Name:	Student Code:

34th International Chemistry Olympiad

Groningen, Wednesday, 10 July 2002

Theoretical Examination

Chemistry and the Quality of Life go Hand in Hand

Theme I Chemistry of Life

I-1 Oxygen in Your Life
I-2 Nitrogen Cycle in Nature

Theme II Chemistry of Industrial Relevance

II-1 Inulin, a New Renewable Raw Material
II-2 Production of Methanol
II-3 Aramids, High-Performance Polymeric Materials

Theme III Chemistry of Functional Molecules in Nature

III-1 Phospholipids in Membranes
III-2 Glutathione, an Essential Mini-Peptide

Theme IV Chemistry Related to Light and Energy

IV-1 Lighting Lamps
IV-2 Red Ruby
IV-3 Vehicle Traction Batteries

Name:	Student Code:

- Write your name and student code (posted at your station) on all the pages of the theoretical examination.
- You have 5 hours to complete all the tasks and record your results in the answer boxes, you must stop your work immediately after the STOP command is given. A delay in doing this by 3 minutes will lead to cancellation of the current task and will result in zero points for the task.
- All results must be written in the appropriate boxes on the pages. Anything written elsewhere will not be marked. Do not write anything on the back of your answer sheets. If you need additional sheets or a replacement sheet, request it from the supervisor.
- For a sanitary stop: ask your supervisor for permission.
- When you have finished the examination, you must put all of your papers into the envelope provided, then you must seal the envelope. Only papers in the sealed envelope will be marked.
- A receipt will be issued for your sealed envelope. Do not leave the examination room until you are directed to do so.
- Use only the pen and calculator provided.
- A copy of the Periodic Table of the Elements is provided.
- This examination paper has 31 pages of problems including answer boxes.
- An official English-language version is available only on request.

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Theme 1 - Chemistry of Life

Life runs on chemistry. Understanding and monitoring life processes receive much attention in chemistry.

Problem I-1 Oxygen in Your Life — Score: 6 points

	1	2	3	4	5
Marks	**25**	**25**	**15**	**25**	**10**

Oxygen is of vital importance for all of us. Oxygen enters the body via the lungs and is transported to the tissues in our body by blood. There it can deliver energy by the oxidation of sugars:

$$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O$$

This reaction releases 400 kJ of energy per mol of oxygen. O_2 uptake by blood is at four heme (Hm) groups in the protein hemoglobin (Hb).
Free Hm consists of an Fe^{2+} ion attached to four N atoms of a porphyrin^{2-} ligand. Oxygen can bind at the coordination site of Fe^{2+} giving a $Hm{\cdot}O_2$ complex. Carbon monoxide can be complexed similarly, giving a Hm·CO complex. CO is a poison as it binds more strongly to Hm than O_2 does. The equilibrium constant K_1 for the reaction:

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

is 10000 times larger than the equilibrium constant K_2 for the reaction:

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

Each Hb molecule can take up four molecules of O_2. Blood in contact with O_2 absorbs a fraction of this amount, depending on the oxygen pressure, as shown in Figure 1 (curve 1). Also shown are the curves (2) and (3) for blood with two kinds of deficient Hb. These occur in patients with certain hereditary diseases.

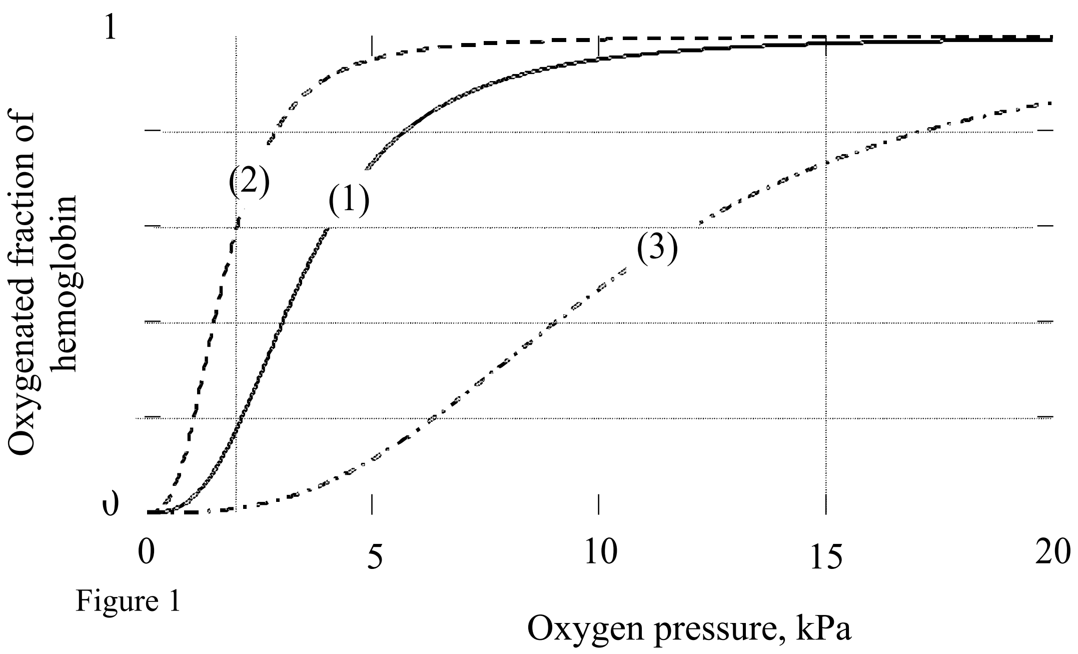

Figure 1

Relevant data: O_2 pressure in lungs is 15 kPa; in the muscles it is 2 kPa. The maximum flow of blood through heart and lungs is 4 _ 10^{-4} m^3 s^{-1}. The red cells in blood occupy 40% of the blood volume; inside the cells the concentration of Hb is 340 kg m^{-3}; Hb has a molar mass of 64 kg mol^{-1}. R = 8.314 J mol^{-1} K^{-1}. T = 298 K.

I-1-1 Using the relation between K and the standard Gibbs energy ΔG^0 for a reaction, calculate the difference between the ΔG^0 values for the heme reactions (1) and (2).

Answer:

Calculation:

I-1-2 Estimate from Figure 1 (to 2 significant figures) how many moles of O_2 are deposited in muscle tissue when one mole of Hb travels from the lungs to the muscles and back again for the three different types of Hb.

Hb type 1:

Hb type 2:

Hb type 3:

I-1-3 The special S-shaped uptake curve 1 is the result of subtle structural features of Hb. The deficient Hb shown in curve 2 is not optimal because:

- ☐ The binding with O_2 is too weak.
- ☐ The binding with O_2 is too strong.
- ☐ The maximum oxygen capacity is too low.
- ☐ The deficiency is caused by carbon monoxide poisoning.

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I-1-4 Calculate how much oxygen (in mol s^{-1}) can be deposited in tissue by blood with normal Hb (1).

Answer:

Calculation:

I-1-5 Calculate the maximum power that the body can produce (assuming it is limited by oxygen transfer).

Answer:

Calculation:

Problem I-2 Nitrogen Cycle in Nature

Score: 7 points

	1	2	3	4	5
Marks	**15**	**15**	**20**	**25**	**25**

Ammonia is a toxic substance to marine animals at levels exceeding 1 ppm. Nitrifying bacteria play an important role in the conversion of NH_3 first to nitrite and then to nitrate, the storage form of nitrogen in the soil.

$$NH_3 + 2\,O_2 + NADH \xrightarrow[\textit{bacteria}]{\textit{Nitrosomonas}} NO_2^- + 2\,H_2O + NAD^+$$

NADH is the biochemical reducing agent of the coenzyme nicotinamide dinucleotide (NAD), NAD^+ is the oxidized form of the coenzyme NAD.

$$2\,NO_2^- + O_2 \xrightarrow[\textit{bacteria}]{\textit{Nitrobacter}} 2\,NO_3^-$$

I-2-1 Give the oxidation states of N in the following series: (Use the boxes below the compounds)

$$NH_3 \longrightarrow NO_2^- \longrightarrow NO_3^-$$

The spectrophotometric analysis of nitrite is based on a reaction with an indicator. The coloured product then obtained has an absorbance maximum at λ = 543 nm.

For quantitative analyses a calibration curve has to be made, in which absorbance at the maximum absorbance wavelength λ = 543 nm is plotted against nitrite concentration in a series of standards.

I-2-2 The measurements are performed at the wavelength with the maximal absorbance because:

- ❑ There is no interference of impurities
- ❑ There is no contribution of stray light
- ❑ There is optimal accuracy of the measurement
- ❑ None of these statements

Mark the correct answer.

The absorption is measured with a single beam spectrophotometer. However 5% of the light, the so-called stray light I_s, strikes the detector directly (see Figure 2).

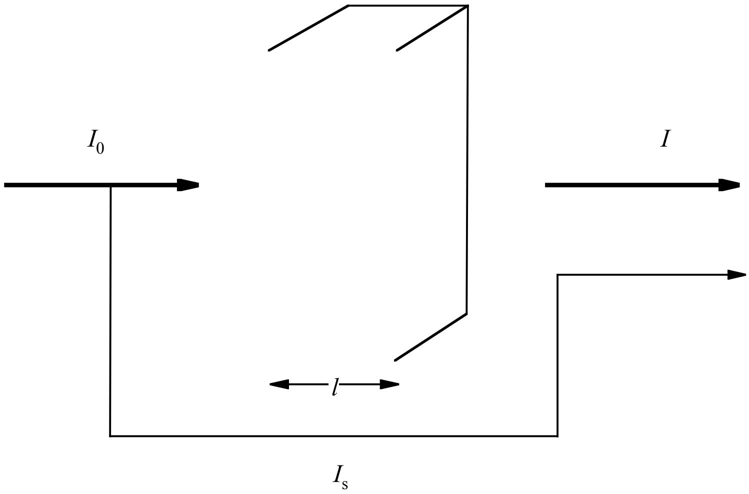

Figure 2

I-2-3 Calculate the value of the absorbance A shown by the spectrophotometer if $\varepsilon = 6000\ M^{-1}\ cm^{-1}$, $l = 1$ cm and $c = 1$ _ 10^{-4} M

Answer:

Calculation:

For a nitrite determination in water the following data have been measured.

concentration of nitrite nitrogen (ppm)	absorbance at 543 nm (1.000 cm cuvet)
blank	0.003 (due to impurities in the solvent)
0.915	0.167
1.830	0.328

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I-2-4 Determine from the data given above, using the values corrected for the solvent impurities, the slope *m* and the intercept *b* of the calibration curve $A = m\,c + b$.

Answer:

Calculation of *m*:

Calculation of *b*:

\The duplicate analyses of a water sample are given below. The measurements have been performed at a wavelength of 543 nm and in a 2.000 cm cuvet.

water sample	absorbance
analysis 1	0.562
analysis 2	0.554

For the calculation of the concentration of the nitrite nitrogen (c in ppm) the equation obtained by the method of least squares

corrected absorbance = $0.1769\,c + 0.0015$

may be applied, using the measurements in a 1.000 cm cuvet.

I-2-5 Calculate the average nitrite nitrogen concentration in ppm and $\mu g\ mL^{-1}$. Hint: Take the blank from problem I-2-4.

Answer:

Calculation:

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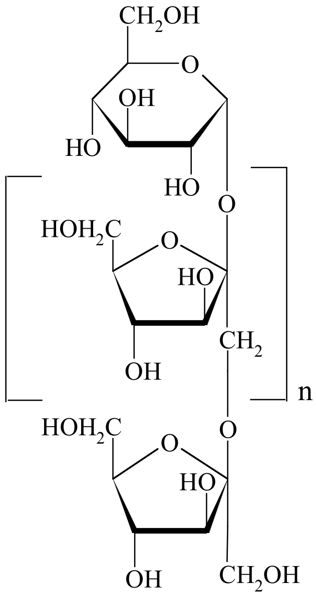
Theme II - Chemistry of Industrial Relevance

In our daily life we use many products that are produced on an industrial scale. Mastering the underlying chemistry is at the heart of this business.

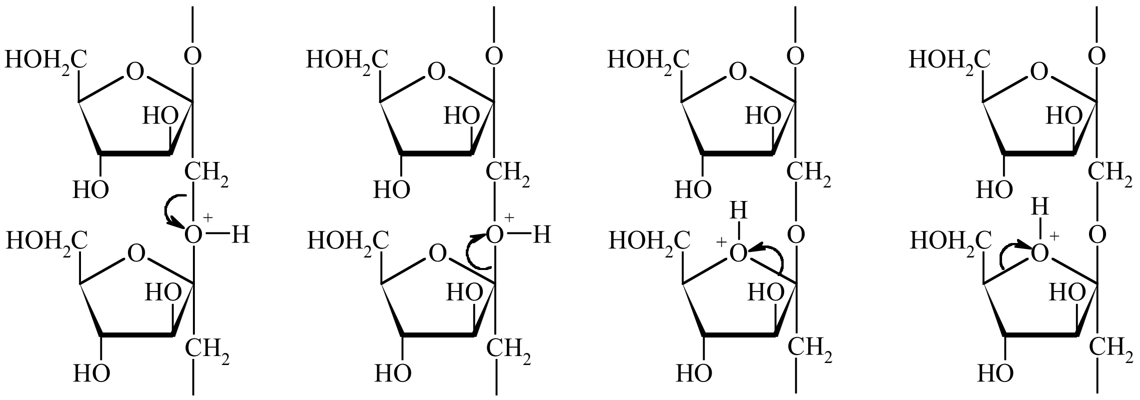
Problem II-1 Inulin, a New Renewable Raw Material Score: 6 points

	1	2	3	4	5
Marks	**15**	**15**	**30**	**10**	**30**



Inulin, which is produced from chicory roots in Belgium and The Netherlands, is used as a food additive as it has a beneficial effect on the intestinal flora. It is also used as source of fructose which is 1.9 times sweeter than sucrose, and for the production of mannitol which is used in chewing gum. Inulin is a linear polymer of fructose units with a glucose unit at one end; its Haworth projection formula is shown at the left. In this problem inulin has 10 fructose units (n = 9).

II-1-1 Inulin may be hydrolyzed under H^+-catalysis conditions. Of the four options below (**A**, **B**, **C** and **D**) indicate which C-O bond cleavage is most likely to occur.



A **B** **C** **D**

☐

Mark the correct cleavage mechanism for the most efficient hydrolysis.

Hydrolysis with isotopically labelled water can provide information about the mechanism of hydrolysis using modern NMR techniques, which can "see" deuterium (^2H) and the oxygen isotope ^{17}O.

II-1-2 Indicate which labelled water can **best** be used for this purpose. Mark the correct answer.

- ☐ ^2H_2O
- ☐ $H_2{}^{17}O$
- ☐ $^2H_2{}^{17}O$
- ☐ None of them.

Upon catalytic hydrogenation glucose gives sorbitol (**S**), whilst fructose (**F**) gives mannitol (**M**) and sorbitol (**S**).

II-1-3 Draw the Fischer projections of fructose (**F**), sorbitol (**S**) and mannitol (**M**).

$\longrightarrow$ +

F **S** **M**

1.00 Mole of inulin in 2.00 kg of water with added catalysts, is subjected to hydrolysis and hydrogenation at 95 °C in a one step process. The selectivity of the hydrogenation of fructose to mannitol / sorbitol is 7 / 3.

II-1-4 How many moles of mannitol and sorbitol are obtained?

M: **S**:

After completion of the reactions the catalysts are removed and the reaction mixture is cooled to 25 °C. The solubility of **M** is 0.40 mol kg^{-1} in water at 25 °C and the solubility of **S** is so high that it will not precipitate.

II-1-5 Calculate how many moles of **M** will precipitate.

Answer: Calculation:

Name:	Student Code:

Problem II-2 Production of Methanol Score: 6 points

	1	2	3	4	5
Marks	**15**	**20**	**15**	**25**	**25**

Methanol (CH_3OH) is a chemical that is used for the production of additives in gasoline and many common plastics. A factory, producing methanol, is based on the reaction:

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

Hydrogen and CO are obtained by the reaction:

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

The three units of the factory, namely, the "reformer" for the hydrogen / carbon monoxide production, the "methanol reactor" and a "separator" to separate methanol from CO and H_2, are schematically shown in Figure 1. Four positions are indicated by α, β, γ and δ.

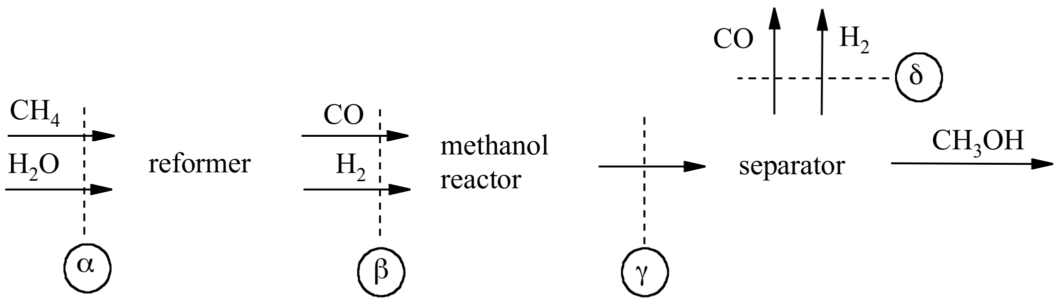


Figure 1

The flow of methanol at position γ is n [CH_3OH, γ] = 1000 mol s^{-1}. The factory is so designed that 2/3 of the CO is converted to methanol. Excess CO and H_2 at position δ are used to heat the first reactor. Assume that the reformer reaction goes to completion.

II-2-1 Calculate the flow of CO and H_2 at position β.

II-2-2 Calculate the flow of CO and H_2 at position γ.

II-2-3 Calculate the flows of CH_4 and H_2O needed at position α.

II-2-4 At point γ all species are gases. Calculate the partial pressures in MPa for CO, H_2 and CH_3OH at position γ using the equation:

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

wherein n_i is the flow and p_i the partial pressure of the compound i, n_{tot} is the total flow at the position considered, and p the total pressure in the system. (p = 10 MPa)

Answer *p*[CO, γ]: Answer *p*[H_2, γ]: Calculations:

When the methanol reactor is large enough the reaction goes to equilibrium. The partial pressures at point γ obey the equation:

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

wherein p_0 is a constant (0.1 MPa) and K_p is a function of temperature as is shown in Figure 2 (the vertical scale is logarithmic).

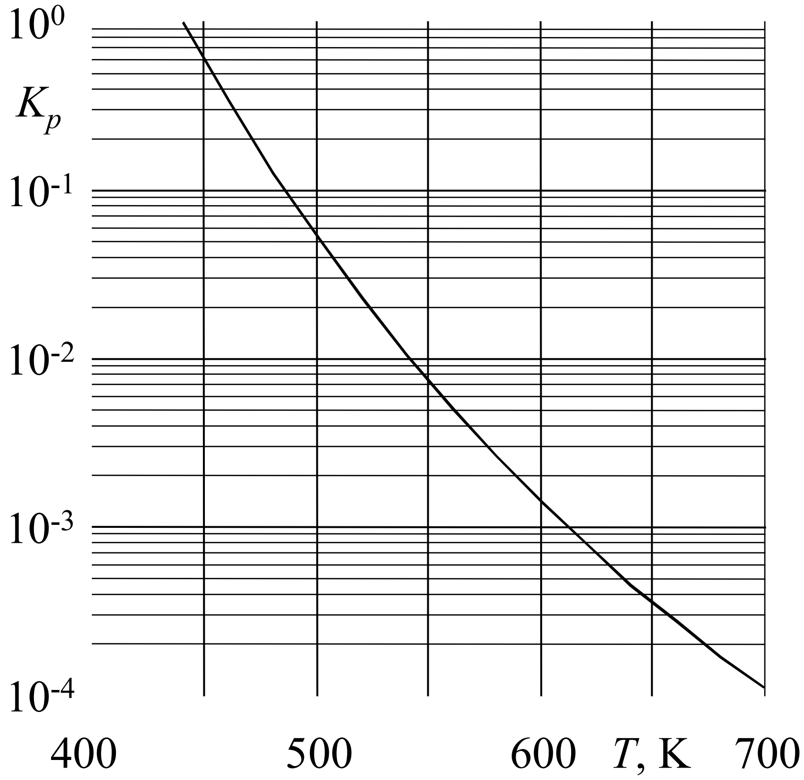


Figure 2

II-2-5 Calculate K_p and indicate at which temperature T the reaction must be operated to achieve this equilibrium.

Answer K_p:

Answer T_γ:

Calculation:

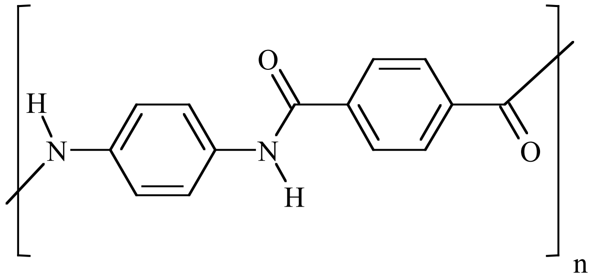
Name:	Student Code:

Problem II-3 Aramids, High-Performance Polymeric Materials

Score: 6 points

	1	2	3	4
Marks	**20**	**30**	**25**	**25**

Aromatic polyamides (aramids) are high strength, high performance polymer fibers that find use in composite materials, bullet-proof vests, high quality skis, safety helmets, etc. Aramid PPTA is marketed under the names Kevlar® (DuPont) and Twaron® (Teijin), and amongst others manufactured in the north of The Netherlands. The PPTA chains are neatly packed into fibers with a sheet type structure.



PPTA

II-3-1 Draw the structure of these sheets (three chains suffice).

For a polymerisation of equimolar amounts of two monomers the average chain length is $\overline{P}_n$, the degree of conversion is p, which equals the fraction of functional groups that have reacted, the total number of chains is N_t and the total initial number of monomers is U_0.

Assuming that the polymerization equilibrium can fully be described by:

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

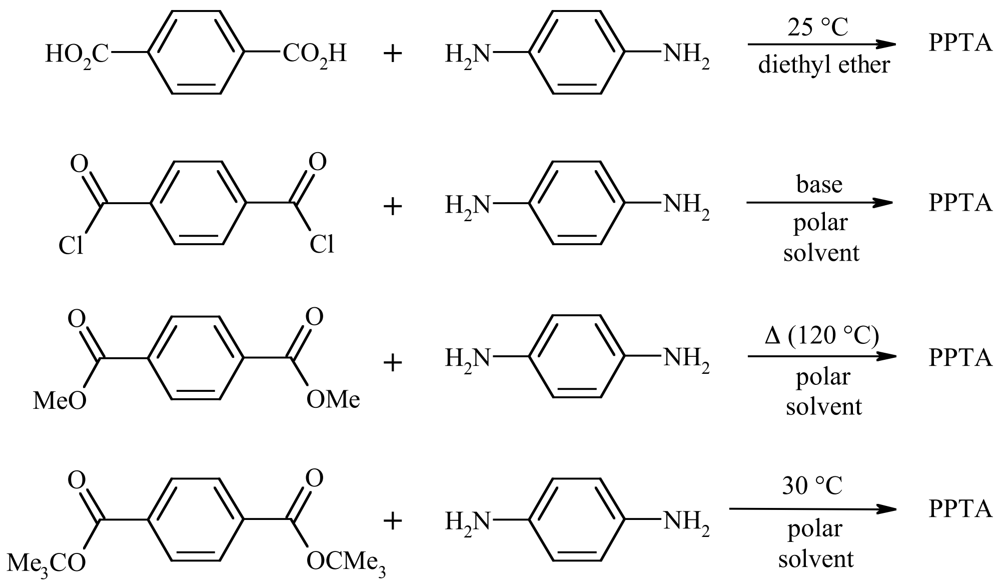
Where C stands for any $-CO_2$ group, A stands for any $-NH_2$ group and Am stands for any amide group.

II-3-2 Calculate the degree of conversion needed to obtain an average chain length of 500.

Answer:

Calculation:

II-3-3 For the synthesis of PPTA the following possibilities are considered. Which of the following reactions will work? Mark the correct answer(s).



II-3-4 Another type of aramid can be produced from 4-aminobenzoic acid (4-aminobenzene-carboxylic acid) by heating.

(a) Give the structure of this aramid (n = 4)

(b) Calculate the average chain length at equilibrium (reaction is carried out in a closed vessel). The equilibrium constant $K = 576$.

Answer: $\overline{P}_n$ =

Calculation:

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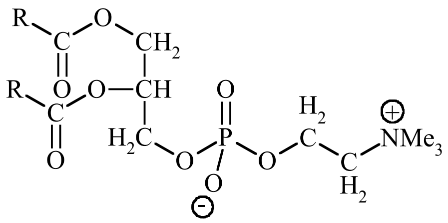
Theme III - Chemistry of Functional Molecules in Nature

A challenge in chemistry is to discover what nature does and how the structures of biologically active molecules are related to what they do.

Problem III-1 Phospholipids in Membranes — Score: 6 points

	1	2	3	4	5
Marks	**20**	**20**	**20**	**20**	**20**

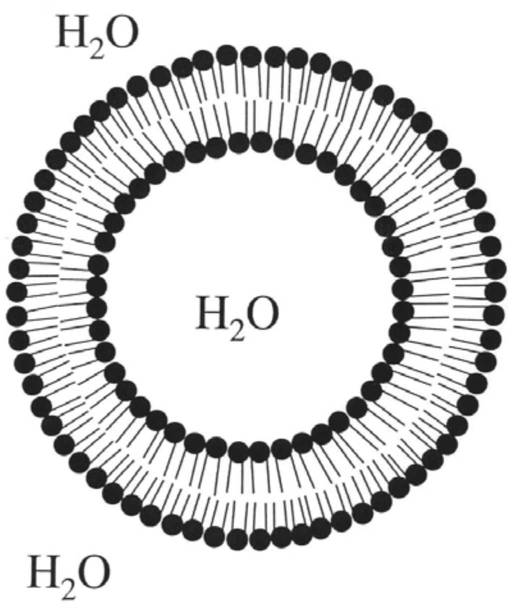
Biological cell membranes are complex, functional, non-covalent molecular assemblies, largely consisting of lipids and proteins. Their function is of vital importance for life processes. They separate the cell from its environment and also determine the specific flow of information between the cell contents and the environment. Phospholipids are among the most important components of cell membranes. An example is compound **A**.

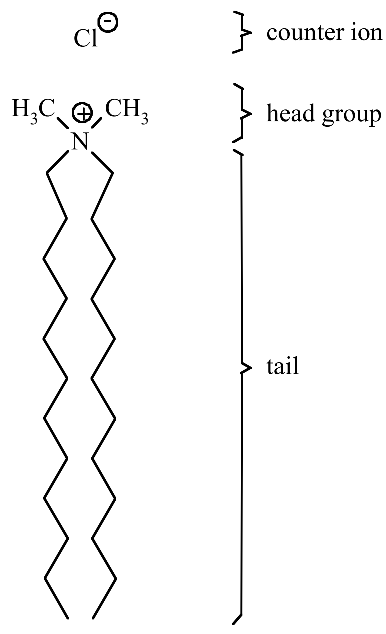


A

R = n-$C_{17}H_{35}$

Upon dispersion in water (above a low critical concentration) compound **A** forms closed bilayer structures, called liposomes, which are employed as model compounds for aspects of the chemistry of the structurally much more complex cell membranes. Liposomes are globular aggregates with the polar or ionic head groups in contact with water and with the alkyl tails sequestered in a hydrophobic core. The bilayer structure encloses an aqueous inner compartment.
Double-tailed *synthetic* surfactants also form closed bilayer assemblies similar to liposomes but now called vesicles. An example is di-n-dodecyldimethylammonium chloride (**DDAC**).

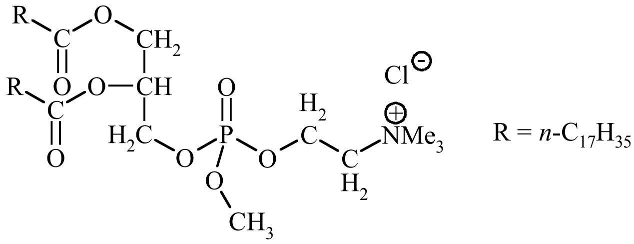




DDAC

III-1-1 **(a)** How many stereoisomers are possible for compound **A**?

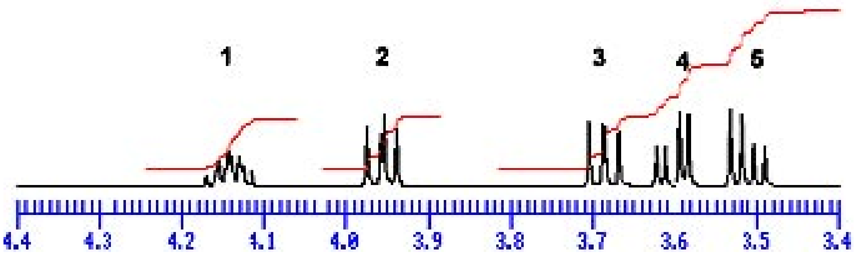
(b) How many stereoisomers are possible for the trialkylphosphate **B**?

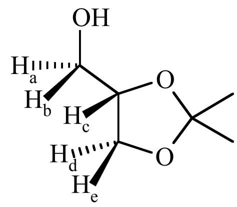


B

A precursor for the synthesis of compound **A** is the acetonide **C** derived from glycerol. Part of the ^{1}H-NMR spectrum of compound **C** is shown below.

III-1-2 Which signal number in the ^{1}H-NMR spectrum corresponds to proton $\mathbf{H_c}$?





C

$\mathbf{H_c}$ =

The bilayer of a liposome can be characterized by V (the volume of the hydrocarbon chains), a_0 (optimal cross-sectional surface area of the head groups of the phospholipid in the aggregate) and l_c (the maximum chain length that the alkyl group can assume). A good approximation for unbranched alkyl tails containing n carbon atoms yields:

$V = (27.4 + 26.99\ n) \times 10^{-3}\ \text{nm}^3$

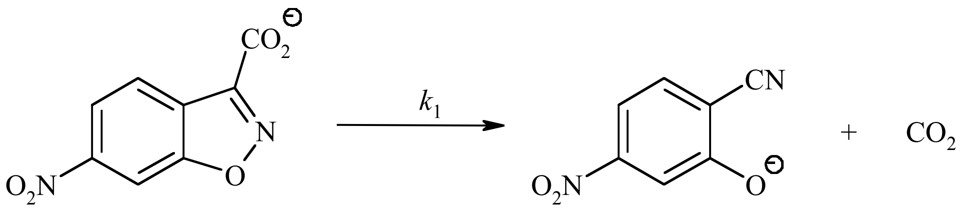
$l_c = (0.154 + 0.1265\ n)$ nm

For very large n values, the intertail interactions dominate over the head group repulsions.

III-1-3 Calculate the minimum cross-sectional surface area of the head groups for such very large *n* values.

Answer: Calculation:

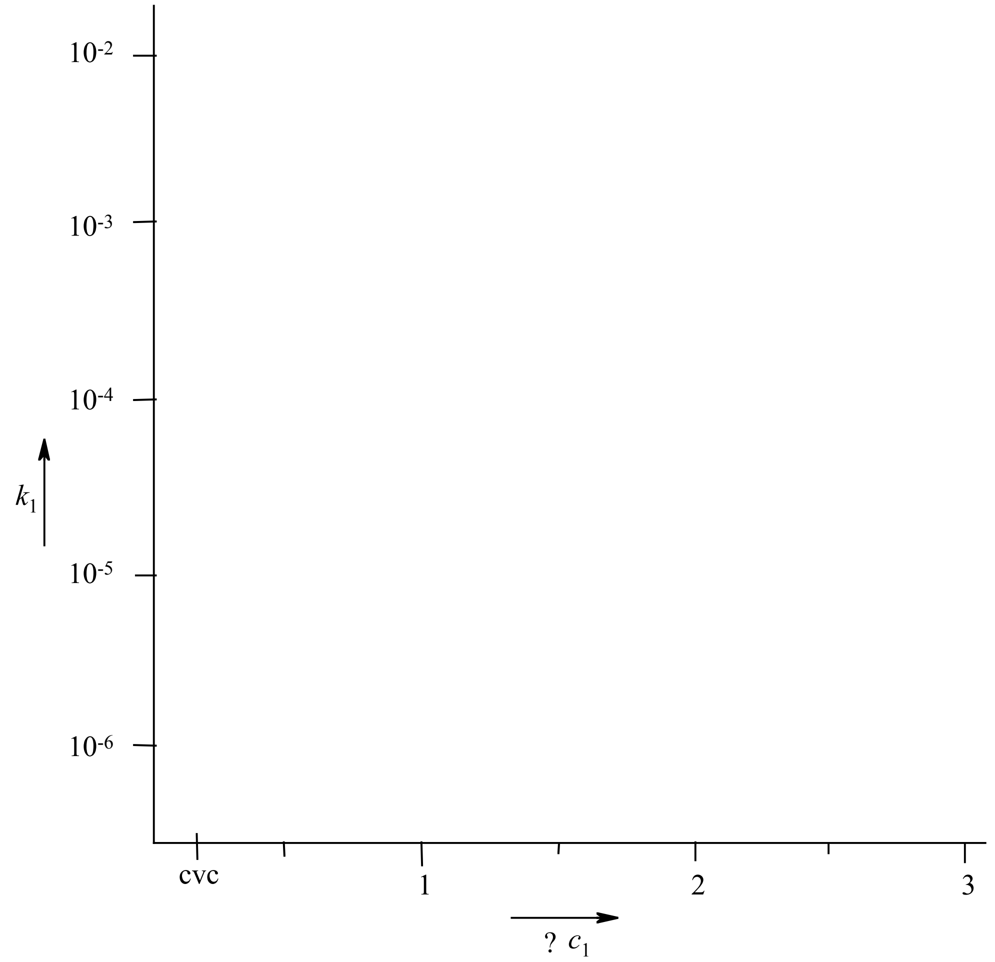
Vesicles formed from **DDAC** (above its critical vesicle concentration, cvc) catalyse the unimolecular decarboxylation of 6-nitro-benzisoxazole-3-carboxylate (**6-NBIC**).



6-NBIC

In water at 25 ºC k_1 = 3.1 _ 10^{-6} s^{-1}. At the concentration c_1 of **DDAC** at which **6-NBIC** becomes fully bound to the vesicles, k_1 = 2.1 _ 10^{-3} s^{-1}.

III-1-4 Sketch a plot of k_1 vs. [**DDAC**] for [**DDAC**] = 0 → 3 c_1.



III-1-5 The main reason for the efficient catalysis of the decarboxylation of **6-NBIC** by **DDAC** vesicles is:

- ❑ The decarboxylation is catalysed by the Cl^- ions bound to the surface of the vesicles.
- ❑ Efficient loss of hydration of the carboxylate group of vesicle-bound 6-NBIC.
- ❑ Strong binding of CO_2 in the interior of the vesicle.
- ❑ Strong binding of the organic reaction product to the vesicles relative to that of 6-NBIC.

Mark the correct answer.

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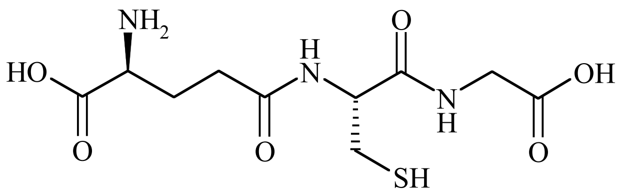
Problem III-2 Glutathione, an Essential Mini-Peptide Score: 6 points

	1a	1b	2a	2b	2c	3
Marks	**10**	**24**	**18**	**8**	**25**	**15**

Glutathione, abbreviated as GSH, is a small peptide that is present in almost all tissues of animals. GSH fulfils important biological functions, such as detoxification of electrophilic chemicals and reduction of (organic) peroxides in blood. An electrophilic compound reacts irreversibly with GSH, especially in the liver, to give a primary product that is converted by a series of biotransformations into a so-called *mercapturic acid*, which is excreted via the urine. Oxidants react with GSH to give the disulfide GSSG, which can be enzymatically reverted to GSH with reductases. The ratio GSH/GSSG in most cells is ≥ 500.



GSH

III-2-1 **(a)** How many amino acid residues are present in GSH?

(b) Draw the structures of the corresponding amino acids and mark the chiral centers with an asterisk.

A mercapturic acid **A** isolated from urine of a person who has been exposed to acrylonitrile ($H_2C=CH-CN$) has the molecular formula $C_8H_{12}N_2O_3S$. The ^{1}H-NMR spectrum of **A** in $(CD_3)_2SO$ is shown in Figure 1. When the product is pretreated with D_2O, the signals at δ 12.8 and δ 6.8 are no longer present and the signal 3 is simplified.

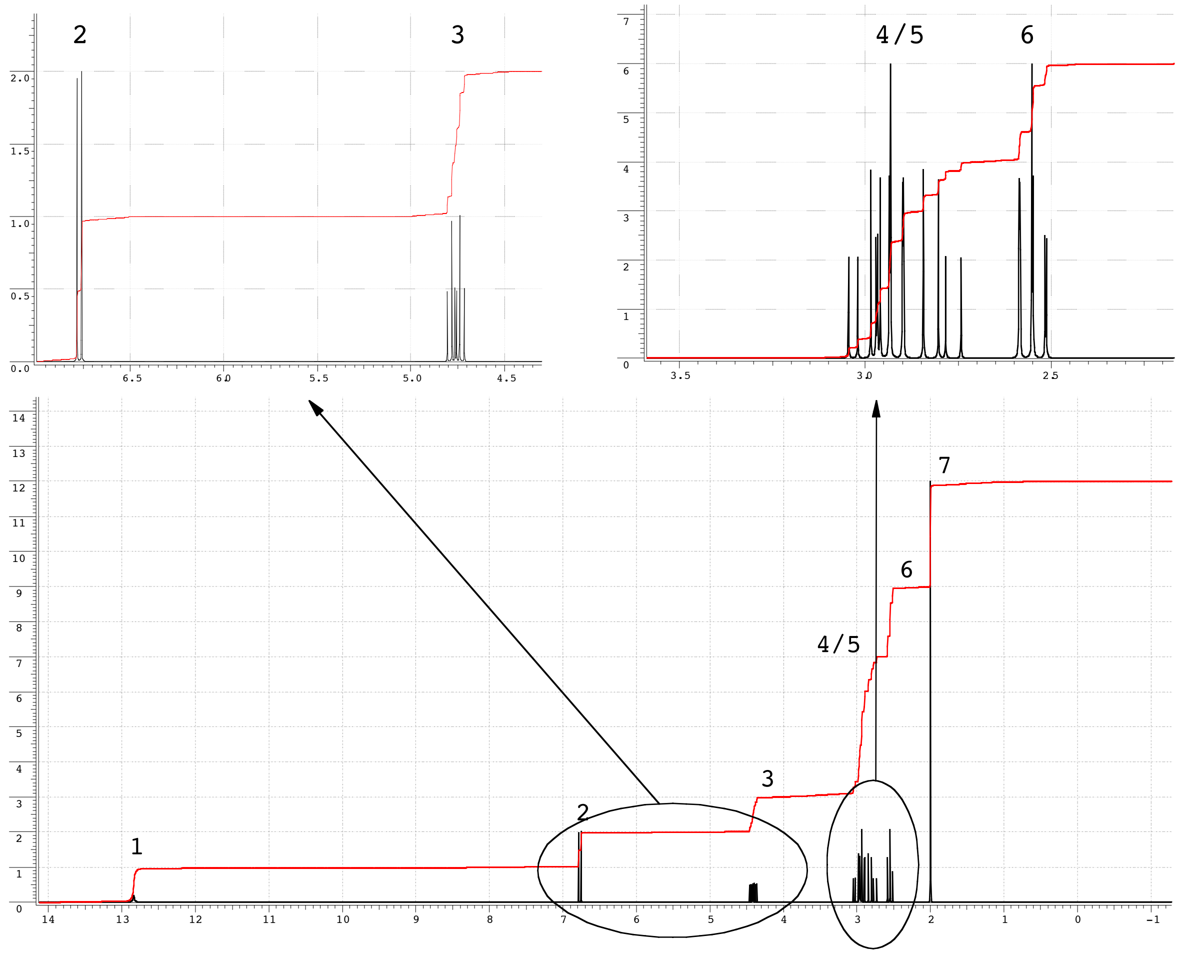


Figure 1

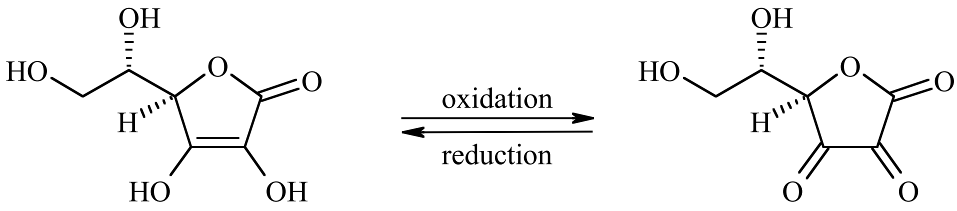
III-2-2 **(a)** The NMR-signals correspond with protons in the following groups: CH, CH_2, CH_3, OH and NH. Indicate the appropriate proton group in the boxes for the signals 1-7.

Signals	1	2	3	4/5	6	7
Protons						

(b) How many carbon atoms are present in compound **A** that do not carry any protons?

(c) Draw the structure of compound **A**.

Vitamin C (ascorbic acid) reacts with oxidants to give dehydroascorbic acid **D**



vitamin C **D**

III-2-3 Eating fresh fruit and vegetables is healthy

- ❑ because vitamin C forms a complex with GSH.
- ❑ because vitamin C reacts with electrophilic compounds.
- ❑ because vitamin C removes oxidants and prevents undesired depletion of GSH.
- ❑ for many reasons, but none of them has anything to do with GSH.

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Theme IV - Chemistry Related to Light and Energy

Chemistry plays a major role in meeting our needs of light and energy. Our life is unthinkable without artificial light and energy for mobility.

Problem IV-1 Lighting Lamps — Score: 7 points

	1	2	3	4	5
Marks	**10**	**25**	**25**	**35**	**5**

Since 1891 lighting lamps have been manufactured in The Netherlands. The improvement today in comparison to the first lamp is enormous, especially with the introduction of the gas discharge lamps. The life-time has increased by orders of magnitude. The colour is also an important aspect. Rare earth metal compounds like $CeBr_3$ are now included to reach a colour temperature of 6000 K in the lamp. These compounds are ionic solids at room temperature, and upon heating they sublime partially to give a vapour of neutral metal halide molecules. To achieve a high vapour pressure, the sublimation enthalpy should be as low as possible.

IV-1-1 Give a thermochemical cycle (Law of Hess) for sublimation of $CeBr_3$, via a vapour of mononuclear ions. ($H_l = H_{lattice}$; $H_e = H_{electrostatic}$; $H_s = H_{sublimation}$;H is not absolute, H means ΔH)

$-H_l$ → +

+ $+H_e$ →

+

$+H_s$ → ; $H_s = -H_l + H_e$

The lattice energy of the solid can be calculated using the Born–Landé formula:

$$H_l = f\frac{Z_+ Z_- A e^2}{r_+ + r_-}\left(1 - \frac{1}{n}\right)$$

The factor fe^2 (necessary in order to calculate the lattice energy in kJ mol^{-1}) amounts to 139 when the ionic radii are substituted in nm. The Madelung constant A for the lattice is 2.985. The Born exponent n is 11. The charges of the ions Z_+ and Z_- are integer numbers (Z_- is negative) . For the calculation of the energy of gaseous $CeBr_3$ (when formed from ions) the same Born-Landé formula can be used without A. The structure of $CeBr_3$ in the gas phase is planar triangular. The radius of Ce^{3+} is 0.115 nm and of Br^- is 0.182 nm.

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IV-1-2 Calculate the enthalpy of sublimation of $CeBr_3$ (in integers; be aware of the signs!)

Answer:

Calculation:

Attempts to make a better lamp have been undertaken by adding a stoichiometric amount of CsBr to the $CeBr_3$ in the lamp leading at room temperature to solid $CsCeBr_4$. When the sublimation temperature decreases the life time of the lamp will increase likewise. The $CsCeBr_4$ lattice has a NaCl structure with Cs^+ as cations and tetrahedral $CeBr_4^-$ as complex anions. Sublimation of $CsCeBr_4$ leads to a vapour of CsBr and $CeBr_3$ molecules.

IV-1-3 Give the reaction equations of the thermochemical cycle (Law of Hess) for this process in which some steps involve $CeBr_4^-$ ions, mononuclear ions and/or neutral molecules in the gas phase.

Step 1: $\xrightarrow{+H_1}$ +

Step 2: + $\xrightarrow{+H_2}$

Step 3: + $\xrightarrow{+H_3}$

Step 4: + $\xrightarrow{+H_4}$

+

Total: $(CsCeBr_4)_{lattice} \xrightarrow{+H_{total}} (CeBr_3)_{molecule} + (CsBr)_{molecule}$

IV-1-4 Calculate the enthalpy of sublimation of $CsCeBr_4$ (in integers). Use the Born–Landé formula for all steps in the process and report the separate energies also (be aware of the signs!). The Madelung constant for NaCl is 1.75. The Cs–Ce distance in the lattice is 0.617 nm. The $CeBr_4^-$ anion is a tetrahedron in which the ratio between the edge and the distance between a corner of the tetrahedron and the centre of gravity (body-radius) amounts to $(2\sqrt{6})/3 = 1.633$. The Born exponent of CsBr is 11. The radius of Cs^+ is 0.181 nm.

Answer Step 1: H_1 =

Calculation:

Answer Step 2: H_2 =

Calculation:

Answer Step 3: H_3 =

Calculation:

Answer Step 4: H_4 =

Calculation:

Answer total sum: H_{total} =

Calculation:

IV-1-5 Conclusion in relation to the previous answers: Was adding CsBr a good idea? Mark the correct answer.

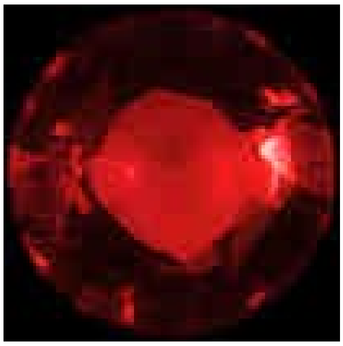
- ❑ Adding CsBr is counterproductive
- ❑ Adding CsBr has no influence
- ❑ Adding CsBr is advantageous
- ❑ From these data no clear answer can be given

Name:	**Student Code:**

Problem IV-2 Red Ruby **Score: 5 points**

	1	2	3	4	5
Marks	**20**	**20**	**20**	**20**	**20**

Ruby crystals have a deep red colour and are well known for their use in jewellery. Not many people know that the heart of the first laser, built in 1960 by Maiman, was a big ruby crystal. The red colour of ruby originates from the absorption of light by Cr^{3+} ions that are incorporated in colourless aluminium oxide (Al_2O_3) crystals. The Cr^{3+} ion has 3 electrons in the 3*d* shell and the absorption of light is due to electronic transitions between 3*d* orbitals of lower and higher energy.



N.B.: A colour picture of the ruby crystal is shown in the Appendix.

IV-2-1 Indicate which of the four absorption spectra belongs to ruby.

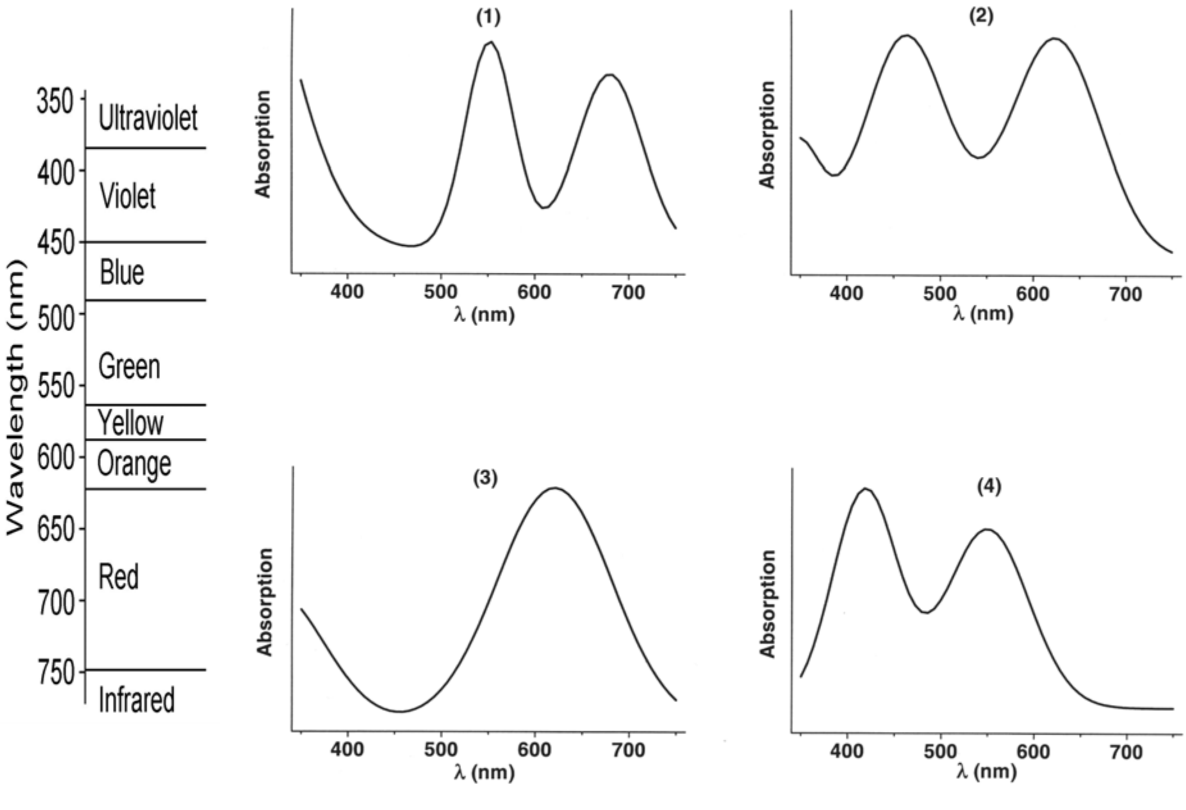


Figure 1

The rod used in ruby lasers is a cylinder with a length of 15.2 cm and a diameter of 1.15 cm. The amount of Cr^{3+} ions is 0.050 mass%. The density of Al_2O_3 is 4.05 g cm^{-3}. The atomic mass of Cr = 52u. (1u=1.67 _ 10^{-27} kg).

Name: **Student Code:**

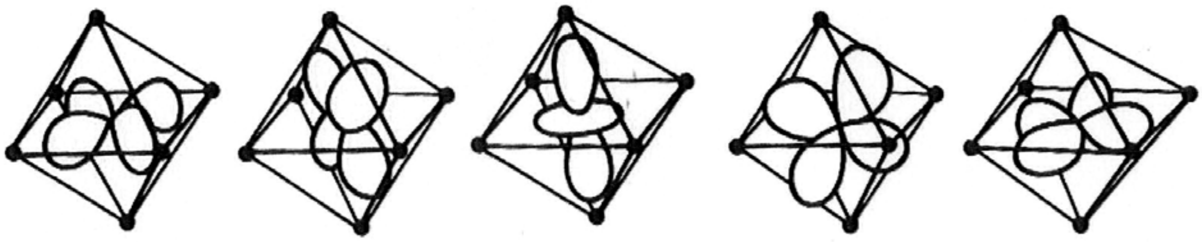
IV-2-2 Calculate how many Cr^{3+} ions are in this laser rod.

Answer:

Calculation:

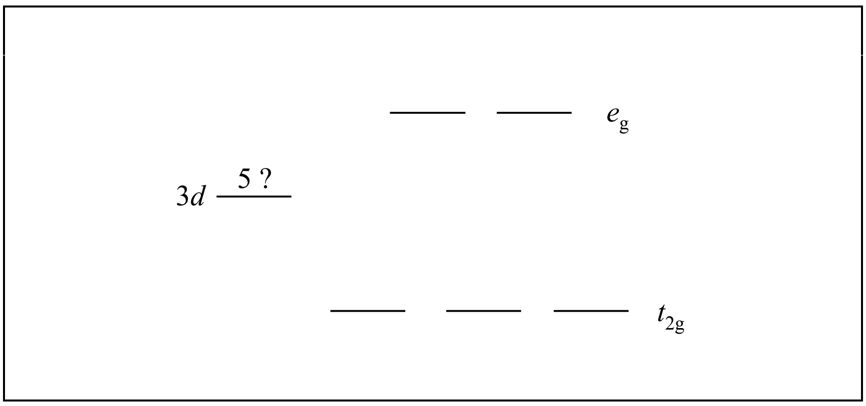
In rubies the Cr^{3+} ions are coordinated by an octahedron of 6 oxygen ions. The shape of the five 3*d* orbitals is shown below. The box below shows the splitting of the five 3*d* orbitals into a group of three orbitals at lower energy (t_{2g}) and a group of two at higher energy (e_g)..

IV-2-3 Indicate in the boxes below which of the 3*d* orbitals (d_{z^2}, d_{xy}, d_{yz}, $d_{x^2-y^2}$, d_{xz}) belong to the t_{2g} group and which belong to the e_g group.



$d_{x^2-y^2}$ d_{yz} d_{z^2} d_{xz} d_{xy}

IV-2-4 Indicate with arrows the distribution and the direction of the magnetic spin moment of the three 3*d* electrons of Cr^{3+} over the five *d* orbitals in the lowest energy state of Cr^{3+}.



Name:	Student Code:

The ruby is placed on a (non-magnetic) scale. When the scale is in balance (Figure 2) a magnet is placed directly under the side with the ruby.

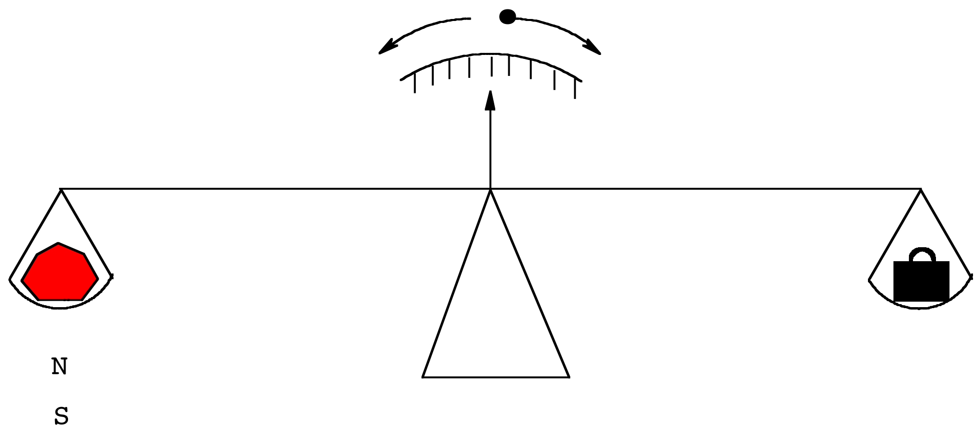


Figure 2

IV-2-5 Indicate what will happen with the ruby (mark the correct answer)

- ❑ The magnet attracts the ruby (the ruby moves down)
- ❑ The magnet has no influence on the ruby (the ruby does not move)
- ❑ The magnet repels the ruby (the ruby moves up)
- ❑ The magnet has an oscillating effect on the ruby (the ruby moves up and down)

Name:	Student Code:

Problem IV-3 Vehicle Traction Batteries **Score: 5 points**

	1	2	3	4
Marks	**25**	**25**	**20**	**30**

Battery-powered electric vehicles (EV's) are likely to become increasingly common in the next 50 years because of growing concern over pollution caused by vehicles using combustion engines. The reason for the current meagre commercial success of EV's is that the battery specifications must have a performance and cost profile comparable to conventionally powered vehicles.

Lead-acid batteries are extensively used as portable power sources for vehicles and traction. A lead-acid battery capable of efficient recharging has an energy density of 45 Wh/kg.

In the current evolution of EV batteries, the most promising long-term solution is the rechargeable light weight lithium-ion battery. Such batteries are under intensive investigation worldwide and hold also promise for the storage of electricity from solar cells. Their weight is 1/3 of a lead-acid battery. Lithium is used as a negative electrode. It has a high specific capacity and electrode potential. A common positive electrode material is the environmentally benign spinel-type $LiMn_2O_4$. The spinel structure comprises a matrix of cubic close-packed oxide ions, stabilised by lithium ions in tetrahedral sites and manganese ions in octahedral sites. In $LiMn_2O_4$ half of the manganese ions has an oxidation state +3 and half the oxidation state +4.

A lead-acid battery is represented by:

$Pb(s) \mid PbSO_4(s) \mid H_2SO_4(aq) \mid PbSO_4(s) \mid PbO_2(s) \mid (Pb(s))$

A lithium battery is represented by:

$Li(s) \mid Li^+$-conducting (solid) electrolyte(s) $\mid LiMn_2O_4(s)$

Upon discharge the insertion product $Li_2Mn_2O_4$ is formed. Charging the battery leads to the products Li(s) and $LiMn_2O_4$.

IV-3-1 Give the electrochemical reactions at the electrodes of the lead-acid battery during discharge.

Reaction at the negative electrode:

Reaction at the positive electrode:

Name:	Student Code:

IV-3-2 Give the electrochemical reactions at the electrodes of the lithium-ion battery upon discharge.

Reaction at the negative electrode:

Reaction at the positive electrode:

IV-3-3 Give the coordination numbers of the lithium ions and of the manganese ions in the spinel structure of $LiMn_2O_4$.

Li-ions: Mn-ions:

A typical family car of 1000 kg requires at least 5 kWh of energy to move 50 km, which corresponds with the consumption of about 5.0 L or 3.78 kg of petrol. This conventional car has a petrol tank volume of 50 L. The weight of the tank is 10 kg. The fuel consumption is 10 km L^{-1}.

IV-3-4 Calculate the extra weight of the car if the petrol tank is replaced by an equivalent battery in an EV based on (**a**) lead-acid battery and (**b**) lithium battery. Assume that in all cases the engine efficiency is the same.

(**a**) Extra weight of a lead-acid battery car:

Answer:

Calculation:

(**b**) Extra weight of a lithium battery car:

Answer:

Calculation:

Periodic Table of Elements

Atomic weights based on $^{12}C = 12$
(Numbers) = most stable isotope

s block **d block** Transition Metals **p block**

I	II											III	IV	V	VI	VII	VIII
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 105.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	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 (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 **Ac 227.03	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (?)											

Metals Non-metals

f block

*Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	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 173.04	71 Lu 174.97
**Actinides	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

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