

**34<sup>th</sup>**



**International Chemistry Olympiad**

**10 theoretical problems  
3 practical problems**

# THE THIRTY-FOURTH INTERNATIONAL CHEMISTRY OLYMPIAD 5–14 JULY 2002, GRONINGEN, THE NETHERLANDS

## THEORETICAL PROBLEMS

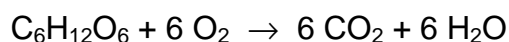
### Theme 1 - Chemistry of Life

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

### PROBLEM 1

#### OXYGEN IN YOUR LIFE

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:

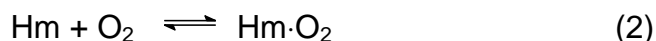


This reaction releases 400 kJ of energy per mol of oxygen. O<sub>2</sub> uptake by blood is at four heme (Hm) groups in the protein hemoglobin (Hb).

Free Hm consists of an Fe<sup>2+</sup> ion attached to four N atoms of a porphyrin<sup>2-</sup> ligand. Oxygen can bind at the coordination site of Fe<sup>2+</sup> giving a Hm·O<sub>2</sub> complex. Carbon monoxide can be complexed similarly, giving a Hm·CO complex. CO is a poison as it binds more strongly to Hm than O<sub>2</sub> does. The equilibrium constant  $K_1$  for the reaction:



is 10 000 times larger than the equilibrium constant  $K_2$  for the reaction:



Each Hb molecule can take up four molecules of O<sub>2</sub>. Blood in contact with O<sub>2</sub> 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.

Relevant data: O<sub>2</sub> pressure in lungs is 15 kPa; in the muscles it is 2 kPa. The maximum

flow of blood through heart and lungs is  $4 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$ . The red cells in blood occupy 40 % of the blood volume; inside the cells the concentration of Hb is  $340 \text{ kg m}^{-3}$ ; Hb has a molar mass of  $64 \text{ kg mol}^{-1}$ .  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .  $T = 298 \text{ K}$ .

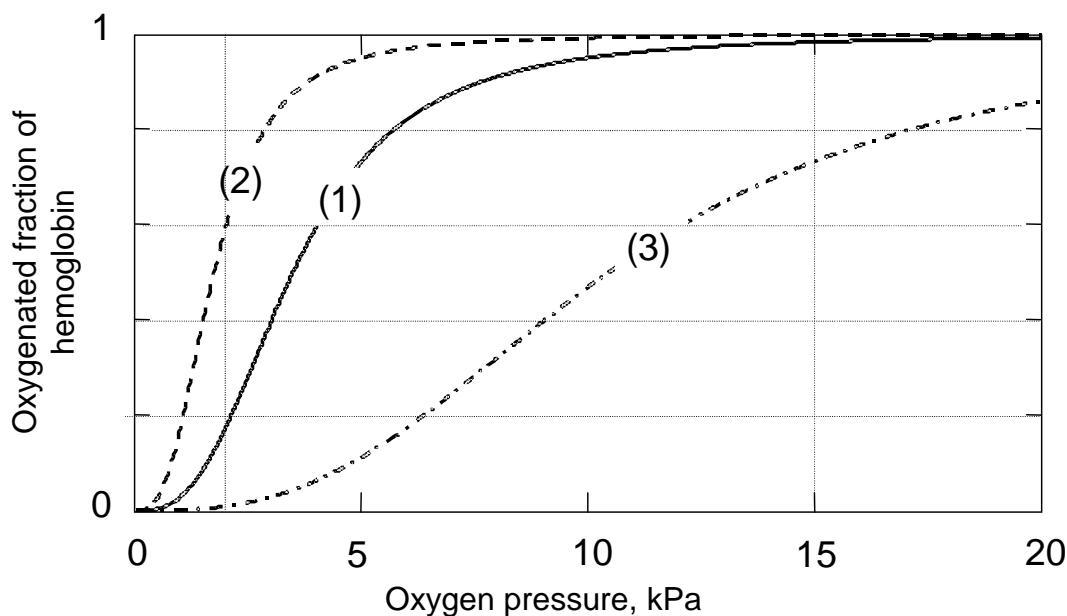


Figure 1

- 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).
- 1.2 Estimate from Figure 1 (to 2 significant figures) how many moles of  $\text{O}_2$  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.
- 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  $\text{O}_2$  is too weak.
  - The binding with  $\text{O}_2$  is too strong.
  - The maximum oxygen capacity is too low.
  - The deficiency is caused by carbon monoxide poisoning.
- 1.4 Calculate how much oxygen (in  $\text{mol s}^{-1}$ ) can be deposited in tissue by blood with normal Hb (1).
- 1.5 Calculate the maximum power that the body can produce (assuming it is limited by oxygen transfer).

**SOLUTION**

**1.1**  $\Delta G_1^0 = -RT \ln K_1$      $\Delta G_2^0 = -RT \ln K_2$

$$\Delta G_2^0 - \Delta G_1^0 = RT \ln \frac{K_1}{K_2}$$

$$\Delta G_2^0 - \Delta G_1^0 = (8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln 10\,000) \text{ J} = 23 \text{ kJ mol}^{-1}$$

**1.2** Hb-Typ 1:  $(0.98 - 0.17) \text{ mol} \times 4 = 3.2 \text{ mol}$

Hb-Typ 2:  $(1.00 - 0.60) \text{ mol} \times 4 = 1.6 \text{ mol}$

Hb-Typ 3:  $(0.73 - 0.01) \text{ mol} \times 4 = 2.9 \text{ mol}$

**1.3** Correct answer: The binding with O<sub>2</sub> is too strong.

**1.4**  $(4 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}) \times 0.4 \times (340 \text{ kg m}^{-3}) \times (3.2 \text{ mol O}_2 / \text{mol Hb}) / (64 \text{ kg mol}^{-1}) =$   
 $= 2.72 \times 10^{-3} \text{ mol s}^{-1}$

**1.5**  $(2.72 \times 10^{-3} \text{ mol s}^{-1}) \times (400 \text{ kJ mol}^{-1}) = 1088 \text{ W}$ 

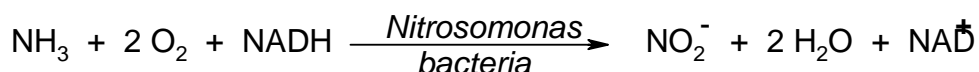
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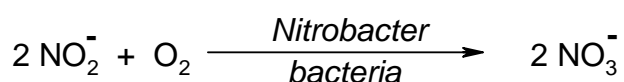
## PROBLEM 2

### Nitrogen Cycle in Nature

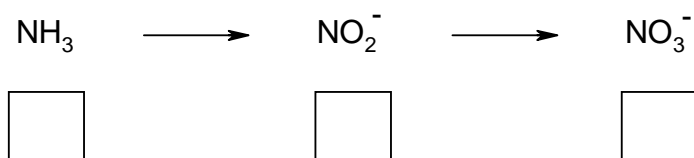
Ammonia is a toxic substance to marine animals at levels exceeding 1 ppm. Nitrifying bacteria play an important role in the conversion of  $\text{NH}_3$  first to nitrite and then to nitrate, the storage form of nitrogen in the soil.



NADH is the biochemical reducing agent of the coenzyme nicotinamide dinucleotide (NAD),  $\text{NAD}^+$  is the oxidized form of the coenzyme NAD.



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

2.2 The measurements are performed at the wavelength with the maximum 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).

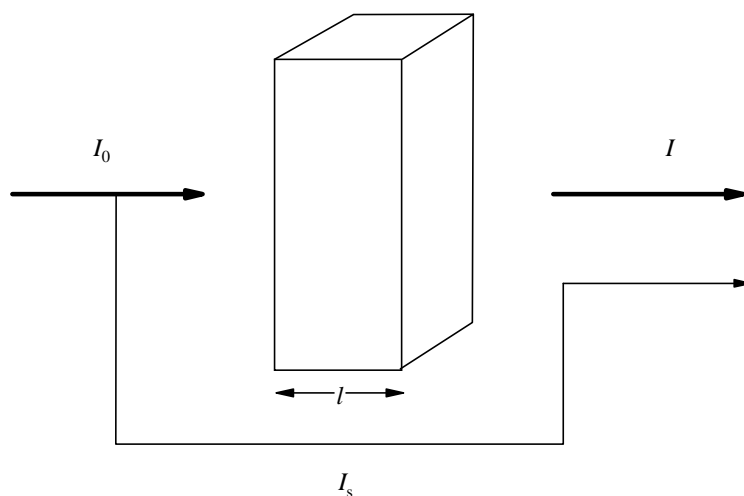


Figure 2

- 2.3** Calculate the value of the absorbance  $A$  shown by the spectrophotometer if  $\varepsilon = 6000 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $l = 1 \text{ cm}$  and  $c = 1 \times 10^{-4} \text{ M}$

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

Table 1

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

- 2.4** Determine (show calculation) from the data given above, using the values corrected for the solvent impurities, the slope  $m$  and the intercept  $b$  of the calibration curve  $A = m c + b$ .

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 cell.

Table 2

| 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

$$\text{corrected absorbance} = 0.1769 c + 0.0015 \quad (\text{a})$$

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

**2.5** Calculate the average nitrite nitrogen concentration in ppm and  $\mu\text{g cm}^{-3}$ .

Hint: Take the blank from problem 2.4.

## SOLUTION

**2.1**  $\text{NH}_3$ : -III (-3)       $\text{NO}_2^-$ : III (3)       $\text{NO}_3^-$ : V (5)

**2.2** Correct answer: There is optimal accuracy of the measurement.

**2.3**  $I_S = 0.05 \times I_0$      $A = \log \frac{I_0}{I + I_S}$       (see Figure 2)

The absorption of the solution  $A_{\text{sol}}$  is given by the relation:

$$A_{\text{sol}} = \log 0.95 \times \frac{I_0}{I} = \varepsilon c d$$

$$I = 0.95 \times I_0 \times 10^{-6000 \cdot 0.0001 \cdot 1} = 0.95 I_0 \times 10^{-0.6}$$

$$A = \log \frac{I_0}{0.95 \times I_0 \times 10^{-0.6} + 0.05 \times I_0} = 0.54$$

**2.4** The absorbance of the blank solution (see Table):  $A = 0.003$ .

Slope  $m$  of the calibration curve:

$$m = \frac{\Delta A}{\Delta c} = \frac{A_2 - A_1}{c_2 - c_1} = \frac{0.325 - 0.164}{1.830 - 0.915} = \frac{0.161}{0.915 \text{ M}} = 0.176 \text{ M}^{-1}$$

Note: Corrected absorbance values were used in the calculation.

$$A = 0.176 c + b$$

For  $c = 0$ ,  $A = 0.003$ .

Thus:  $b = 0.003$

- 2.5** The average absorption in a 2 cm cell is 0.558; thus, in a 1 cm cell is 0.279.  
Regarding the blank value (0.003) the corrected absorption has the value 0.276.  
Substituting this value into the equation (a) gives:

$$c = \frac{0.276 - 0.0015}{0.1769} \text{ ppm}$$

$$c = 1.55 \text{ ppm} = 1.55 \mu\text{g cm}^{-3}$$

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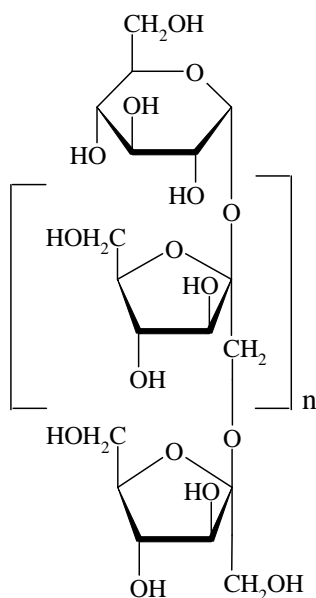


## Theme II - Chemistry of Industrial Relevance

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.

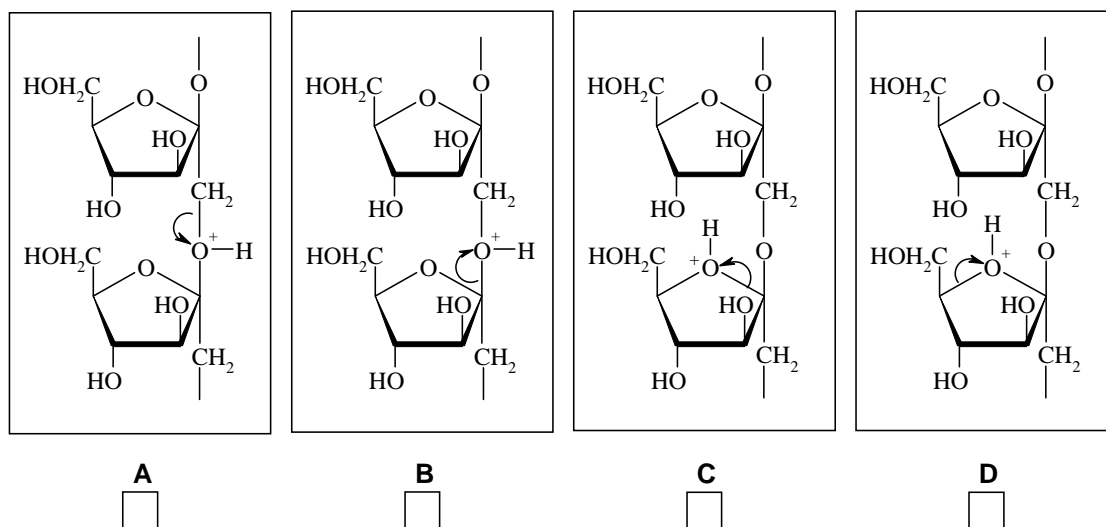
### PROBLEM 3

#### Inulin, a New Renewable Raw Material



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 ( $n = 9$ ).

3.1 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.



Mark the correct cleavage mechanism for the most efficient hydrolysis.

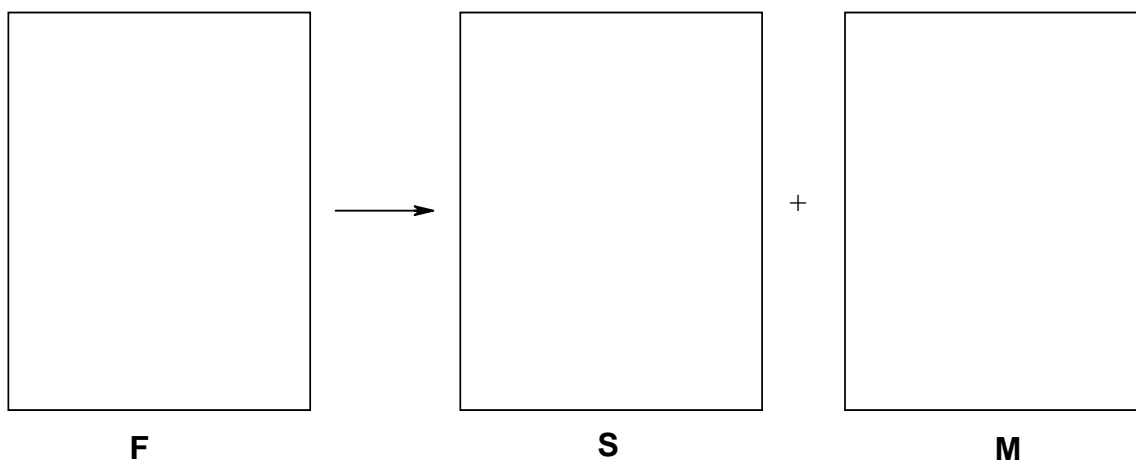
Hydrolysis with isotopically labelled water can provide information about the mechanism of hydrolysis using modern NMR techniques, which can “see” deuterium ( $^2\text{H}$ ) and the oxygen isotope  $^{17}\text{O}$ .

**3.2** Indicate which labelled water can best be used for this purpose. Mark the correct answer.

- $^2\text{H}_2\text{O}$   
  $\text{H}_2^{17}\text{O}$   
  $^2\text{H}_2^{17}\text{O}$   
 None of them.

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

**3.3** Draw the Fischer projections of fructose (**F**), sorbitol (**S**) and mannitol (**M**).



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

**3.4** How many moles of mannitol and sorbitol are obtained?

**M:**

**S:**

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

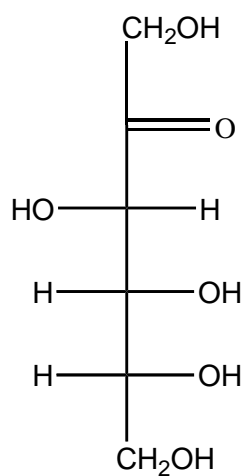
**3.5** Calculate how many moles of **M** will precipitate.

**SOLUTION**

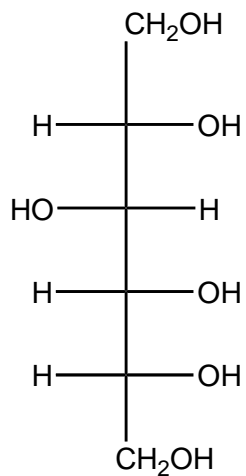
3.1 B is correct.

3.2  $\text{H}_2^{17}\text{O}$ 

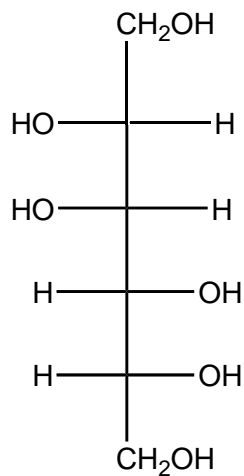
3.3



F



S



M

3.4  $n(\text{M}): 7 \text{ mol}$        $n(\text{S}): 4 \text{ mol}$ 

3.5 Remaining amount of water:

$$m(\text{H}_2\text{O}) = 2 \text{ kg} - (10 \times 0.018 \text{ kg}) = 1.82 \text{ kg}$$

$$n(\text{M})_{\text{total}} = 7 \text{ mol}$$

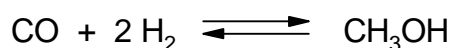
$$n(\text{M})_{\text{dissolved}} = 1.82 \times 0.4 \text{ mol} = 0.73 \text{ mol}$$

$$n(\text{M})_{\text{precipitated}} = 7.00 - 0.73 = 6.27 \text{ mol}$$

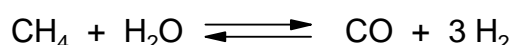
## PROBLEM 4

### Production of Methanol

Methanol (CH<sub>3</sub>OH) 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:



Hydrogen and CO are obtained by the reaction:



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<sub>2</sub>, are schematically shown in Figure 1. Four positions are indicated by  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ .

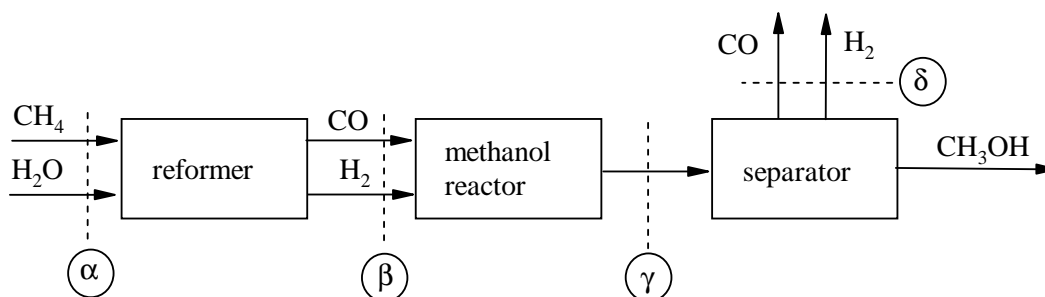


Figure 1

The flow of methanol at position  $\gamma$  is  $\eta[\text{CH}_3\text{OH}, \gamma] = 1000 \text{ mol s}^{-1}$ . The factory is so designed that  $2/3$  of the CO is converted to methanol. Excess CO and H<sub>2</sub> at position  $\delta$  are used to heat the first reactor. Assume that the reformer reaction goes to completion.

- 4.1 Calculate the flow of CO and H<sub>2</sub> at position  $\beta$ .
- 4.2 Calculate the flow of CO and H<sub>2</sub> at position  $\gamma$ .
- 4.3 Calculate the flows of CH<sub>4</sub> and H<sub>2</sub>O needed at position  $\alpha$ .
- 4.4 At point  $\gamma$  all species are gases. Calculate the partial pressures in MPa for CO, H<sub>2</sub> and CH<sub>3</sub>OH at position  $\gamma$  using the equation:

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

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

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

$$K_p = \frac{p_{\text{CH}_3\text{OH}} p_0^2}{p_{\text{CO}} p_{\text{H}_2}^2}$$

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).

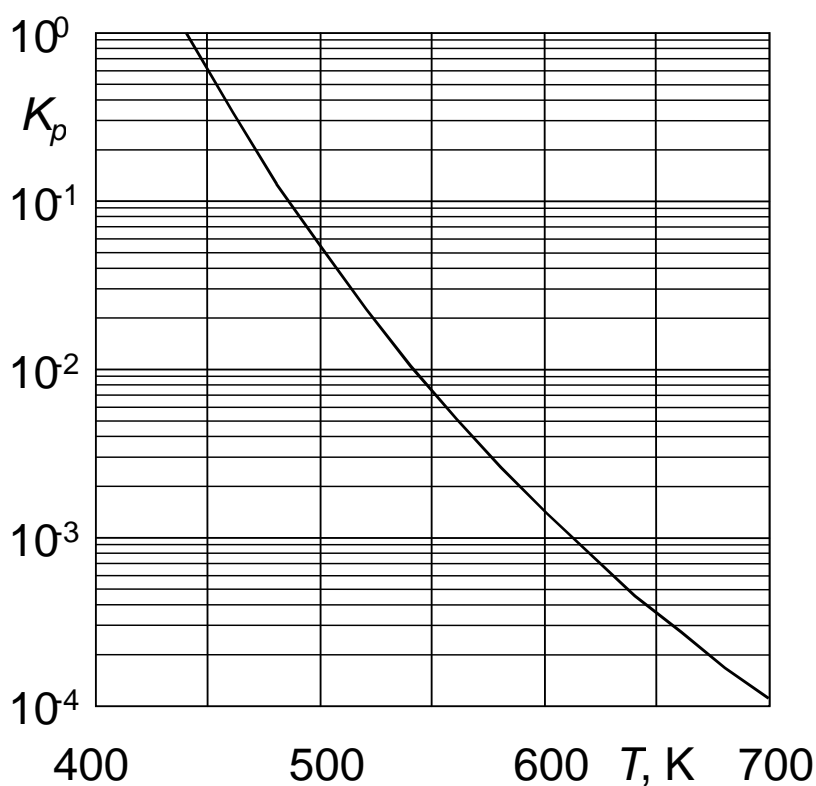


Figure 2

4.5 Calculate  $K_p$  and indicate at which temperature  $T$  the reaction must be operated to achieve this equilibrium.

## SOLUTION

$$4.1 \quad n(\text{CO}, \beta) = 3/2 \times n(\text{CH}_3\text{OH}, \gamma) = 1500 \text{ mol s}^{-1}$$

$$n(\text{H}_2, \beta) = 3 \times n(\text{CO}, \beta) = 4500 \text{ mol s}^{-1}$$

**4.2**  $n(\text{CO}, \gamma) = n(\text{CO}, \beta) - n(\text{CH}_3\text{OH}, \gamma) = (1500 - 1000) \text{ mol s}^{-1} = 500 \text{ mol s}^{-1}$   
 $n(\text{H}_2, \gamma) = n(\text{H}_2, \beta) - 2 \times n(\text{CH}_3\text{OH}, \gamma) = (4500 - 2 \times 1000) \text{ mol s}^{-1} = 2500 \text{ mol s}^{-1}$

**4.3**  $n(\text{CH}_4, \alpha) = n(\text{CO}, \beta) = 1500 \text{ mol s}^{-1}$   
 $n(\text{H}_2\text{O}, \alpha) = n(\text{CO}, \beta) = 1500 \text{ mol s}^{-1}$

**4.4**  $n_{\text{tot}} = (1000 + 500 + 2500) \text{ mol s}^{-1} = 4000 \text{ mol s}^{-1}$   
 $p_i = p_{\text{tot}} \cdot (n_i/n_{\text{tot}})$   
 $p(\text{CO}, \gamma) = 10 \text{ MPa} \times (500/4000) = 1,25 \text{ MPa}$   
 $p(\text{H}_2, \gamma) = 10 \text{ MPa} \times (2500/4000) = 6,25 \text{ MPa}$   
 $p(\text{CH}_3\text{OH}, \gamma) = 10 \text{ MPa} \times (1000/4000) = 2,50 \text{ MPa}$

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

The temperature corresponding to this value (see Fig. 2) is  $\approx 630 \text{ K}$ .

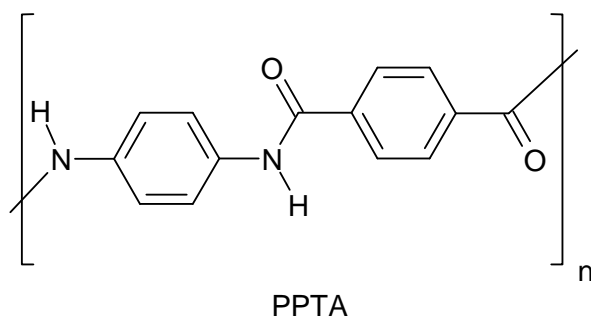
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## PROBLEM 5

### Aramids, High-performance Polymeric Materials

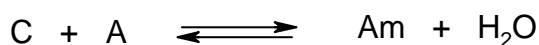
Aromatic polyamides (aramids) are high strength, high performance polymer fibers that find use in composite materials, bullet-proof vests, high quality skis, safety helmets, etc. Aramid PPTA is marketed under the names Kevlar® (DuPont) and Twaron® (Teijin), and amongst others manufactured in the north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



5.1 Draw the structure of these sheets (three chains suffice).

For a polymerisation of equimolar amounts of two monomers the average chain length is  $\bar{P}_n$ , 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  $U_0$ .

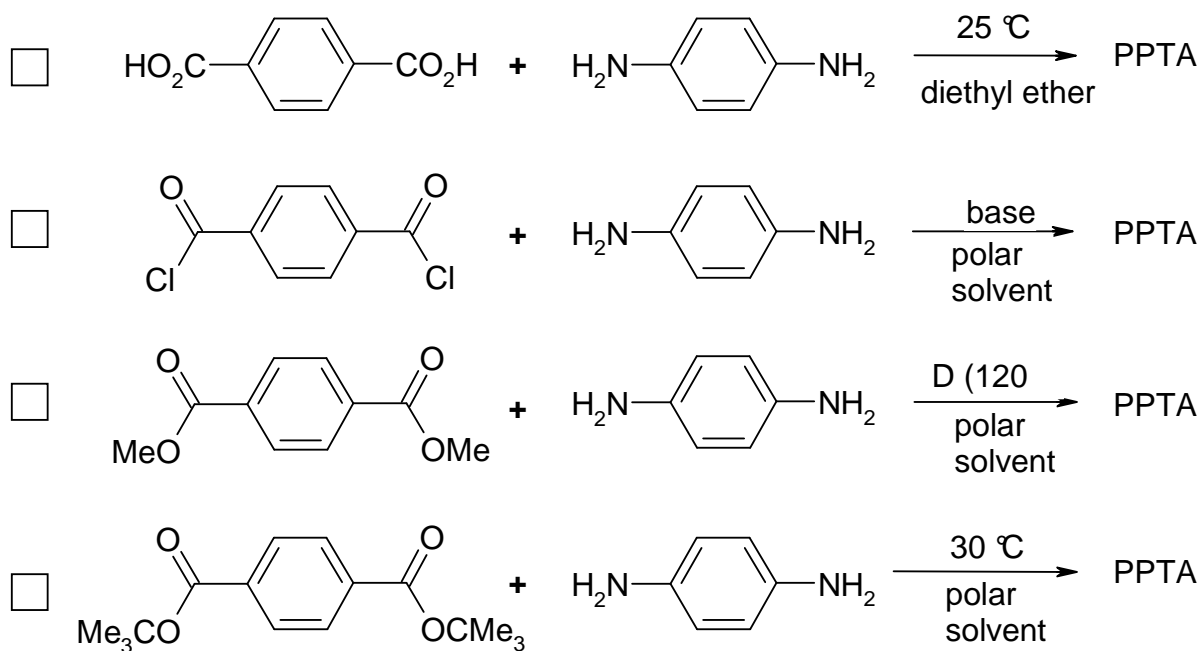
Assuming that the polymerization equilibrium can fully be described by:



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

5.2 Calculate the degree of conversion needed to obtain an average chain length of 500.

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

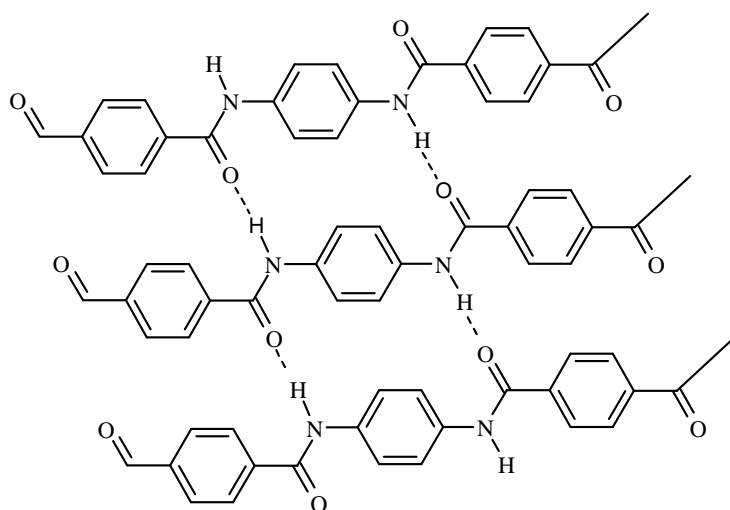


5.4 Another type of aramid can be produced from 4-aminobenzoic acid (4-aminobenzene-carboxylic acid) by heating.

- Give the structure of this aramid ( $n = 4$ )
- Calculate the average chain length at equilibrium (reaction is carried out in a closed vessel). The equilibrium constant  $K = 576$ .

## SOLUTION

5.1





$$5.2 \quad \bar{P}_n = \frac{U_0}{N_t}, \quad p = \frac{U_0 - N_t}{U_0} \rightarrow$$

$$p = 1 - \frac{N_t}{U_0}, \quad \frac{N_t}{U_0} = 1 - p \rightarrow \bar{P}_n = \frac{1}{1-p}$$

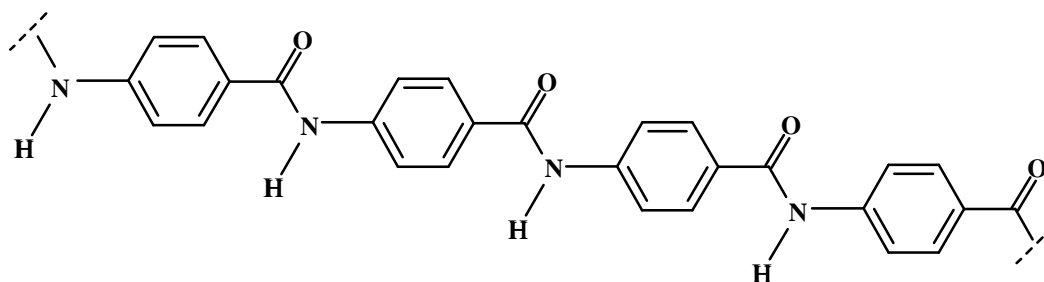
$$500 = \frac{1}{1-p} \quad p = \frac{499}{500} = 0.998$$

5.3

2 and 3

5.4

a)



$$b) \quad K = \frac{[Am] \times [H_2O]}{[C] \times [A]} = \frac{p U_0 \times p U_0}{(1-p)^2 \times U_0^2} = \frac{p^2}{(1-p)^2} = 576 \Rightarrow p = 0.96$$

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

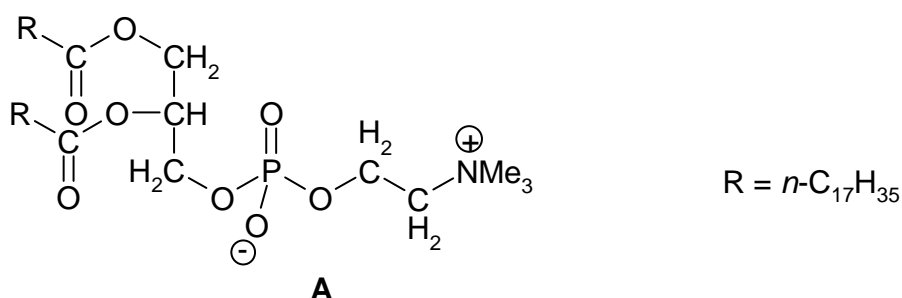
### Theme III - Chemistry of Functional Molecules in Nature

*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 6

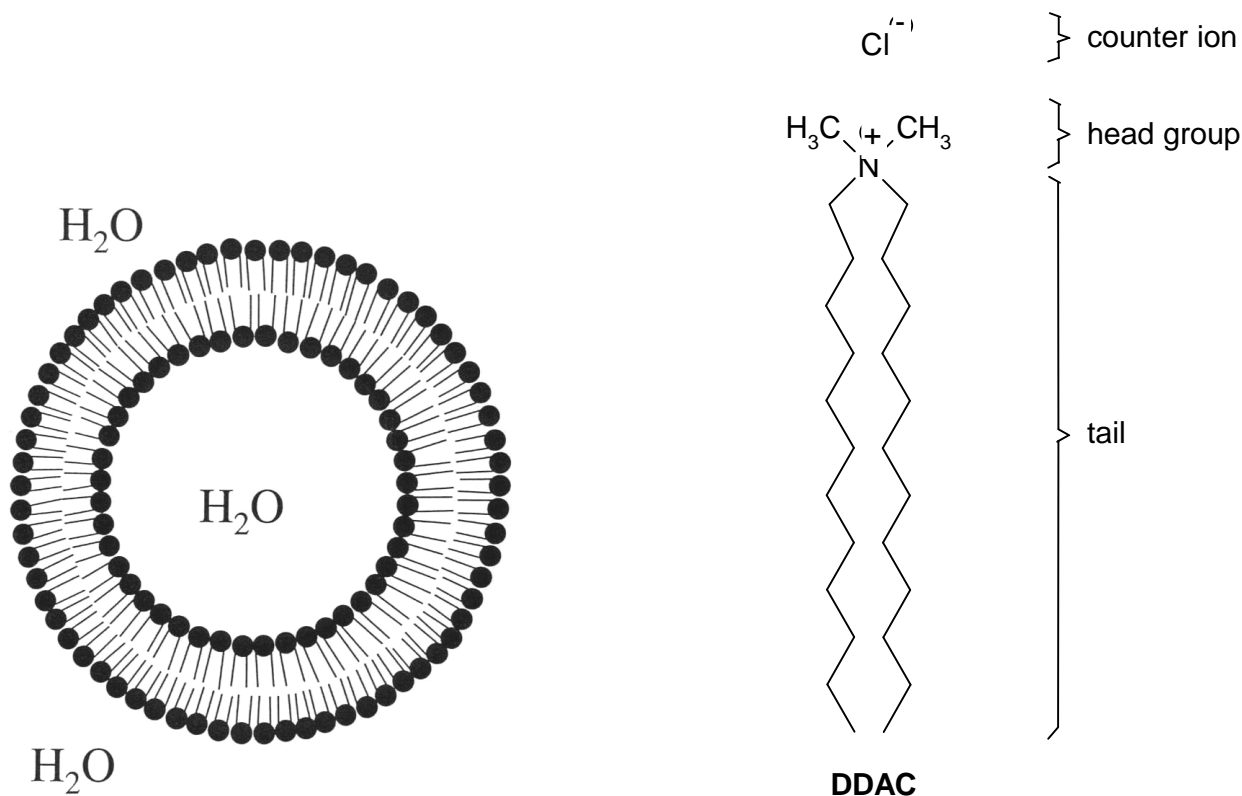
### Phospholipids in Membranes

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**.

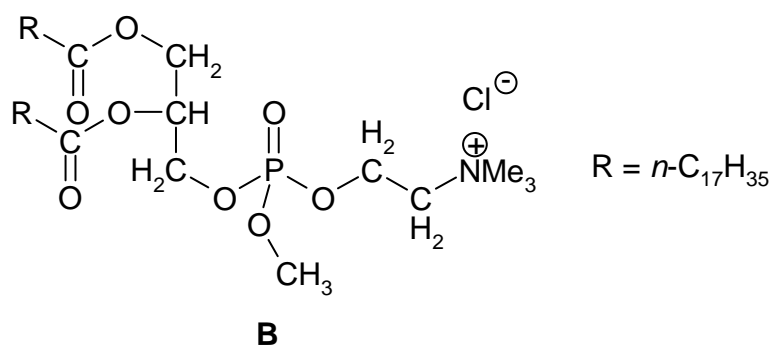


Upon dispersion in water (above a low critical concentration) compound **A** forms closed bilayer structures, called liposomes, which are employed as model compounds for aspects of the chemistry of the structurally much more complex cell membranes. Liposomes are globular aggregates with the polar or 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**).

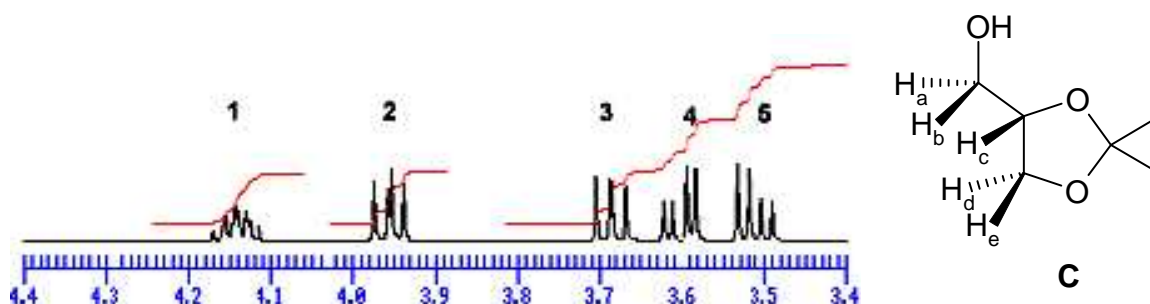


- 6.1 (a)** How many stereoisomers are possible for compound **A**?
- (b)** How many stereoisomers are possible for the trialkylphosphate **B**?



A precursor for the synthesis of compound **A** is the acetone **C** derived from glycerol. Part of the <sup>1</sup>H-NMR spectrum of compound **C** is shown below.

- 6.2** Which signal number in the <sup>1</sup>H-NMR spectrum corresponds to proton **H<sub>c</sub>**?



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:

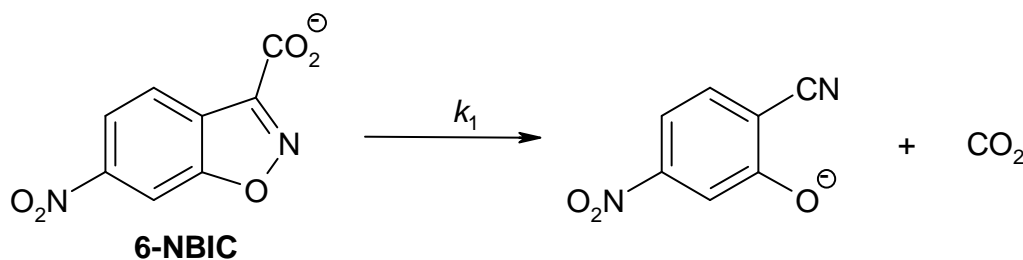
$$V = (27.4 + 26.99 n) \times 10^{-3} \text{ nm}^3$$

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

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

**6.3** Calculate the minimum cross-sectional surface area of the head groups for such very large  $n$  values.

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



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

**6.4** Sketch a plot of  $k_1$  vs.  $[\text{DDAC}]$  for  $[\text{DDAC}] = 0 \rightarrow 3 c_1$ .

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

- The decarboxylation is catalysed by the  $\text{Cl}^-$  ions bound to the surface of the vesicles.
- Efficient loss of hydration of the carboxylate group of vesicle-bound 6-NBIC.
- Strong binding of  $\text{CO}_2$  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.

**SOLUTION**

6.1 (a) 2; (b) 4

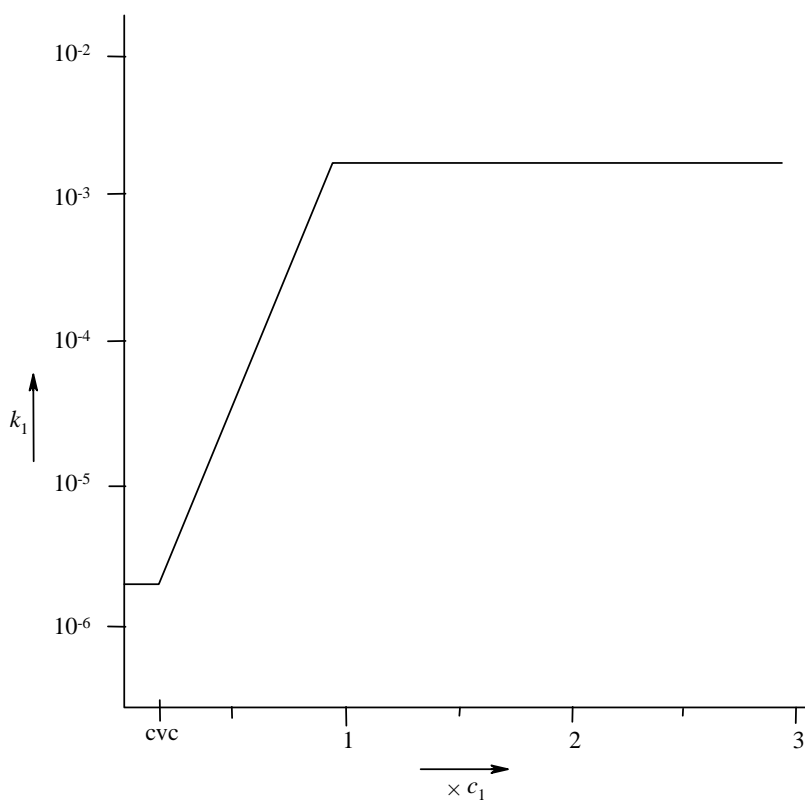
6.2 Signal No 1.

$$6.3 \quad a_0(\text{min}) = \frac{V}{l_c} = \frac{(27.4 + 26.99 n) \times 10^{-3}}{(0.154 + 0.1265 n)} \text{ nm}^2$$

$$\text{For a large value of } n: \quad a_0(\text{min}) = \frac{26.99 \times 10^{-3}}{0.1265} \text{ nm}^2$$

$$a_0(\text{min}) = 0.213 \text{ nm}^2$$

6.4



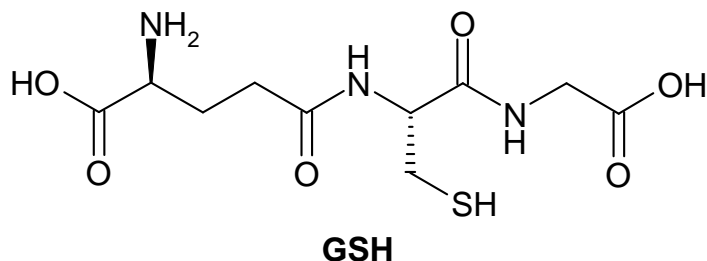
We expect curved bends in the graph, however, sharp corners (see the Figure) are also accepted.

6.5 The second answer is correct: Efficient loss of hydration of the carboxylate group of vesicle-bound 6-NBIC.

## PROBLEM 7

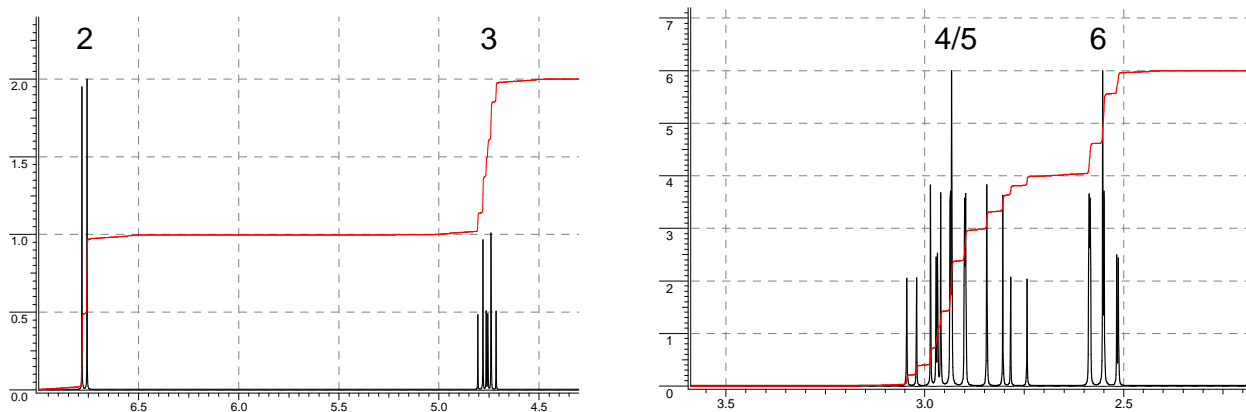
### Glutathione, an Essential Mini-Peptide

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  $\geq 500$ .



- 7.1 (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 ( $\text{H}_2\text{C}=\text{CH}-\text{CN}$ ) has the molecular formula  $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_3\text{S}$ . The  $^1\text{H}$ -NMR spectrum of **A** in  $(\text{CD}_3)_2\text{SO}$  is shown in Figure 1. When the product is pretreated with  $\text{D}_2\text{O}$ , the signals at  $\delta$  12.8 and  $\delta$  6.8 are no longer present and the signal 3 is simplified.



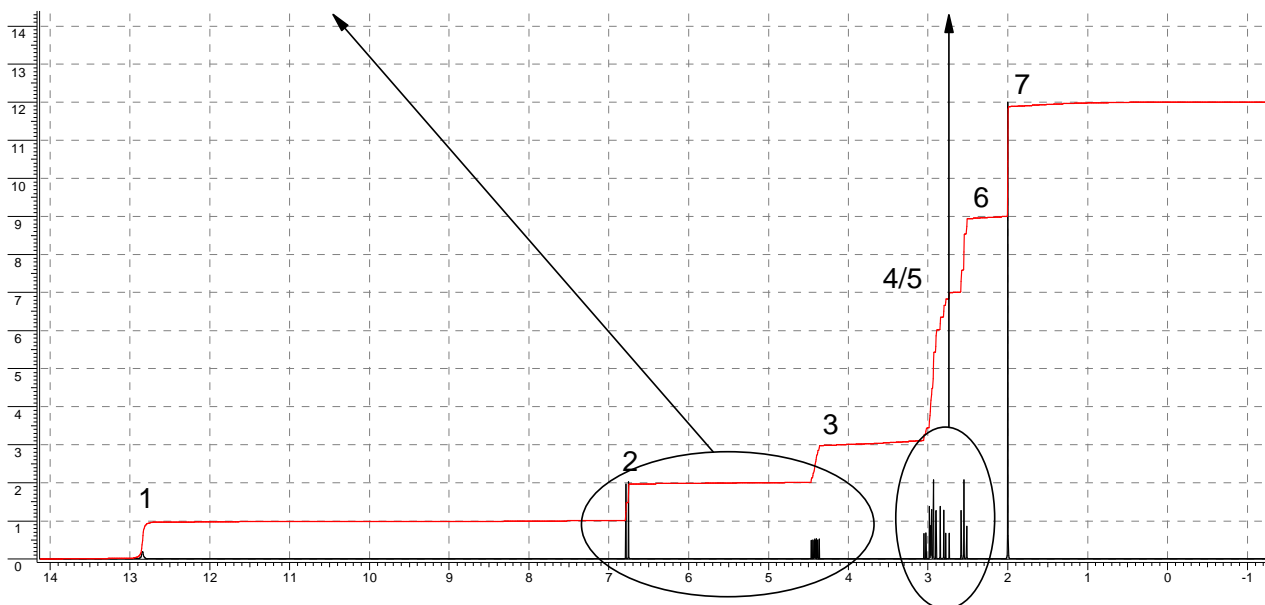


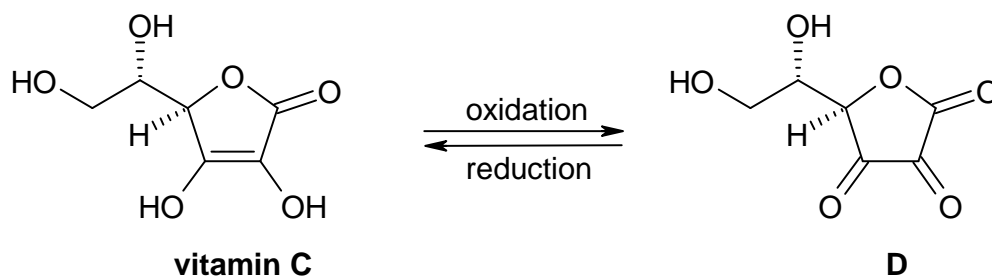
Figure 1

**7.2 (a)** The NMR-signals correspond with protons in the following groups: CH, CH<sub>2</sub>, CH<sub>3</sub>, 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 | <input type="text"/> | <input type="text"/> | <input type="text"/> | <input type="text"/> | <input type="text"/> | <input type="text"/> |

- (b)** How many carbon atoms are present in compound **A** that do not carry any protons?
- (c)** Draw the structure of compound **A**.

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



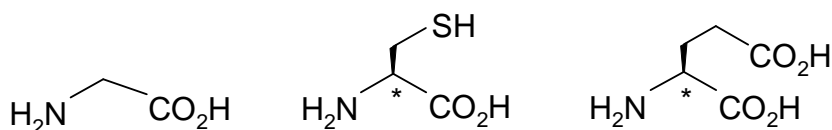
## 7.3 Eating fresh fruit and vegetables is healthy

- 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.

**SOLUTION**

7.1 a) Three amino acid residues.

b)

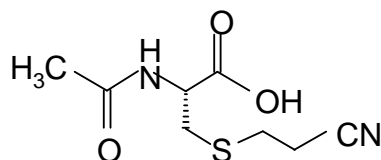


7.2 a)

| Signal           | 1  | 2  | 3  | 4/5             | 6               | 7               |
|------------------|----|----|----|-----------------|-----------------|-----------------|
| Group of protons | OH | NH | CH | CH <sub>2</sub> | CH <sub>2</sub> | CH <sub>3</sub> |

b) 3

c)



7.3 The third answer is correct: Vitamin C removes oxidants and prevents undesired depletion of GSH.



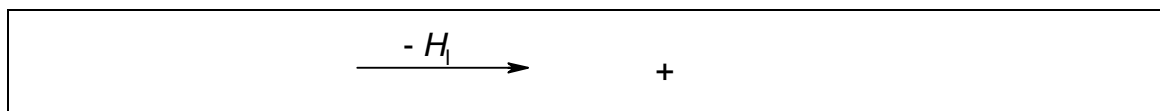
**Theme IV - Chemistry Related to Light and Energy**

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 8****LIGHTING LAMPS**

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  $\text{CeBr}_3$  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.

- 8.1** Give a thermochemical cycle (Law of Hess) for sublimation of  $\text{CeBr}_3$ , via a vapour of mononuclear ions. ( $H_l = H_{\text{lattice}}$ ;  $H_e = H_{\text{electrostatic}}$ ;  $H_s = H_{\text{sublimation}}$ ;  $H$  is not absolute,  $H$  means  $\Delta H$ )



+



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

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

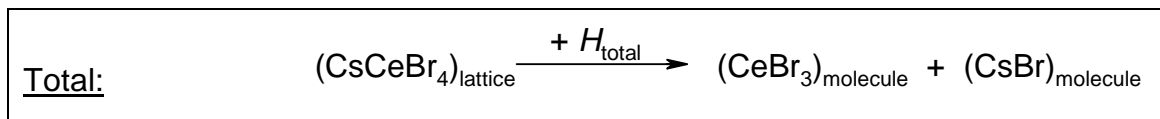
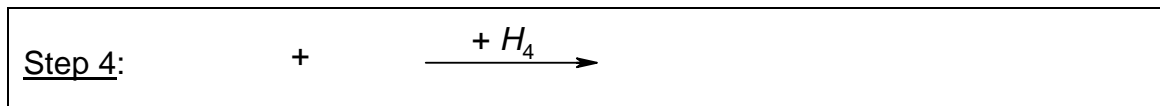
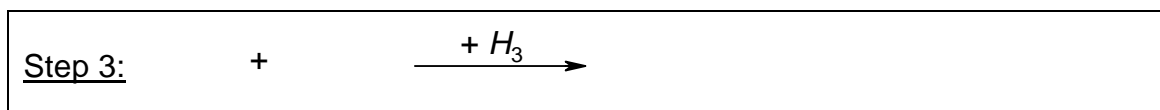
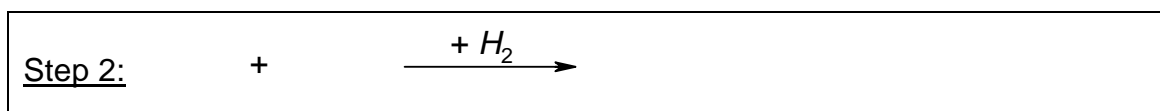
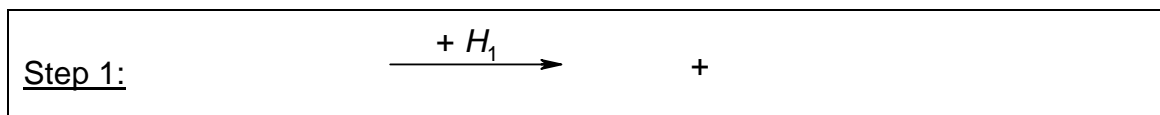
The factor  $f e^2$  (necessary in order to calculate the lattice energy in  $\text{kJ mol}^{-1}$ ) amounts to 139 when the ionic radii are substituted in nm. The Madelung constant  $A$  for the lattice is

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  $\text{CeBr}_3$  (when formed from ions) the same Born-Landé formula can be used without  $A$ . The structure of  $\text{CeBr}_3$  in the gas phase is planar triangular. The radius of  $\text{Ce}^{3+}$  is 0.115 nm and of  $\text{Br}^-$  is 0.182 nm.

**8.2** Calculate the enthalpy of sublimation of  $\text{CeBr}_3$  (in integers; be aware of the signs!)

Attempts to make a better lamp have been undertaken by adding a stoichiometric amount of  $\text{CsBr}$  to the  $\text{CeBr}_3$  in the lamp leading at room temperature to solid  $\text{CsCeBr}_4$ . When the sublimation temperature decreases the life time of the lamp will increase likewise. The  $\text{CsCeBr}_4$  lattice has a NaCl structure with  $\text{Cs}^+$  as cations and tetrahedral  $\text{CeBr}_4^-$  as complex anions. Sublimation of  $\text{CsCeBr}_4$  leads to a vapour of  $\text{CsBr}$  and  $\text{CeBr}_3$  molecules.

**8.3** Give the reaction equations of the thermochemical cycle (Law of Hess) for this process in which some steps involve  $\text{CeBr}_4^-$  ions, mononuclear ions and/or neutral molecules in the gas phase.



**8.4** Calculate the enthalpy of sublimation of  $\text{CsCeBr}_4$  (in integers).

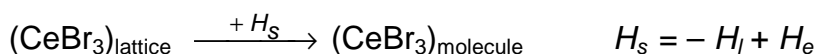
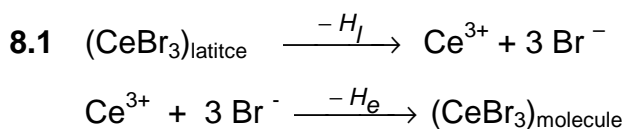
Use the Born–Landé formula for all steps in the process and report the separate energies also (be aware of the signs!). The Madelung constant for NaCl is 1.75. The

Cs–Ce distance in the lattice is 0.617 nm. The  $\text{CeBr}_4^-$  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  $\text{Cs}^+$  is 0.181 nm.

8.5 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.

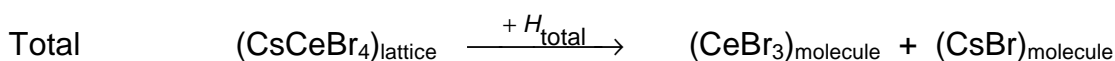
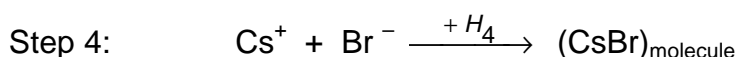
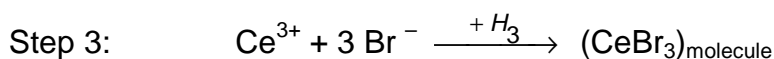
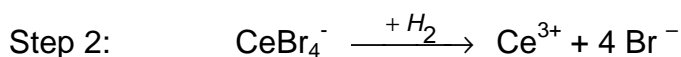
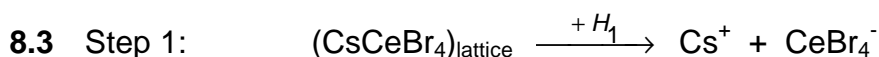
## SOLUTION



$$8.2 \quad H_l = -\frac{139 \times 3 \times 1 \times 2.985}{0.297} \times \frac{10}{11} \text{ kJ mol}^{-1} = -3810 \text{ kJ mol}^{-1}$$

$$H_e = \left( -3 \times \frac{139 \times 3 \times 1}{0.297} \times \frac{10}{11} \right) + \left( 3 \times \frac{139 \times 1 \times 1}{0.297 \sqrt{3}} \times \frac{10}{11} \right) \text{ kJ mol}^{-1} = -3092 \text{ kJ mol}^{-1}$$

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



**8.4** Step 1: The lattice energy of CsCeBr<sub>4</sub> with opposite sign is:

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

Step 2:

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

Step 3: The electronic energy in the gas phase of CeBr<sub>3</sub> is (see answer 8.2):

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

Step 4: The electrostatic energy in the gas phase of CsBr is

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

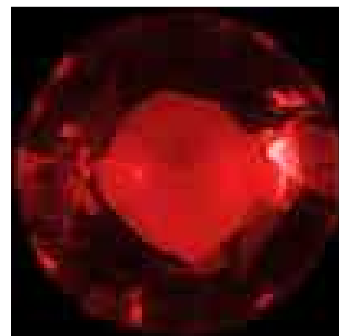
Total sum:

$$H_{\text{total}} = H_1 + H_2 + H_3 + H_4 = 461 \text{ kJ mol}^{-1}$$

**8.5** The third answer is correct: Adding CsBr is advantageous.

**PROBLEM 9****RED RUBY**

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  $\text{Cr}^{3+}$  ions that are incorporated in colourless aluminium oxide ( $\text{Al}_2\text{O}_3$ ) crystals. The  $\text{Cr}^{3+}$  ion has 3 electrons in the 3d shell and the absorption of light is due to electronic transitions between 3d orbitals of lower and higher energy.



**9.1** Indicate which of the four absorption spectra belongs to ruby.

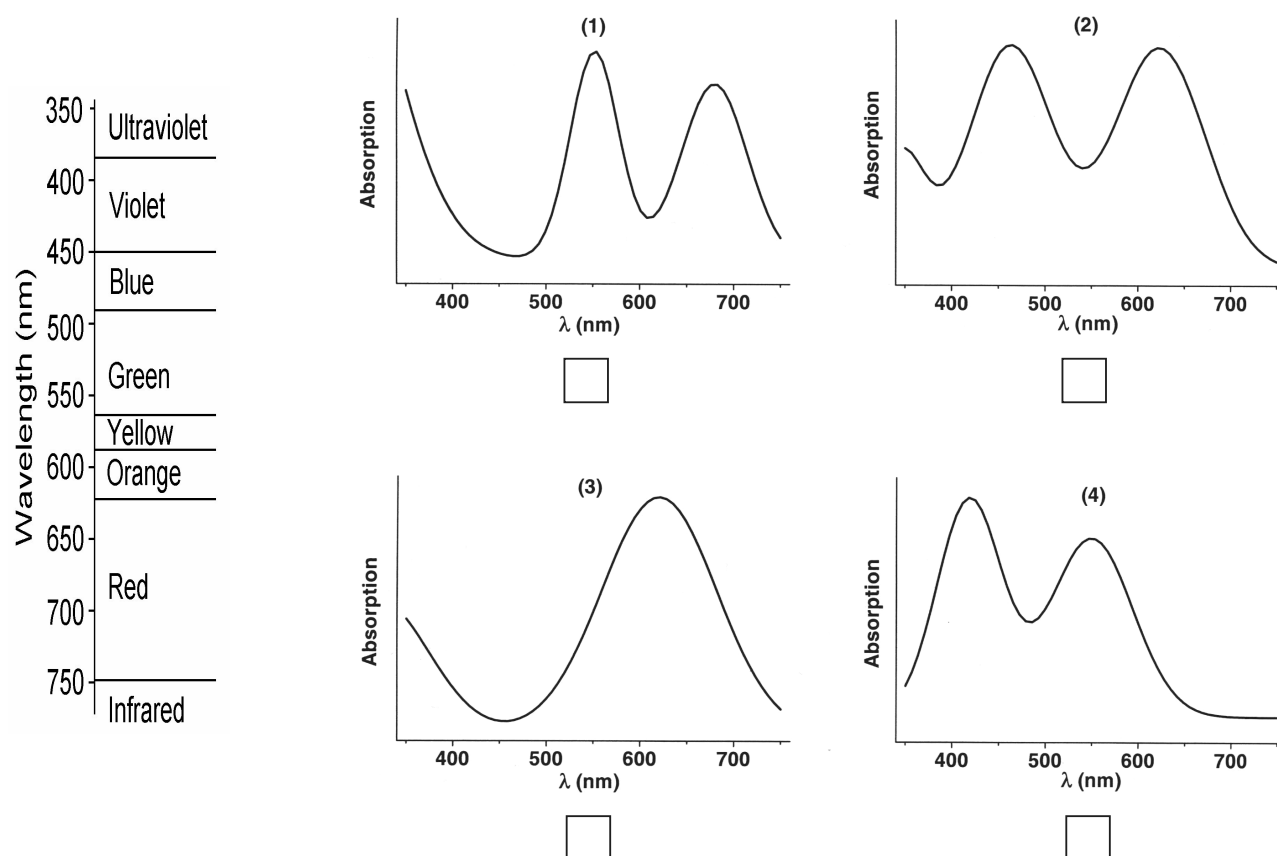


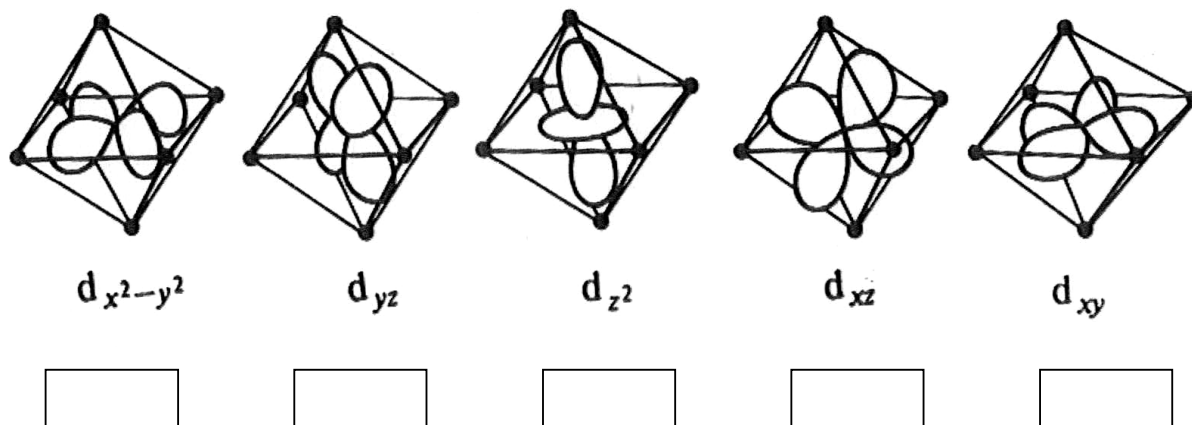
Figure 1

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  $\text{Cr}^{3+}$  ions is 0.050 mass %. The density of  $\text{Al}_2\text{O}_3$  is  $4.05 \text{ g cm}^{-3}$ . The atomic mass of  $\text{Cr} = 52\text{u}$ . ( $1\text{u} = 1.67 \times 10^{-27} \text{ kg}$ ).

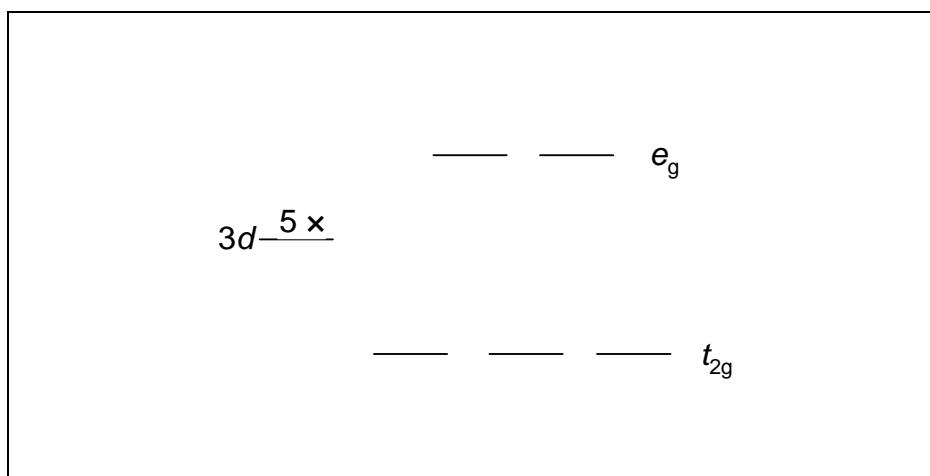
**9.2** Calculate how many  $\text{Cr}^{3+}$  ions are in this laser rod.

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

**9.3** Indicate in the boxes below which of the 3d 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.



**9.4** Indicate with arrows the distribution and the direction of the magnetic spin moment of the three 3d electrons of  $\text{Cr}^{3+}$  over the five d orbitals in the lowest energy state of  $\text{Cr}^{3+}$ .



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.

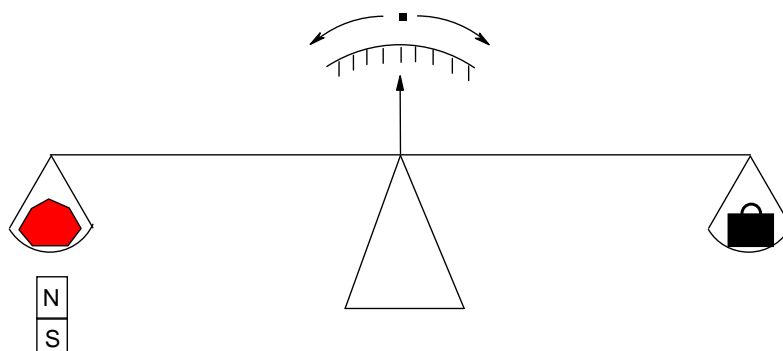


Figure 2

9.5 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)

## SOLUTION

9.1 The fourth spectrum is correct.

9.2 Volume of the rod =  $\pi \times r^2 \times l$

$$V = \pi \times 0.575^2 \times 15.2 \text{ cm}^3 = 15.79 \text{ cm}^3$$

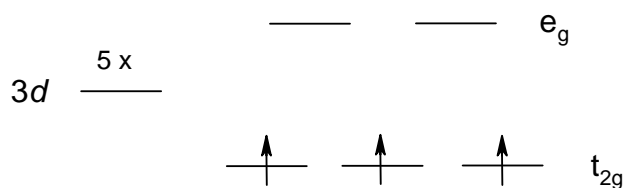
Mass of the rod:  $m = 15.79 \times 4.05 \text{ g} = 63.94 \text{ g}$

Mass of chromium in the rod:  $m_{\text{Cr}} = 63.94 \text{ g} \times 0.05 / 100 = 0.0319 \text{ g}$

Number of chromium ions:  $N = 0.0319 \times 10^{-3} \text{ kg} / (52 \times 1.67 \times 10^{-27}) = 3.68 \times 10^{20}$ .

9.3  $d_{x^2-y^2}$ :  $e_g$        $d_{yz}$ :  $t_{2g}$        $d_{z^2}$ :  $e_g$        $d_{xz}$ :  $t_{2g}$        $d_{xy}$ :  $t_{2g}$

9.4



9.5 The correct answer: The magnet attracts the ruby (the ruby moves down).

## PROBLEM 10

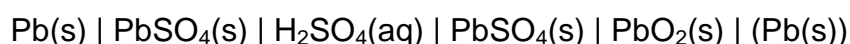
### Vehicle Traction Batteries

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.

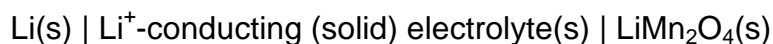
Lead-acid batteries are extensively used as portable power sources for vehicles and traction. A lead-acid battery capable of efficient recharging has an energy density of 45 Wh/kg.

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  $\text{LiMn}_2\text{O}_4$ . 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  $\text{LiMn}_2\text{O}_4$  half of the manganese ions has an oxidation state +3 and half the oxidation state +4.

A lead-acid battery is represented by:



A lithium battery is represented by:



Upon discharge the insertion product  $\text{Li}_2\text{Mn}_2\text{O}_4$  is formed. Charging the battery leads to the products  $\text{Li(s)}$  and  $\text{LiMn}_2\text{O}_4$ .

- 10.1** Give the electrochemical reactions at the electrodes of the lead-acid battery during discharge.
- 10.2** Give the electrochemical reactions at the electrodes of the lithium-ion battery upon discharge.



**10.3** Give the coordination numbers of the lithium ions and of the manganese ions in the spinel structure of  $\text{LiMn}_2\text{O}_4$ .

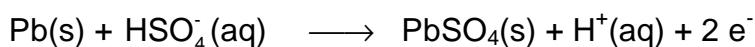
A typical family car of 1000 kg requires at least 5 kWh of energy to move 50 km, which corresponds with the consumption of about 5.0 litres or 3.78 kg of petrol. This conventional car has a petrol tank volume of 50 L. The weight of the tank is 10 kg. The fuel consumption is  $10 \text{ km L}^{-1}$ .

**10.4** 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. Calculate:

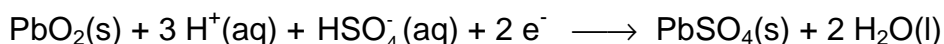
- (a) Extra weight of a lead-acid battery car.  
 (b) Extra weight of a lithium battery car.

## SOLUTION

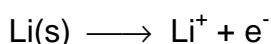
**10.1** Reaction at the negative electrode:



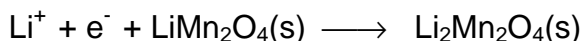
Reaction at the positive electrode:



**10.2** Reaction at the negative electrode:



Reaction at the positive electrode:



**10.3** Li – ions: coordination number = 4                      Mn – ions: coordination number = 6

**10.4** Distance of the petrol car = 500 km  $\Rightarrow$  50 kWh

Mass of petrol tank = 10 kg + 50  $\times$  (3.78 / 5) = 47.8 kg

(a) Mass of a lead-acid battery = 50000 Wh / 45 Wh  $\text{kg}^{-1}$  = 1111.1 kg

Extra weight of a lead-acid battery car = 1111.1 kg – 47.8 kg = 1063.3 kg

(b) Mass of the lithium battery = 1/3 of the mass of a lead-acid battery

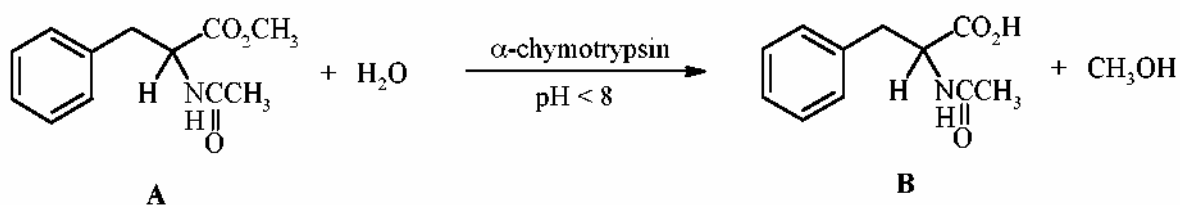
Extra weight of a lithium battery car = 1111.1 kg / 3 – 47.8 kg = 322.6 kg.

## PRACTICAL PROBLEMS

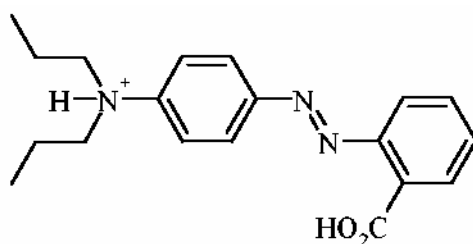
### PROBLEM 1 (Practical)

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

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



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  $\alpha$ -chymotrypsin will be supplied in a sample vial by the laboratory assistant on request.*

Racemic methyl *N*-acetyl-phenylalaninate **A** [500 mg, the exact mass ( $\pm 1$  mg) is indicated on the label of the vial marked as NacPheOMe] is transferred quantitatively into a 50 cm<sup>3</sup> Erlenmeyer flask and dissolved in methanol ( $\sim 2.5$  cm<sup>3</sup>). Subsequently, propyl red (0.02 % solution in ethanol; 4 drops) is added. The kinetic experiment is started by adding  $\alpha$ -chymotrypsin (10.0 cm<sup>3</sup> 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 cm<sup>3</sup> versus time is constructed, in order to visualize the kinetic course of this enzymatic reaction.

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## **SOLUTION**

The competitors were expected to show on the answer sheet the following data, tables, graphs or calculations:

1. Amount of the starting racemic methyl *N*-acetyl-phenylalaninate **A** (in mg and mmol).
  2. Table with time measured and the total consumption of NaOH in cm<sup>3</sup>.
  3. A graph of the total consumption of NaOH vs time.
  4. Calculation of the amount of 0.100 M NaOH consumed in this experiment in mmol.
  5. Calculation of the degree of hydrolysis of methyl *N*-acetyl-(*R,S*)-phenylalaninate **A** in mol %.
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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 cm<sup>3</sup>) 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.

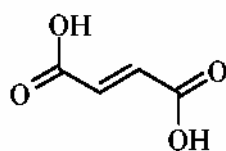
**SOLUTION**

The competitors were expected to show the following data, tables, graphs or calculations on the answer sheet:

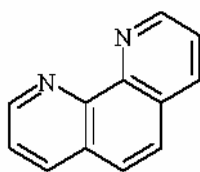
1. Mass of your starting material **A** (see label on the vial) in mg.
  2. Amount of benzyhydantoin **C** obtained.
  3. Calculation of the yield of benzyhydantoin **C** in %.
  4.  $R_f$  value of urea derivative **B**.
  5.  $R_f$  value of benzyhydantoin **C**.
  6. A copy of the TLC diagram with indication of the front base line of the solvent.
  7. 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.
  8. Appearance of benzyhydantoin **C**: white colour, yellowish colour, sticky, crystalline, powder.
  9. Melting point of benzyhydantoin **C** was determined by the examination committee.
  10. The TLC plate was necessary to pack in an envelope and leave it to a laboratory supervisor.
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**PROBLEM 3 (Practical)****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:

**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 cm<sup>3</sup> beaker with the aid of a small amount of distilled water. Hydrochloric acid (5 cm<sup>3</sup>, 4 M) is added. The content of the beaker is heated up to approximately 60 °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 cm<sup>3</sup>) and the final volume adjusted by adding distilled water and with regular mixing. An amount of 10 cm<sup>3</sup> is pipetted from this solution and transferred into a volumetric flask of 100 cm<sup>3</sup>. Again the volume is adjusted with distilled water while mixing the content of the flask.

From this solution, 10 cm<sup>3</sup> is pipetted and transferred into a volumetric flask of 100 cm<sup>3</sup>. Subsequently, 1,10-phenanthroline solution (10 cm<sup>3</sup>) and hydroxylammonium chloride solution (1 cm<sup>3</sup>) 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 cell.

Calculate the amount of iron in the iron pill on basis of the known molar absorptivity (extinction coefficient,  $\epsilon$ ) of the iron(II)phenanthroline complex at 510 nm. The molar absorptivity of the iron(II)phenanthroline complex at 510 nm is 11100 M<sup>-1</sup>cm<sup>-1</sup>.

#### 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.*

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## **SOLUTION**

The competitors were expected to show the following data, tables, graphs or calculations:

1. Weight of the iron pill in mg.
2. Reading of the spectrophotometer and corrected absorbance.
3. Calculation of the concentration of iron(II)phenanthroline complex in the cell in mmol dm<sup>-3</sup>.
4. Calculation of the total amount of iron(II) in the pill in mg.
5. Calculation of the iron content of the pill in weight %.