on an open Petri dish.

### The reaction of ammonium rhodanilate with amino acids

Dissolve 0.35 g proline in 15 cm<sup>3</sup> 0.25 mol/dm<sup>3</sup> aqueous HCl in a beaker. In a separate beaker dissolve 1.5 g ammonium rhodanilate in 20 cm<sup>3</sup> methanol. Mix the two solutions. Filter the precipitate on a glass filter. Wash with three 10 cm<sup>3</sup> portions of distilled water. Dry the product in an open Petri dish.

### TLC experiments

Dissolve appr. 10 mg samples of alanine, proline, phenylalanine and glutamic acid (separately) in 1 cm<sup>3</sup> of water. Additionally, make a sample mixing the four standard solutions. In a separate test tube mix 0.1 cm<sup>3</sup> samples of these solutions with 0.1 cm<sup>3</sup> ammonium rhodanilate solution (5 % in methanol). Filter the solutions on paper using a small funnel.

Analyze the solutions by TLC on silica plates. Find an appropriate eluent by mixing 50% acetic acid and *n*-butanol. Visualise the spots with ninhydrin\*. Summarize your results. Explain your findings!

		R phrases	S phrases
KCr(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	solid		22-24/25
KSCN	solid	20/21/22-32-52/53	13-61
Aniline†		23/24/25-40-41-43-48/23/24/25-50-68	26-27-36/37/39-45-46-61-63
L-Alanine	solid		
L-Phenylalanine	solid		
L-Proline	solid		22-24/25
L-Glutamic acid	solid		
Methanol	abs.	11-23/24/25-39/23/24/25	7-16-36/37-45
Ninhydrin	0.5% (in acetone)	11-22-36/37/38-66-67	9-16-26
<i>n</i> -butanol		10-22-37/38-41-67	13-26-37/39-46-7/9
NH <sub>3</sub>	conc.	34-50	26-36/37/39-45-61
Acetic acid	100%	10-35	23-26-45
Acetic acid	50%	34	23-26-45
HCl	0.25 mol/dm <sup>3</sup>	34-37	26-36/37/39-45

\* Ninhydrin is a selective reagent for amino acids. Dip the developed and dried plates in a 0.5% acetone solution of ninhydrin, dry the plates and heat them for a short time with a heat-gun. Contact of the reagent with skin should be avoided since it produces a rather long-lasting purple discoloration. Use forceps!