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# 34th International Chemistry Olympiad

# Groningen, Wednesday, 10 July 2002

# Theoretical Examination

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***Chemistry and the Quality of Life go Hand in Hand***

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| **Name:** | **Student Code:** |
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- 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 $Hm{\cdot}CO$ 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.

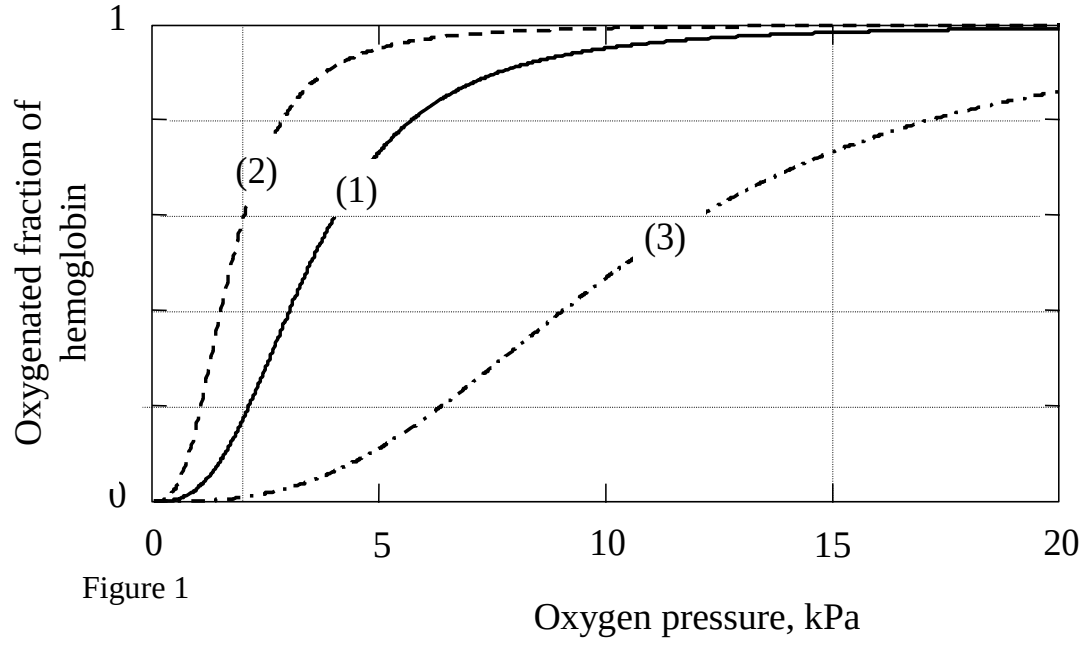


Figure 1

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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 $4 \times 10^{-4}$ $m^3$ $s^{-1}$. 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 $\Delta G^0$ for a reaction, calculate the difference between the $\Delta G^0$ 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:

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## Problem I-2 Nitrogen Cycle in Nature — Score: 7 points

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

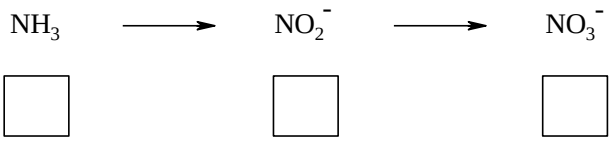
Ammonia is a toxic substance to marine animals at levels exceeding 1 ppm. Nitrifying bacteria play an important role in the conversion of $NH_3$ first to nitrite and then to nitrate, the storage form of nitrogen in the soil.

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

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)




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

For quantitative analyses a calibration curve has to be made, in which absorbance at the maximum absorbance wavelength $\lambda = 543$ 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).

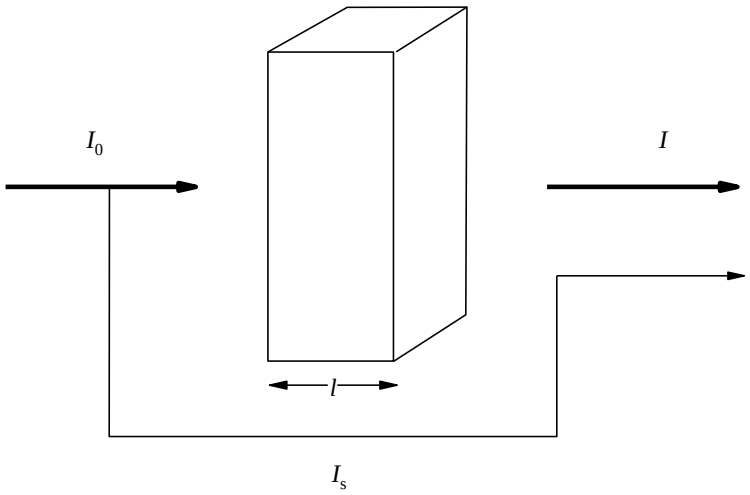



Figure 2

**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 $c = 1 \times 10^{-4}$ 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 |

**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

$$\text{corrected absorbance} = 0.1769\,c + 0.0015$$

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

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

Answer:

Calculation:

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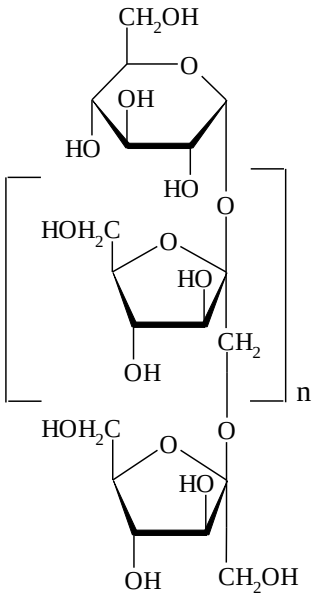
## Theme II - Chemistry of Industrial Relevance

*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.*

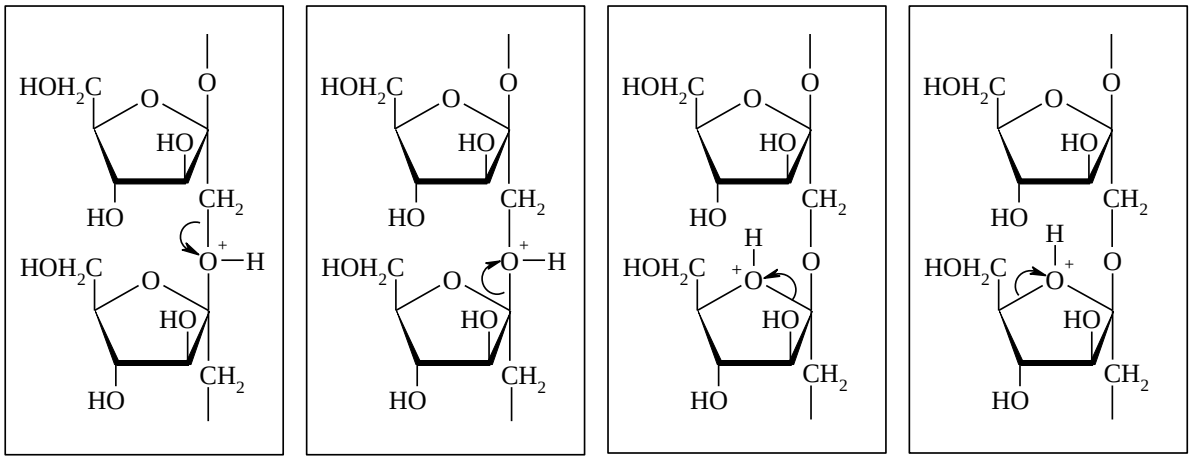
## Problem II-1 Inulin, a New Renewable Raw Material Score: 6 points

| | 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.

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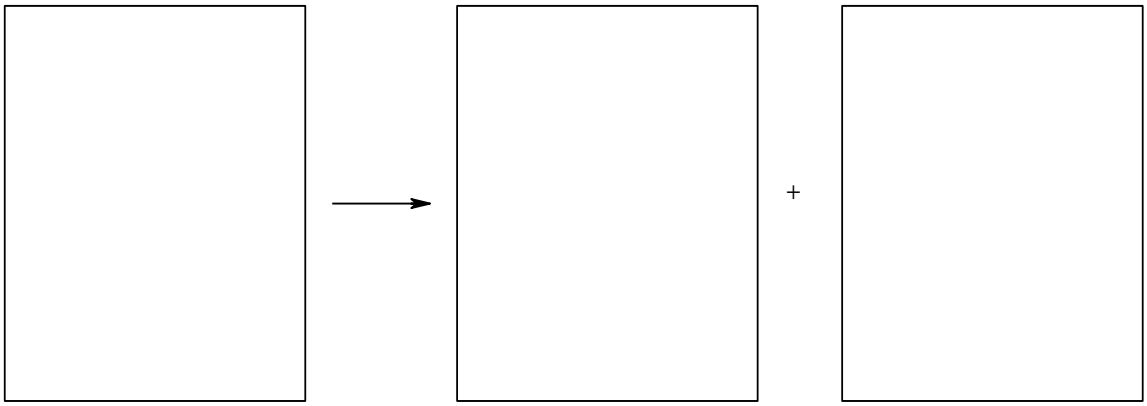
Hydrolysis with isotopically labelled water can provide information about the mechanism of hydrolysis using modern NMR techniques, which can "see" deuterium ($^2H$) and the oxygen isotope $^{17}O$.

**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**).




**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 $^oC$ 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 $^{o}$C. The solubility of **M** is 0.40 mol kg$^{-1}$ in water at 25 $^{o}$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:

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## 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.

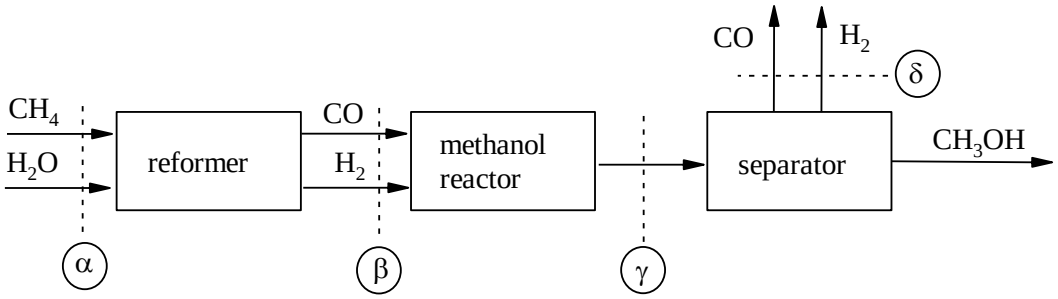


Figure 1

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).

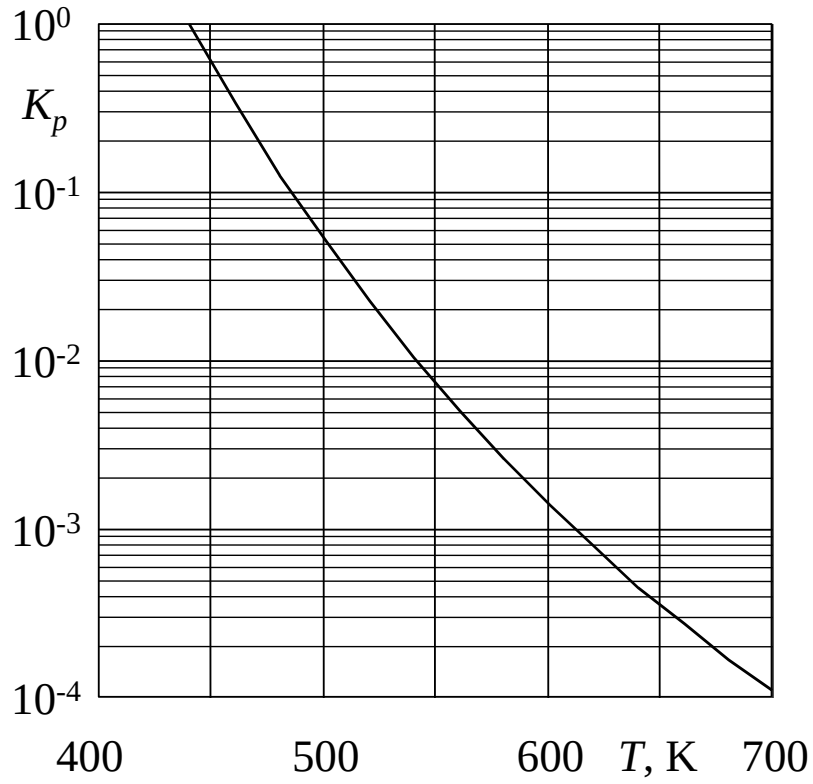


Figure 2

**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 $T_\gamma$:

Calculation:

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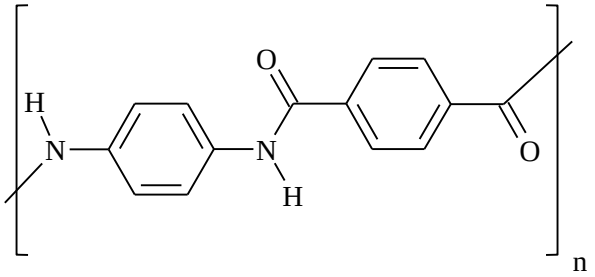
## Problem II-3 Aramids, High-Performance Polymeric Materials

**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).

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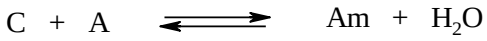
For a polymerisation of equimolar amounts of two monomers the average chain length is $\overline{P}_n$, the degree of conversion is $p$, which equals the fraction of functional groups that have reacted, the total number of chains is $N_t$ and the total initial number of monomers is $U_0$.

Assuming that the polymerization equilibrium can fully be described by:



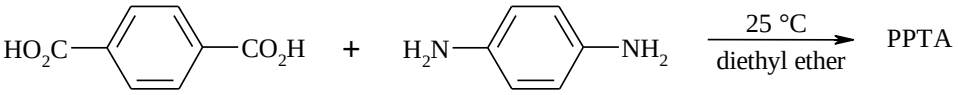

Where C stands for any $–CO_2$ group, A stands for any $–NH_2$ group and Am stands for any amide group.

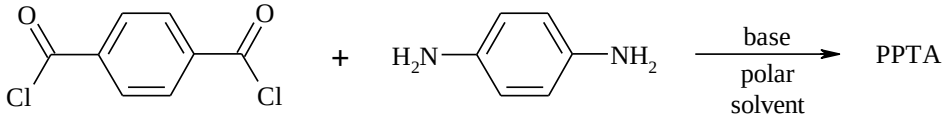
**II-3-2** Calculate the degree of conversion needed to obtain an average chain length of 500.

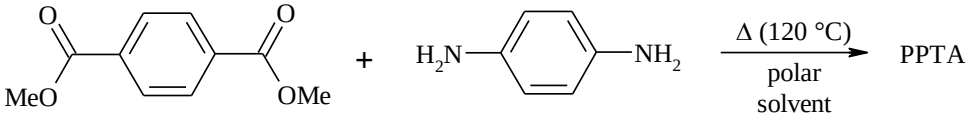
Answer:

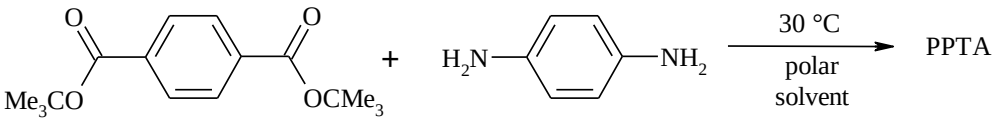
Calculation:

**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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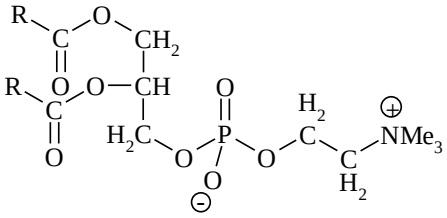
## Theme III - Chemistry of Functional Molecules in Nature

*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**.

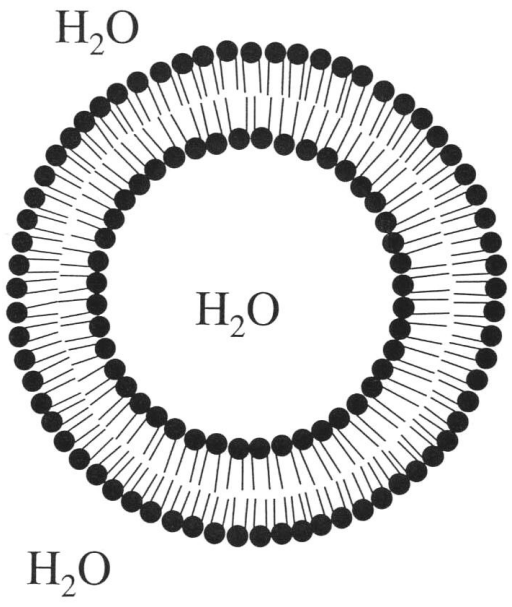


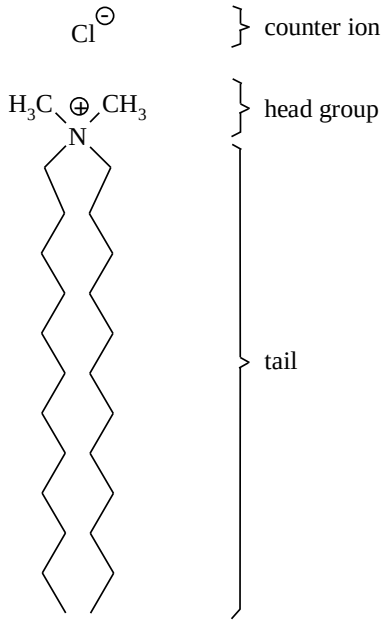
**A**

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**

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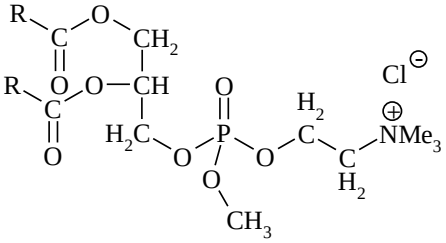
**III-1-1** **(a)** How many stereoisomers are possible for compound **A**?

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

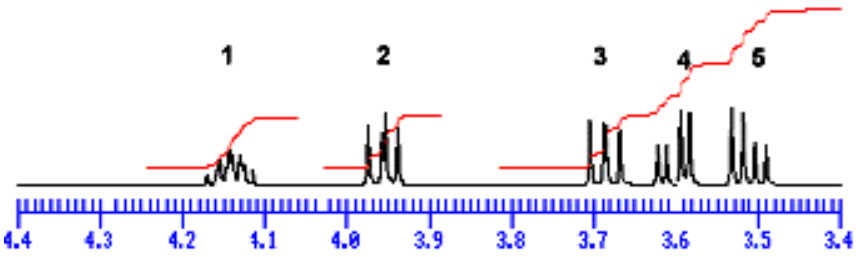


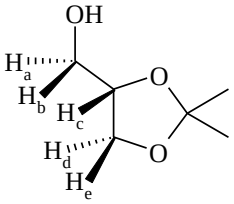
R = *n*-$C_{17}H_{35}$

**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:

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

$l_c = (0.154 + 0.1265\ n)\ \text{nm}$

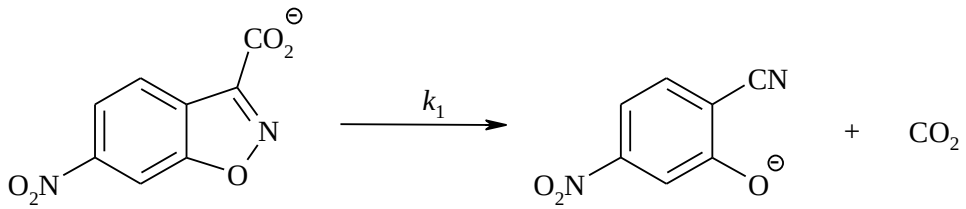
For very large $n$ values, the intertail interactions dominate over the head group repulsions.

**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 $k_1 = 3.1 \times 10^{-6}$ s$^{-1}$. At the concentration $c_1$ of **DDAC** at which **6-NBIC** becomes fully bound to the vesicles, $k_1 = 2.1 \times 10^{-3}$ s$^{-1}$.

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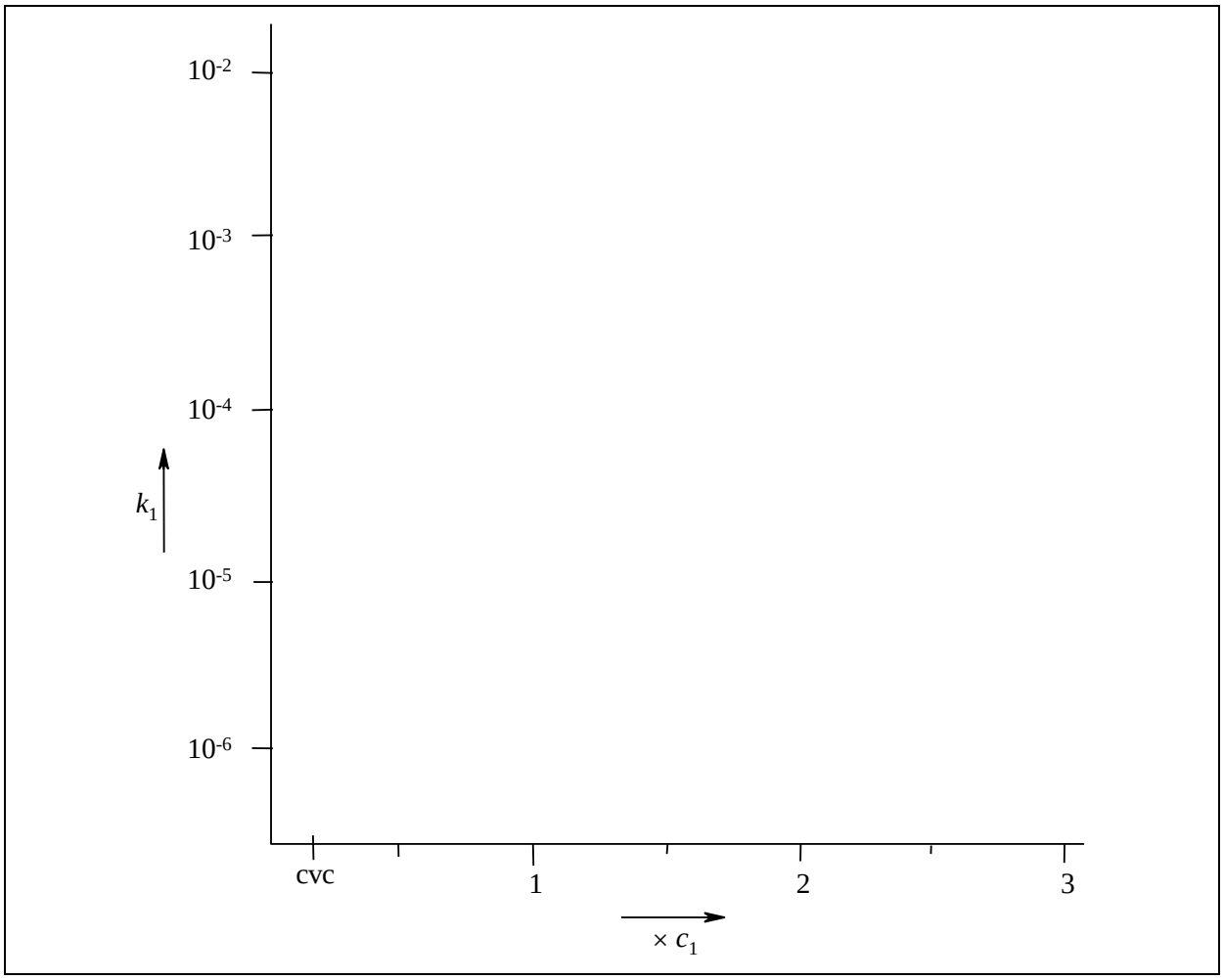
**III-1-4** Sketch a plot of $k_1$ vs. [**DDAC**] for [**DDAC**] = 0 → 3 $c_1$.




**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.

| Name: | Student Code: |
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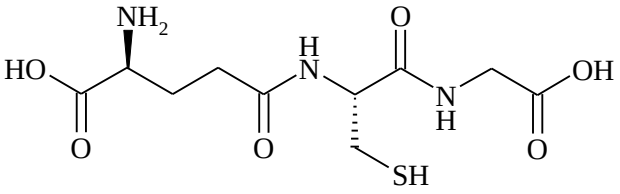
## Problem III-2 Glutathione, an Essential Mini-Peptide Score: 6 points

| | 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.

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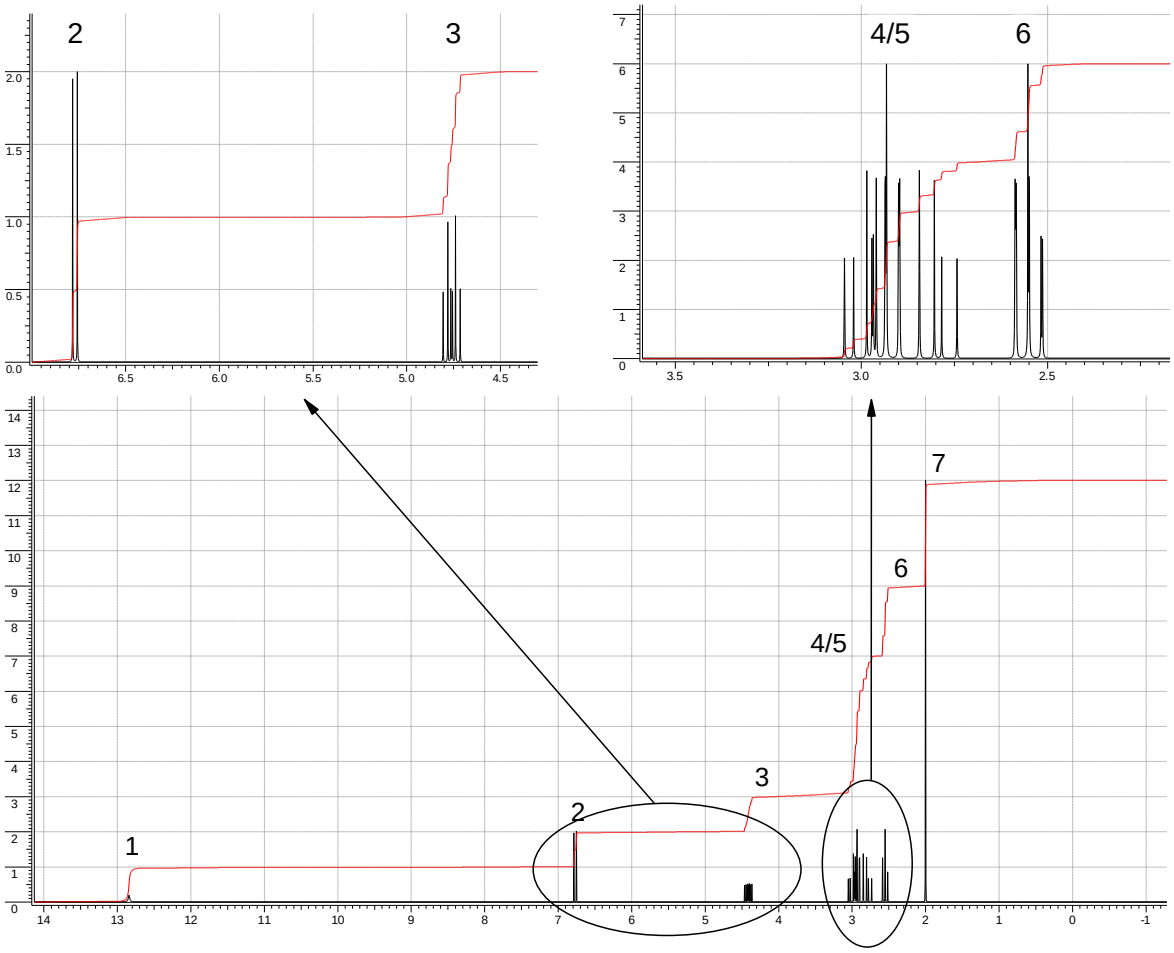


Figure 1

**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**.

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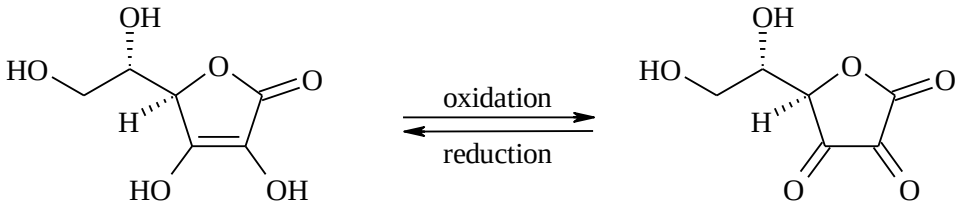
Vitamin C (ascorbic acid) reacts with oxidants to give dehydroascorbic acid **D**




**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.*

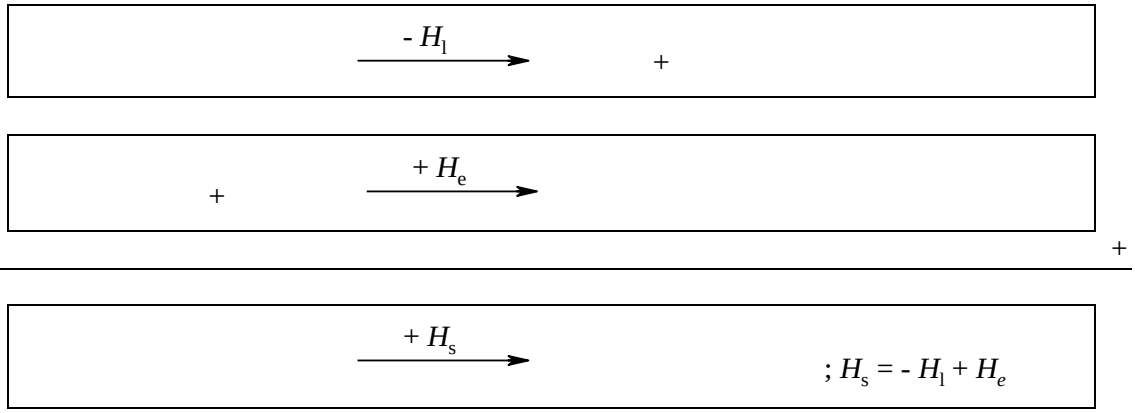
## Problem IV-1 Lighting Lamps

**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 $\Delta H$)




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

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**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

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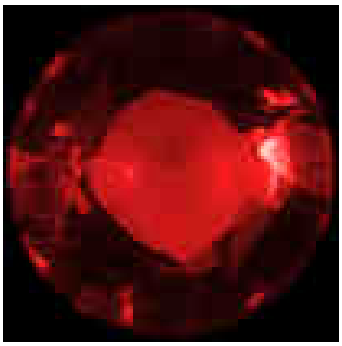
## Problem IV-2 Red Ruby

**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.

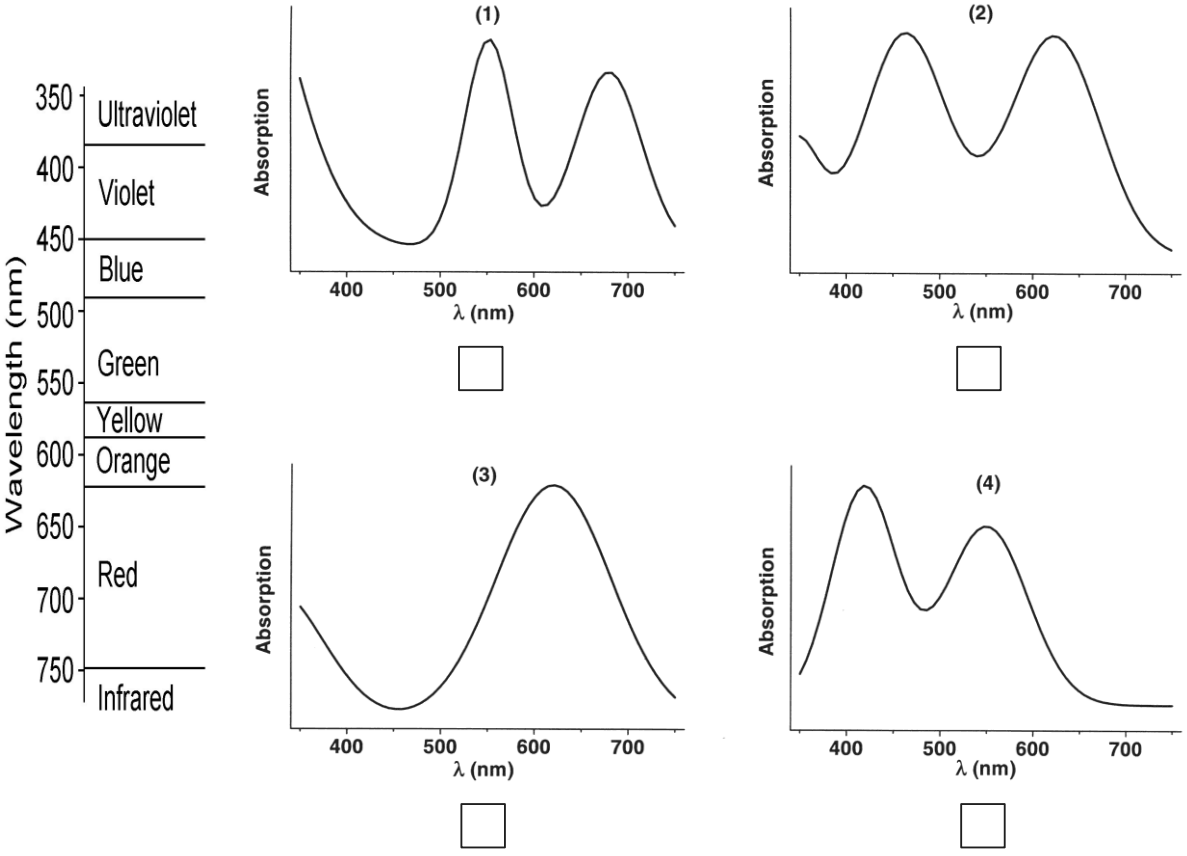



Figure 1

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).

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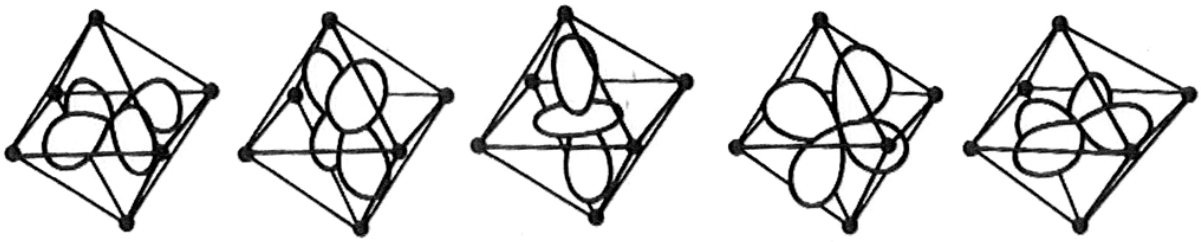
**IV-2-2** Calculate how many $Cr^{3+}$ ions are in this laser rod.

Answer:

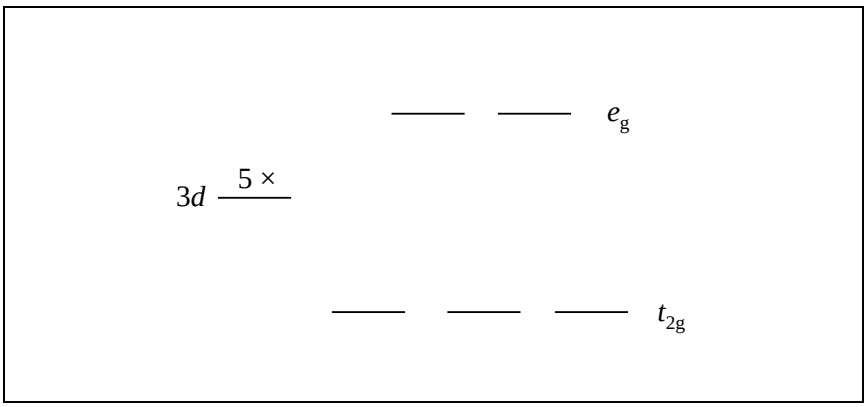
Calculation:

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.




**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 $Cr^{3+}$.



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.

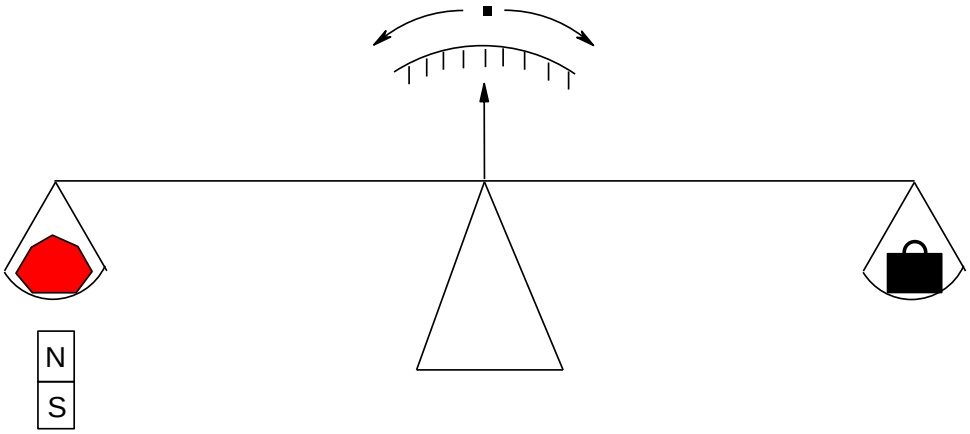



Figure 2

**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)

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## 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:

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

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:

**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:

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# 34th International Chemistry Olympiad

# Groningen, Wednesday, 10 July 2002

# Theoretical Examination

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***Chemistry and the Quality of Life go Hand in Hand***

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| **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 32 pages of problems including answer boxes.
- An official English-language version is available only on request.

| Name: | Student Code: |
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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 $Hm{\cdot}CO$ 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.

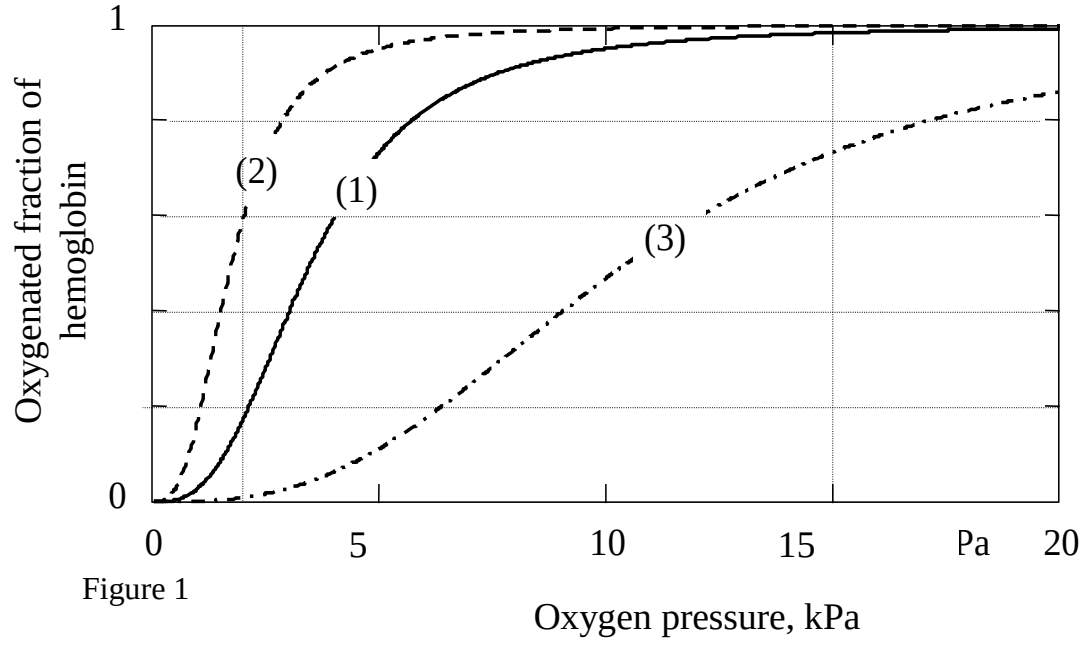


Figure 1

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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 $4 \times 10^{-4}$ $m^3$ $s^{-1}$. 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 $\Delta G^0$ for a reaction, calculate the difference between the $\Delta G^0$ values for the heme reactions (1) and (2).

Answer: 23 kJ $mol^{-1}$

Calculation:

$K_1 = \exp(-\Delta G^0_1/(RT))$ $\quad\quad$ $\Delta G^0_1 = -RT \ln(K_1)$

$K_2 = \exp(-\Delta G^0_2/(RT))$ $\quad\quad$ $\Delta G^0_2 = -RT \ln(K_2)$ **10**

$\Delta G^0_2 - \Delta G^0_1 = RT \ln(K_1/K_2) = (2477 \text{ J mol}^{-1}) \times \ln(10^4) = 23 \text{ kJ mol}^{-1}$ **10 + 5**

**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: (0.98 - 0.17) × 4 = 3.2 mol **Factor 4 correct 10 points**
**Hb-type correct fraction 5 points**

Hb type 2: (1.00 - 0.60) × 4 = 1.6 mol **Hb-type correct fraction 5 points**

Hb type 3: (0.73 - 0.01) × 4 = 2.9 mol **Hb-type correct fraction 5 points**

**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: $2.72 \times 10^{-3}$ mol $s^{-1}$

Calculation:
$(4 \times 10^{-4}\ m^3\ s^{-1}) \times 0.4 \times (340\ kg\ m^{-3}) \times (3.2\ mol\ O_2/\ mol\ Hb) / (64\ kg\ mol^{-1}) = 2.72 \times 10^{-3}$ mol $s^{-1}$

**-10 points for each missing factor**

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

Answer: 1088 W

Calculation:
$(2.72 \times 10^{-3}\ mol\ s^{-1}) \times (400\ kJ\ mol^{-1}) = 1088$ W

**10 or 5 or 0**

| Name: | Student Code: |
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## Problem I-2 Nitrogen Cycle in Nature

**Score: 7 points**

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

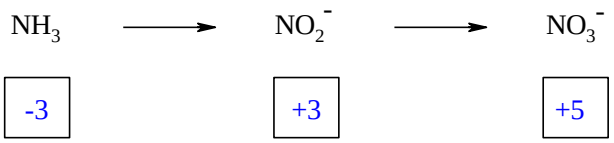
Ammonia is a toxic substance to marine animals at levels exceeding 1 ppm. Nitrifying bacteria play an important role in the conversion of $NH_3$ first to nitrite and then to nitrate, the storage form of nitrogen in the soil.

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

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)




**5 + 5 + 5**

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

For quantitative analyses a calibration curve has to be made, in which absorbance at the maximum absorbance wavelength $\lambda$ = 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.

**15**

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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).

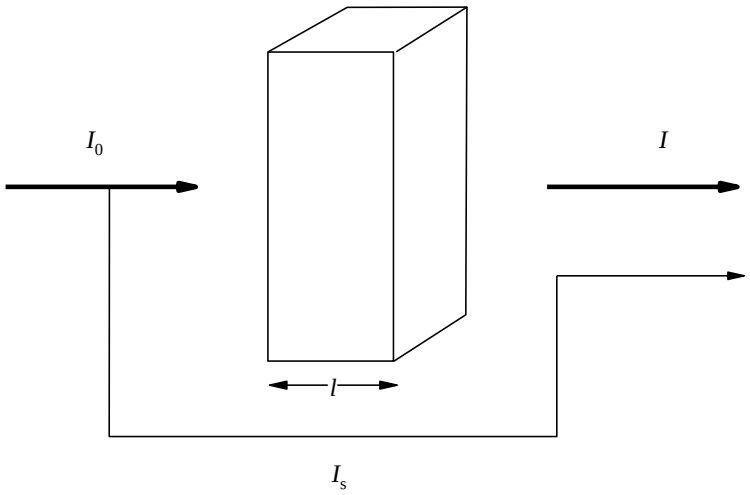



Figure 2

**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 $c = 1 \times 10^{-4}$ M

Answer: $A = 0.50$

Calculation: $I_s = 0.05\ I_0$ **5**

$$A = \log \frac{I_0}{I + I_s}$$ **5**

$I = 0.95\ I_0 \times 10^{-(6000 \times 0.0001 \times 1)} = 0.95\ I_0 \times 10^{-0.6}$ **5**

$$A = \log \frac{I_0}{0.95\ I_0 \times 10^{-0.6} + 0.05\ I_0} = \log \frac{I_0}{0.29\ I_0} = 0.50$$ **5**

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 |

**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: $m = 0.176$
$b = 0.003$

Calculation of *m*:
Slope *m* of the calibration curve:

$$m = \frac{\Delta A}{\Delta c} = \frac{A_2 - A_1}{c_2 - c_1} \quad \textbf{5} \rightarrow \quad m = \frac{0.325 - 0.164}{1.830 - 0.915} = \frac{0.161}{0.915} = 0.176$$

**Correct absorbances 5** **Calculation of m 5**

(Explanation: From the *corrected* absorbance values $A_2 = 0.325$ and $A_1 = 0.164$, and the concentrations $c_2 = 1.830$ ppm and $c_1 = 0.915$ ppm, follows the value of *m*)

Calculation of *b*:
From the corrected absorbance $A = 0.325$
the concentration $c = 1.830$ ppm
and the slope $m = 0.176$
follows the value of *b*:

$0.325 = 0.176 \times 1.830 + b$
$b = 0.325 - 0.322 = 0.003$ **Calculation of b 10**

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 μg $mL^{-1}$. Hint: Take the blank from problem I-2-4.

Answer: 1.55 ppm

Calculation:
The average absorbance in a 2.000 cm cuvet is 0.558 **5**
The average absorbance in a 1.000 cm cuvet is 0.279 **5**
The corrected average absorbance in a 1 cm cuvet is 0.276
Substituting this value into the equation gives:
Corrected absorbance = $0.1769\,c + 0.0015$

$c = (0.276 - 0.0015) / 0.1769 = 1.55$ ppm **10**

*c* is also 1.55 μg $mL^{-1}$ **5**

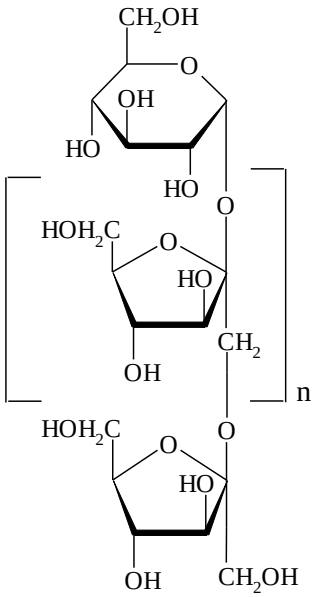
| Name: | Student Code: |
|---|---|

## 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.*

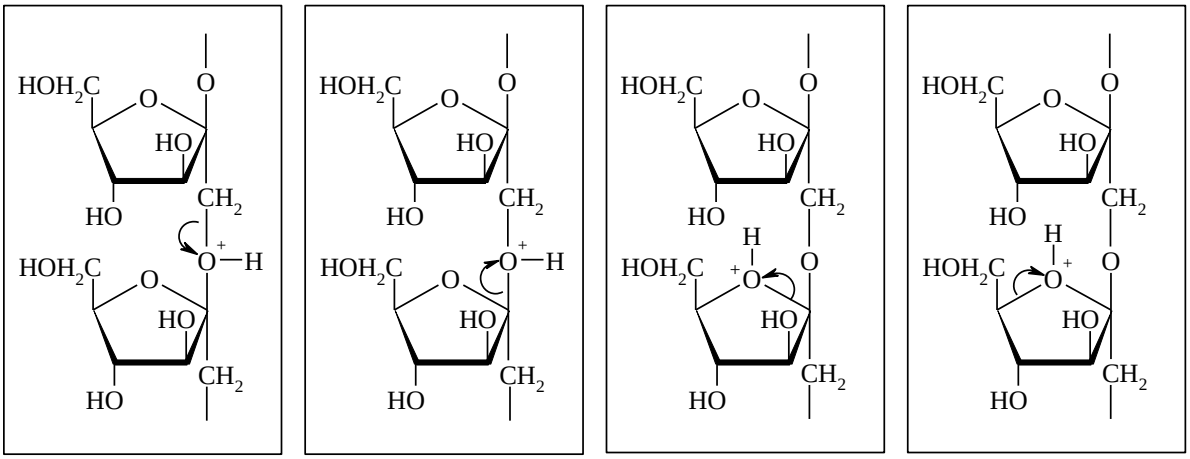
## Problem II-1 Inulin, a New Renewable Raw Material Score: 6 points

| | 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. **15**

| **Name:** | **Student Code:** |
|---|---|

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

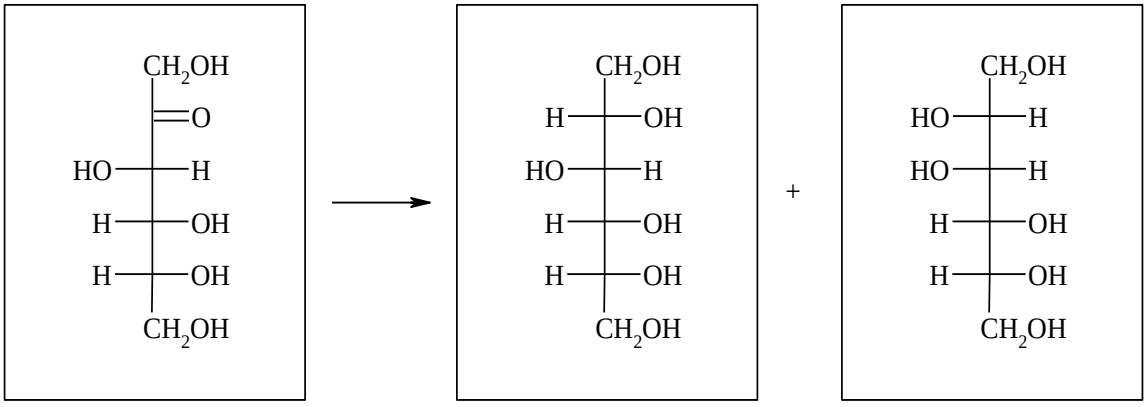
**II-1-2** Indicate which labelled water can **best** be used for this purpose. Mark the correct answer.

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

**15**

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**).




**F** **S** **M**

**10 + 10 + 10**

1.00 Mole of inulin in 2.00 kg of water with added catalysts, is subjected to hydrolysis and hydrogenation at 95 $^{o}C$ 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**: | 7.00 |
|---|---|

| **S**: | 4.00 |
|---|---|

**10 or 0**

| **Name:** | **Student Code:** |
|---|---|

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

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

Answer: 6.27 mol

Calculation:

Remaining amount of water: $2.00 - (10 \times 0.018) = 1.82$ kg
$\mathbf{M}_{total} = 7.00$ mol; $\mathbf{M}_{dissolved} = 1.82 \times 0.40 = 0.73$ mol ==> $\mathbf{M}_{precipitated} = 7.00 - 0.73 = 6.27$ mol

**30 (-25 when reacting water is neglected)**

| 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.

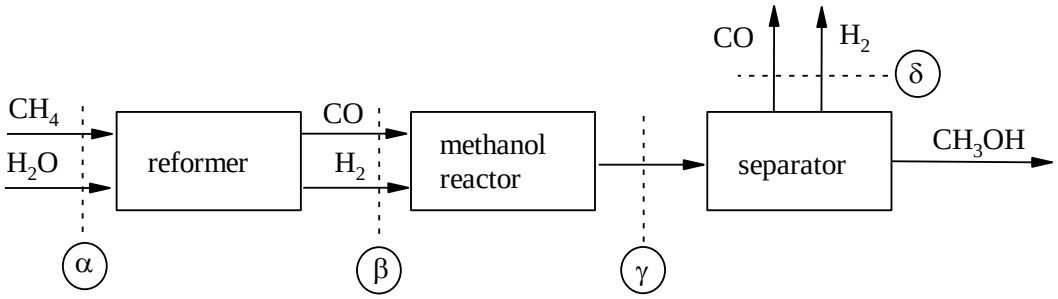



Figure 1

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.

$n$[CO, β] = (3/2) × $n$[$CH_3OH$, γ] = 1500 mol $s^{-1}$
$n$[$H_2$, β] = 3 × $n$[CO, β] = 4500 mol $s^{-1}$
**15 (only one -10)**

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

$n$[CO, γ] = $n$[CO, β] - $n$[$CH_3OH$, γ] = 1500 - 1000 = 500 mol $s^{-1}$
$n$[$H_2$, γ] = $n$[$H_2$, β] - 2 × $n$[$CH_3OH$, γ] = 4500 - 2 × 1000 = 2500 mol $s^{-1}$
**10 + 10**

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

$n$[$CH_4$, α] = $n$[CO, β] = 1500 mol $s^{-1}$
$n$[$H_2O$, α] = $n$[CO, β] = 1500 mol $s^{-1}$
**15 (only one -10)**

**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]: 1.25 MPa

Answer $p$[$H_2$, γ]: 6.25 MPa

Calculations:

| | |
|---|---|
| $n_{tot}$ = 1000 + 500 + 2500 = 4000 | **10 + 5** |
| ***p*[$CH_3OH$, γ] = 10 Mpa × 1000 / 4000 = 2.5 Mpa** | |
| $p$[CO, γ] = 10 MPa × 500 / 4000 = 1.25 Mpa | **5** |
| $p$[$H_2$, γ] = 10 MPa × 2500 / 4000 = 6.25 Mpa | **5** |

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).

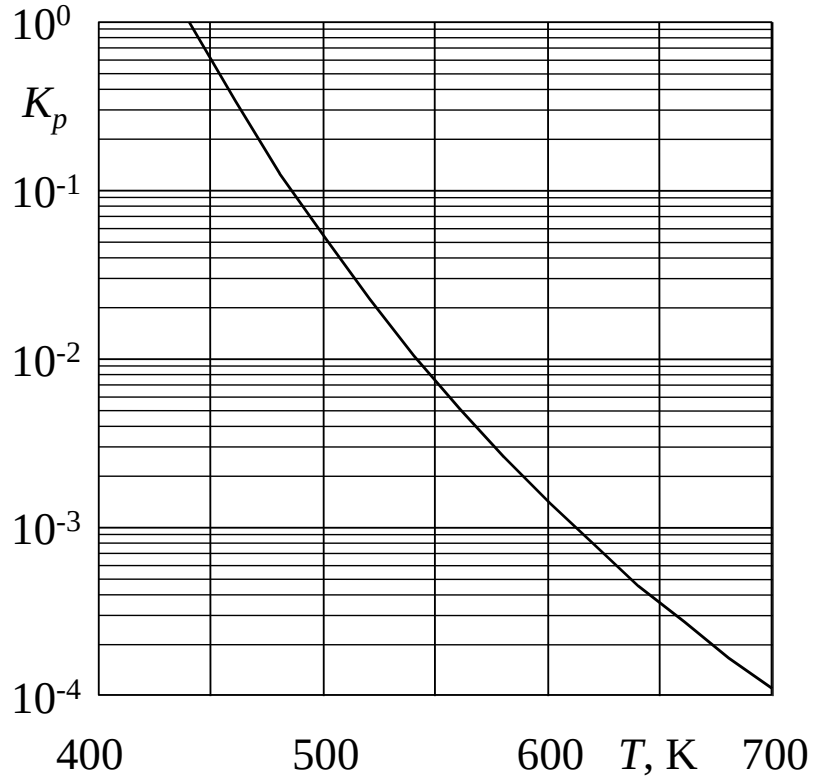



Figure 2

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

Answer $K_p$: $5.12 \times 10^{-4}$

Answer $T_\gamma$: 630 K Read from the graph at $5.1 \times 10^{-4}$ on the y-axis
**Temperature 620 – 640 K 10 points, else 0 points**

Calculation:
$K_p = (2.5 \times 0.1^2) / (1.25 \times 6.25^2) = 5.12 \times 10^{-4}$ **15**

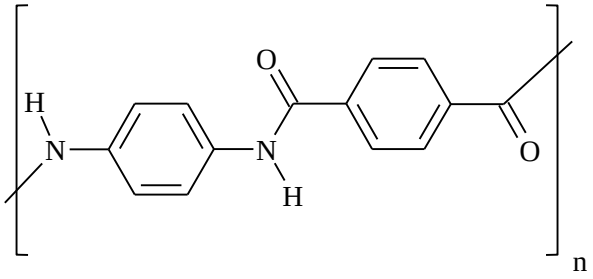
| Name: | Student Code: |
|---|---|

## Problem II-3 Aramids, High-Performance Polymeric Materials

**Score: 6 points**

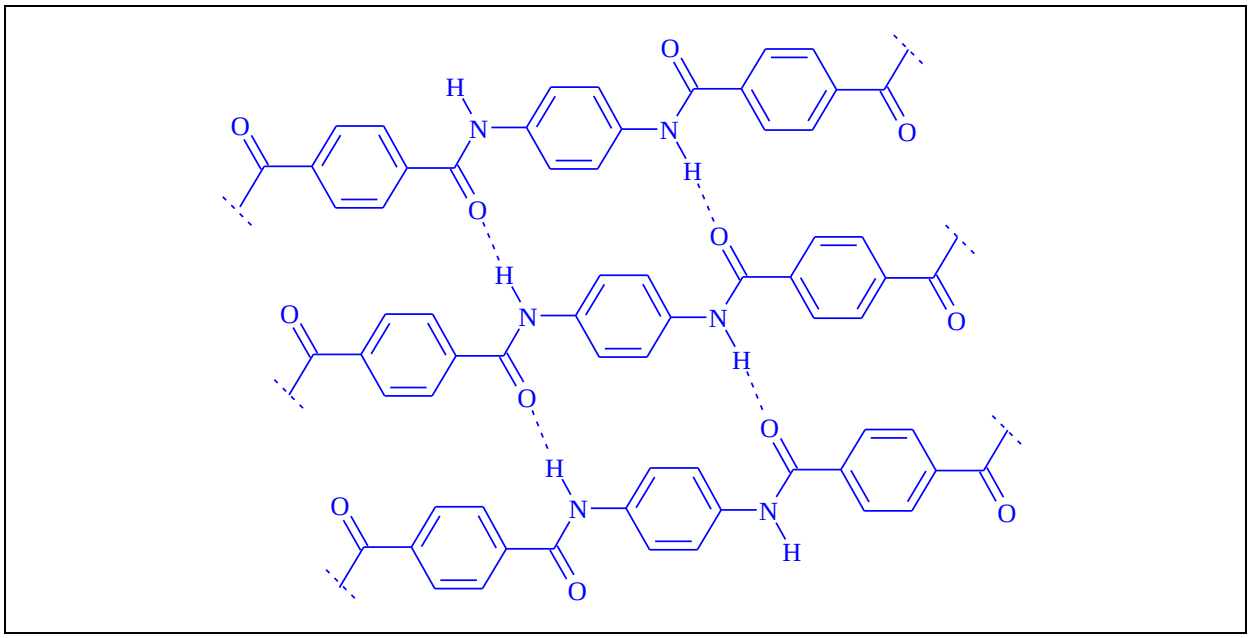
| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Marks | **20** | **30** | **25** | **25** |

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).

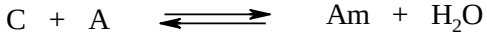



**2 strings -10, only one H-bridge -10, H-bridge to nitrogen half of the points**

| **Name:** | **Student Code:** |
|---|---|

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:




Where C stands for any $-CO_2H$ 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: 0.998

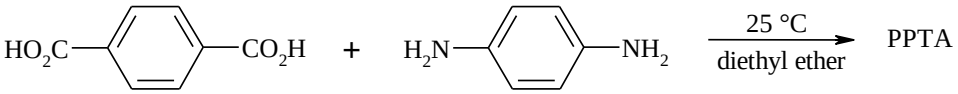
Calculation:

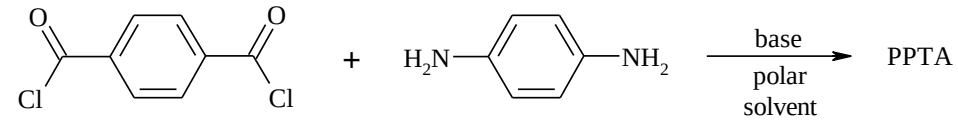
$$\overline{P}_n = \frac{U_0}{N_t} \qquad p = \frac{U_0 - N_t}{U_0} \Longrightarrow p = 1 - \frac{N_t}{U_0} \Longrightarrow \frac{N_t}{U_0} = 1 - p \qquad \overline{P}_n = \frac{1}{1-p}$$

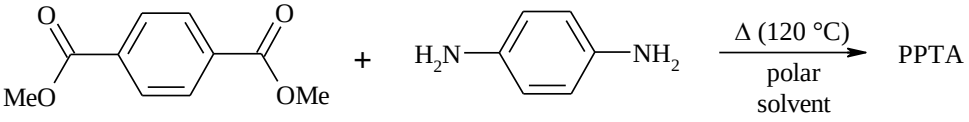
$$500 = \frac{1}{1-p} \qquad p = \frac{499}{500} = 0.998$$

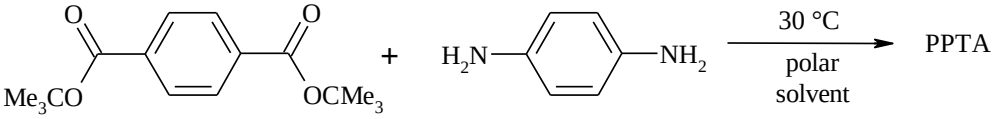
**Formula correct 15, calculation correct 15**

**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).

☐ 


■ 


■ 

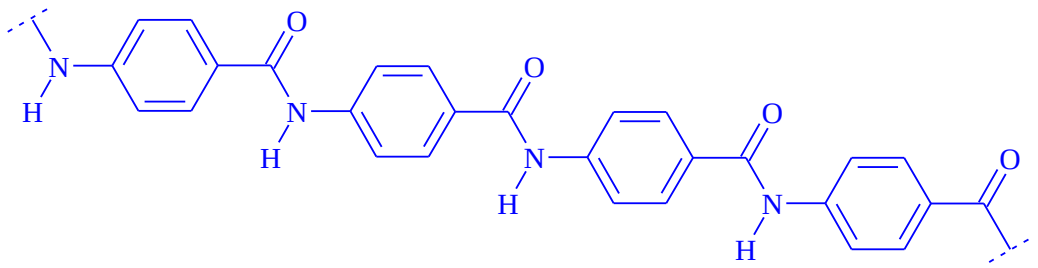

☐ 


**option b 15, option c 10**

| **Name:** | **Student Code:** |
|---|---|

**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)



**10**

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

Answer: $\overline{P}_n = 25$

Calculation:

$K = 576$

$$K = \frac{[\text{Am}]\,[\text{H}_2\text{O}]}{[\text{C}]\times[\text{A}]} = \frac{p\,U_0 \times p\,U_0}{(1-p)^2\,U_0^2} = \frac{p^2}{(1-p)^2} = 576 \Longrightarrow p = 0.96$$

$$\overline{P}_n = \frac{1}{1-p} = \frac{1}{1-0.96} = 25$$

***K* correct 10 points, $P_n$ correct 5 points**

| Name: | Student Code: |
|---|---|

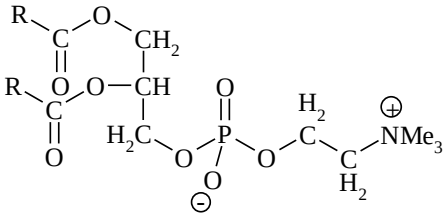
## Theme III - Chemistry of Functional Molecules in Nature

*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** |

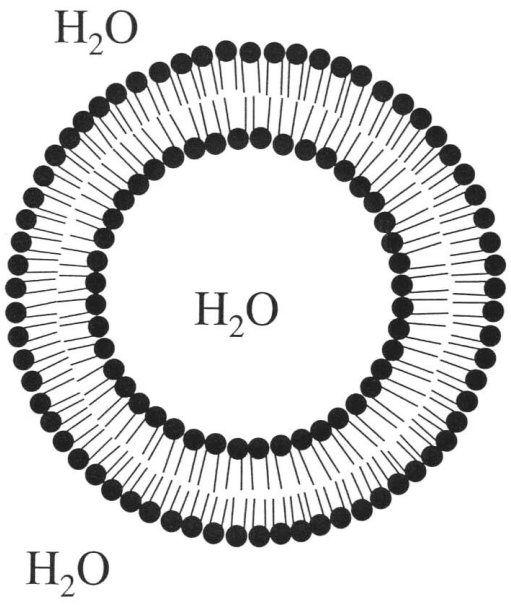
Biological cell membranes are complex, functional, non-covalent molecular assemblies, largely consisting of lipids and proteins. Their function is of vital importance for life processes. They separate the cell from its environment and also determine the specific flow of information between the cell contents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

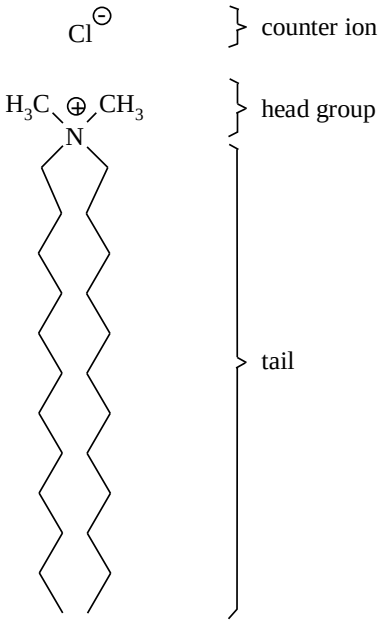


**A**

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**

| **Name:** | **Student Code:** |
|---|---|

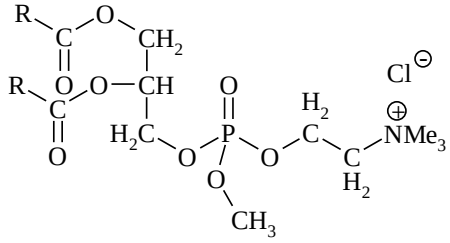
**III-1-1** **(a)** How many stereoisomers are possible for compound **A**?

| 2 |
|---|

**10**

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

| 4 |
|---|



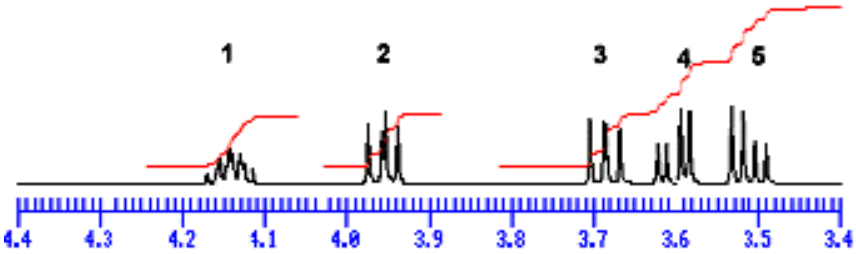
R = *n*-$C_{17}H_{35}$

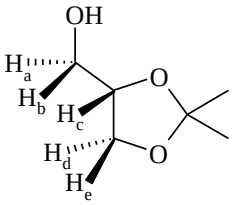
**B**

**10**

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**

| $\mathbf{H_c}$ = 1 |
|---|

**20**

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:

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

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: 0.213 $\text{nm}^2$ **10** |
|---|
| Calculation: |

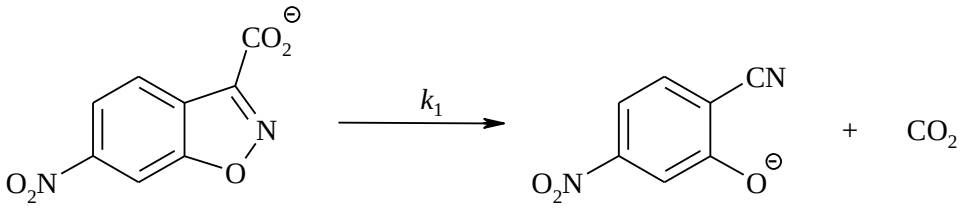
| **Name:** | **Student Code:** |
|---|---|

$a_0(\text{min}) = \dfrac{V}{l_c} = \dfrac{(27.4 + 26.99\,n) \times 10^{-3}}{(0.154 + 0.1265\,n)}$ nm$^2$

$n \rightarrow$ large $\Longrightarrow \dfrac{26.99 \times 10^{-3}}{0.1265} = 0.213$ nm$^2$

**10**

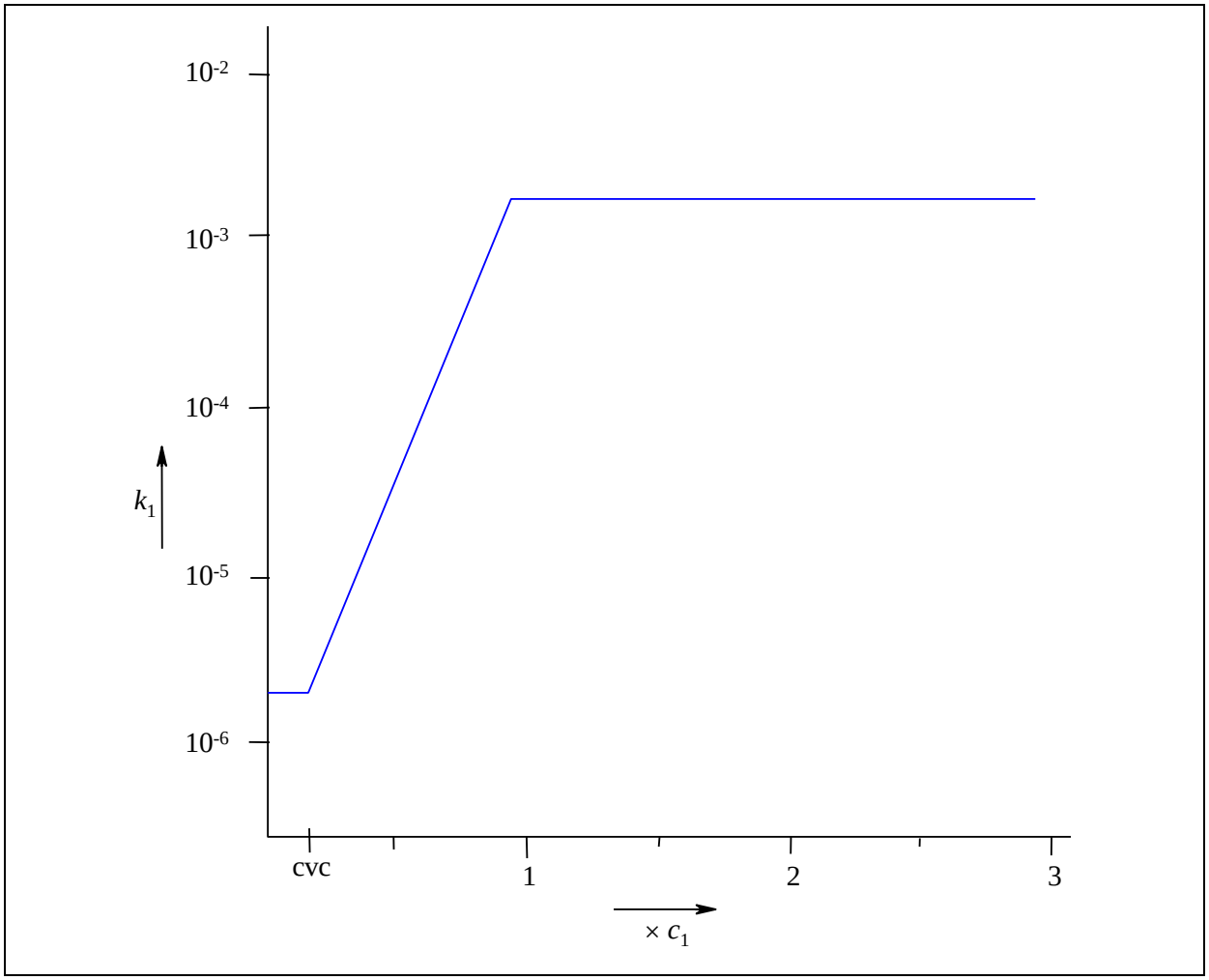
Vesicles formed from **DDAC** (above its critical vesicle concentration, cvc) catalyse the unimolecular decarboxylation of 6-nitro-benzisoxazole-3-carboxylate (**6-NBIC**).




**6-NBIC**

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

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




**We expect curved bends in the graph, sharp corners are also accepted 20**
**Cvc not included -5, above $c_1$ not constant -15**

| **Name:** | **Student Code:** |
|---|---|

**III-1-5** The main reason for the efficient catalysis of the decarboxylation of **6-NBIC** by **DDAC** vesicles is: **20 or 0**

- ❑ 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.

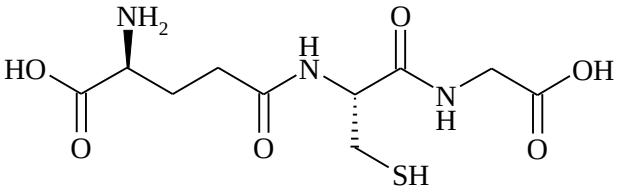
Mark the correct answer.

| Name: | Student Code: |
|---|---|

## 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.

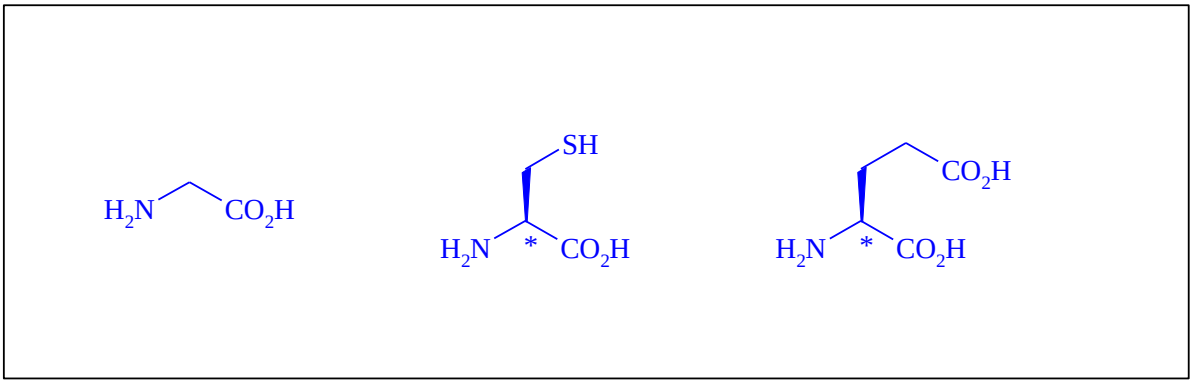



**GSH**

**III-2-1** **(a)** How many amino acid residues are present in GSH? **10 or 0**

| 3 |
|---|

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




**Each amino acid correct 4, each chiral center correct 4**

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 at δ 4.4~~ signal 3 is simplified ~~to a triplet~~.

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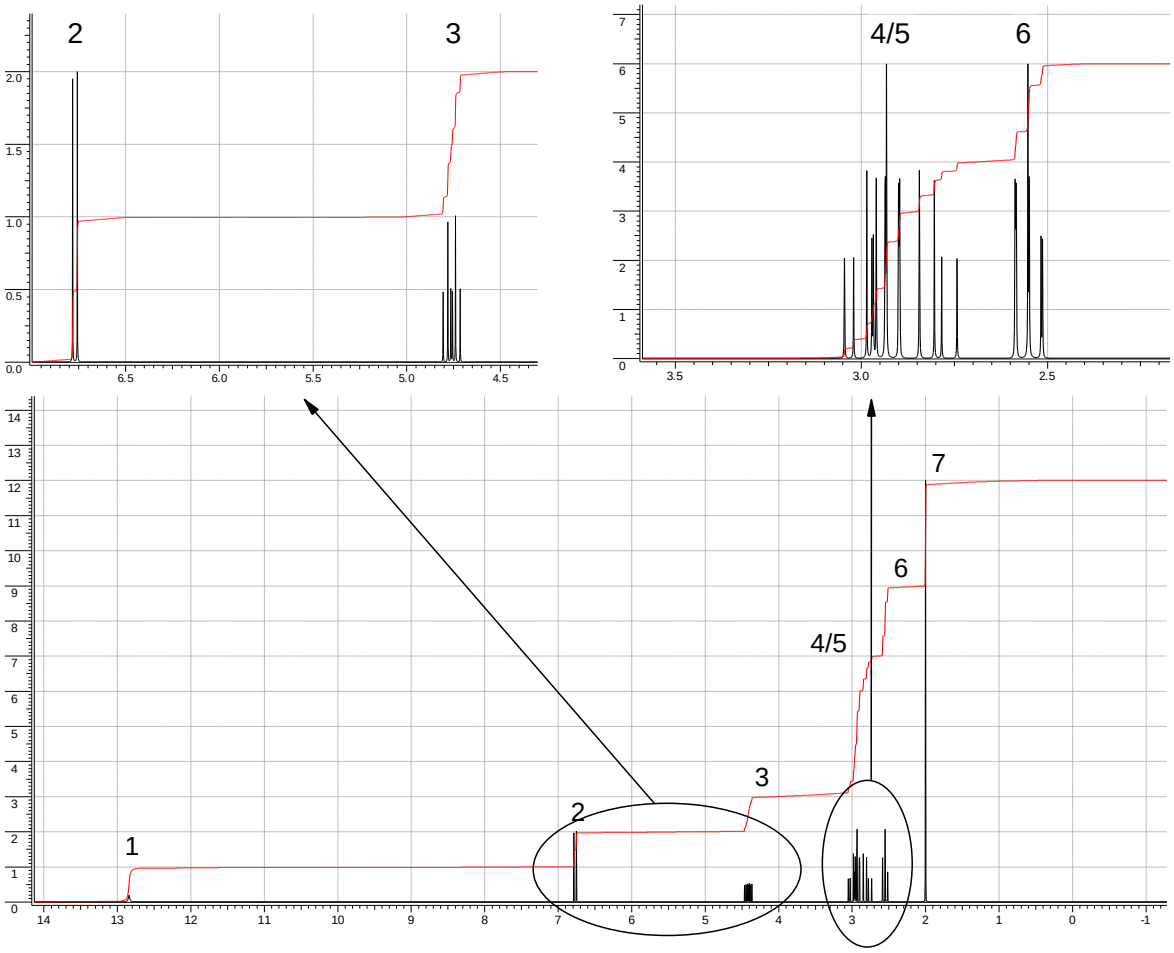



Figure 1

**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 | OH | NH | CH | $CH_2$ | $CH_2$ | $CH_3$ |

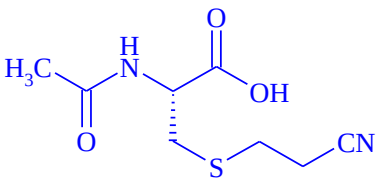
**3 points per correct signal**

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

**8 or 0**

3

**(c)** Draw the structure of compound **A**. **20, no acetyl or $-CH_2-CH_2-CN$ -10**



| **Name:** | **Student Code:** |
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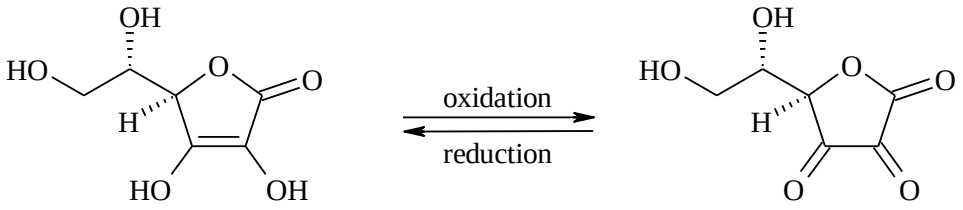
Vitamin C (ascorbic acid) reacts with oxidants to give dehydroascorbic acid **D**




**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.

**20 or 0**

| Name: | Student Code: |
|---|---|

## 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.*

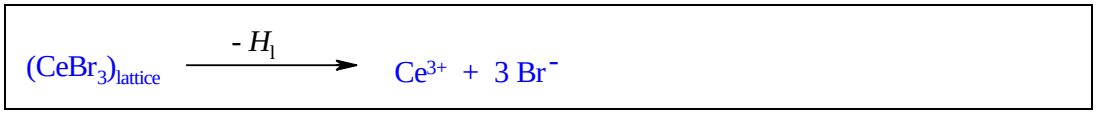
## Problem IV-1 Lighting Lamps

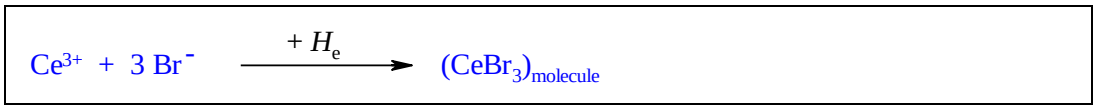
**Score: 7 points**

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

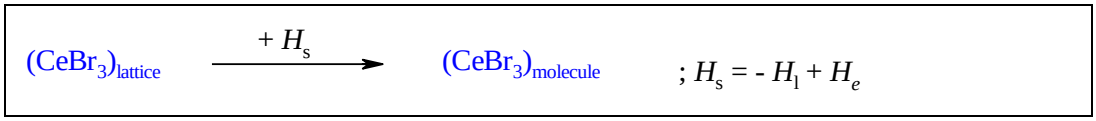
Since 1891 lighting lamps have been manufactured in The Netherlands. The improvement today in comparison to the first lamp is enormous, especially with the introduction of the gas discharge lamps. The life-time has increased by orders of magnitude. The colour is also an important aspect. Rare earth metal 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 $\Delta H$)




+




**10 or 0**

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.

| **Name:** | **Student Code:** |
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**IV-1-2** Calculate the enthalpy of sublimation of $CeBr_3$ (in integers; be aware of the signs!)

Answer: $H_s = 718$ kJ mol$^{-1}$

Calculation:

$$H_l = -\frac{139\times 3\times 1\times 2.985}{0.297}\times\frac{10}{11} = -3810 \text{ kJ mol}^{-1}$$

$$H_e = -3\times\frac{139\times 3\times 1}{0.297}\times\frac{10}{11} + 3\times\frac{139\times 1\times 1}{0.297\sqrt{3}}\times\frac{10}{11} = -3829 \text{ kJ mol}^{-1} + 737 \text{ kJ mol}^{-1} = -3092 \text{ kJ mol}^{-1}$$

$$H_s = 3810 - 3092 = 718 \text{ kJ mol}^{-1}$$

**$H_l$ = 8 points, $H_e$ = 14 points, $H_s$ = 3 points**
**Each mistake -3 points**

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: $(CsCeBr_4)_{lattice} \xrightarrow{+H_1} Cs^+ + CeBr_4^-$

Step 2: $CeBr_4^- \xrightarrow{+H_2} Ce^{3+} + 4\ Br^-$

Step 3: $Ce^{3+} + 3\ Br^- \xrightarrow{+H_3} (CeBr_3)_{molecule}$

Step 4: $Cs^+ + Br^- \xrightarrow{+H_4} (CsBr)_{molecule}$

+

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

**25 or 0, all steps are interchangable**

| **Name:** | **Student Code:** |
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**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: $H_1 = +358$ kJ mol$^{-1}$ **8**

Calculation:
The lattice energy of $CsCeBr_4$ with opposite sign is

$$H_1 = +\frac{139 \times 1 \times 1 \times 1.75}{0.617} \times \frac{10}{11} = +358 \text{ kJ mol}^{-1}$$

Answer Step 2: $H_2 = +3543$ kJ mol$^{-1}$ **12**

Calculation:
$CeBr_4^-$ in the gas phase is

$$H_2 = 4 \times \frac{3 \times 1 \times 139}{0.297} \times \frac{10}{11} - 6 \times \frac{1 \times 1 \times 139}{0.297 \times \frac{2}{3}\sqrt{6}} \times \frac{10}{11} = 5106 - 1563 = +3543 \text{ kJ mol}^{-1}$$

Answer Step 3: $H_3 = -3092$ kJ mol$^{-1}$ **5**

Calculation:
The electrostatic energy in the gas phase of $CeBr_3$ is (see answer IV-1-2):

$$H_3 = -3 \times \frac{139 \times 3 \times 1}{0.297} \times \frac{10}{11} + 3 \times \frac{139 \times 1 \times 1}{0.297\sqrt{3}} \times \frac{10}{11} = -3829 + 737 = -3092 \text{ kJ mol}^{-1}$$

Answer Step 4: $H_4 = -348$ kJ mol$^{-1}$ **5**

Calculation:
The electrostatic energy in the gas phase of CsBr is

$$H_4 = -\frac{139 \times 1 \times 1}{0.363} \times \frac{10}{11} = -348 \text{ kJ mol}^{-1}$$

Answer total sum: $H_{total} = +461$ kJ mol$^{-1}$ **5**

Calculation:
$H_{total} = H_1 + H_2 + H_3 + H_4 = +358 + 3543 - 3092 - 348 = +461$ kJ mol$^{-1}$

**Each mistake -3 points**

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**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

**5**

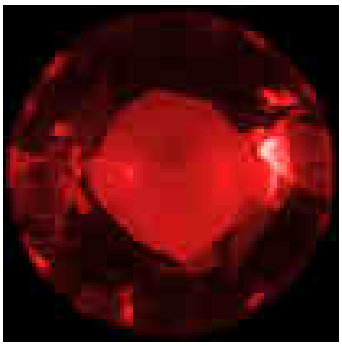
| Name: | Student Code: |
|---|---|

## 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. **20**

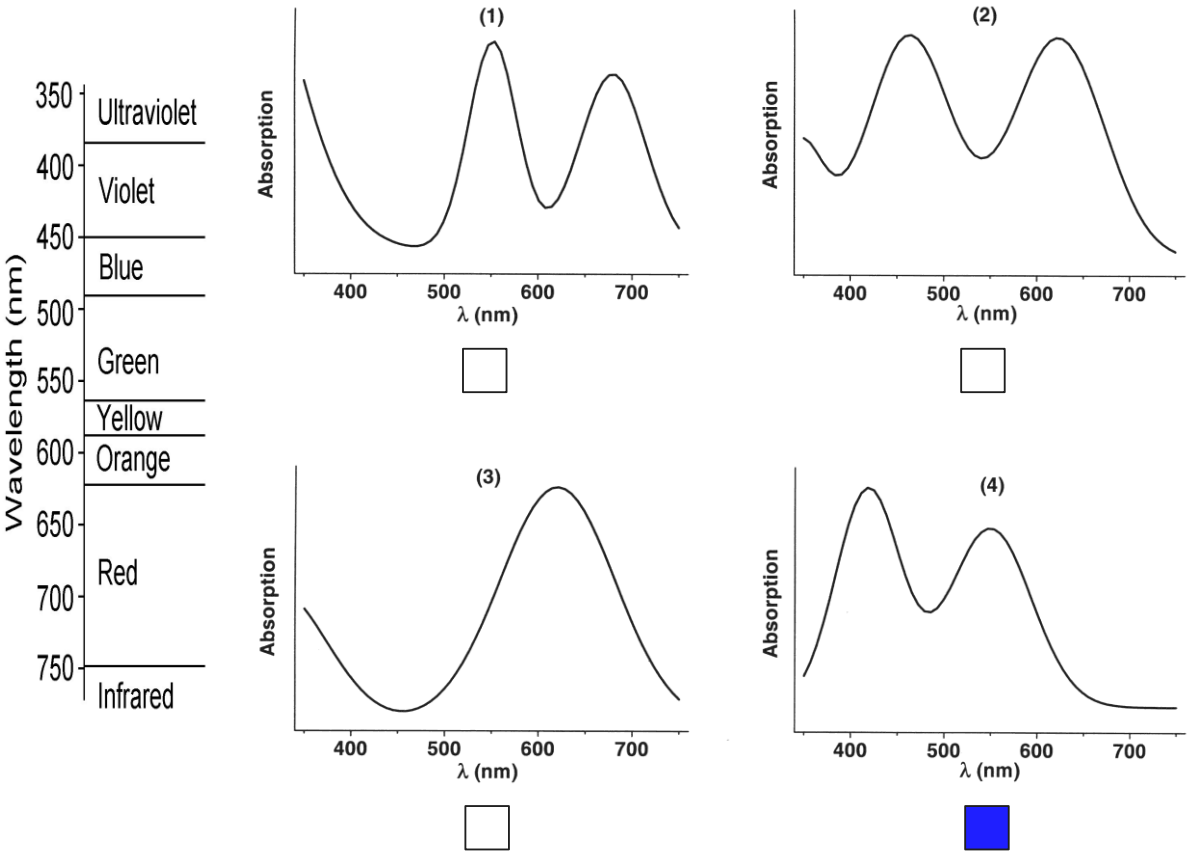



Figure 1

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).

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

Answer: $3.68 \times 10^{20}$ $Cr^{3+}$ ions.

Calculation:

The volume of the rod is $\pi r^2 l = \pi \times 0.575^2 \times 15.2 = 15.79$ cm$^3$. **5**

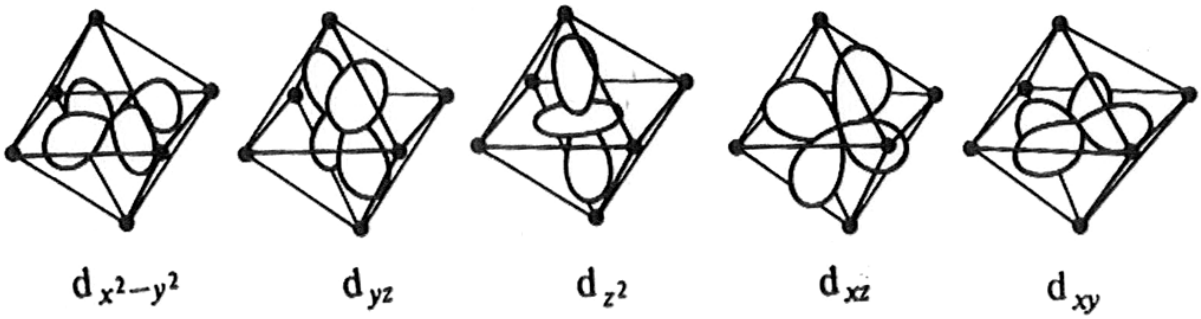
The total weight is $15.79 \times 4.05 = 63.94$ g. **5**

The amount of Cr is then $0.05\% \times 63.94 = 0.0319$ g. **5**

0.0319 g of Cr corresponds to $(0.0319 \times 10^{-3}$ kg) / $(52 \times 1.67 \times 10^{-27}$ kg) = $3.68 \times 10^{20}$ $Cr^{3+}$ ions. **5**

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 ($e_g$)..

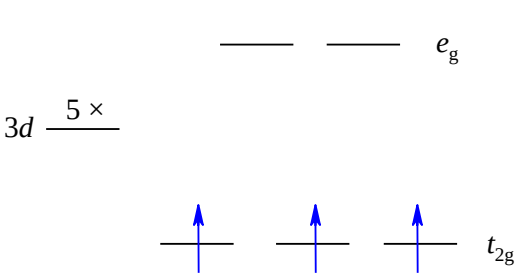
**IV-2-3** Indicate in the boxes below which of the 3*d* orbitals ($d_z^2$, $d_{xy}$, $d_{yz}$, $d_{x^2-y^2}$, $d_{xz}$) belong to the $t_{2g}$ group and which belong to the $e_g$ group.




| $e_g$ | $t_{2g}$ | $e_g$ | $t_{2g}$ | $t_{2g}$ |
|---|---|---|---|---|

**20 or 0**

**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 $Cr^{3+}$.




**10 for correct state, 10 for correct spin**

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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.

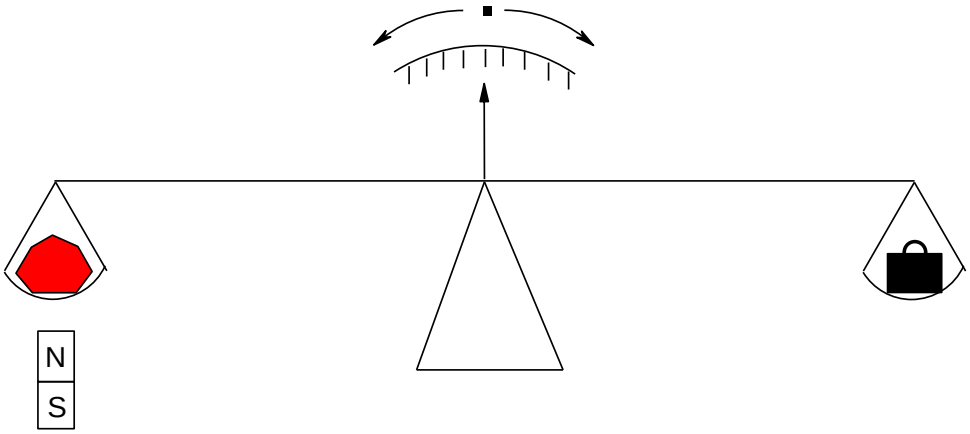


Figure 2

**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)

**20 or 0**

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|---|---|

## 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:

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

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

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

Reaction at the negative electrode: **10**

$Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\,e^-$

Reaction at the positive electrode: **15**

$PbO_2(s) + 3\,H^+(aq) + HSO_4^-(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$

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

Reaction at the negative electrode: **10**

$Li(s) \longrightarrow Li^+ + e^-$

Reaction at the positive electrode: **15**

$Li^+ + e^- + LiMn_2O_4(s) \longrightarrow Li_2Mn_2O_4(s)$

**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: 4 **10**

Mn-ions: 6 **10**

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: **20**

Answer: 1063.2 kg

Calculation:
Distance of the petrol car = 500 km ➔ 50 kWh
Weight of petrol tank plus fuel: 10 kg + 50 × (3.4 / 4.5) = 47.8 kg
Weight of the Pb-battery: 50,000 / 45 = 1111 kg
Extra weight for Pb-battery car: 1111 – 47.8 = 1063.2 kg

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(**b**) Extra weight of a lithium battery car: **10**

Answer: 322.2 kg

Calculation:
Weight of the Li-battery: 1/3 of the Pb-battery ➔ 1111 kg / 3 = 370 kg
Extra weight for Li-battery car: 370 – 47.8 = 322.2 kg

| Name: | Student Code: |
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# 34th International Chemistry Olympiad

# Groningen, Monday, 8 July 2002

# Practical Examination

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***Chemistry and the Quality of Life go Hand in Hand***

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**Enzymatic Hydrolysis of Methyl *N*-Acetyl-phenylalaninate**

**Synthesis of Benzylhydantoin**

**Determination of Iron in Iron Pills**

| **Name:** | **Student Code:** |
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# Introductory Remarks

- At all times while you are in the laboratory you should wear safety spectacles or your own spectacles if they have been approved. Use only a pipette filler bulb for pipetting. Eating of any kind of food is strictly prohibited in the laboratory.

- Participants are expected to work safely, to behave socially and to keep equipment and work environment clean. Violation of these rules may result in penalty points. Do not hesitate to ask a laboratory assistant if you have any questions concerning safety issues.

- When you enter the laboratory, check the emergency exits and the place of the safety shower.

- Please carefully read the text of the entire experimental task and study the layout of the answer forms before you begin your experimental work. Check where instruments are located. You have 15 minutes to prepare yourself for the experimental tasks.

- Work may only begin when the start signal is given.

- You have **5** hours to complete all of the experimental tasks, and record your results on the answer sheets. There will be a pre-warning 15 minutes before the end of your time. You must stop your work immediately after the stop command is given. A delay in doing this by 5 minutes will lead to cancellation of the current task and will result in zero points for that task.

- **This practical examination comprises three experiments. In order to use the available time efficiently, it is necessary to make a work plan. Read the content of all three experiments carefully. Conducting experiments simultaneously may save a considerable amount of time.**

- Write your name and personal identification code (posted at your work station) in the appropriate box of the answer sheets.

- All results must be written in the answer boxes on the answer sheets. Data written elsewhere will not be marked. Do not write anything on the back of your answer sheets. If you need more paper for working or a replacement answer sheet, request it from the laboratory assistant.

- When you have finished the examination, you must put all papers into the envelope provided, then you must seal the envelope. Only papers in the sealed envelope will be marked.

- Do not leave the examination room until you have permission to do so. A receipt for your sealed envelope will be issued to you as you leave.

- Use only the tools and calculator provided.

- A copy of the Periodic Table of the Elements is provided.

- The number of significant figures in numerical answers must conform to the rules of evaluation of experimental error. The inability to perform calculations correctly will result in penalty points, even if your experimental technique is flawless.

- This examination has 5 pages of answer sheets.

- An official English-language version is available only on request.

| Name: | Student Code: |
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## Safety

The rules described in the Preparatory Problems "safety rules" should be followed strictly.

## Disposal of waste chemicals, spills, and glassware

Organic filtrates and organic washings and any other waste should be placed in the waste beaker or bottle.

Use the appropriate waste containers for disposals of chemical and other waste materials.

Broken glass should be placed in the waste bucket.

## Cleaning up

The lab bench should be wiped clean with a wet tissue.

## Instructions for the Texas Instruments TL-83 plus calculator

The following instruction is sufficient for this Olympiad. This machine is a gift from Texas Instruments to mark this Olympiad. The calculator is able to perform many, many calculations, more than necessary for this examination. Other options can be found in the book, but do not use the book today.

On: Press on the button 'ON'.
Off: First press the button '2nd' and then press the button 'ON'.
Adding, subtracting, multiplying and dividing is as usual:
e.g. adding: Number 1 + Number 2 'enter'
Brackets can easily be used (on the panel above 8 and 9 resp.).
The buttons for ln, log, $x^{-1}$ and $x^2$ are on the panel.
For $e^x$ first press the button '$2^{nd}$' and then the button 'ln' ; press the number and 'enter'.
For $10^x$ first press the button '$2^{nd}$' and then the button 'log' ; press the number and 'enter'.
For $\sqrt{x}$ first press the button '$2^{nd}$' and then '$x^2$' ; press the number and 'enter'.
For the number e = 2.71828 first press the button '$2^{nd}$' and then press the button ' -:- ' .
For the number $\pi$ =3.14 first press the button '$2^{nd}$' and then press the button ' ^ ' .

In general: The yellow functions can be activated by first pressing '$2^{nd}$' (yellow button) and then the desired function in yellow.

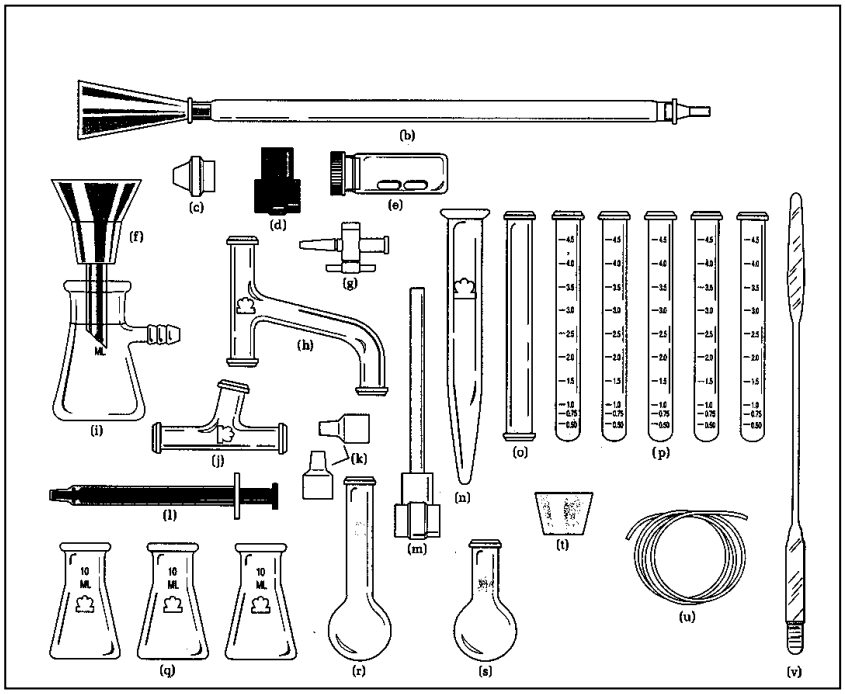
The screen can be cleared by pressing the 'clear' button.

| Name: | Student Code: |
|---|---|

# Chemicals, glassware and equipment:

### Microscale glassware kit

(a) Thermometer (on the bench)
(b) Chromatography column
(c) Thermometer adaptor
(d) Connector
(e) 2 Magnetic stirring bars
(f) Hirsch funnel
(g) One-way stopcock
(h) Distillation head 60 mm
(i) Filter flask 25 mL
(j) Connecting adaptor
(k) Sleeve stopper 8 mm septum
(l) Syringe polyethylene 1 mL
(m) Connector with support rod
(n) Centrifuge Tube 15 mL
(o) Distillation column
(p) Reaction tube 10 x 100 mm
(q) Erlenmeyer flask 10 mL
(r) Long neck flask 5 mL
(s) Short neck flask 5 mL
(t) Filter adapter
(u) Tubing PTFE 1/16”
(v) Spatula




### Glassware and equipment

| | | |
|---|---|---|
| Sand bath (sand supplied separately) | 1 | |
| Erlenmeyer (50 mL) | 1 | |
| Burette (50 mL) | 1 | |
| Burette clamp | 1 | |
| Clamp holder with clamp | 2 | |
| Support stand | 2 | |
| Mortar and pestle | 1 | |
| Beaker 100 mL | 1 | |
| Measuring cylinder 10 mL | 1 | |
| Volumetric flask 250 mL | 1 | |
| Volumetric flask 100 mL | 2 | |
| Glass funnel | 1 | |
| Measuring pipette 10 mL | 2 | |
| Pipetting balloon | 1 | |
| Pasteur pipettes | 10 | |
| Pasteur pipette bulbs | 3 | |
| Weighing paper | 20 | (in location Zernicke near the balances) |
| Magnetic stirrer | 1 | |
| Magnetic stirring bar | 1 | (in location Zernicke in sample tube) |
| Pair of tweezers | 1 | |
| Spoon | 1 | |
| Screw cap bottle (large) for TLC | 1 | |
| Thin layer plates (5 × 10 cm) | 4 | |
| Capillary tubes for TLC (in sample tube) | 5 | |
| Cuvets 1.000 cm | 2 | |

| | |
|---|---|
| Stirring rod | 1 |
| Sample tubes | 4 |
| Stopwatch | 1 |
| Sealing bag | 2 |

### Chemicals

| | |
|---|---|
| Methyl *N*-acetyl-phenylalaninate (NAcPheOMe) | 500 mg (exact weight ± 1 mg) |
| (S)-Phenylalanine (Phe) | 500 mg (exact weight ± 1 mg) |
| Sodium cyanate (NaOCN) | 300 mg |
| α-Chymotrypsin solution (0.05% in water) | 10 mL in a vial, available from the laboratory assistant |
| Iron pill in envelope | 1 pill |
| Methanol (MeOH) | 20 mL |
| Hydrochloric acid (HCl) 4 M | 50 mL |
| Sodium hydroxide (NaOH) 0.1 M | 70 mL (exact titer is given in your examination paper) |
| Sodium hydroxide (NaOH) 1 M | 3 mL in small vial |
| Propyl red solution (0.02% in ethanol) | 3 mL in small vial |
| Buffer solution pH=8 | 150 mL |
| Hydroxylamine.HCl solution ($H_2NOH.HCl$) 100 g $L^{-1}$ | 10 mL |
| 1,10-Phenanthroline solution 1 g $L^{-1}$ | 20 mL |
| Di-isopropylether | 50 mL |
| Acetone (high purity) | 10 mL |
| TLC eluent (2% formic acid in ethyl acetate) | 20 mL |
| pH-paper | 4 pieces |
| Hi-flo filter aid | 5 g |
| Wash bottle with acetone (for cleaning) | 250 mL |
| Wash bottle with "demi" water | 500 mL |

## Available for general use

Cleaning paper
Sponge
Brush
Waste container
Parafilm

## Equipment for general use

Hotplate (only in location Zernicke)
Ultrasonic bath
Vacuumpump
Spectrophotometer
Balance
UV lamp

| Name: | Student Code: |
|---|---|

# R and S phrases

## Acetone

| | |
|---|---|
| Formula | $C_3H_6O$ |
| Molecular weight | 58.08 |
| Melting point | -95 $^oC$ |
| Boiling point | 56 $^oC$ |
| Density | 0.79 g/cm$^3$ |

R11 Highly flammable
S9 Keep container in a well-ventilated place
S16 Keep away from sources of ignition
S23 Do not breathe vapour
S33 Take precautionary measures against static discharges

## Di-isopropyl ether

| | |
|---|---|
| Formula | $C_6H_{14}O$ |
| Molecular weight | 102.17 |
| Melting point | -85 $^oC$ |
| Boiling point | 68 $^oC$ |
| Density | 0.72 g/cm$^3$ |

R11 Highly flammable
R19 May form explosive peroxides.
R66 Repeated exposure may cause skin dryness or cracking
R67 Vapours may cause drowsiness and dizziness
S9 Keep container in a well-ventilated place
S16 Keep away from sources of ignition – No smoking
S29 Do not empty into drains
S33 Take precautionary measures against static discharges

## Ethanol

| | |
|---|---|
| Formula | $C_2H_6O$ |
| Molecular weight | 46.08 |
| Melting point | -114 $^oC$ |
| Boiling point | 78 $^oC$ |
| Density | 0.78 g/cm$^3$ |

R11 Highly Flammable
S7 Keep container tightly closed
S16 Keep away from sources of ignition

## Ethyl acetate

| | |
|---|---|
| Formula | $C_4H_8O_2$ |
| Molecular weight | 88.10 |
| Melting point | -84 $^oC$ |
| Boiling point | 76 $^oC$ |
| Density | 0.90 g/cm$^3$ |

R11 Highly flammable
R36 Irritating to the eyes

| **Name:** | **Student Code:** |
|---|---|

R66 Repeated exposure may cause skin dryness or cracking
R67 Vapours may cause drowsiness and dizziness
S16 Keep away from sources of ignition – No smoking
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advise
S33 Take precautionary measures against static discharges

## Hydrochloric acid

Formula HCl
Molecular weight 36.46
Density 0.909

R11 Highly flammable
R37/37 Irritating to eyes, respiratory system and skin

38
S16 Keep away from sources of ignition – No smoking
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advise
S45 In case of accident of if you feel unwell, seek medical advise immediately (show the label where possible)
S7 Keep container tightly closed

## Hydroxylamine hydrochloride

Formula $H_3NO.HCl$
Molecular weight 69.49
Melting point 155 $^oC$
Density 1.67 $g/cm^3$

R22 Harmful if swallowed
R36/38 Irritating to eyes and skin
R43 May cause sensitisation by skin contact
R48/22 Harmful: danger of serious damage to health by prolonged exposure if swallowed
R50 Very toxic to aquatic organisms
S22 Do not inhale dust
S24 Avoid contact with skin
S37 Wear suitable gloves
S61 Avoid release to the environment.

## *Methanol*

Formula $CH_4O$
Molecular weight 32.04
Melting point -98 $^oC$
Boiling point 65 $^oC$
*Density* *0.79 $g/cm^3$*

*R11 Highly flammable*
*R23-25 Toxic by inhalation, in contact with skin and if swallowed*
*R39/23 24/25 Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed*
*S7 Keep container tightly closed*

*S16 Keep away from sources of ignition –No smoking*
*S36/37 Wear suitable protective clothing and gloves*
*S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)*

## *1,10-Phenanthroline*

Formula $C_{12}H_8N_2$
Molecular weight 180.20
Melting point 117-120 $^oC$

*R25 Toxic when swallowed*
*R50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment*
*S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)*
*S60 This material and its container must be disposed of as hazardous waste*
*S61 Avoid release to the environment*

## L-*Phenylalanine*

*Formula* $C_9H_{11}NO_2$
*Molecular weight 165.19*
*Melting point 270-275 $^oC$*

*S24/25 Avoid contact with skin and eyes*

## *Sodium Cyanate*

*Formula NaOCN*
*Molecular weight 65.00*
*Melting point 550 $^oC$*

*R22 Harmful if swallowed*
*R52/53 Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment*
*S24/25 Avoid contact with skin and eyes*
*S61 Avoid release to the environment*

## *Sodium hydroxide*

*Formula NaOH*
*Molecular weight 40.00*
*Melting point 318 $^oC$*

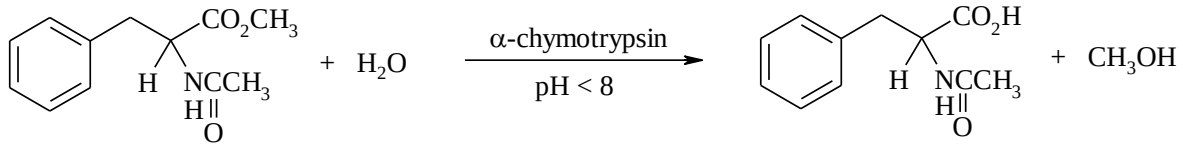
*R35 Causes severe burns*
*S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice*
*S37/39 Wear suitable gloves and eye/face protection*
*S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)*

| **Name:** | **Student Code:** |
|---|---|

# Enzymatic Hydrolysis of Methyl *N*-Acetyl-phenylalaninate

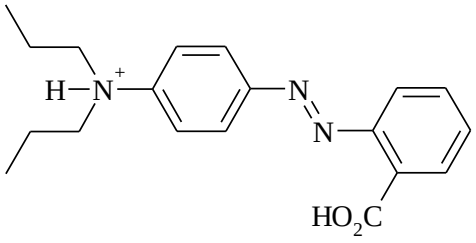
## Introduction

α-Chymotrypsin, a protease enzyme recognizing derivatives of natural α-amino acids, catalyses the hydrolysis of esters. In this experiment the enzymatic hydrolysis of racemic methyl *N*-acetyl-phenylalaninate **A** is investigated (Scheme).




**A** **B**

*The rate of formation of* N-*acetyl-phenylalanine **B** can be monitored by titration with 0.100 M NaOH in the presence of propyl red as a pH indicator.*




Propyl red (protonated form)
At pH < 5: pink; at pH > 6: yellow

**Procedure**

***Note: the required amount of α-chymotrypsin will be supplied in a sample vial by the laboratory assistant on request.***

**Racemic methyl *N*-acetyl-phenylalaninate** A **[500 mg, the exact weight (± 1 mg) is indicated on the label of the vial marked as NacPheOMe] is transferred quantitatively into a 50 mL Erlenmeyer flask and dissolved in methanol (~ 2.5 mL). Subsequently, propyl red (0.02% solution in ethanol; 4 drops) is added. The kinetic experiment is started by adding α-chymotrypsin (10.0 mL of a 0.05% solution in distilled water) in one portion (*start the stopwatch*).**

**When the reaction mixture turns pink, it is immediately titrated with 0.100 M NaOH until the colour changes to yellow. When the pink colour reappears, add just enough titrant to restore the pale yellow colour, swirling the flask continually during the addition. You only need to record the reading on the burette every 5 minutes. (*Note: at the beginning colour changes occur very frequently.*)**

**Monitor the reaction for 75 minutes. A graph showing the amounts of NaOH consumed in mL versus time is constructed, in order to visualize the kinetic course of this enzymatic reaction.**

| **Name:** | **Student Code:** |
|---|---|

**34th IChO Laboratory Task** **Answer Sheet 1**

**Score 12 points**

# Enzymatic Hydrolysis of Methyl *N*-Acetyl-phenylalaninate

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| **Marks** | **10** | **30** | **30** | **10** | **10** | **10** |

**1** Amount of the starting racemic methyl *N*-acetyl-phenylalaninate **A**

mg = mmol

**2** Record the time in minutes and the total consumption of NaOH in mL (accuracy ± 0.05 mL), according to the scheme below. Final recording after 75 minutes.

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (min) | | | | | | | | | | | | | | | 75 |
| NaOH (mL) | | | | | | | | | | | | | | | |

**3** Construct a graph of the total consumption of NaOH vs time on the supplied graph paper.
Put minutes on the x-axis: 5 min. per cm
Put mL NaOH on the y-axis: 1.0 mL per cm

**4** Calculate the amount of 0.100 M NaOH consumed in this experiment in mmol

Answer:

Calculation:

| **Name:** | **Student Code:** |
|---|---|

**Enzymatic Hydrolysis… (Cont'd)** **Answer Sheet 2**

**5** Calculate the degree of hydrolysis of methyl *N*-acetyl-(*R*,*S*)-phenylalaninate **A** in mol%
Answer:

Calculation:

**6** Which of the following statements is in accordance with your experimental results? Mark the appropriate box.

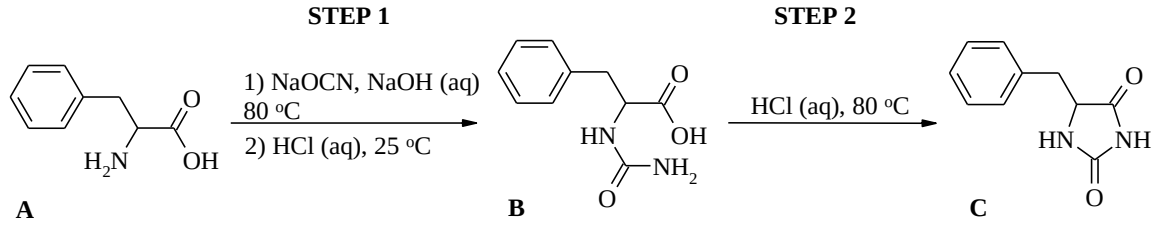
- ❑ The enzyme catalyses the hydrolysis to give methyl *N*-acetyl-(*S*)-phenylalaninate and *N*-acetyl-(*R*)-phenylalanine.
- ❑ The enzyme catalyses the hydrolysis to give *N*-acetyl-(*R*,*S*)-phenylalanine.
- ❑ The enzyme catalyses the hydrolysis to give methyl *N*-acetyl-(*R*)-phenylalaninate and *N*-acetyl-(*S*)-phenylalanine
- ❑ The enzyme loses its catalytic activity during the course of the reaction.

| **Name:** | **Student Code:** |
|---|---|

# Synthesis of Benzylhydantoin

## Introduction

α-Amino acids are the building blocks for peptides and proteins. They are also frequently used as starting material for the synthesis of pharmaceuticals. In this experiment natural *S*-phenylalanine **A** is converted in two steps into benzylhydantoin **C**, which is a useful intermediate for the preparation of various physiologically active derivatives.




**A** Molecular Weight =165.19 **B** Molecular Weight =208.22 **C** Molecular Weight =190.20

**Procedure**

**STEP 1**

***Retain a tiny amount of starting material*** *A* ***for the TLC analysis (see below).*** **A long-necked round-bottomed flask is charged with (*S*)-phenylalanine** A **(500 mg, 3 mmol, the exact amount is indicated on the label of the vial), sodium cyanate (300 mg, 4.6 mmol), water (3 mL) and a stirring bar. Two drops of aqueous sodium hydroxide (1 M) are added to the stirred suspension. The flask is equipped with a condenser (distillation column) and the reaction mixture is heated to 80 °C on a sand bath while stirring magnetically.**

***Important***

***In order to reach the appropriate temperature in time and not lose too much time, start the electric heating of the sand bath immediately at the beginning of this experiment. Check the temperature of the sand bath regularly and carefully with a thermometer.***

**After heating the reaction mixture at 80 °C for at least 30 minutes, the resulting clear solution is cooled to room temperature and poured into a small Erlenmeyer flask. Rinse the round-bottomed flask with a little water. The solution is acidified by dropwise addition of hydrochloric acid (4 M) to pH < 3 with magnetic stirring. Some water is added to the resulting white suspension in order to facilitate stirring.**

**The white precipitate is then filtered off by suction, washed with ample water (on the filter) and then washed twice with a small amount of di-isopropyl ether to remove most of the adhering water. The urea derivative** B **is left on the filter under suction for at least 3 minutes to remove as much solvent as possible.**

A small amount of the obtained urea derivative **B** is retained for TLC-analysis later.

**STEP 2**

The urea derivative **B** is now transferred into a long-necked round-bottomed flask and hydrochloric acid (4 M, 3 mL) is added. A stirring bar is introduced and the suspension is stirred thoroughly whilst heating at 80 °C on a sand bath. A clear solution is obtained. After a reaction time of 30 minutes, the reaction mixture, which may already contain some precipitate, is cooled to room temperature. The obtained suspension is filtered by suction, washed thoroughly with water and finally washed twice

with a small amount of di-isopropyl ether. The product is left on the filter under suction for at least 3 minutes. It is then collected on a filter paper and dried in the air for at least 30 minutes.

The final product **C**, its precursor **B** and starting material **A** (see above) are subjected to TLC-analysis. For this purpose small amounts of either compound are dissolved in a tiny amount of pure acetone. Small samples of these solutions are applied to a TLC plate, using the supplied capillary tubes. The analysis is carried out with two TLC plates in one run. The TLC-plates are developed with a solution of 2% formic acid in ethyl acetate as the eluent. After the elution the TLC-plates are analysed using a UV-lamp. The starting line, solvent front and the UV-active spots are clearly marked with a pencil. Copy the diagram in the box on the answer sheet. The $R_f$ values are determined. Finally, the TLC-plate with the best analysis is wrapped in parafilm and placed in a plastic bag with a sealing strip.

The final product **C** is transferred into a sample vial of which the empty weight has been pre-determined (weight is indicated on the label). Weigh the vial with product and calculate the yield of the product **C**.

The examination committee will check the quality of the benzylhydantoin that you have prepared by determining its melting point using an automatic melting point apparatus.

| **Name:** | **Student Code:** |
|---|---|

**34th IChO Laboratory Task** **Answer Sheet 3**

**Score 18 points**

## Synthesis of Benzylhydantoin

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| **Marks** | **10** | **20** | **10** | **10** | **20** | **10** | **10** | **10** |

Weight of your starting material **A** (see label on the vial): mg

Weight of the empty sample vial: mg
(see label on the vial: YOUR PRODUCT)

**1** Weight of the sample vial containing your product **C**: mg

**2** Amount of benzylhydantoin **C** obtained: mg

Calculate the yield of benzylhydantoin **C:**
Answer: %

Calculation:

**3** $R_f$ value of urea derivative **B**
Answer:

Calculation:

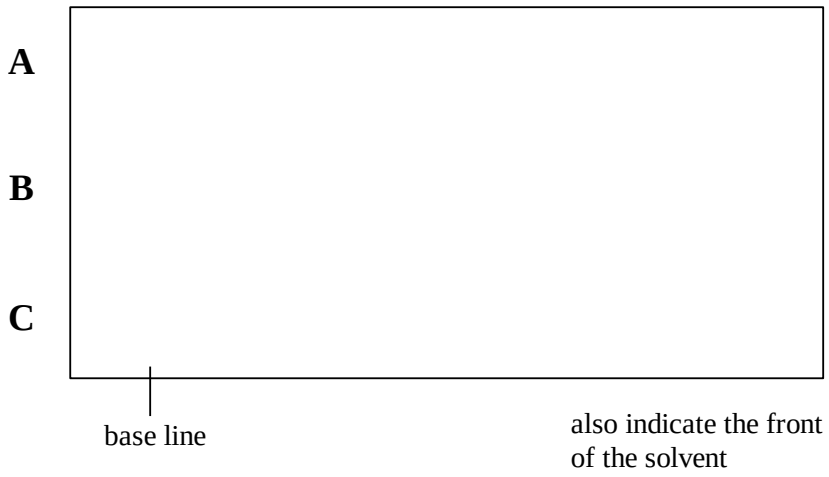
**4** $R_f$ value of benzylhydantoin **C**
Answer:

Calculation:

| **Name:** | **Student Code:** |
|---|---|

**Synthesis of Benzylhydantoin (Cont'd)** **Answer Sheet 4**

**5** Copy the TLC diagram in the box below




**6** Conclusions from the TLC analysis:

Compound **B**:

- ❑ is pure
- ❑ contains some **A**
- ❑ contains several contaminants

Compound **C**:

- ❑ is pure
- ❑ contains some **B**
- ❑ contains some **A** and **B**
- ❑ contains several contaminants

**7** Appearance of benzylhydantoin **C,** mark what is appropriate for your product.

- ❑ White colour
- ❑ Yellowish colour
- ❑ Sticky
- ❑ Crystalline
- ❑ Powder

**8** Melting point of benzylhydantoin **C** will be determined later by the examination committee - $^{o}$C

Place your packed TLC plate (see procedure) in an envelope with your name and student number.

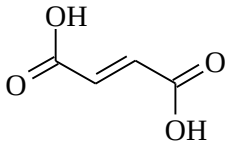
| **Name:** | **Student Code:** |
|---|---|

# Determination of Iron in Iron Pills

Introduction

Iron is an essential component of hemoglobin, transporting oxygen in the blood to all parts of the body. It also plays a vital role in many metabolic reactions. Iron deficiency can cause anaemia resulting from low levels of hemoglobin in the blood. Iron deficiency is the most widespread mineral nutritional deficiency worldwide. One way to reduce iron shortage is by treatment with iron pills.

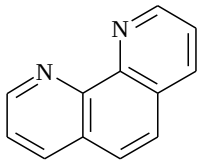
The active ingredient in the iron pill to be examined, is iron(II) present as iron(II) fumarate. Besides this organic iron(II) compound the pill contains other compounds such as binding agents. The structure of fumaric acid is:




Fumaric acid

Iron(II) and 1,10-phenanthroline form an orange/red coloured complex $[(C_{12}H_8N_2)_3Fe]^{2+}$. The absorbance of this complex, determined at 510 nm in a buffer solution (pH=8) is a measure for the iron content of the iron pill. Since 1,10-phenanthroline only binds to iron(II) and iron(II) is readily oxidized to iron(III), hydroxylammonium chloride is added to reduce all iron(III) to iron(II). A simplified reaction scheme is:

$$2\ NH_2OH\ +\ 4\ Fe^{3+} \rightarrow N_2O\ +\ 4\ H^{+}\ +\ H_2O\ +\ 4\ Fe^{2+}$$




1,10-Phenanthroline

Procedure

The weight of the iron pill is determined with an accuracy of 1 mg using a balance. The pill is carefully pulverized in a mortar and transferred quantitatively into a 100 mL beaker with the aid of a small amount of distilled water. Hydrochloric acid (5 mL, 4 M) is added. The content of the beaker is heated up to approximately 60 $^{o}$C on a hotplate. The solution turns a yellow colour.

The beaker is then placed in an ultrasonic bath for at least 5 minutes. The beaker is kept in place by styrofoam. The suspension is filtered by suction using a Hirsch funnel containing a small layer of moistened hi-flow filter aid pressed onto the filter. The hi-flow filter aid is washed with ample distilled water. The filtrate is carefully transferred into a volumetric flask (250 mL) and the final volume adjusted by adding distilled water and with regular mixing. An amount of 10 mL is pipetted from this solution and transferred into a volumetric flask of 100 mL. Again the volume is adjusted with distilled water while mixing the content of the flask.

From this solution, 10 mL is pipetted and transferred into a volumetric flask of 100 mL. Subsequently, 1,10-phenanthroline solution (10 mL) and hydroxylammonium chloride solution (1 mL) are added. Then the volume is adjusted with buffer solution (pH 8).

The absorbance of this solution is measured with a spectrophotometer at 510 nm against water as a blank in a 1.000 cm cuvet.

Calculate the amount of iron in the iron pill on basis of the known molar absorptivity (extinction coefficient, ε) of the iron(II)phenanthroline complex at 510 nm. The molar absorptivity of the iron(II)phenanthroline complex at 510 nm is 11100 $M^{-1}cm^{-1}$.

| **Name:** | **Student Code:** |
|---|---|

## *Important*

*In order to eliminate deviations in absorbance typically connected to the spectrophotometer used, a correction factor is denoted on the spectrophotometer you will be using for your experiment. The absorbance observed must be multiplied by this factor in order to obtain the correct absorbance of the solution of the iron complex.*

| Name: | Student Code: |
|---|---|

**34th IChO Laboratory Task** **Answer Sheet 5**

**Score 10 points**

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| **Marks** | **15** | **40** | **20** | **10** | **15** |

# Determination of Iron in Iron Pills

**1** Weight of the iron pill mg

Number of the spectrophotometer

Correction factor

**2** Reading of the spectrophotometer: ; corrected absorbance: AU

**3** Concentration of iron(II)phenanthroline complex in the cuvet: mmol $L^{-1}$
Calculation:

**4** Total amount of iron(II) in the pill: mg
Calculation:

**5** Calculate the iron content of the pill in weight%
*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
f block
Metals
Non-metals
*Lanthanides
**Actinides

| Name: | Student Code: |
|---|---|

# Scientific Committee of the 34th International Chemistry Olympiad

**Chairperson:**

| | |
|---|---|
| Prof.dr. B. Zwanenburg | University of Nijmegen |

**Section Theory:**

| | |
|---|---|
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| Prof.dr. H.P.J. Bloemers | University of Nijmegen |
| Prof.dr. F.B. van Duijneveldt | University of Utrecht |
| Prof.dr. J.B.F.N. Engberts | University of Groningen |
| Dr. G.A. van der Marel | University of Leiden |
| Prof.dr. E.W. Meijer | Eindhoven University of Technology |
| Prof.dr. A. Meijerink | University of Utrecht |
| Prof.dr. A. Oskam | University of Amsterdam |
| Prof.dr. J. Schoonman | Delft University of Technology |
| Prof.dr. A.J. Schouten | University of Groningen |
| Ms. Prof.dr. N.H. Velthorst | Free University, Amsterdam |
| Prof.ir. J.A. Wesselingh | University of Groningen |

**Section Practical:**

| | |
|---|---|
| Prof.dr. J.F.J. Engbersen | Twente University of Technology |
| Dr. E. Joling | University of Amsterdam |
| Dr. A.J.H. Klunder | University of Nijmegen |
| Dr. A.J. Minnaard | University of Groningen |
| Dr. J.A.J.M. Vekemans | Eindhoven University of Technology |
| Mr.Ing. T. van Weerd | University of Nijmegen |
| Dr. W.H. de Wolf | Free University, Amsterdam |

**Consultants:**

Drs. P. de Groot
Drs. A.M Witte
Drs. W. Davids

**Secretariat:** University of Nijmegen

Dr. R. Ruinaard
J. Brinkhorst
Ms. M.V. Versteeg

| Name: | Student Code: |
|---|---|

# 34th International Chemistry Olympiad

# Groningen, Monday, 8 July 2002

# Practical Examination

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***Chemistry and the Quality of Life go Hand in Hand***

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**Enzymatic Hydrolysis of Methyl *N*-Acetyl-phenylalaninate**

**Synthesis of Benzylhydantoin**

**Determination of Iron in Iron Pills**

| **Name:** | **Student Code:** |
|---|---|

# Introductory Remarks

- At all times while you are in the laboratory you should wear safety spectacles or your own spectacles if they have been approved. Use only a pipette filler bulb for pipetting. Eating of any kind of food is strictly prohibited in the laboratory.

- Participants are expected to work safely, to behave socially and to keep equipment and work environment clean. Violation of these rules may result in penalty points. Do not hesitate to ask a laboratory assistant if you have any questions concerning safety issues.

- When you enter the laboratory, check the emergency exits and the place of the safety shower.

- Please carefully read the text of the entire experimental task and study the layout of the answer forms before you begin your experimental work. Check where instruments are located. You have 15 minutes to prepare yourself for the experimental tasks.

- Work may only begin when the start signal is given.

- You have **5** hours to complete all of the experimental tasks, and record your results on the answer sheets. There will be a pre-warning 15 minutes before the end of your time. You must stop your work immediately after the stop command is given. A delay in doing this by 5 minutes will lead to cancellation of the current task and will result in zero points for that task.

- **This practical examination comprises three experiments. In order to use the available time efficiently, it is necessary to make a work plan. Read the content of all three experiments carefully. Conducting experiments simultaneously may save a considerable amount of time.**

- Write your name and personal identification code (posted at your work station) in the appropriate box of the answer sheets.

- All results must be written in the answer boxes on the answer sheets. Data written elsewhere will not be marked. Do not write anything on the back of your answer sheets. If you need more paper for working or a replacement answer sheet, request it from the laboratory assistant.

- When you have finished the examination, you must put all papers into the envelope provided, then you must seal the envelope. Only papers in the sealed envelope will be marked.

- Do not leave the examination room until you have permission to do so. A receipt for your sealed envelope will be issued to you as you leave.

- Use only the tools and calculator provided.

- A copy of the Periodic Table of the Elements is provided.

- The number of significant figures in numerical answers must conform to the rules of evaluation of experimental error. The inability to perform calculations correctly will result in penalty points, even if your experimental technique is flawless.

- This examination has 5 pages of answer sheets.

- An official English-language version is available only on request.

| Name: | Student Code: |
|---|---|

## Safety

The rules described in the Preparatory Problems "safety rules" should be followed strictly.

## Disposal of waste chemicals, spills, and glassware

Organic filtrates and organic washings and any other waste should be placed in the waste beaker or bottle.

Use the appropriate waste containers for disposals of chemical and other waste materials.

Broken glass should be placed in the waste bucket.

## Cleaning up

The lab bench should be wiped clean with a wet tissue.

## Instructions for the Texas Instruments TL-83 plus calculator

The following instruction is sufficient for this Olympiad. This machine is a gift from Texas Instruments to mark this Olympiad. The calculator is able to perform many, many calculations, more than necessary for this examination. Other options can be found in the book, but do not use the book today.

On: Press on the button 'ON'.
Off: First press the button '2nd' and then press the button 'ON'.
Adding, subtracting, multiplying and dividing is as usual:
e.g. adding: Number 1 + Number 2 'enter'
Brackets can easily be used (on the panel above 8 and 9 resp.).
The buttons for ln, log, $x^{-1}$ and $x^2$ are on the panel.
For $e^x$ first press the button '$2^{nd}$' and then the button 'ln' ; press the number and 'enter'.
For $10^x$ first press the button '$2^{nd}$' and then the button 'log' ; press the number and 'enter'.
For $\sqrt{x}$ first press the button '$2^{nd}$' and then '$x^2$' ; press the number and 'enter'.
For the number e = 2.71828 first press the button '$2^{nd}$' and then press the button ' -:- ' .
For the number $\pi$ =3.14 first press the button '$2^{nd}$' and then press the button ' ^ ' .

In general: The yellow functions can be activated by first pressing '$2^{nd}$' (yellow button) and then the desired function in yellow.

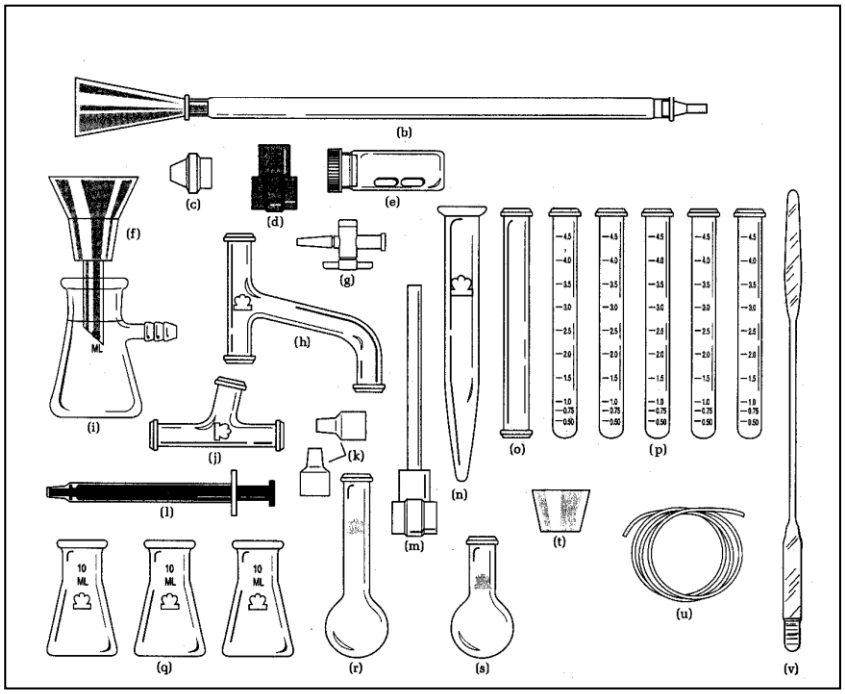
The screen can be cleared by pressing the 'clear' button.

| Name: | Student Code: |
|---|---|

# Chemicals, glassware and equipment:

### Microscale glassware kit

(a) Thermometer (on the bench)
(b) Chromatography column
(c) Thermometer adaptor
(d) Connector
(e) 2 Magnetic stirring bars
(f) Hirsch funnel
(g) One-way stopcock
(h) Distillation head 60 mm
(i) Filter flask 25 mL
(j) Connecting adaptor
(k) Sleeve stopper 8 mm septum
(l) Syringe polyethylene 1 mL
(m) Connector with support rod
(n) Centrifuge Tube 15 mL
(o) Distillation column
(p) Reaction tube 10 x 100 mm
(q) Erlenmeyer flask 10 mL
(r) Long neck flask 5 mL
(s) Short neck flask 5 mL
(t) Filter adapter
(u) Tubing PTFE 1/16”
(v) Spatula




### Glassware and equipment

| | | |
|---|---|---|
| Sand bath (sand supplied separately) | 1 | |
| Erlenmeyer (50 mL) | 1 | |
| Burette (50 mL) | 1 | |
| Burette clamp | 1 | |
| Clamp holder with clamp | 2 | |
| Support stand | 2 | |
| Mortar and pestle | 1 | |
| Beaker 100 mL | 1 | |
| Measuring cylinder 10 mL | 1 | |
| Volumetric flask 250 mL | 1 | |
| Volumetric flask 100 mL | 2 | |
| Glass funnel | 1 | |
| Measuring pipette 10 mL | 2 | |
| Pipetting balloon | 1 | |
| Pasteur pipettes | 10 | |
| Pasteur pipette bulbs | 3 | |
| Weighing paper | 20 | (in location Zernicke near the balances) |
| Magnetic stirrer | 1 | |
| Magnetic stirring bar | 1 | (in location Zernicke in sample tube) |
| Pair of tweezers | 1 | |
| Spoon | 1 | |
| Screw cap bottle (large) for TLC | 1 | |
| Thin layer plates (5 × 10 cm) | 4 | |
| Capillary tubes for TLC (in sample tube) | 5 | |
| Cuvets 1.000 cm | 2 | |

| | |
|---|---|
| Stirring rod | 1 |
| Sample tubes | 4 |
| Stopwatch | 1 |
| Sealing bag | 2 |

### Chemicals

| | |
|---|---|
| Methyl *N*-acetyl-phenylalaninate (NAcPheOMe) | 500 mg (exact weight ± 1 mg) |
| (S)-Phenylalanine (Phe) | 500 mg (exact weight ± 1 mg) |
| Sodium cyanate (NaOCN) | 300 mg |
| α-Chymotrypsin solution (0.05% in water) | 10 mL in a vial, available from the laboratory assistant |
| Iron pill in envelope | 1 pill |
| Methanol (MeOH) | 20 mL |
| Hydrochloric acid (HCl) 4 M | 50 mL |
| Sodium hydroxide (NaOH) 0.1 M | 70 mL (exact titer is given in your examination paper) |
| Sodium hydroxide (NaOH) 1 M | 3 mL in small vial |
| Propyl red solution (0.02% in ethanol) | 3 mL in small vial |
| Buffer solution pH=8 | 150 mL |
| Hydroxylamine.HCl solution ($H_2NOH.HCl$) 100 g $L^{-1}$ | 10 mL |
| 1,10-Phenanthroline solution 1 g $L^{-1}$ | 20 mL |
| Di-isopropylether | 50 mL |
| Acetone (high purity) | 10 mL |
| TLC eluent (2% formic acid in ethyl acetate) | 20 mL |
| pH-paper | 4 pieces |
| Hi-flo filter aid | 5 g |
| Wash bottle with acetone (for cleaning) | 250 mL |
| Wash bottle with "demi" water | 500 mL |

## Available for general use

Cleaning paper
Sponge
Brush
Waste container
Parafilm

## Equipment for general use

Hotplate (only in location Zernicke)
Ultrasonic bath
Vacuumpump
Spectrophotometer
Balance
UV lamp

| Name: | Student Code: |
|---|---|

# R and S phrases

## Acetone

| | |
|---|---|
| Formula | $C_3H_6O$ |
| Molecular weight | 58.08 |
| Melting point | -95 $^oC$ |
| Boiling point | 56 $^oC$ |
| Density | 0.79 g/cm$^3$ |

R11 Highly flammable
S9 Keep container in a well-ventilated place
S16 Keep away from sources of ignition
S23 Do not breathe vapour
S33 Take precautionary measures against static discharges

## Di-isopropyl ether

| | |
|---|---|
| Formula | $C_6H_{14}O$ |
| Molecular weight | 102.17 |
| Melting point | -85 $^oC$ |
| Boiling point | 68 $^oC$ |
| Density | 0.72 g/cm$^3$ |

R11 Highly flammable
R19 May form explosive peroxides.
R66 Repeated exposure may cause skin dryness or cracking
R67 Vapours may cause drowsiness and dizziness
S9 Keep container in a well-ventilated place
S16 Keep away from sources of ignition – No smoking
S29 Do not empty into drains
S33 Take precautionary measures against static discharges

## Ethanol

| | |
|---|---|
| Formula | $C_2H_6O$ |
| Molecular weight | 46.08 |
| Melting point | -114 $^oC$ |
| Boiling point | 78 $^oC$ |
| Density | 0.78 g/cm$^3$ |

R11 Highly Flammable
S7 Keep container tightly closed
S16 Keep away from sources of ignition

## Ethyl acetate

| | |
|---|---|
| Formula | $C_4H_8O_2$ |
| Molecular weight | 88.10 |
| Melting point | -84 $^oC$ |
| Boiling point | 76 $^oC$ |
| Density | 0.90 g/cm$^3$ |

R11 Highly flammable
R36 Irritating to the eyes

R66 Repeated exposure may cause skin dryness or cracking
R67 Vapours may cause drowsiness and dizziness
S16 Keep away from sources of ignition – No smoking
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advise
S33 Take precautionary measures against static discharges

## Hydrochloric acid

Formula HCl
Molecular weight 36.46
Density 0.909

R11 Highly flammable
R37/37 Irritating to eyes, respiratory system and skin

38
S16 Keep away from sources of ignition – No smoking
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advise
S45 In case of accident of if you feel unwell, seek medical advise immediately (show the label where possible)
S7 Keep container tightly closed

## Hydroxylamine hydrochloride

Formula $H_3NO.HCl$
Molecular weight 69.49
Melting point 155 $^oC$
Density 1.67 $g/cm^3$

R22 Harmful if swallowed
R36/38 Irritating to eyes and skin
R43 May cause sensitisation by skin contact
R48/22 Harmful: danger of serious damage to health by prolonged exposure if swallowed
R50 Very toxic to aquatic organisms
S22 Do not inhale dust
S24 Avoid contact with skin
S37 Wear suitable gloves
S61 Avoid release to the environment.

## *Methanol*

Formula $CH_4O$
Molecular weight 32.04
Melting point -98 $^oC$
Boiling point 65 $^oC$
*Density* *0.79 $g/cm^3$*

*R11 Highly flammable*
*R23-25 Toxic by inhalation, in contact with skin and if swallowed*
*R39/23 24/25 Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed*
*S7 Keep container tightly closed*

*S16 Keep away from sources of ignition –No smoking*
*S36/37 Wear suitable protective clothing and gloves*
*S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)*

## *1,10-Phenanthroline*

Formula $C_{12}H_8N_2$
Molecular weight 180.20
Melting point 117-120 $^oC$

*R25 Toxic when swallowed*
*R50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment*
*S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)*
*S60 This material and its container must be disposed of as hazardous waste*
*S61 Avoid release to the environment*

## L-*Phenylalanine*

*Formula* $C_9H_{11}NO_2$
*Molecular weight 165.19*
*Melting point 270-275 $^oC$*

*S24/25 Avoid contact with skin and eyes*

## *Sodium Cyanate*

*Formula NaOCN*
*Molecular weight 65.00*
*Melting point 550 $^oC$*

*R22 Harmful if swallowed*
*R52/53 Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment*
*S24/25 Avoid contact with skin and eyes*
*S61 Avoid release to the environment*

## *Sodium hydroxide*

*Formula NaOH*
*Molecular weight 40.00*
*Melting point 318 $^oC$*

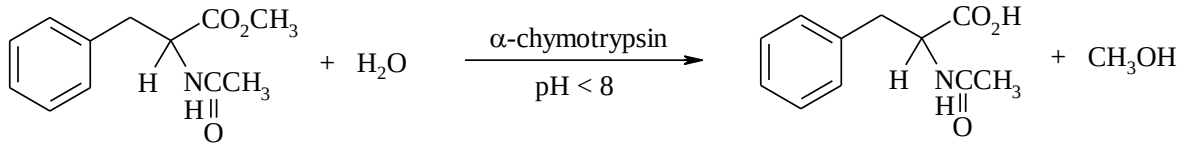
*R35 Causes severe burns*
*S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice*
*S37/39 Wear suitable gloves and eye/face protection*
*S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)*

| **Name:** | **Student Code:** |
|---|---|

# Enzymatic Hydrolysis of Methyl *N*-Acetyl-phenylalaninate

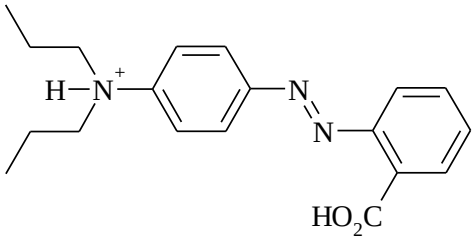
## Introduction

α-Chymotrypsin, a protease enzyme recognizing derivatives of natural α-amino acids, catalyses the hydrolysis of esters. In this experiment the enzymatic hydrolysis of racemic methyl *N*-acetyl-phenylalaninate **A** is investigated (Scheme).




**A** **B**

*The rate of formation of* N-*acetyl-phenylalanine **B** can be monitored by titration with 0.100 M NaOH in the presence of propyl red as a pH indicator.*




Propyl red (protonated form)
At pH < 5: pink; at pH > 6: yellow

**Procedure**

***Note: the required amount of α-chymotrypsin will be supplied in a sample vial by the laboratory assistant on request.***

**Racemic methyl *N*-acetyl-phenylalaninate** A **[500 mg, the exact weight (± 1 mg) is indicated on the label of the vial marked as NacPheOMe] is transferred quantitatively into a 50 mL Erlenmeyer flask and dissolved in methanol (~ 2.5 mL). Subsequently, propyl red (0.02% solution in ethanol; 4 drops) is added. The kinetic experiment is started by adding α-chymotrypsin (10.0 mL of a 0.05% solution in distilled water) in one portion (*start the stopwatch*).**

**When the reaction mixture turns pink, it is immediately titrated with 0.100 M NaOH until the colour changes to yellow. When the pink colour reappears, add just enough titrant to restore the pale yellow colour, swirling the flask continually during the addition. You only need to record the reading on the burette every 5 minutes. (*Note: at the beginning colour changes occur very frequently.*)**

**Monitor the reaction for 75 minutes. A graph showing the amounts of NaOH consumed in mL versus time is constructed, in order to visualize the kinetic course of this enzymatic reaction.**

| **Name:** | **Student Code:** |
|---|---|

**34th IChO Laboratory Task** **Answer Sheet 1**

**Score 12 points**

# Enzymatic Hydrolysis of Methyl *N*-Acetyl-phenylalaninate

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| **Marks** | **10** | **30** | **30** | **10** | **10** | **10** |

**1** Amount of the starting racemic methyl *N*-acetyl-phenylalaninate **A**

mg = mmol

**2** Record the time in minutes and the total consumption of NaOH in mL (accuracy ± 0.05 mL), according to the scheme below. Final recording after 75 minutes.

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (min) | | | | | | | | | | | | | | | 75 |
| NaOH (mL) | | | | | | | | | | | | | | | |

**3** Construct a graph of the total consumption of NaOH vs time on the supplied graph paper.
Put minutes on the x-axis: 5 min. per cm
Put mL NaOH on the y-axis: 1.0 mL per cm

**4** Calculate the amount of 0.100 M NaOH consumed in this experiment in mmol

Answer:

Calculation:

| **Name:** | **Student Code:** |
|---|---|

**Enzymatic Hydrolysis… (Cont'd)** **Answer Sheet 2**

**5** Calculate the degree of hydrolysis of methyl *N*-acetyl-(*R*,*S*)-phenylalaninate **A** in mol%
Answer:

Calculation:

**6** Which of the following statements is in accordance with your experimental results? Mark the appropriate box.

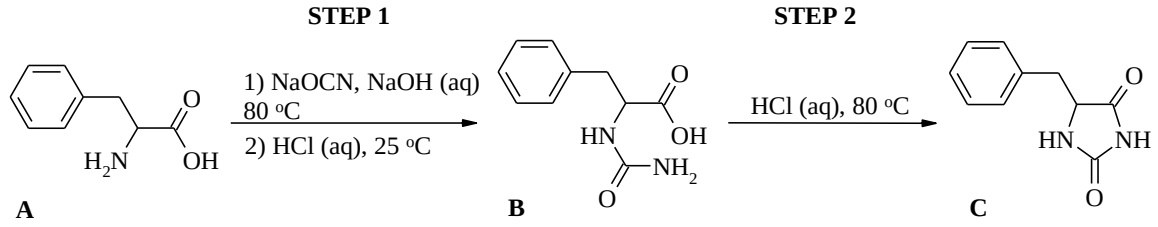
- ❑ The enzyme catalyses the hydrolysis to give methyl *N*-acetyl-(*S*)-phenylalaninate and *N*-acetyl-(*R*)-phenylalanine.
- ❑ The enzyme catalyses the hydrolysis to give *N*-acetyl-(*R*,*S*)-phenylalanine.
- ❑ The enzyme catalyses the hydrolysis to give methyl *N*-acetyl-(*R*)-phenylalaninate and *N*-acetyl-(*S*)-phenylalanine
- ❑ The enzyme loses its catalytic activity during the course of the reaction.

| **Name:** | **Student Code:** |
|---|---|

# Synthesis of Benzylhydantoin

## Introduction

α-Amino acids are the building blocks for peptides and proteins. They are also frequently used as starting material for the synthesis of pharmaceuticals. In this experiment natural *S*-phenylalanine **A** is converted in two steps into benzylhydantoin **C**, which is a useful intermediate for the preparation of various physiologically active derivatives.




Molecular Weight =165.19 Molecular Weight =208.22 Molecular Weight =190.20

**Procedure**

**STEP 1**

***Retain a tiny amount of starting material*** *A* ***for the TLC analysis (see below).*** **A long-necked round-bottomed flask is charged with (*S*)-phenylalanine** A **(500 mg, 3 mmol, the exact amount is indicated on the label of the vial), sodium cyanate (300 mg, 4.6 mmol), water (3 mL) and a stirring bar. Two drops of aqueous sodium hydroxide (1 M) are added to the stirred suspension. The flask is equipped with a condenser (distillation column) and the reaction mixture is heated to 80 °C on a sand bath while stirring magnetically.**

***Important***

***In order to reach the appropriate temperature in time and not lose too much time, start the electric heating of the sand bath immediately at the beginning of this experiment. Check the temperature of the sand bath regularly and carefully with a thermometer.***

**After heating the reaction mixture at 80 °C for at least 30 minutes, the resulting clear solution is cooled to room temperature and poured into a small Erlenmeyer flask. Rinse the round-bottomed flask with a little water. The solution is acidified by dropwise addition of hydrochloric acid (4 M) to pH < 3 with magnetic stirring. Some water is added to the resulting white suspension in order to facilitate stirring.**

**The white precipitate is then filtered off by suction, washed with ample water (on the filter) and then washed twice with a small amount of di-isopropyl ether to remove most of the adhering water. The urea derivative** B **is left on the filter under suction for at least 3 minutes to remove as much solvent as possible.**

A small amount of the obtained urea derivative **B** is retained for TLC-analysis later.

**STEP 2**

The urea derivative **B** is now transferred into a long-necked round-bottomed flask and hydrochloric acid (4 M, 3 mL) is added. A stirring bar is introduced and the suspension is stirred thoroughly whilst heating at 80 °C on a sand bath. A clear solution is obtained. After a reaction time of 30 minutes, the reaction mixture, which may already contain some precipitate, is cooled to room temperature. The obtained suspension is filtered by suction, washed thoroughly with water and finally washed twice

with a small amount of di-isopropyl ether. The product is left on the filter under suction for at least 3 minutes. It is then collected on a filter paper and dried in the air for at least 30 minutes.

The final product **C**, its precursor **B** and starting material **A** (see above) are subjected to TLC-analysis. For this purpose small amounts of either compound are dissolved in a tiny amount of pure acetone. Small samples of these solutions are applied to a TLC plate, using the supplied capillary tubes. The analysis is carried out with two TLC plates in one run. The TLC-plates are developed with a solution of 2% formic acid in ethyl acetate as the eluent. After the elution the TLC-plates are analysed using a UV-lamp. The starting line, solvent front and the UV-active spots are clearly marked with a pencil. Copy the diagram in the box on the answer sheet. The $R_f$ values are determined. Finally, the TLC-plate with the best analysis is wrapped in parafilm and placed in a plastic bag with a sealing strip.

The final product **C** is transferred into a sample vial of which the empty weight has been pre-determined (weight is indicated on the label). Weigh the vial with product and calculate the yield of the product **C**.

The examination committee will check the quality of the benzylhydantoin that you have prepared by determining its melting point using an automatic melting point apparatus.

| Name: | Student Code: |
|---|---|

**34th IChO Laboratory Task** **Answer Sheet 3**

**Score 18 points**

## Synthesis of Benzylhydantoin

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| **Marks** | **10** | **20** | **10** | **10** | **20** | **10** | **10** | **10** |

Weight of your starting material **A** (see label on the vial): mg

Weight of the empty sample vial: mg
(see label on the vial: YOUR PRODUCT)

**1** Weight of the sample vial containing your product **C**: mg

**2** Amount of benzylhydantoin **C** obtained: mg

Calculate the yield of benzylhydantoin **C:**
Answer: %

Calculation:

**3** $R_f$ value of urea derivative **B**
Answer:

Calculation:

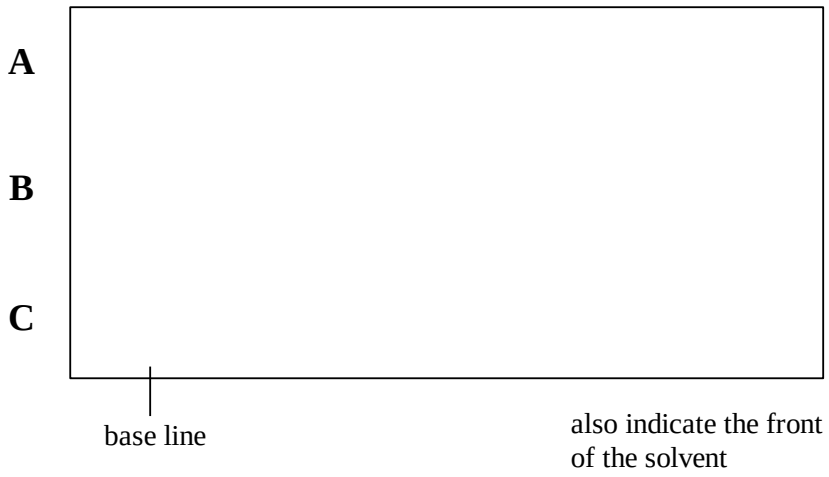
**4** $R_f$ value of benzylhydantoin **C**
Answer:

Calculation:

| **Name:** | **Student Code:** |
|---|---|

**Synthesis of Benzylhydantoin (Cont'd)** **Answer Sheet 4**

**5** Copy the TLC diagram in the box below




**6** Conclusions from the TLC analysis:

Compound **B**:

- ❑ is pure
- ❑ contains some **A**
- ❑ contains several contaminants

Compound **C**:

- ❑ is pure
- ❑ contains some **B**
- ❑ contains some **A** and **B**
- ❑ contains several contaminants

**7** Appearance of benzylhydantoin **C,** mark what is appropriate for your product.

- ❑ White colour
- ❑ Yellowish colour
- ❑ Sticky
- ❑ Crystalline
- ❑ Powder

**8** Melting point of benzylhydantoin **C** will be determined later by the examination committee - $^{o}$C

Place your packed TLC plate (see procedure) in an envelope with your name and student number.

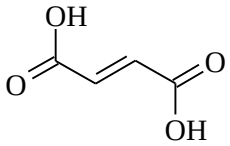
| **Name:** | **Student Code:** |
|---|---|

# Determination of Iron in Iron Pills

Introduction

Iron is an essential component of hemoglobin, transporting oxygen in the blood to all parts of the body. It also plays a vital role in many metabolic reactions. Iron deficiency can cause anaemia resulting from low levels of hemoglobin in the blood. Iron deficiency is the most widespread mineral nutritional deficiency worldwide. One way to reduce iron shortage is by treatment with iron pills.

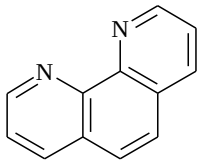
The active ingredient in the iron pill to be examined, is iron(II) present as iron(II) fumarate. Besides this organic iron(II) compound the pill contains other compounds such as binding agents. The structure of fumaric acid is:




Fumaric acid

Iron(II) and 1,10-phenanthroline form an orange/red coloured complex $[(C_{12}H_8N_2)_3Fe]^{2+}$. The absorbance of this complex, determined at 510 nm in a buffer solution (pH=8) is a measure for the iron content of the iron pill. Since 1,10-phenanthroline only binds to iron(II) and iron(II) is readily oxidized to iron(III), hydroxylammonium chloride is added to reduce all iron(III) to iron(II). A simplified reaction scheme is:

$$2\ NH_2OH\ +\ 4\ Fe^{3+} \rightarrow N_2O\ +\ 4\ H^{+}\ +\ H_2O\ +\ 4\ Fe^{2+}$$




1,10-Phenanthroline

Procedure

The weight of the iron pill is determined with an accuracy of 1 mg using a balance. The pill is carefully pulverized in a mortar and transferred quantitatively into a 100 mL beaker with the aid of a small amount of distilled water. Hydrochloric acid (5 mL, 4 M) is added. The content of the beaker is heated up to approximately 60 $^{o}$C on a hotplate. The solution turns a yellow colour.

The beaker is then placed in an ultrasonic bath for at least 5 minutes. The beaker is kept in place by styrofoam. The suspension is filtered by suction using a Hirsch funnel containing a small layer of moistened hi-flow filter aid pressed onto the filter. The hi-flow filter aid is washed with ample distilled water. The filtrate is carefully transferred into a volumetric flask (250 mL) and the final volume adjusted by adding distilled water and with regular mixing. An amount of 10 mL is pipetted from this solution and transferred into a volumetric flask of 100 mL. Again the volume is adjusted with distilled water while mixing the content of the flask.

From this solution, 10 mL is pipetted and transferred into a volumetric flask of 100 mL. Subsequently, 1,10-phenanthroline solution (10 mL) and hydroxylammonium chloride solution (1 mL) are added. Then the volume is adjusted with buffer solution (pH 8).

The absorbance of this solution is measured with a spectrophotometer at 510 nm against water as a blank in a 1.000 cm cuvet.

Calculate the amount of iron in the iron pill on basis of the known molar absorptivity (extinction coefficient, ε) of the iron(II)phenanthroline complex at 510 nm. The molar absorptivity of the iron(II)phenanthroline complex at 510 nm is 11100 $M^{-1}cm^{-1}$.

## *Important*

*In order to eliminate deviations in absorbance typically connected to the spectrophotometer used, a correction factor is denoted on the spectrophotometer you will be using for your experiment. The absorbance observed must be multiplied by this factor in order to obtain the correct absorbance of the solution of the iron complex.*

| **Name:** | **Student Code:** |
|---|---|

**34th IChO Laboratory Task** **Answer Sheet 5**

**Score 10 points**

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| **Marks** | **15** | **40** | **20** | **10** | **15** |

# Determination of Iron in Iron Pills

**1** Weight of the iron pill mg

Number of the spectrophotometer

Correction factor

**2** Reading of the spectrophotometer: ; corrected absorbance: AU

**3** Concentration of iron(II)phenanthroline complex in the cuvet: mmol $L^{-1}$
Calculation:

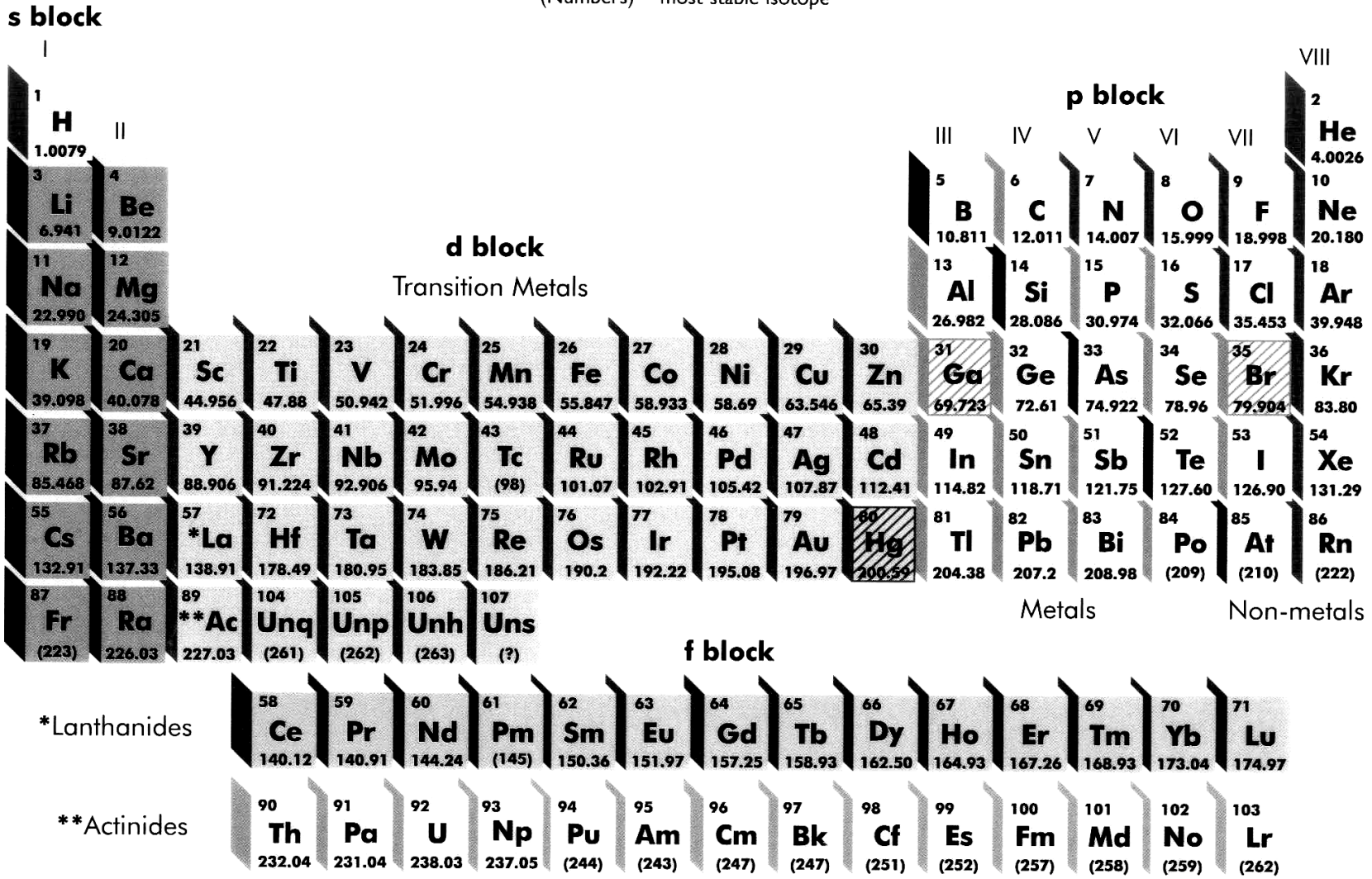
**4** Total amount of iron(II) in the pill: mg
Calculation:

**5** Calculate the iron content of the pill in weight%
*Answer:*

*Calculation:*

# Periodic Table of Elements

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




Name:

Student Code:

| Name: | Student Code: |
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# EXPERIMENTAL EXAMINATION – IChO34

## Grading Protocol Enzymatic Hydrolysis of Methyl N-Acetylphenylalaninate

General:

In this experiment the student titrates the enzyme solution around its equivalence point. If the experiment is performed correctly, only enzymatic hydrolysis of the S-isomer occurs. In that case 11.3 mL of 0.1 M NaOH will be needed. Too basic conditions lead to additional chemical hydrolysis, too acidic conditions lead to a slower enzymatic hydrolysis. The evaluation of the answers on items 2 and 3 are interconnected.

Item 1: 500 mg = 2.26 mmol 2.24 – 2.26 mmol = **10 points**

Item 2: (a) The regularity of the titration data is considered.
13-15 data points with correct intervals (5 ± 0.5 min) = **10 points**.
10-12 data points (5 ± 0.5 min) = **5 points**.

(b) The amount of NaOH consumed after 5 minutes is a good indication whether the enzyme reaction has started correctly. About 4.0 mL of NaOH is needed (tolerance 3.8 – 5.0 mL): **5 points**

The enzyme reaction proceeds during the first 20 minutes in an almost linear fashion. Measurements after 10, 15 and 20 minutes are considered.
10 min: 6.25 – 7.75 mL
15 min: 8.00 – 9.50 mL
20 min: 9.25 – 10.50 mL 2 out of 3 in the correct range = **5 points**

In the time range 40 – 70 minutes the reaction approaches completion. Volume of additional NaOH: 0.1 – 0.5 mL = **5 points**

Final total volume of NaOH at 75 min between 11.0 – 12.2 mL = **5 points**

Item 3: Correct X and Y axes with units and data points = **10 points**
Correct drawing of curve (with interpolation) = **5 points**
Curve between margins (*see figure*) = **10 points**
Correct shape of curve = **5 points**

Item 4: Amount of NaOH needed in mmol = volume NaOH after 75 min × 0.1 mol $L^{-1}$ = **10 points**

Item 5: Degree of hydrolysis = (exp. mmol NaOH / calc. mmol A) × 100% = **10 points**

Item 6: Third option is correct if experiment is performed correctly = **10 points**
The answer must agree with the experimental observations.

## Grading Protocol Synthesis of Benzylhydantoin

Item 1: Weight of the sample vial containing product max 10 points
Weight influenced by
– balance dependency ± 5 mg
- evaporation of solvent + 5 mg

Student weight: error ≤ +10 mg and ≤ -5 mg = **10 points**

Student weight: error > +10 mg ≤ +15 mg and > -5 mg ≤ -10 mg = **5 points**
Student weight: error > +15 mg and > -10 mg = **0 points**

Item 2: Amount of benzylhydantoin max 20 points

Yields are only accepted as real when m.p. in range 160 – 190 $^{o}$C
Average yield by experts: 72-75 %, points allocated via histogram
Student yield in range 65 – 80 % = **20 points**
Student yield in range 81 – 90 % (slightly wet) = **15 points**
Student yield in range >90% (considerably wet) = **10 points**
Student yield in range 60 – 64 % = **15 points**
Student yield in range 50 - 59 % = **10 points**
Student yield in range 25 – 49 % = **5 points**
Student yield in range <25 % = **0 points**

If calculation of yield incorrect **–5 penalty points**

Item 3: $R_f$ value of urea derivative **B** max 10 points
Average value by experts 0.50 – 0.55; Histogram made
Students $R_f$-value in range 0.50 – 0.55 = **10 points**
Students $R_f$-value in range 0.45 – 0.49 = **5 points**
Students $R_f$-value in range < 0.45 = **0 points**
Students $R_f$-value in range 0.56 – 0.60 = **5 points**
Students $R_f$-value in range > 0.60 = **0 points**

Item 4: Rf –value of benzylhydantoin **C** max 10 points
Average value by experts 0.70 – 0.75; Histogram made
Students $R_f$-value in range 0.70 – 0.75 = **10 points**
Students $R_f$-value in range 0.65 – 0.69 = **5 points**
Students $R_f$-value in range < 0.65 = **0 points**
Students $R_f$-value in range 0.76 – 0.80 = **5 points**
Students $R_f$-value in range > 0.80 = **0 points**

Item 5: TLC-analysis max 20 points
The following criteria have been applied

- position of front line > 5 cm = **5 points**
- quality and marking of spots* = **5 points**
- pure product **B** (single spot) = **5 points**
- pure product **C** (single spot) = **5 points**

* When (S)-phenylalanine A is not marked **–5 penalty points**

Item 6: Conclusions for the TLC analysis max 10 points
Compound B if correct = **5 points**
Compound C if correct = **5 points**

Item 7: Appearance of benzylhydantoin **C** max 10 points
Colour if correct = **5 points**
Texture if correct = **5 points**

Item 8: Melting points of benzylhydantoin C max 10 points

Literature value 184 $^{o}$C; Histogram made
Average value obtained by experts 178 – 180 $^{o}$C
Students m.p. in range 176 – 190 $^{o}$C = 10 points
Students m.p. in range 172 – 175 $^{o}$C = 5 points
Students m.p. in range < 172 $^{o}$C = 0 points
Students m.p. in range > 190 $^{o}$C = 0 points

## Grading Protocol Determination of Iron in Iron Pills

Item 1: max 15 points
Dimension error = **-10 penalty points**
Weight of pill no in range 315 – 332 = **-5 penalty points**

Item 2: max 40 points
Only 1 value (observed or corrected) = **-10 penalty points**
Value in range 0.475 – 0.575 = **40 points**
Value in range 0.376 – 0.475 = **20 points**
Value in range < 0.375 **= 0 points**
Value in range 0.575 – 0.659 = **20 points**
Value in range > 0.659 = **0 points**

Item 3: max 20 points
Lambert-Beer formula = **10 points**
Correct calculation = **10 points**
Dimension error = **-10 penalty points**

Item 4: max 10 points
Factor 10 wrong in calculation = -5 penalty points
Factor 4 wrong in calculation = -5 penalty points
Factor 2.5 wrong in calculation = -5 penalty points
No molecular mass in calculation = -5 penalty points

Item 5: max 15 points
Correct calculation = **5 points**
Iron-value 15 – 25 % = **10 points**
Iron value 10 - 15 % = **5 points**
Iron value < 10 % = **0 points**
Iron value 25 – 30 % = **5 points**
Iron value > 30 % = **0 points**