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The 2002 Chemistry Olympiad in Groningen

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Abstract: At the 2002 Chemistry Olympiad in Groningen, in contrast to previous years, the Swiss students won no medals, although two of them missed the bronze medal only by one point.

Keywords: International Chemistry Olympiad · Swiss students

Delegations from 57 countries took part in the 34th International Chemistry Olympiad in Groningen, Netherlands from 5th to 14th July, 2002. The International Chemistry Olympiad is an annual competition for high school students younger than 20 years old. The competition lasts ten days. Two days are devoted to competition, one for practical work in the laboratory, and one for solving theoretical problems. After correction and grading the best students are awarded gold, silver and bronze medals like in any real Olympic games.

In the present Olympiad, the best result was obtained by M. Zhu, from China. Unlike previous year there were no medals for Switzerland this time, although Martin Kotyrba and Severin Schneebeli missed the bronze medals by only one point. Generally speaking the most successful countries were China, Korea, Taiwan, and other Asian countries. Students from European countries seem to have some difficulty in competing with their far-eastern friends.

The four members of the Swiss team were:

– Martin Kotyrba, b. 1982, 5313 Klingnau.
– Peter Ludwig, b. 1984, 8400 Winterthur.
– Vinitha Pazhepurackel, b. 1984, 8046 Zürich.
– Severin Schneebeli, b. 1984, 8708 Männedorf.

At the beginning of the Olympiad the mentors meet to create and define the problems of the Olympiad. The level of these problems is usually extremely high, so that the contestants must be seriously trained in advance in their original countries. In Switzerland the preparation was done in winter weekends followed by one week in April in the Gymnase de Chamblandes, Pully-Lausanne.

The two Swiss mentors were Jochen Müller, Gymnasium Hohe Promenade, Zürich, and Blenda Weibel, Gymnase de la Cité, 1000 Lausanne. Mentors were hosted in one of the best luxury hotels in Groningen. The organization was perfect.

After the competition the mentors and the candidates had a lot of opportunities for sightseeing and visiting parks, museums, industries, *etc*. in the vicinity.

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The next Olympiads will be 2003 Greece, 2005 Taiwan, 2006 Korea, 2007 Turkey, 2008 England, and 2009 Singapore. The Swiss Chemical Society (SCS) should have organized the 2004 Olympiad. Unfortunately the SCS decided in January 2002 to retract its commitment made in June 2000 and not to organize the 2004 Olympiad in Switzerland. It was a shame for our country, as we had already found half a million francs and many devoted people. But it is so.

Theoretical Problems

The theoretical problems of the 2002 Olympiad will now be presented, with their answers.

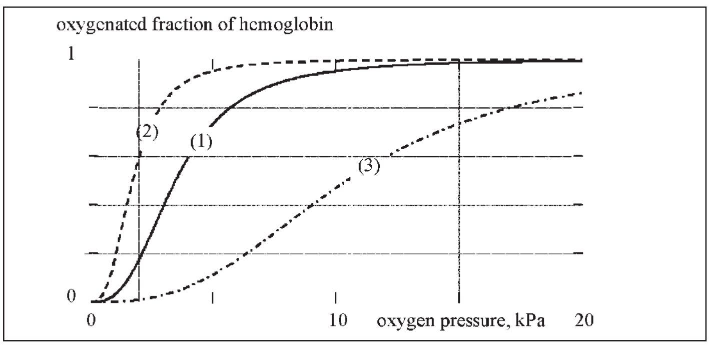
Problem I-1. Hemoglobin

Heme Hm is part of the hemoglobin molecule which reacts with O_2 and CO to produce the complexes $Hm{\cdot}O_2$ and $Hm{\cdot}CO$.

$$Hm + CO \rightleftharpoons Hm{\cdot}CO \qquad (1)$$

$$Hm + O_2 \rightleftharpoons Hm{\cdot}O_2 \qquad (2)$$

The equilibrium constants K_1 for reaction (1) and K_2 for reaction (2) are related as follows: $K_1 = 10^4\ K_2$. The ratio $Hm{\cdot}O_2$ / ($Hm{\cdot}O_2$ + Hm) is reported in the Fig. (curve 1) *versus* the partial pressure of oxygen in air. The two curves (2) and (3) have been obtained with two modified hemoglobins related to hereditary illnesses.



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Some useful data: O_2 pressure is 15 kPa in the lungs and 2 kPa in the muscular tissue. Hemoglobin (molar mass 64000 g/mol) contains four heme groups. Its concentration in the blood is 340 g/l. Maximum blood rate of flow is 0.4 l/s in the heart and lungs. Red corpuscles make up 40% of the blood volume.

I-1-1. Determine the difference between ΔG° of the two reactions (1) and (2).
Answer. ΔΔG° = 23 kJ mol^{-1}.

I-1-2. How many moles O_2 will be discharged in the muscles when 1 mol Hb leaves the lungs, crosses the muscle and go back to the heart? Same question for the three types of hemoglobin.
Answers. Type 1: 3.2 mol; type 2: 1.6 mol; type 3: 2.9 mol.

I-1-3. Why is the curve (2) different from (1)? a) the bond with O_2 is too weak; b) the bond with O_2 is too strong; c) the maximum reaction capacity with O_2 is too low; d) the blood has been poisoned by CO.
Answer. b.

I-1-4. How much oxygen (in mol s^{-1}) can be delivered to muscle with normal hemoglobin?
Answer. 2.72 mmol s^{-1}.

I-1-5. What is the maximum power of the body muscles, assuming that this performance is defined by the oxygen transport capacity?
Answer. 1088 W.

Problem I-2. Nitrogen and Spectroscopy

I-2-1. Determine the oxidation states of N in NH_3, NO_2^-, and NO_3^-.
Answers. –3, +3, +5.

I-2-2. Nitrogen in nitrites is determined by spectrophotometry. Nitrite is first transformed into a colored compound with the absorption maximum at λ = 543 nm. Later on all measurements will be done at this wavelength. Why this choice?
a) Because these measurements are not influenced by impurities.
b) Because diffused light does not interfere at this wavelength.
c) Because the measurements are more precise at his wavelength.
d) For other reasons.
Answer. c.

I-2-3. Determine the absorbance A, with ε = 6000 M^{-1} cm^{-1}, l = 1 cm and $c = 10^{-4}$ M.
Answer. A = 0.50.

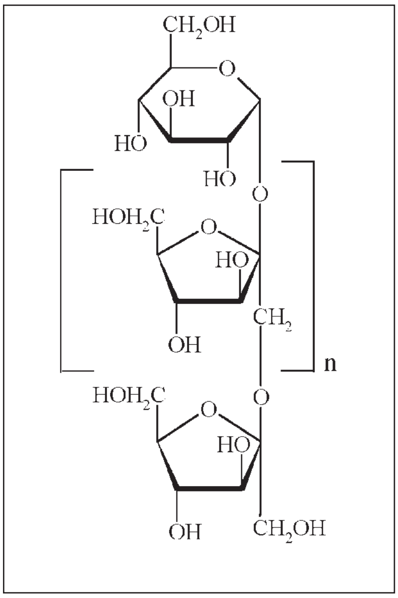
I-2-4. The following measurements have been made from a diluted nitrite solution, with a 1 cm cuvette

Concentration c of N from nitrite	Absorption A at 543 nm
Pure water (Zero effect)	0.003 (due to impurities)
0.915 ppm	0.167
1.830 ppm	0.328

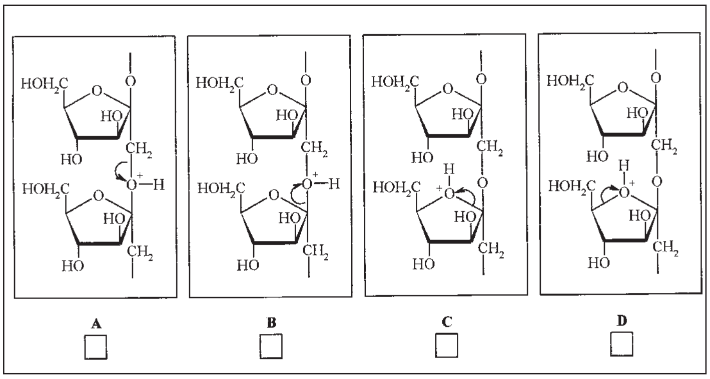
These points are aligned on a straight line $A = mc + b$. Determine the slope m and the parameter b.
Answer. m = 0.176, b = 0.003.

Problem II-1. Inulin Chemistry

Inulin is a natural polymer extracted from chicory or endive. Its molecule is a long chain made of ten fructose units with a glucose unit at one end. The Fig. shows the Hawoth projection of inulin (n = 9).



II-1-1. Inulin can be hydrolyzed in an acidic solution. Determine the correct mechanism for the rupture of the C–O bond.



Answer. B

II-1-2. This hydrolysis can be performed with isotopically labeled water, using for example deuterium (^{2}H) or the oxygen isotope ^{17}O. Which one of the following molecules is recommended for later use in NMR spectroscopy? ^2H_2O, $H_2{}^{17}O$, $^2H_2{}^{17}O$, none of these.
Answer. $H_2{}^{17}O$

II-1-3. 1.0 mol Inulin is dissolved in 2 kg of water, then hydrolyzed and reduced at 95 °C with a suitable catalyst producing mannitol and sorbitol from fructose. The selectivity of the hydrogenation of fructose to mannitol/sorbitol is 7 : 3. How many moles of mannitol and sorbitol are obtained?
Answer. 7 mol mannitol, 4 mol sorbitol.

II-1-4. At the end of the reaction, the catalyst is removed, and the solution cooled down to room temperature. Sorbitol remains dissolved. But mannitol solubility is only 0.40 mol/kg at 25 °C. So some mannitol is deposited. How many moles?
Answer. 6.27 mol.

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Problem II-2. Industrial Synthesis of Methanol

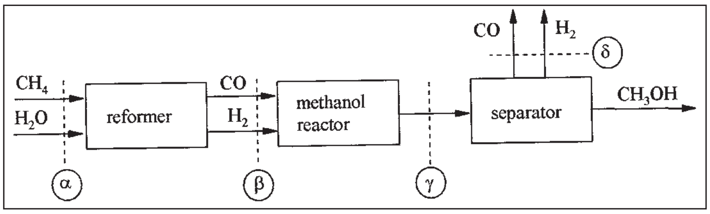
Methanol is industrially produced by the reaction:

$$CO + 2\,H_2 \rightleftharpoons CH_3OH$$

Hydrogen and carbon monoxide are obtained by the reaction:

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2$$

Technically speaking, CH_4 and H_2O are first transformed in a so-called reformer unit. The gases are then reacted in a methanol reactor, and pass through a separator, where CH_3OH is separated from unused CO and H_2. See the Fig., where four different positions are described with Greek letters.



At the point γ, the flow rate of CH_3OH is 1000 mol s^{-1}. Assume that: 1) the yield in the reformer is 100%; 2) 2/3 of the entering CO is transformed into methanol at β; 3) all CO and H_2 exiting at δ is burned to heat the reformer.

II-2-1and -2. Determine the flow rate of CO and H_2 at β and γ.
Answers. In β: CO: 1500 mol s^{-1}, H_2: 4500 mol s^{-1}; in γ: CO: 500 mol s^{-1}, H_2: 2500 mol s^{-1}.

II-2-3. Determine the required initial flow rate of CH_4 and H_2O at α.
Answer. CO and H_2O: 1500 mol s^{-1}.

II-2-4. Determine the partial pressure of CO, H_2 and CH_3OH at γ, using the following equation:

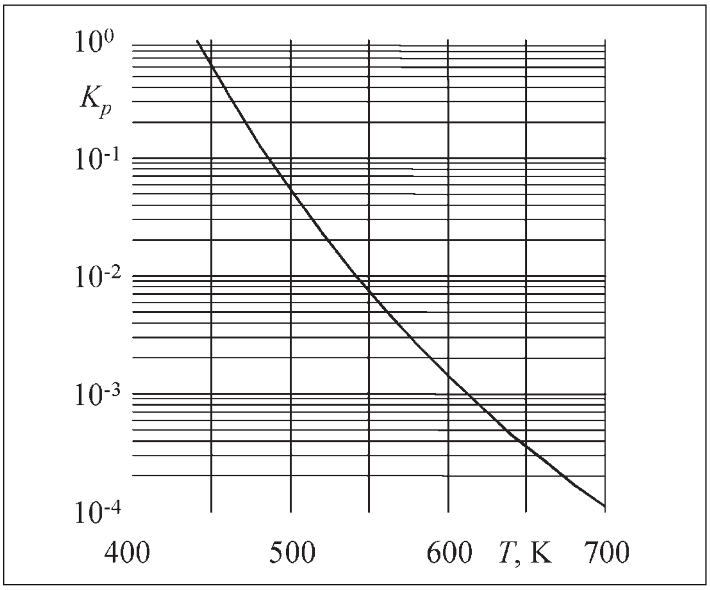
$$p_i = p\frac{n_i}{n_{tot}}$$

where n_i is the flow rate and p_i the partial pressure of the i-th component, n_{tot} the total flow rate and p the total pressure of the system. (p = 10 MPa).
Answer. $p(CO)$ = 1.25 MPa ; $p(H_2)$ = 6.25 MPa.

II-2-5. With large reactors, the reaction goes to equilibrium. The corresponding constant K_p is defined from the different partial pressures.

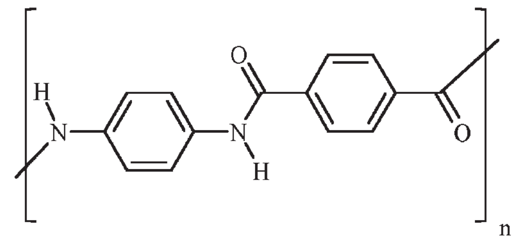
$$K_p = \frac{p_{CH_3OH}\, p_0^2}{p_{CO}\, p_{H_2}^2}$$

where p_0 is 0.1 MPa. Assume that K_p changes with temperature as in the next Fig. Determine the experimental value K_p and the temperature needed to obtain this equilibrium.
Answer. 5.12 10^{-4}.



Problem II-3. Structure of Polymers

PPTA is an industrial polymer belonging to the Aramid class, sold under the trade name of Kevlar® or Twaron®. The polymer chain is packed in sheets.



PPTA

II-3-1. Draw the structure of three chains of this polymer.
Answer. Draw hydrogen bonds between O from CO and H from NH in next chains.

To produce this polymer, two monomers are mixed in equal amounts, then reacted. Assume that: 1) U_0 is the total number of monomer molecules at the beginning of the reaction; 2) at the end of the reaction, a fraction p (p <100%) of the functional groups have reacted; 3) the total number of chains is N_t, and 4) the average length of the chain is $\overline{P}_n$.

The polymerization equilibrium can be described by the following equation:

$$C + A \rightleftharpoons Am + H_2O$$

where C is any free $–CO_2H$ group, A is any free $–NH_2$ group and Am is any –CO-NH- group.

II-3-2. Determine the so-called degree of polymerization p, if the average length of the chain is 500.
Answer. p = 0.998.

II-3-3. Which of the following possibilities can be used to produce PPTA?

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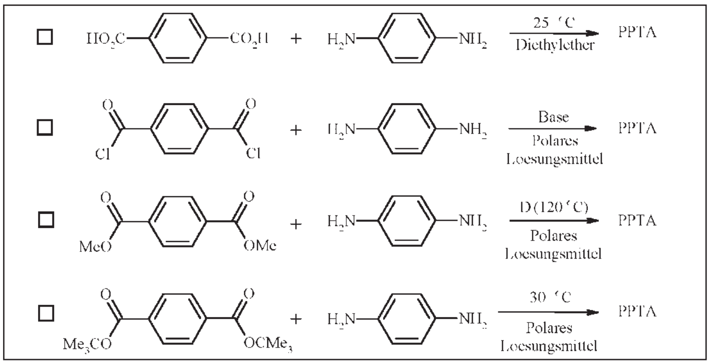
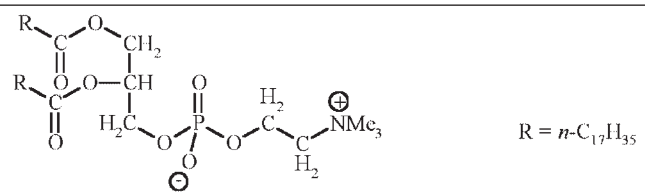


Answer. Line 2 or 3.

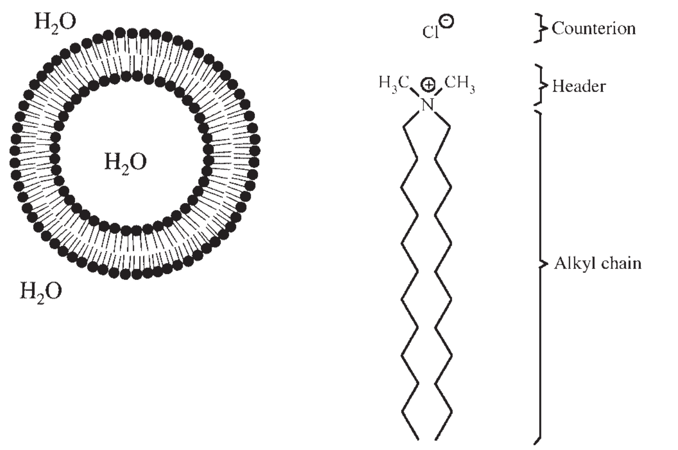
II-3-4. Another polymer can be produced by heating 4-aminobenzoic acid. What is the structure of this polymer, with n = 4? And what is the average length of the chain in a closed system with an equilibrium constant $K = 576$?
Answer. $\overline{P}_n = 25$.

Problem III-1. Phospholipids in Membranes



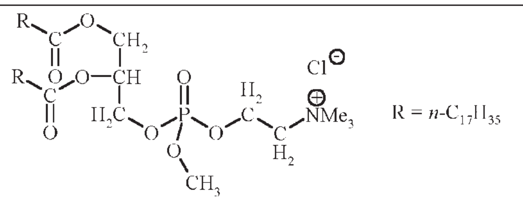
A

The phospholipid **A** is a constituent of the cell membranes. In highly diluted solutions its molecules are separated and independent. If their concentration is higher than a critical value they stack together and produce double-layered spherical structures called liposomes. Polar or ionic groups stay in contact with the solvent water. The long alkyl chains stay in the core of the membrane, producing a double layer. See the Fig.



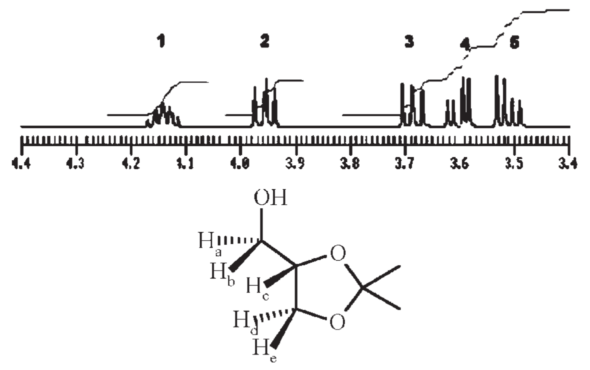
DDAC

III-1-1. How many different stereoisomers are there in the molecule **A** and in the following trialkylphosphate **B**?
Answers. 2 in **A**, 4 in **B**.



B

III-1-2. **A** can be synthesized from **C**, which is itself obtained from glycerol and acetone. The ^{1}H-NMR spectrum of **C** is given. Which signal of the NMR spectrum corresponds to the given H atoms?



C

Answer. $H_c = 1$.

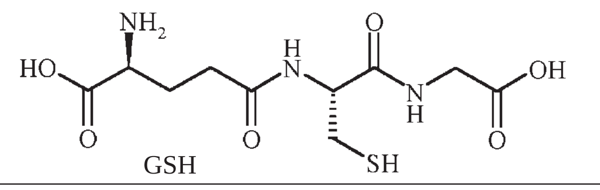
III-1-3. The double layer of the liposome depends upon the length l_c and the volume V of the alkyl chain. It depends also on the cross-section a_0 of the head group in the phospholipid molecule. The following values may be assumed for alkyl chains with n C atoms :

$V = (27.4 + 26.99\ n) \cdot 10^{-3}$ nm^3
$l_c = (0.154 + 0.1265\ n)$ nm

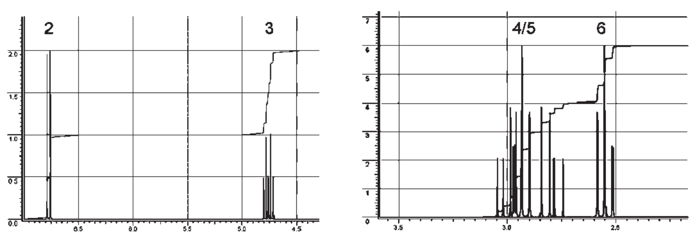
When n is big enough, the repulsion between end charges can be neglected. Determine the minimal cross-section of the head group for these high values of n.
Answer. 0.213 nm^2.

Problem III-2. Glutathion

III-2-1. Glutathion (GSH) is a simple peptide as described in the Fig. How many amino-acids does it contain? Draw the structure of these amino-acids, with stars at chiral centers.
Answer. Three amino acids.



III-2-2. Glutathion reacts with blood poisons like acrylonitrile CH_2=CHCN, and transforms it in the body into a mercaptur acid A ($C_8H_{12}N_2O_3S$), which can be eliminated in the urine. The ^{1}H-NMR spectrum of A in $(CD_3)_2SO$ is displayed. When A is previously treated by D2O, the signals at 12.8 and 6.8 disappear; the signal at 3 is simplified.



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Assume that the H atoms of the spectrum belong to either CH or CH_2 or CH_3 or OH or NH_2. a) Assign the signals 1 to 7 to a correct proton group; b) How many C atoms are not connected to any H atom? c) Draw the structure of **A**.
Answers. a) 1 to OH, 2 to NH, 3 to CH, 4/5 to CH_2, 6 to CH_2, 7 to CH_3 ; b) 3 C atoms; c) CH_3-CO-NH-CH(COOH)-CH_2-S-CH_2-CH_2-CN.

Problem IV-1. Thermochemistry

IV-1-1. Define the chemical equation for the following three phenomena: complete separation of Ce and Br from the solid $CeBr_3$ (requiring a lattice energy H_1), formation of ions from gaseous atoms (producing an electrostatic energy H_e), sublimation of $CeBr_3$ (requiring an energy H_s).
Answers: $CeBr_3$(s) → Ce^{3+}(g) + 3 Br^-(g) with $-H_1$, then: Ce^{3+}(g) + 3 Br^-(g) → $CeBr_3$(g) with $+H_e$, then: $CeBr_3$(s) → $CeBr_3$(g), with $+H_s$.

IV-1-2. The lattice energy H_1 of a solid can be calculated with the Born-Landé formula

$$H_1 = f\frac{Z_+Z_-Ae^2}{r_+ + r_-}(1-\frac{1}{n})$$

The factor fe^2 is equal to 139, and takes into account the different distance (in nm) and energy units (kJ mol^{-1}). The Madelung constant A is 2.985. The Bohr exponent is n = 11. The ionic charges Z_+ and Z_- are integers (Z_- is negative). The radius r_+ of Ce^{3+} is 0.115 nm and the radius r_- of Br^- is 0.182 nm. When gaseous $CeBr_3$ is formed from ions the corresponding energy can be calculated from Born-Landé formula using A = 1. Gaseous $CeBr_3$ is trigonal and planar. Determine the sublimation enthalpy of $CeBr_3$.
Answer. 718 kJ mol^{-1}.

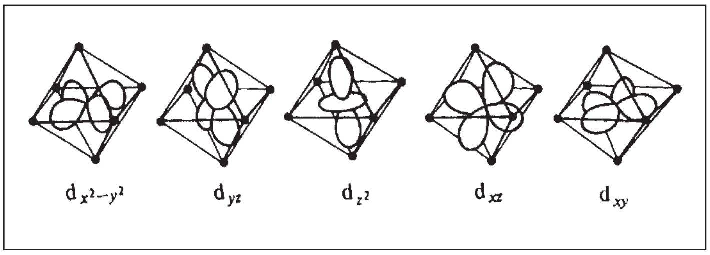
IV-1-3. $CsCeBr_4$ is a substance whose sublimation produces a gaseous mixture of CsBr and $CeBr_3$. The lattice of $CsCeBr_4$ has the NaCl structure with a cation Cs^+ and a tetrahedral anion $CsBr_4^-$. Determine a thermodynamic cycle in four steps for the sublimation of $CsCeBr_4$ using the Hess law.
Answers. Step 1 produces Cs^+ and $CeBr_4^-$, with H_1; step 2 transforms $CeBr_4^-$ into Ce^{3+} and 4 Br^- ions, with H_2; step 3 and 4 are the synthesis of the gaseous $CeBr_3$ then CsBr molecules.

IV-1-4. Calculate the numerical value of the sublimation enthalpy of $CsCeBr_4$.
The Madelung constant for NaCl is 1.75. The distance Cs–Ce in the lattice is 0.617 nm. The apexes of two tetrahedron are separated by $(2\sqrt{6})/3$ = 1.633 times the distance from apex to the center of the tetrahedron. The Born exponent of CsBr is 11 and the radius of Cs^+ is 0.181 nm.
Answer. [kJ mol^{-1}]. 358 + 3543 – 3092 – 348 = 461.

Problem IV-2. 3d Orbitals

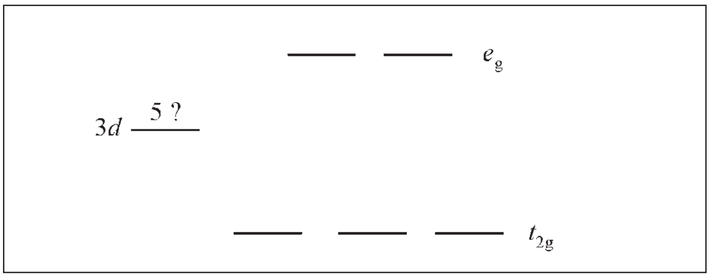
IV-2-1. Red ruby is made of colorless aluminum oxide, containing chromium ions as impurities. Cr^{3+} ion has three electrons in the 3d shell, which may absorb light. Usually Cr^{3+} concentration is 0.050% in mass. A cylindrical ruby crystal is 15.2 cm long with 1.15 cm diameter. Its density is 4.05 g cm^{-3}. Calculate the amount of chromium in the ruby cylinder.
Answer. 3.68 10^{20} ions.

IV-2-2. In ruby Cr^{3+} ions are octahedrically surrounded by six oxide ions. The geometry of the five *3d* shells are described below. Later on a box describes the splitting of the five *3d* shells in one group of three orbitals with low energy (t_{2g}) and a second group of two orbitals with a higher energy (e_g). Determine which orbitals *3d* belong to t_{2g} and which to e_g



Answer. d_{xy}, d_{yz}, and d_{xz} are t_{2g}.

IV-2-3. Complete the following scheme by adding three arrows for the three electrons of Cr^{3+}.
Answer: One arrow on each t_{2g}.



IV-2-4. A piece of ruby is deposited on a non-magnetic balance. Then a magnet is approached from under the ruby. What is the effect of this magnet?
Answer. The ruby is attracted by the magnet, and moves down.

Problem IV-3. Electrochemistry

IV-3-1. A lead storage cell is described by the following scheme:
Pb(s) | $PbSO_4$(s) | H_2SO_4(aq) | $PbSO_4$(s) | PbO_2(s) | (Pb(s))
Determine the equations of the reactions at both electrodes.
Answers: Pb + HSO_4^- → $PbSO_4$ + H^+ + 2 e^-. Then PbO_2 + 3 H^+ + HSO_4^- + 2 e^- → $PbSO_4$ + 2 H_2O.

IV-3-2. A lithium storage cell is described by the scheme:
Li(s) | Li^+- ceramic electrolyte | $LiMn_2O_4$(s)
The end product is $Li_2Mn_2O_4$. Determine the equations of reactions at both electrodes.
Answer. Cathode : Li^+ + e^- + $LiMn_2O_4$ → $Li_2Mn_2O_4$.

IV-3-3. $LiMn_2O_4$ has a spinel structure: the oxide ions make up a face-centered cubic lattice. The Li^+ ions occupy the tetrahedral gaps, and the Mn ions occupy the octahedral gaps. Half Mn ions are Mn(III) and half Mn(IV). Determine the coordination numbers of Li and Mn in the spinel structure of $LiMn_2O_4$.
Answer. Li 4, Mn 6.

IV-3-4. A typical car weighs 1000 kg, has a 50 l tank weighing 10 kg, and needs 5 kwh or 3.78 kg gas (5 l) to drive 50 km. Calculate the mass change produced by the replacement of the gas tank by a) a lead storage cell; b) a lithium cell.
Answer. 1063 kg.

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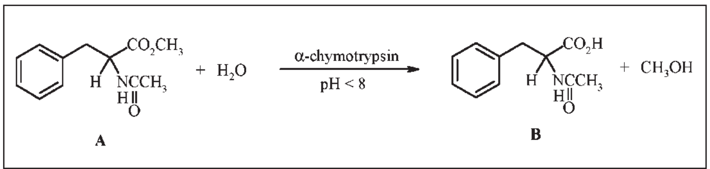
Practical Tasks

Practical Task 1. Kinetics of an Enzymatic Ester Hydrolysis

The ester **A** to be used is methyl N-acetyl-phenylalaninate. But its exact structure is of no use for the rest of the problem. In the presence of an enzyme called chymotrypsine, this ester **A** is hydrolyzed and produces an acid **B** which can be titrated by NaOH.

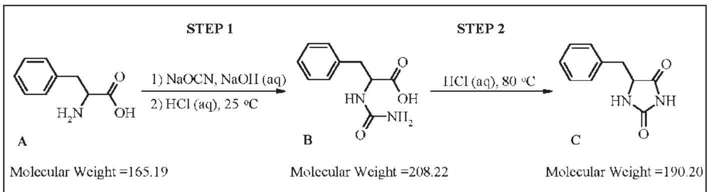


The reaction starts when 0.05 g of enzyme (dissolved in 10 ml of water) is introduced into a solution of the ester **A** (0.5 g in 2.5 ml of methanol) containing also propyl red, as indicator (red at pH < 5, and yellow at pH > 7).

When the yellow reaction mixture turns pink, time is written down, and 0.1M NaOH is immediately added until the color changes to lemon yellow. Later on, new NaOH is added, each time the salmon-pink color re-appears. This amount should just restore the pale yellow color. This procedure is repeated for 75 min. The total volume of the NaOH solution is recorded at time intervals of approximately 5 min. The total volume of NaOH, plotted *versus* time, visualizes the kinetics of the reaction.

Practical Task 2. Conversion of Phenylalanine to Benzylhydantoin

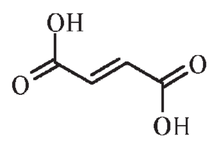
In this experiment natural (*S*)-phenylalanine **A** is converted in two steps into benzylhydantoin **C**.



0.5 g (*S*)-phenylalanine A, 0.3 g sodium cyanate, 0.3 ml water, 2 drops of 1M NaOH are heated for 30 min. to 80 °C. The resulting solution is cooled to room temperature and acidified by HCl to pH <3. The white precipitate B is then filtered off, mixed with 3 ml of 4M HCl and heated for 30 min to 80 °C. A clear solution is obtained. After cooling down to room temperature, the obtained suspension is filtered and C is dried, weighed and subjected to TLC analysis. The melting point of the benzylhydantoin is determined by an automatic melting point apparatus.

Practical Task 3. Determination of Iron in a Pill

The pill to be examined contains iron(II) fumarate and binding agents. The structure of fumaric acid is:



Fumaric acid

The pill is weighed, then dissolved in 5 ml of 4M HCl at 60 °C. The yellow solution is filtered, then transferred into a volumetric flask (250 ml) and the final volume adjusted by adding water. Then 10 ml are transferred into a volumetric flask of 100 ml containing 1,10-phenanthroline solution (10 ml) and hydroxylammonium chloride solution (1 ml). Then the volume is adjusted with a buffer solution (pH 8). The amount of iron is obtained from the absorbance of the solution at 510 nm, where the extinction coefficient for the iron(II)phenanthroline complex is 11100 $M^{-1}cm^{-1}$.

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