

**16<sup>th</sup>**



**International Chemistry Olympiad**

**8 theoretical problems  
2 practical problems**

# THE SIXTEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–10 JULY 1984, FRANKFURT AM MAIN, GERMAN FEDERAL REPUBLIC

## THEORETICAL PROBLEMS

### PROBLEM 1

A)

The element carbon consists of the stable isotopes  $^{12}\text{C}$  (98.90 percent of atoms) and  $^{13}\text{C}$  (1.10 percent of atoms). In addition, carbon contains a small fraction of the radioisotope  $^{14}\text{C}$  ( $t_{1/2} = 5730$  years), which is continuously formed in the atmosphere by cosmic rays as  $\text{CO}_2$ .  $^{14}\text{C}$  mixes with the isotopes  $^{12}\text{C}$  and  $^{13}\text{C}$  via the natural  $\text{CO}_2$  cycle.

The decay rate of  $^{14}\text{C}$  is described by ( $N$  = number of  $^{14}\text{C}$  atoms;  $t$  = time;  $\lambda$  = decay constant):

$$\text{decay rate} = -\frac{dN}{dt} = \lambda N \quad (1)$$

Integration of (1) leads to the well-known rate law (2) for the radioactive decay:

$$N = N_0 e^{-\lambda t} \quad (2)$$

$N_0$  = number of  $^{14}\text{C}$  atoms at  $t = 0$

- 1.1 What is the mathematical relationship between the parameters  $\alpha$  and  $t_{1/2}$  (= half life)?
- 1.2 The decay rate of carbon, which is a part of the natural  $\text{CO}_2$  cycle, is found to be 13.6 disintegrations per minute and gram of carbon. When a plant (e. g. a tree) dies, it no longer takes part in the  $\text{CO}_2$  cycle. As a consequence, the decay rate of carbon decreases.

In 1983, a decay rate of 12.0 disintegrations per minute and gram of carbon was measured for a piece of wood which belongs to a ship of the Vikings. In which year was cut the tree from which this piece of wood originated?

- 1.3 Assume that the error of the decay rate of 12.0 disintegrations per minute and gram of carbon is 0.2 disintegrations per minute and gram of carbon. What is the corresponding error in the age of the wood in question b)?
- 1.4 What is the isotope  $^{12}\text{C}/^{14}\text{C}$  ratio of carbon, which takes part in the natural  $\text{CO}_2$  cycle (1 year = 365 days)?

B)

The elements strontium and rubidium have the following isotope composition:

Strontium: 0.56 %  $^{84}\text{Sr}$  ; 9.86 %  $^{86}\text{Sr}$  ; 7.00 %  $^{87}\text{Sr}$  ; 82.58 %  $^{88}\text{Sr}$  (these isotopes are all stable).

Rubidium: 72.17 %  $^{85}\text{Rb}$  (stable) ; 27.83 %  $^{87}\text{Rb}$  (radioactive;  $t_{1/2} = 4.7 \times 10^{10}$  years).

The radioactive decay of  $^{87}\text{Rb}$  leads to  $^{87}\text{Sr}$ .

In Greenland one finds a gneiss (= silicate mineral) containing both strontium and rubidium.

- 1.5 What is the equation rate law describing the formation of  $^{87}\text{Sr}$  from  $^{87}\text{Rb}$  as a function of time?
- 1.6 Assume that the isotope ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  (as determined by mass spectrometry) and the isotope ratio  $^{87}\text{Rb} : ^{86}\text{Sr}$  are known for the gneiss. What is the mathematical relationship with which one can calculate the age of the gneiss?

## SOLUTION

A)

- 1.1 The relationship is:

$$\alpha = \frac{\ln 2}{t_{1/2}}$$

1.2

$$t = \frac{t_{1/2}}{\ln 2} \times \ln \left( \frac{N_0}{N} \right) = \frac{5730}{0.6930} \times \ln \left( \frac{13.6}{12.0} \right) = 1035 \text{ years}$$

- 1.3 For  $N_0/N = 13.6/12.0$      $t = 1035$  years  
 For  $N_0/N = 13.6/12.2$      $t = 898$  years  
 For  $N_0/N = 13.6/11.8$      $t = 1174$  years

Thus, the tree was cut 1035 (+ 139/–137) years ago.

#### 1.4

$$N = \frac{13.6 \times t_{1/2}}{\ln 2} = 5.91 \times 10^{10} \text{ atoms } ^{14}\text{C} / \text{g carbon}$$

$$1 \text{ g} \approx 0.989 \text{ g } ^{12}\text{C}; \quad 0.989 \text{ g } ^{12}\text{C} \approx (0.989/12) \times 6.023 \times 10^{23} \text{ atoms } ^{12}\text{C}$$

$$^{12}\text{C} / ^{14}\text{C} = \frac{0.989 \times 6.023 \times 10^{23}}{12 \times 5.91 \times 10^{10}} = 8.40 \times 10^{11} : 1$$

#### B)

1.5 Equation (2) describes the decay of the  $^{87}\text{Rb}$ :

$$^{87}\text{Rb} = ^{87}\text{Rb}_0 \cdot \exp(-\lambda t)$$

The symbol  $^{87}\text{Rb}$  stands for the number of atoms of this nuclide.

Consequently, one obtains for the formation of  $^{87}\text{Sr}$  from  $^{87}\text{Rb}$ :

$$^{87}\text{Sr} = ^{87}\text{Rb}_0 - ^{87}\text{Rb} = ^{87}\text{Rb} \cdot \exp(\lambda t) - ^{87}\text{Rb} \quad (\text{a})$$

1.6 The formation of the radiogenic  $^{87}\text{Sr}$  follows equation (a).

One has to take into account that at time  $t = 0$ , when the mineral was formed, there was some non-radiogenic strontium in it already:

$$^{87}\text{Sr} = (^{87}\text{Sr})_0 + ^{87}\text{Rb} \cdot [\exp(\lambda t) - 1]$$

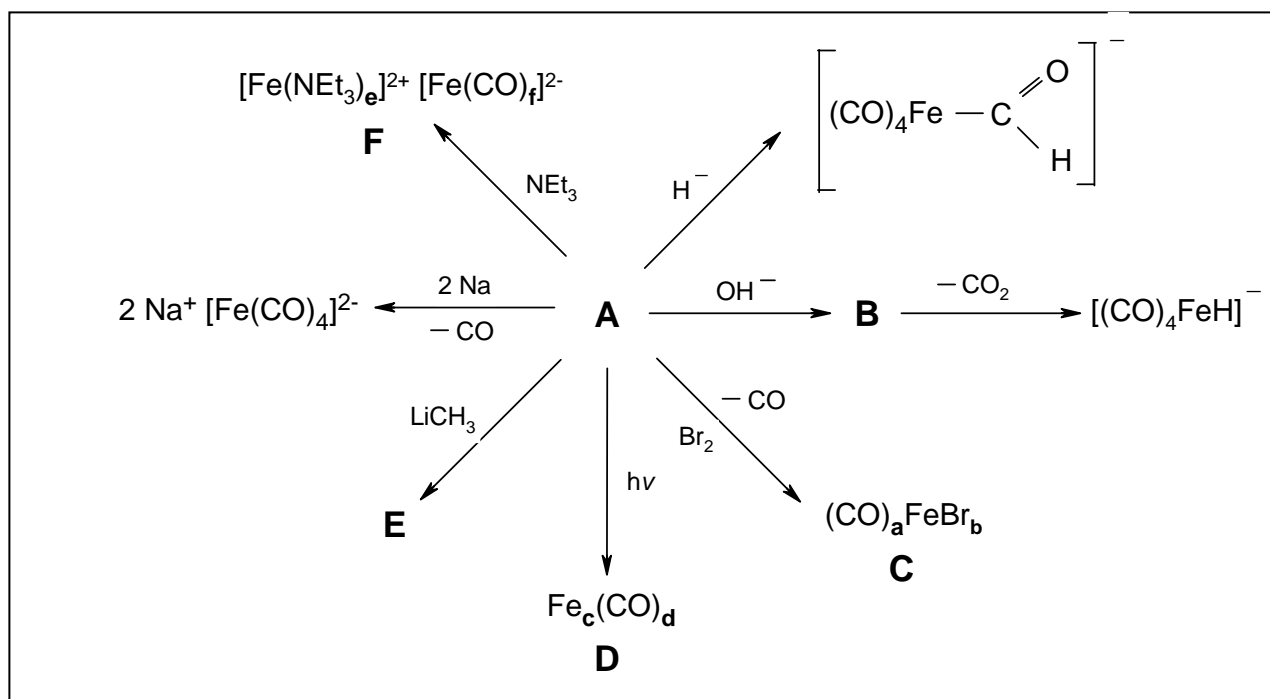
The isotope ratio  $(^{87}\text{Sr} / ^{86}\text{Sr})_0$  follows from the isotope composition of strontium. The time  $t$  in this equation corresponds to the age of the gneiss.

## PROBLEM 2

Ludwig Mond discovered before the turn of this century that finely divided nickel reacts with carbon monoxide forming tetracarbonylnickel,  $\text{Ni}(\text{CO})_4$ , a colourless, very volatile liquid. The composition of  $\text{Ni}(\text{CO})_4$  provides an example of the noble gas rule ("EAN rule").

Problems:

- Use the eighteen-electron rule (noble gas rule) to predict the formula of the binary carbonyls of  $\text{Fe}(0)$  and  $\text{Cr}(0)$ .
- What composition would the eighteen-electron rule predict for the most simple binary chromium(0)-nitrosyl compound?
- Explain why  $\text{Mn}(0)$  and  $\text{Co}(0)$  do not form so-called mononuclear carbonyl complexes of the type  $\text{M}(\text{CO})_x$  ( $\text{M} = \text{metal}$ ), but rather compounds with metal-metal bonding.
- Suggest structures of  $\text{Ni}(\text{CO})_4$ ,  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Co}_2(\text{CO})_8$ .
- State whether  $\text{V}(\text{CO})_6$  and the compounds mentioned in a) and d) are diamagnetic or paramagnetic.
- Why are the carbon monoxide ligands bound to metals much more strongly than to boron in borane adducts (e.g.  $\text{R}_3\text{B}-\text{CO}$ ;  $\text{R} = \text{alkyl}$ )?
- Determine the composition of the compounds labeled **A** - **F** in the following reaction scheme:



Hints:

- C** has the following analysis: C, 14.75 % ; Br, 48.90 % .
- D** contains 30.70 % Fe; the molecular mass is 363.8 a.m.u.
- Excess triethylamine is used for the synthesis of **F**. **F** contains 5.782 % C and 10.11 % N.

**2.8** Why is the compound **F** formed in the disproportionation reaction (given in g)), and not the compositional isomer  $[\text{Fe}(\text{CO})_f]^{2+}[\text{Fe}(\text{NEt}_3)_e]^{2-}$  ?

**2.9** The eighteen-electron rule is also satisfied by a compound prepared from elementary chromium and benzene.

- Draw the formula of this complex.
- Which complex with the analogous structure is prepared by the reaction of iron powder with cyclopentadiene? Write the chemical equation for its formation.

## SOLUTION

**2.1**  $\text{Fe}(\text{CO})_5$ ,  $\text{Cr}(\text{CO})_6$

**2.2**  $\text{Cr}(\text{NO})_4$

**2.3** Explanation: the odd number of electrons in the  $\text{Mn}(\text{CO})_5$  and  $\text{Co}(\text{CO})_4$  fragments.

**2.4**  $\text{Ni}(\text{CO})_4$ : tetrahedral geometry

$\text{Mn}_2(\text{CO})_{10}$ : - octahedral  $\text{Mn}(\text{CO})_5$ -structure having a Mn-Mn bond,

- relative orientation (conformation) of the carbonyl groups.

$\text{Co}_2(\text{CO})_{10}$ : CO-bridges and Co-Co bond

**2.5**  $\text{Fe}(\text{CO})_5$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Co}_2(\text{CO})_{10}$  are diamagnetic,

$\text{V}(\text{CO})_6$  is paramagnetic.

**2.6** Explanation using the so-called "back-bonding concept"

**2.7** **A** =  $[\text{Fe}(\text{CO})_5]$

**B** =  $[\text{HOCOF}(\text{CO})_4]$

**C** =  $[\text{FeBr}_2(\text{CO})_4]$

**D** =  $[\text{Fe}_2(\text{CO})_9]$

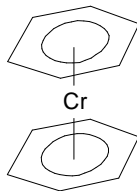
**E** =  $[(\text{CO})_4\text{Fe}=\text{C}(\text{OLi})\text{CH}_3]$

**F** =  $[\text{Fe}(\text{NEt}_3)_6][\text{Fe}(\text{CO})_4]$

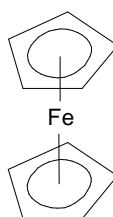
**2.8** This observation is due to differing back bonding capability of  $\text{NEt}_3$  and CO.

**2.9**

i) Structural formula of dibenzenechromium



ii) Structural formula of ferrocene.



**PROBLEM 3**

A weak acid of total concentration  $2 \times 10^{-2}$  M is dissolved in a buffer of pH = 8.8. The anion  $A^-$  of this acid is coloured and has a molar decadic absorption coefficient  $\varepsilon$  of  $2.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ . A layer  $l$  of the solution with 1.0 cm thickness absorbs 60 percent of the incident luminous intensity  $I_0$ .

- 3.1 What is the equation relating the extinction to the thickness of the absorbing layer?  
 3.2 How large is the concentration of the acid anion in the buffer solution?  
 3.3 How large is the  $pK_a$  of the acid?

**SOLUTION**

- 3.1 The Lambert-Beer law e.g.:

$$\log(I_0/I) = A = \varepsilon \cdot c \cdot l$$

- 3.2  $\log[(100-60)/100] = -2.1 \times 10^4 \times [A^-] \times 1$

$$[A^-] = 1.895 \times 10^{-5} \text{ mol cm}^{-3} = 1.895 \times 10^{-2} \text{ mol dm}^{-3}$$

- 3.3 According to the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log \frac{[A^-]_{\text{eq}}}{[HA]_{\text{eq}}}$$

and with the total concentration

$$[HA]_{\text{tot}} = [HA]_{\text{eq}} + [A^-]_{\text{eq}} = 2 \times 10^{-2} \text{ mol dm}^{-3}$$

$$8.8 = pK_a + \log \frac{1.895 \times 10^{-2}}{2 \times 10^{-2} - 1.895 \times 10^{-2}}$$

$$pK_a = 7.5$$



**PROBLEM 4**

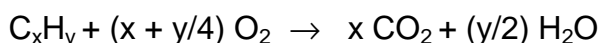
15 cm<sup>3</sup> of a gaseous hydrocarbon C<sub>x</sub>H<sub>y</sub> are mixed with 120 cm<sup>3</sup> oxygen and ignited. After the reaction the burned gases are shaken with concentrated aqueous KOH solution. A part of the gases is completely absorbed while 67.5 cm<sup>3</sup> gases remain. It has the same temperature and pressure as the original unburned mixture.

- 4.1 What is the composition of the remaining gas? Explain.
- 4.2 How large is the change in the amount of substance per mole of a hydrocarbon C<sub>x</sub>H<sub>y</sub> when this is burned completely?
- 4.3 What is the chemical formula of the hydrocarbon used for the experiment? Give the steps of the calculation.

**SOLUTION**

4.1 The remaining gas is oxygen since the burning products CO<sub>2</sub> and H<sub>2</sub>O are completely absorbed in concentrated KOH solution.

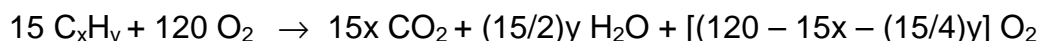
4.2 The general stoichiometric equation for complete combustion of a hydrocarbon C<sub>x</sub>H<sub>y</sub> is as follows:



The change in amount of substance per mole of hydrocarbon is

$$[x + (y/2) - (1 + x + y/4)] \text{ mol} = [(y/4) - 1] \text{ mol}$$

4.3 The equation of chemical conversion at the experimental condition is as follows:



For the residual oxygen:

$$(1) \quad 120 - 15x - (15/4)y = 67.5$$

and for the total balance of amount of substance:

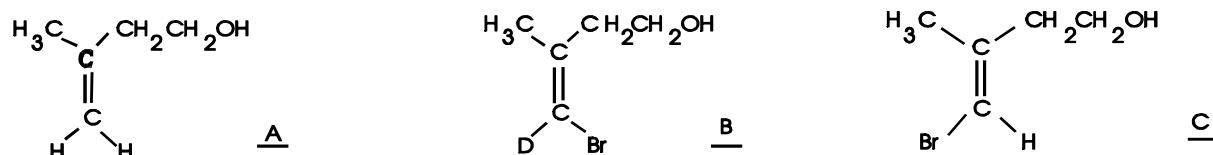
$$(2) \quad 15x + (15/2)y + 67.5 = 15 + 120 + 15[(y/4) - 1]$$

From equation (1) and (2) follows:  $x = 2$  and  $y = 6$ .

The hydrocarbon in question is ethane.

**PROBLEM 5**

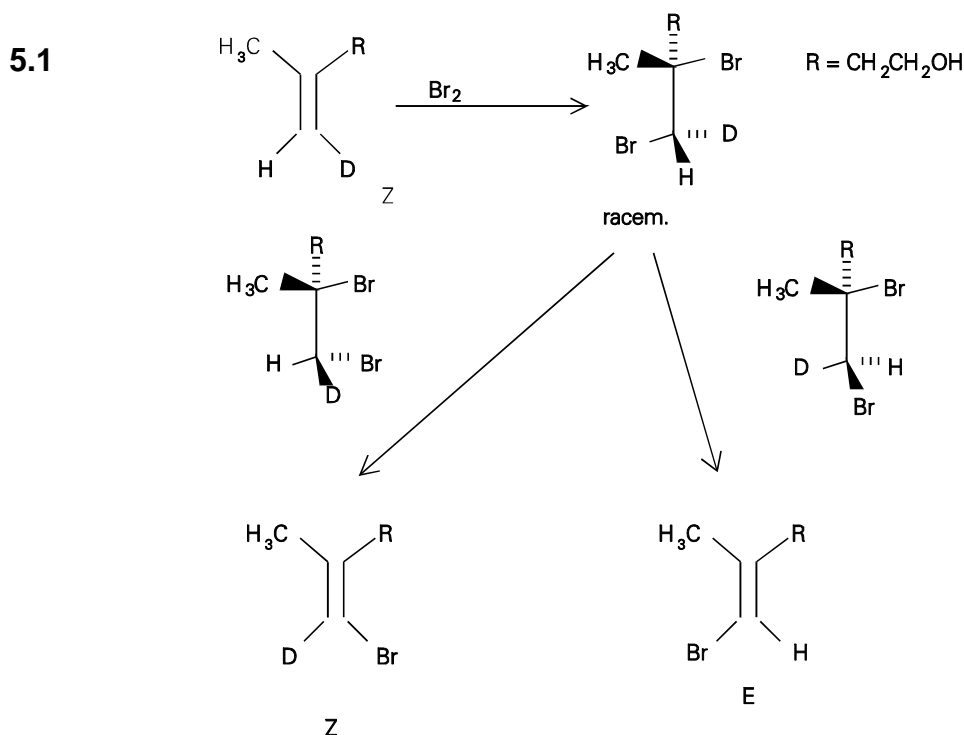
One of the diastereotopic methylene protons at the double bond of **A** was selectively substituted by deuterium. Bromination and subsequent dehydrobromation yields the



deuteriated product **B** and the non-deuteriated product **C**.

**5.1** Which configuration follows for the monodeuteriated **A** from the given reaction products?

**5.2** The solution of this question requires the formulation of the reaction and a short argumentation why only **B** and **C** are formed.

**SOLUTION**

**5.2** The addition of bromine occurs trans (antarafacial). The elimination of HBr via an E2 mechanism also requires an anti-periplanar (= trans) arrangement of H and Br. The products given in this problem are only formed from a Z-configured adduct.

The bromination of **A** and subsequent dehydrobromination yield both E,Z isomeric bromoolefins that have to be separated. Substitution of the bromine by deuterium in the Z-isomer proceeds by treatment with a metal (best: Na/t-BuOD) under retention to **A**.

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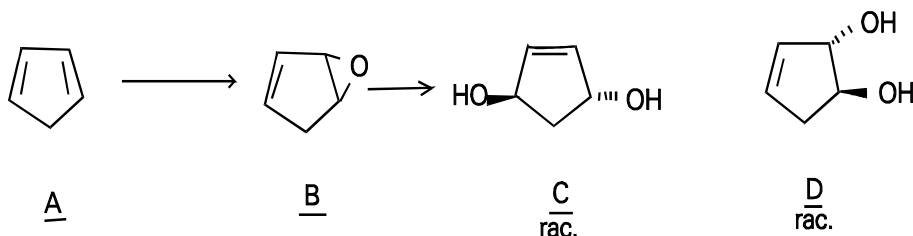
**PROBLEM 6**

A technical interesting C<sub>5</sub> hydrocarbon **A** is separated via dimerization from the for-runnings of the benzene-pyrolysis fraction. This is achieved either by heating to 140 – 150 °C under pressure or by heating over several hours at 100° C. Then it is distilled out at 200 °C. Treatment of **A** with peroxyacetic acid under neutral conditions (sodium acetate and sodium carbonate) in dichloromethane at 20° C yields a product **B**. **B** yields two isomeric products **C** and **D** (summary formula C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>) by the reaction with aqueous sodium carbonate solution. The main product **C** contains three different bound carbon atoms whereas in the minor product **D** five different carbon atoms are present. **C** is chiral.

- 6.1 Write the formulas of **A**, **B**, **C**, and **D** considering the stereochemical representation.
- 6.2 What is the name of the chemical reaction which is used for the above mentioned separation procedure?
- 6.3 Which stereochemical rules hold for the dimerization reaction?
- 6.4 Give the structure of the dimerization product.
- 6.5 Give the mechanism of the formation of **C** and **D** from **B**.
- 6.6 Which kind of isomers are **C** and **D** ?
- 6.7 How many stereoisomers of **C** and **D** are principally (regardless of their synthetic availability) possible? Give their mutual stereochemical relations. Write their structural formulas.

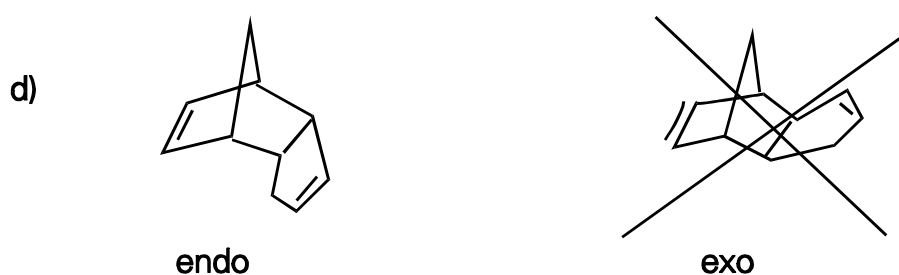
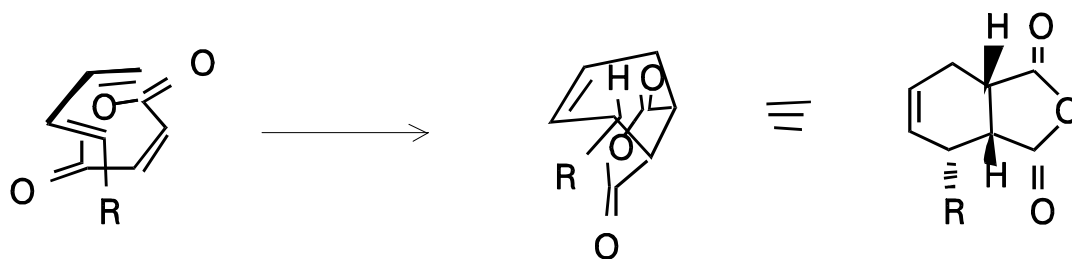
**SOLUTION**

6.1



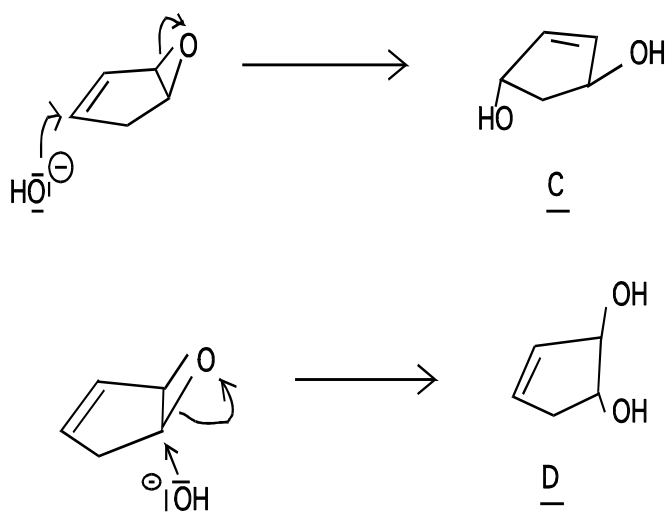
6.2 Diels-Alder-reaction, 4+2-cycloaddition

6.3 cis-addition = suprafacial addition with respect to diene and dienophile endo-rule: a substituent at the dienophile is oriented primarily toward the diene . E.g.



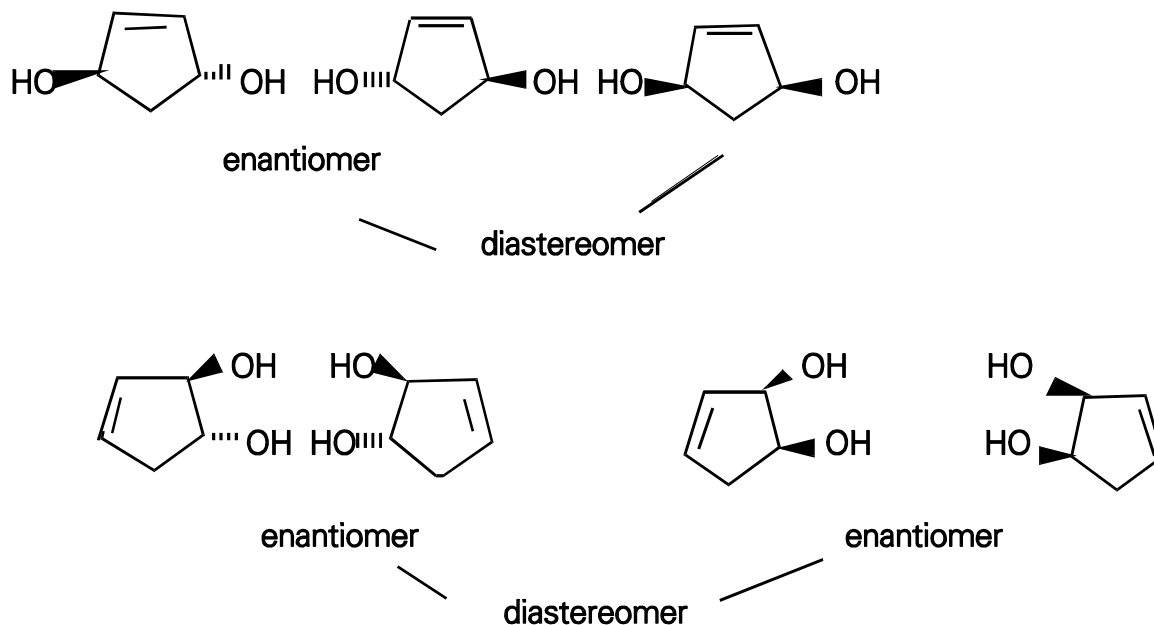
6.4

6.5 **C** is formed via a  $S_N2$  reaction. This reaction can lead to a cis or a trans product. Because **C** is chiral, the trans product is formed. **D** is formed via  $S_N2$  reaction.



6.6 **C** and **D** are constitutional isomers.

6.7 There exist two diastereomers (cis and trans) of **C**. The trans form is chiral, i.e. there exists a pair of enantiomers. The cis form is achiral (reduction of the number of stereoisomers caused by constitutional symmetry, meso-form). **D** forms two diastereomers, each of them is chiral.



**PROBLEM 7**

Deoxyribonucleic acid (DNA) represents the genetic program of all living beings. The human genetic program is subdivided into 23 chromosomes.

**7.1** Calculate the mass of a DNA thread in grams, which reaches from earth to the moon (340,000 km). A mass of 1 g represents 1,000 nucleotide pairs.

One nucleotide pair (base pair) has a length of 0.34 nm.

**7.2** Give estimation on how many nucleotide pairs are stored in the chromosome set of a human being. Human cells can synthesize 50,000 different proteins, which are on the average 300 amino acids long. Only 2 % of the DNA code for proteins.

**7.3** The DNA of the bacteriophage M13 shows the following base composition:

A: 23 %, T: 36 %, G: 21 %, C: 20 % (mole %)

What does the base composition tell about the structure of the DNA?

**SOLUTION**

**7.1** 1. Number of nucleotide pairs as calculated from the given length

$$\frac{3.4 \times 10^8 \text{ m}}{3.4 \times 10^{-10} \text{ m}} = 10^{18} \text{ nucleotide pairs}$$

2. Calculation of the mass:

$$1,000 \text{ nucleotide pairs} = 10^{-18} \text{ g}$$

$$10^{18} \text{ nucleotide pairs} = 1 \text{ mg}$$

The mass of 340.000 km DNA is 1 mg.

**7.2** Human DNA codes for  $50,000 \times 300$  amino acids in form of proteins: Each amino acid is encoded by 3 nucleotides or due to the double stranded structure of DNA by 3 nucleotide pairs. This amounts to  $4.5 \times 10^7$  nucleotide pairs. Since only 2% of the DNA code for proteins one can calculate the number of nucleotide pairs in human DNA to  $2.25 \times 10^9$  nucleotide pairs.

**7.3** The DNA has to be single stranded, since the ratio of adenine : thymine and guanine : cytosine is different from one.

## PROBLEM 8

The sequence of the amino acids in a peptide can be determined by a combination of chemical and enzymatic methods. The peptide in question functions in the human body as a pain reliever.

- Hydrolysis of the peptide in 6 M HCl at 110° C followed by an analysis of the liberated amino acids, resulted in a molar ratio of Gly, Leu, and aromatic amino acids Phe, Tyr 2 : 1 : 1 : 1.
- Reacting the peptide with 2,4-dinitrofluorobenzene (DNFB), followed by hydrolysis and chromatographic analysis, yielded the tyrosine derivative.
- Partial hydrolysis with chymotrypsin yielded Leu, Tyr and a smaller peptide. After hydrolysis of this peptide Gly and Phe were identified in a ratio 2 : 1. Chymotrypsin is a protease which cleaves a peptide bond following an aromatic amino acid.

Problems:

- Determine the amino acid sequence from the given information.
  - Write the structural formula of the DNFB- and the dansyl derivative of tyrosine. What is the advantage of the dansylation in comparison to the DNFB-modification?  
Dansyl means 5-N,N-dimethylaminonaphtalene-4-sulphonyl.
  - In a similar peptide which shows the same biological activity, leucine is replaced by methionine. Explain from the chemical structure of both amino acids why the replacement is possible without loss of biological activity.
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## SOLUTION

- It can be derived from data in part 1 that the net composition of the peptide is 2 Gly, 1 Leu, 1 Phe and 1 Tyr.

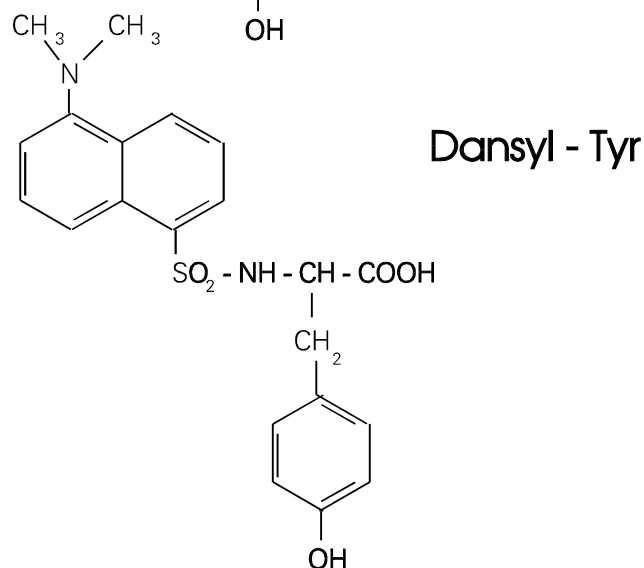
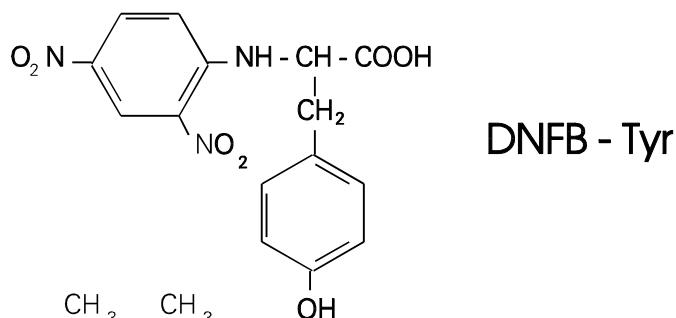
From part 2 one can conclude that the N-terminal amino acid has to be Tyr since DNFB is specific for the N-terminus.

Part 3 shows that the internal peptide has to be Gly-Gly-Phe.

The sequence is Tyr-Gly-Gly-Phe-Leu.

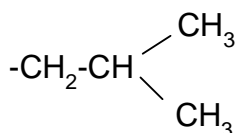
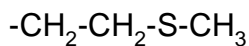


8.2 The trivial name of the peptide is Leu-Enkephaline. It acts as a pain killer in the human body.



Dansyl derivatives give increased sensitivity since they are highly fluorescent.

8.3 The compound is Met-Enkephaline. Leu and Met are both non-polar amino acids. Both side chains show comparable van der Waals radii.



**PRACTICAL PROBLEMS****PROBLEM 1 (practical)**

Nitration of phenacetine (4-ethoxyacetanilide) with nitric acid in acetic acid as solvent

Caution:

Both acetic acid and 65 % nitric acid attack the skin. If it happens, the skin must be rinsed with water immediately and washed with a saturated aqueous solution of sodium carbonate. Vapours of nitric acid damage the respiratory tract; moreover, nitric gases evolved in the reaction flask are very toxic.

The glass joints of the various apparatus must be only slightly greased.

*Apparatus:*

250 ml four-necked flask with laboratory stirrer, thermometer, reflux condenser with gas vent, water bath, Bunsen burner.

*Preparation:*

40 ml of acetic acid are placed with a glass syringe pipette in the four-necked round bottom flask. 2.0 g of phenacetine are then dissolved in the acetic acid. Also, 2.5 ml 65 % nitric acid are added by using a glass syringe pipette under an effective hood. This mixture is heated for five minutes in a water bath at 90 °C.

*Isolation and purification:*

The hot water bath is replaced by ice water. After ca. 10 minutes the gas vent is removed and ca. 120 ml of distilled water are added through the reflux condenser into the flask in order to dilute the original solution. Stirring is continued until a temperature of ca. 5 °C is reached.

The precipitated solid is filtered off and then washed with a total of 100 ml of cold water and finally dried at 60° C for 2.5 hours in a drying oven.

*Evaluation of the experiment:*

## a) Melting points:

The melting point of phenacetine and its reaction product are to be determined and recorded in the note book. The melting point of phenacetine is higher than 120° C and that of the product is higher than 80° C.

## b) Thin-layer chromatogram:

The relative position of the spots of the starting compound and its reaction product must be recorded. In order to reach it, little portions of the both samples must be dissolved in 1-2 ml of acetone. The solutions must be placed on the plate by using a capillary tube. To develop the chromatogram, a mixture of 90 ml toluene, 25 ml acetone, and 5 ml acetic acid is used.

After drying the spots are circled with a pen. The  $R_f$ -values must be recorded.

## c) Developing reagent:

The developed TLC-plate must be sprayed under a hood with the available reagent solution consisting of iron(III) chloride and potassium hexacyanoferrate(III).

Interpretation of the results:

- 1.1 Which nitration product(s) has (have) been formed? The discussion should be focused on the relative position of the spots in your chromatogram; describe your arguments in the note book.
- 1.2 Explain why such "mild conditions" have been used here for the nitration reaction. Explain why the nitration reaction has proceeded in spite of these "mild conditions".
- 1.3 Explain the observed colour reaction of phenacetine with the developing reagent.
- 1.4 Make a brief proposal, how the filtrate should be prepared to avoid environmental damage.

Chemicals:

Acetic acid (analysis grade)

Nitric acid (analysis grade);  $w = 65\%$  by mass

Phenacetine (analysis grade)

Toluene (analysis grade)

Acetone (analysis grade)

Developing reagent: 100 ml solution

200 ml solution

700 ml distilled water.

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## **SOLUTION**

a) Melting points:

4-ethoxy-N-acetylphenylamin (phenacetine) : 135 °C

4-ethoxy-2-nitroacetanilide : 103 °C (theoretical value)

b), c) Documentation, Thin-layer chromatogram

### Interpretation of the results:

**1.1** The  $R_f$ -value of the nitration product is almost twice as great as that of the starting compound phenacetine. Although nitration has occurred, the molecules exhibit less dipolar character that indicates intramolecular hydrogen bridges. This is only possible if the acetyl amino and nitro groups are located in 1.2-positions.

In accordance with the +M-effect of the acetyl amino group one should expect that the nitro group would be favoured in a (free) ortho-position because of the lowered activation energy. On the other hand, one would not expect multiple nitration because of the "mild reaction conditions" (see below) and also because of the electron withdrawing mesomeric effect (-M-effect) and the inductive electron withdrawal (-I-effect) of the nitro group that has entered the molecule.

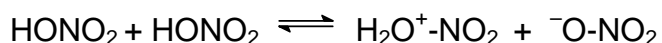
Nitration product: 4-Ethoxy-2-nitroacetanilide

The melting point confirms this observation.

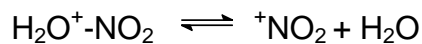
**1.2** The nitration reaction is carried out relatively rapidly, at relatively low temperature in dilute solution and without using fuming nitric acid or "nitration acid".

Instead of sulphuric acid concentrated acetic acid is used. The molecules of the latter compound neither protonate the  $\text{HNO}_3$  sufficiently nor do they do solvate the

$\text{NO}_2^+$  ions. As a result, the equilibrium reactions



and



are shifted far to the left. This effect is counterbalanced by the high reactivity (+M-effect) of phenacetine.

**1.3** Phenacetine is oxidized by iron(III) ions and a molecule of p-quinone type and iron(II) ions are formed. The iron(II) ions react immediately with the hexacyanoferrate(III) ions to give Turnbull's Blue.

**1.4** Neutralization with sodium or potassium hydroxide solution, use of calcium hydroxide solution and argumentation:

$\text{NO}_3^-$ -ions,  $\text{CH}_3\text{COO}^-$  ions and 4-ethoxy-2-nitroacetanilide are removed by biological metabolism.

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**PROBLEM 2 (practical)**Determination of the content of phosphoric acid in a cola drink*Apparatus:*

500 ml round-bottom flask with stirrer, reflux condenser, heating mantle, magnetic stirrer, water bath.

*Preparation of the sample:*

The content of a cola drink bottle is stirred for two or three minutes in a round-bottom flask. Afterwards, 6.0 g powdered active charcoal are added. The entire suspension is carefully heated to reflux and is maintained there for ten minutes. The glass joint of the reflux condenser must not be greased!

The heating mantle is then exchanged with an ice water bath. After the sample has been cooled to 20 °C, it is filtered through a double fluted filter paper. The initial filtrate should be recycled several times.

*Adjustment of the pH-meter:*

The pH-meter is adjusted to the working electrode by using two buffer solutions.

*Titration:*

150 ml of the unknown solution are titrated using pH indication with a standardized sodium hydroxide solution ( $c(\text{NaOH}) = 0.0500 \text{ mol dm}^{-3}$ ).

The first equivalence point of the phosphoric acid is reached after about 6 ml of the NaOH solution have been consumed. The titration is to be continued until more than about 12 ml of sodium hydroxide solution have been added.

*Results of the experiment:*

- Draw the titration curve and determine the first equivalence point.
- Determine the pH value of the heated cola drink and the pH value at the first equivalence point.
- Calculate the concentration of phosphoric acid in the cola drink. Write the calculation and the result in your report.

*Interpretation of the experiment:*

1. Describe and explain your observations during the titration.
2. Is it possible that the active charcoal could have influenced your titration result? Give reasons for your presumption.

*Chemicals:*

Powdered active charcoal

Sodium hydroxide solution;  $c(\text{NaOH}) = 0.0500 \text{ mol dm}^{-3}$

Buffer solutions

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**17<sup>th</sup>**



**International Chemistry Olympiad**

**8 theoretical problems  
1 practical problem**



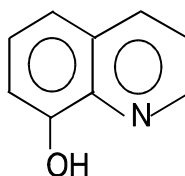
# THE SEVENTEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–8 JULY 1985, BRATISLAVA, CZECHOSLOVAKIA

## THEORETICAL PROBLEMS

### PROBLEM 1

A solution was formed from 0.5284 g of a sample of an alloy containing aluminium. The aluminium was then precipitated as aluminium 8-hydroxyquinolate. The precipitate was separated, dissolved in hydrochloric acid and the 8-hydroxyquinoline formed was titrated with a standard solution of potassium bromate containing potassium bromide. The concentration of the standard potassium bromate solution was 0.0200 M and 17.40 cm<sup>3</sup> of it were required. The resultant product is a dibromo derivative of 8-hydroxyquinoline.

The structural formula of 8-hydroxyquinoline is:



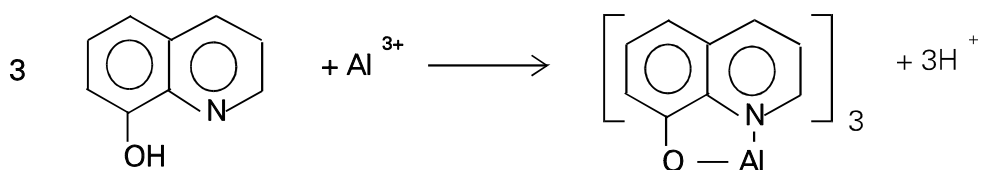
The relative atomic mass of aluminium is 26.98.

Problems:

- 1.1 Write the balanced equation for the reaction of the aluminium (III) ion with 8-hydroxyquinoline, showing clearly the structure of the products.
- 1.2 Give the name of the type of compound which is formed during the precipitation.
- 1.3 Write the balanced equation for the reaction in which bromine is produced.
- 1.4 Write the balanced equation for the reaction of bromine with 8-hydroxyquinoline.
- 1.5 Calculate the molar ratio of aluminium ions to bromate ions.
- 1.6 Calculate the percentage by weight of aluminium in the alloy.

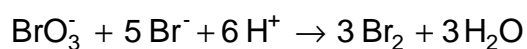
**SOLUTION**

1.1



1.2 Chelate

1.3



1.4



1.5 As  $\text{Al} \triangleq \text{Al}(\text{oxine})_3 \triangleq 3 \text{ oxine} \triangleq 12 \text{ Br} \triangleq 12 \text{ e}$ ,  
the chemical equivalent of Al equals  $26.98/12 = 2.248$ .

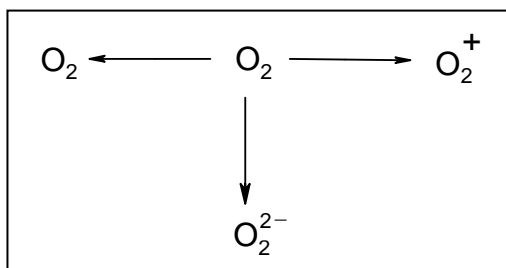
1.6 The percentage of the aluminium in the sample is

$$\% \text{Al} = \frac{17.40 \times 0.1000 \times 2.248 \times 100}{528.4} = 0.74$$

The alloy contains 0.74% of aluminium.

**PROBLEM 2**

It is possible to prepare compounds containing ions  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$  or even  $\text{O}_2^+$ . These ions are usually formed from molecules of oxygen during various reactions, as indicated in the scheme below:



- 2.1** Indicate clearly which of the above reactions correspond to the oxidation and which to the reduction of the oxygen molecule.
- 2.2** For each of the ions in the scheme give the formula of a compound containing that particular ion.
- 2.3** It has been found that one of the species in the scheme is diamagnetic. Which one is it?
- 2.4** Copy out the following table:

Species	Bond order	Interatomic distance	Bonding energy
$\text{O}_2$			
$\text{O}_2^+$			
$\text{O}_2^-$			
$\text{O}_2^{2-}$			

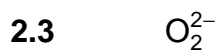
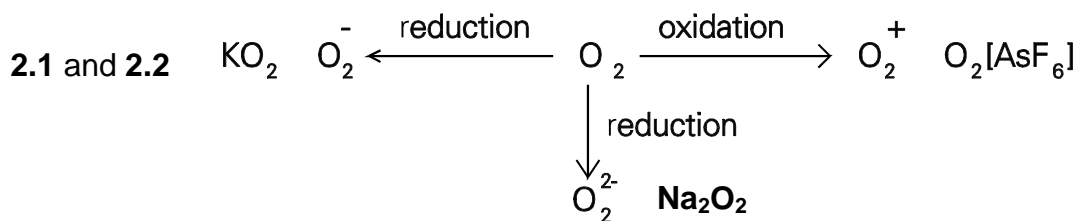
The interatomic distances, O-O, in the above species have the values 112, 121, 132 and about 149 pm. Write these values in the appropriate column in the table.

$$1 \text{ pm} = 10^{-12} \text{ m.}$$

- 2.5** Three of the bond energies,  $E_{\text{O-O}}$ , have the values approximately 200, 490 and 625  $\text{kJ mol}^{-1}$ . The value for one of the species is uncertain and, therefore, not given. Write the values in the appropriate spaces in the table.

- 2.6 Determine the bond order for the individual species and write the answers in the table.
- 2.7 Is it possible to prepare compounds containing the  $F_2^{2-}$  ion? Give reasons for your answer.

## SOLUTION



2.4 - 2.6

Species	Bond order	Interatomic distance (pm)	Bonding energy ( $\text{kJ mol}^{-1}$ )
$\text{O}_2$	2	121	490
$\text{O}_2^+$	2.5	112	625
$\text{O}_2^-$	1.5	132	–
$\text{O}_2^{2-}$	1	149	200

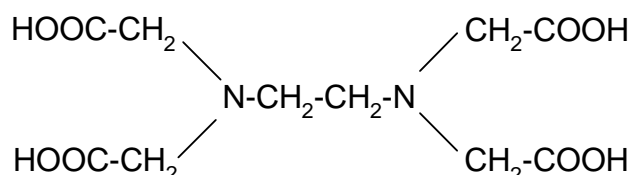
- 2.7 Ion  $F_2^{2-}$  does not exist. The number of electrons in the bonding and antibonding orbitals would be the same and thus, the bonding F–F cannot be formed. Therefore, there exists no compound containing ion  $F_2^{2-}$ .

**PROBLEM 3**

Calcium sulphate is a sparingly soluble compound. Its solubility product is given by:

$$K_s(\text{CaSO}_4) = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 6.1 \times 10^{-5}$$

Ethylenediaminetetraacetic acid (EDTA) has the formula  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$  and the structure:



The anion of this acid,  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}$ , forms a stable complex  $\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{2-}$  with calcium ions. The stability constant of this complex ion is given by:

$$K = \frac{[\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{2-}]}{[\text{Ca}^{2+}][\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}]} = 1.0 \times 10^{11}$$

EDTA is completely dissociated in strongly alkaline solution. The equation for this dissociation is:

Problems:

- 3.1 Calculate the concentration of calcium ions in a saturated solution of calcium sulphate.
- 3.2 Calculate the concentration of free  $\text{Ca}^{2+}$  cations in a solution of 0.1 M  $\text{Na}_2(\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8)$ . You should ignore any protonation of the ligand.
- 3.3 How many moles of calcium sulphate will dissolve in 1 litre of a strongly alkaline solution of 0.1 M  $\text{Na}_4\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8$ ?  
What would be the concentrations of the calcium and sulphate ions in the resulting solution?
- 3.4 Suggest a structure for the complex ion  $[\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8]^{2-}$  assuming that it is approximately octahedral.
- 3.5 Is the structure you have suggested in 4) optically active?  
If your answer is "yes" then draw the structure of the other optical isomer enantiomer).
- 3.6 Explain why the complexes formed by the anion  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}$  are exceptionally stable.

**SOLUTION**

3.1  $[\text{Ca}^{2+}] = 7.8 \times 10^{-3} \text{ mol dm}^{-3}$

3.2  $[\text{Ca}^{2+}] = 1.0 \times 10^{-6} \text{ mol dm}^{-3}$

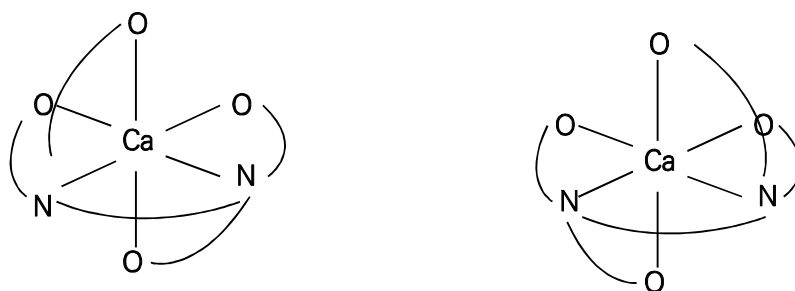
3.3 The  $\text{CaSO}_4$  amount dissolved is 0.1 mol.

$[\text{SO}_4^{2-}] = 0.10 \text{ mol dm}^{-3}$ .

$[\text{Ca}^{2+}] = 6.1 \times 10^{-4} \text{ mol dm}^{-3}$

3.4 + 3.5

The complex is optically active. The structures of both enantiomers are

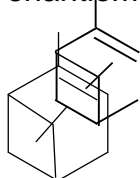


3.6 The high number of the chelate rings. Other factors also contribute to the complex ability, e.g. the character of the donor atoms, the magnitude and distribution of the charges in the anion, etc.

**PROBLEM 4**

At a temperature around 200 °C the racemisation of pinene can be followed in the gaseous phase by measuring the optical rotation.

If, for example, you take the (+)-enantiomer of  $\alpha$ -pinene



an equilibrium is gradually established between the two enantiomers (optical isomers). The two opposing reactions are both of the first order.

In 1927 D. F. Smith obtained the following data in his study of racemisation of  $\alpha$ -pinene:

T/K	$\alpha_1$	$\alpha_2$	t/min
490.9	32.75	18.01	579
490.9	29.51	15.59	587
503.9	30.64	8.74	371
505.4	12.95	8.05	120
510.1	23.22	6.15	216

$\alpha_1$  and  $\alpha_2$  are the values for optical rotation in terms of the dimensions of the polarimeter scale;  $t$  is the time which has elapsed between the two measurements.

Problems:

**4.1** What is the value for the equilibrium constant for the racemisation?

What is the corresponding value of  $\Delta_r G^\circ$  (racemisation)?

What is the relationship between the forward and backward rate constants,  $k_1$  and  $k_{-1}$ , in a state of dynamic equilibrium?

**4.2** State the rate equation for the racemisation of pinene.

Derive a relationship which could be used to calculate the rate constant for the conversion of the (+)-enantiomer into the (-)-enantiomer using the data given in the table.

- 4.3 Calculate the rate constant for this reaction at the four temperatures given in the table.
- 4.4 Calculate the average value of the activation energy for this reaction. You should take the average of the values at a minimum of three temperatures or use a graphical method.

HINT:

If the loss of concentration of a substance obeys the rate equation:

$$-\frac{dc}{dt} = k(2c - \text{constant})$$

Then the dependence of concentration on time is given by:

$$\ln \frac{2c_0 - \text{constant}}{2c - \text{constant}} = 2kt$$

where  $c_0$  is the initial concentration at time  $t = 0$ .

## SOLUTION

- 4.1 The racemisation equilibrium constant equals unity at all temperatures and  $\Delta_r G^\circ = 0$ .
- 4.2 If the concentration of one enantiomer is  $c$  and that of the other is  $c'$ , then it holds for the rate of the loss of  $c$  that

$$-\frac{dc}{dt} = k_1c - k_{-1}c' = k(c - c') \text{ for } k_1 = k_{-1} = k$$

If the initial concentrations are  $c_0$  and  $c_0'$ , then

$$c' = c_0 - c + c_0'$$

can be substituted for  $c'$  in the rate equation, obtaining

$$-\frac{dc}{dt} = k(2c - c_0 - c_0')$$

It then holds for concentrations  $c_1$  and  $c_2$  measured at times  $t_1$  and  $t_2$ , respectively, that

$$\ln \frac{2c_1 - c_0 - c_0'}{2c_2 - c_0 - c_0'} = 2k(t_2 - t_1)$$

and since  $c_0 + c_0' = c_1 + c_1' = c_2 + c_2'$



$$\ln \frac{c_1 - c_1'}{c_2 - c_2'} = 2k(t_2 - t_1)$$

The measured optical rotation  $\alpha$  is proportional to  $c - c'$ ; hence  $\ln \frac{\alpha_1}{\alpha_2} = 2k(t_2 - t_1)$

## 4.3

T/K	490.9	503.9	505.4	510.1
$10^4 k \text{ min}^{-1}$	5.3	16.9	19.8	30.7

$$4.4 \quad \ln \frac{k_2}{k_1} = \frac{E_A}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad E_A = \ln \frac{k_2}{k_1} \times \frac{R T_1 T_2}{T_2 - T_1}$$

If e.g. the value of  $k$  for 490.9 K (the average of two measurements) is combined with each of the remaining three values, three values of activation energy are obtained: 183400 J mol<sup>-1</sup>, 177500 J mol<sup>-1</sup>, 190500 J mol<sup>-1</sup>. The average value equals 187100 J mol<sup>-1</sup>.

**PROBLEM 5**

The equilibrium voltage of the cell,

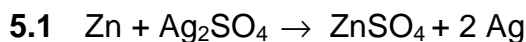


was measured at several temperatures and the results of the measurements are given in the following table:

t / °C	10	20	30
E / V	1.5784	1.5675	1.5566

Problems:

- 5.1 Give the equation for the reaction occurring in this galvanic cell.
- 5.2 Determine the value of the cell voltage at the temperature  $T = 298 \text{ K}$ .
- 5.3 Determine  $\Delta_r G_{298}$  of the cell reaction.
- 5.4 Determine  $\Delta_r H_{298}$  of the cell reaction.

**SOLUTION**

5.2 The temperature dependence is described by the equation,

$$E_T = E_{T_0} + \frac{dE}{dT} \cdot (T - T_0)$$

It follows from the plot for the slope,

$$\frac{dE}{dT} = -1.09 \times 10^{-3} \text{ V K}^{-1}$$

Hence,

$$E_{298} = 1.5675 - 1.09 \times 10^{-3} \times 5 = 1.562 \text{ V}$$

5.3 The relationship,

$$\Delta_r G = -nFE$$

holds for  $\Delta_r G$ . Then

$$\Delta_r G_{298} = -2 \times 96484.6 \times 1.563 = -301417.9 \text{ J mol}^{-1}$$

5.4 The equation,

$$\Delta G = \Delta H - T \Delta S,$$

is employed to calculate  $\Delta_r H_{298}$ , substituting

$$\Delta S = -\frac{dG}{dT}$$

Rearrangement yields the relationship

$$\Delta H = \Delta G - T \frac{dG}{dT}$$

As it holds that

$$\frac{dG}{dT} = -nF \frac{dE}{dT}$$

the final expression is:

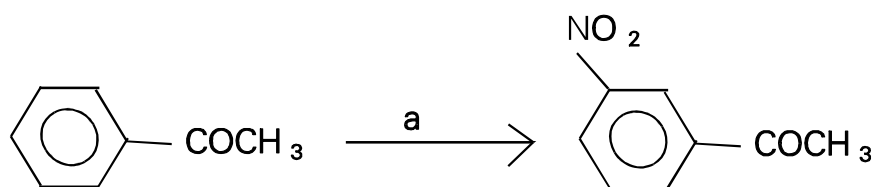
$$\begin{aligned}\Delta_r H_{298} &= \Delta G_{298} + nFT \frac{dE}{dT} \\ &= -301417.9 + [2 \times 96\,484.6 \times 298 \times (-1.09 \times 10^{-3})] = 364098.1 \text{ J mol}^{-1}\end{aligned}$$

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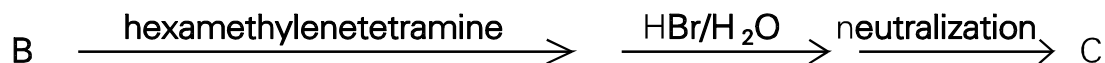
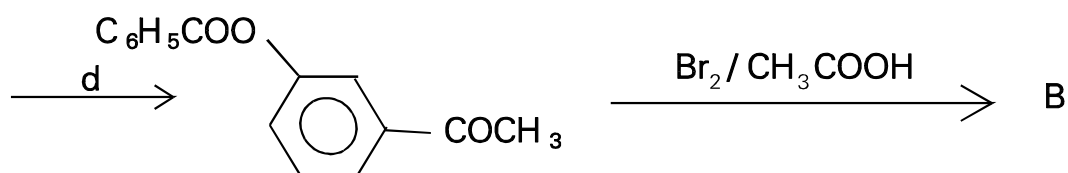
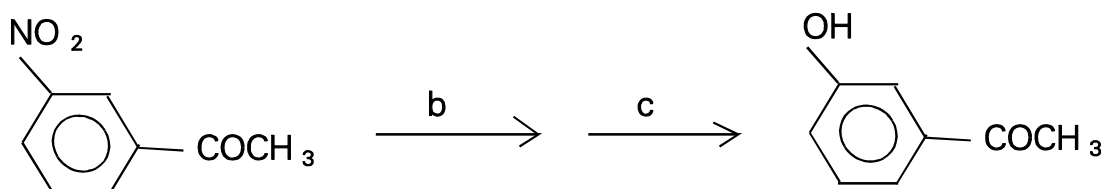
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**PROBLEM 6**

The following scheme describes the synthesis of a compound **D** (with sympathomimetic effects) whose skeleton consists of 2-phenylethylamine.



A Acetophenone



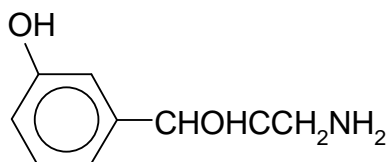
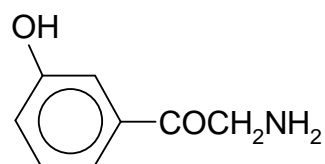
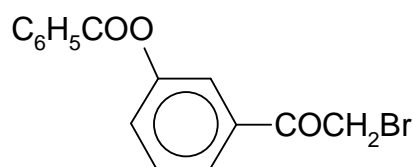
Problems:

- 6.1 What reagents were used in steps **a**, **b**, **c**, and **d**?
- 6.2 Give the structural formulae of compounds **B**, **C** and **D**.
- 6.3 Is it possible to prepare 3-hydroxyacetophenone from the reaction between phenol, acetylchloride and  $\text{AlCl}_3$ ? Give reasons for your answer.
- 6.4 Give the formulae of the compounds that are formed by the reaction of compound **C** with a) 10%  $\text{HCl}$  and b) 10%  $\text{NaOH}$ .
- 6.5 By the asterisk denote the chirality centre in the formula of compound **D**.
- 6.6 Give the spatial formula of enantiomer (R) of compound **D**.

## SOLUTION

- 6.1 a)  $\text{HNO}_3/\text{H}_2\text{SO}_4$   
 b)  $\text{Fe}/\text{H}^+$   
 c)  $\text{NaNO}_2/\text{HCl}$   
 d) benzoylchloride

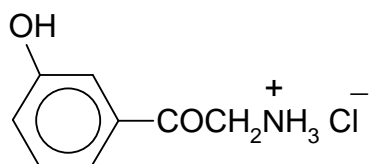
6.2



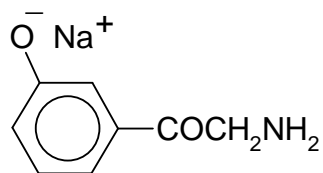
6.3 No

6.4

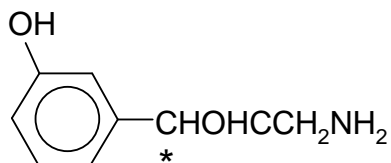
a)



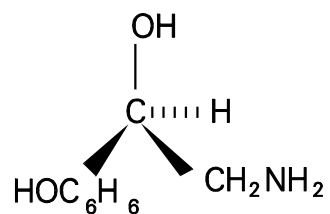
b)



6.5



6.6

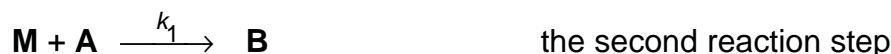
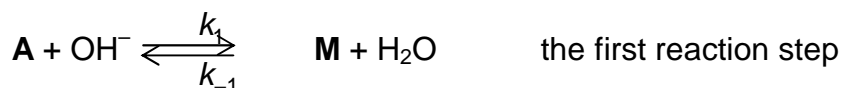


**PROBLEM 7**

Propanal, **A**, reacts in an aqueous-ethanolic solution of sodium hydroxide to yield compound **B** that is readily dehydrated to give compound **C** (C<sub>6</sub>H<sub>10</sub>O).

Problems:

- 7.1** Give the structural formulae of substances **B** and **C**.
- 7.2** Give the formula of intermediate **M** that is formed from propanal **A** by the action of hydroxide ions.
- 7.3** Give the formulae of the two most important mesomeric structures of intermediate **M** and denote the nonbonding electron pairs and the charge distribution.
- 7.4** The reaction of propanal **A** with sodium hydroxide, producing substance **B**, can be described by the scheme:



The rate of the formation of substance **B** is given by the equation:

$$v = k_2 [\text{M}] [\text{A}] \quad (1)$$

The above values of  $k$  are the rate constants for the individual reaction steps.

Assume that the concentration of intermediate **M** is small and constant during the reaction and express this fact by an equation involving terms with constants  $k_1$ ,  $k_{-1}$  and  $k_2$ .

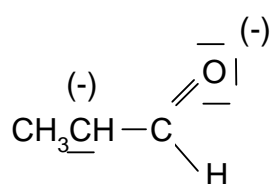
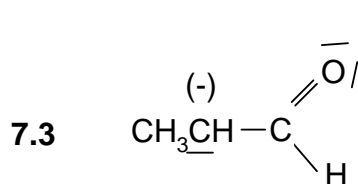
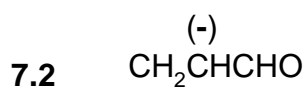
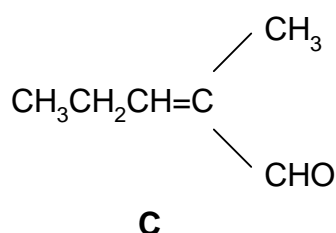
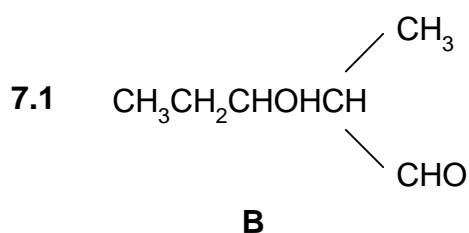
$$\frac{d[\text{M}]}{dt} = 0 \quad (2)$$

Derive an expression for the concentration of **M** from equation 2 and then substitute for  $[\text{M}]$  in equation 1. This gives equation 3 which is the complete rate equation for the formation of substance **B**.

If it is assumed that the second reaction step is rate determining, then the rearrangement of equation 3 gives equation 4, the rate equation.

Give equations 2, 3, and 4.

- 7.5** Determine the overall order of the reaction described by equation 4.

**SOLUTION**

7.4

$$\frac{d[\mathbf{M}]}{dt} = 0 = k_1[\mathbf{A}][\text{OH}^-] - k_{-1}[\mathbf{M}] - k_2[\mathbf{A}][\mathbf{M}] \quad (2)$$

$$[\mathbf{M}] = \frac{k_1[\mathbf{A}][\text{OH}^-]}{k_{-1} + k_2[\mathbf{A}]} \quad v = \frac{k_1 k_2 [\mathbf{A}]^2 [\text{OH}^-]}{k_{-1} + k_2[\mathbf{A}]} \quad (3)$$

for  $k_2[\mathbf{A}][\mathbf{M}] \ll k_{-1}[\mathbf{M}]$  it holds, that

$$v = \frac{k_1 k_2 [\mathbf{A}]^2 [\text{OH}^-]}{k_{-1}} \quad (4)$$

7.5 Rate equation (4) corresponds to the overall reaction order of (3).



**PROBLEM 8**

The following reaction scheme represents part of anaerobic degradation of saccharides, i.e. the glycolysis, involving equilibrium constants  $K_1$  and  $K_2$ :



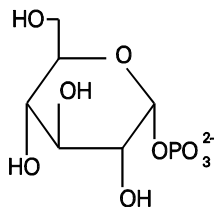
Problems:

- 8.1** Give the structural formulae for all the three reactants (compounds) that are mutually interconverted, i.e.  $\alpha$ -D-glucose-1-phosphate,  $\alpha$ -D-glucose-6-phosphate and  $\alpha$ -D-fructose-6-phosphate.
- 8.2** In the beginning of the reaction the reaction mixture contained 1 mmol of glucose-6-phosphate. Calculate the amounts of glucose-6-phosphate, glucose-1-phosphate and fructose-6-phosphate in the mixture at equilibrium. (As the reaction take place in a constant volume, the ratio of the amounts of substances equals that of their concentrations.)

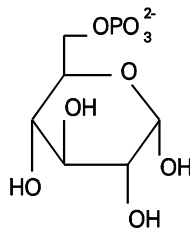
**SOLUTION**

**8.1**

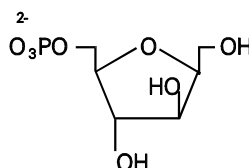
$\alpha$ -D-glucose-1-phosphate



$\alpha$ -D-glucose-6-phosphate



$\alpha$ -D-fructose-6-phosphate



8.2 It holds for the equilibrium constant of the successive reactions, that

$$\frac{\text{Fru-6-P}}{\text{Glc-1-P}} = 19 \times 0.5 = 9.5 \quad (\text{i})$$

If  $y$  mmoles of Glc-6-phosphate are converted into the same number of Glc-1-phosphate and another  $x$  mmoles of Glc-6-phosphate are converted into the same number of mmoles of Fru-6-phosphate, then  $(1 - x - y)$  mmoles of Glc-6-phosphate remain in the reaction mixture at equilibrium. It follows from relationship (i) that

$$\text{Glc-1-phosphate} = y \quad x/y = 9.5$$

$$\text{Fru-6-phosphate} = x \quad x = 9.5 y$$

After substituting,

$$\text{Glc-6-phosphate} = 1 - x - y = 1 - 10.5y,$$

it is possible to write for the reaction mixture at equilibrium that

$$\frac{\text{Glc-6-P}}{\text{Glc-1-P}} = \frac{1 - 10.5y}{y} = 19 \quad 1 - 10.5y = 19 y$$

$$y = 1/29.5 = 0.034 \text{ mmoles Glc-1-phosphate}$$

It is further calculated that

$$x = 9.5y = 9.5 \times 0.034 \text{ or } 9.5/29.5 = 0.322 \text{ mmoles of Fru-6-phosphate}$$

$$1 - x - y = 1 - 0.322 - 0.034 = 0.644 \text{ mmoles of Glc-6-phosphate}$$

At equilibrium the reaction mixture contains 0.034 mmoles Glc-1-phosphate, 0.644 mmoles Glc-6-phosphate and 0.322 mmoles Fru-6-phosphate.

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**PRACTICAL PROBLEMS****PROBLEM 1 (practical)**

Determination of the relative molecular mass of a weak acid by acid-base titration in a non-aqueous solvent

Weak acid whose dissociation constants,  $K_a$ , are smaller than  $1 \times 10^{-7}$  can be satisfactorily titrated in ethanol or in a mixture of ethanol and benzene, using a standard ethanolic solution of potassium hydroxide or potassium alkoxide in the presence of phenolphthalein or thymolphthalein as an indicator.

Task:

Determine the molecular weight (chemical equivalent) of a weak monobasic acid by titration with potassium ethoxide in ethanolic solution using phenolphthalein as an indicator (the acid has the general formula  $C_xH_yO_z$ ).

Chemicals and equipment:

Standard solution of potassium ethoxide in ethanol of concentration  $c = 0.1000 \text{ mol dm}^{-3}$

Indicator: 0.1% solution of phenolphthalein in ethanol

Solvent: A mixture of ethanol and benzene

1.000 g of sample, accurately weighed,

3 titration flasks of volume 200 or 500  $\text{cm}^3$ , one 25  $\text{cm}^3$  burette, one 50  $\text{cm}^3$  pipette, one 250  $\text{cm}^3$  volumetric flask, one 100  $\text{cm}^3$  measuring cylinder, small funnels, beakers, filter paper.

Procedure:

You are provided with 1.000 g of the monobasic acid  $C_xH_yO_z$ . This sample is labelled with a number. This should be written clearly at the top of your answer paper.

Carefully transfer all the acid into the graduated (volumetric) flask and fill the solution in the flask with ethanol up to 250 ml. A portion of 50.00 ml of this solution should be titrated with the 0.1000 M alcoholic solution of potassium ethoxide using 5 drops of phenolphthalein as indicator. The first titration should be a rough titration for estimating the

approximate volume necessary to determine the endpoint. Subsequent titrations should be carried out with precision, using the same quantity of indicator each time.

Record all titration values. An extra titration should be carried out to eliminate any error that might be due to the action of the potassium hydroxide on the solvent, indicator or ethanol. This type of titration is known as a blank titration, its value should be recorded and used to correct the results of previous titrations. Care should be taken to use the same quantity of indicator as in previous titrations.

The correct titration values should be used to calculate the relative molecular mass (molecular weight) of the sample.

Note: The waste material containing organic solvents must not be discharged in a sink. Use labelled containers for this purpose.

Questions:

- 1) Suggest the name and formula of a common, monobasic acid which corresponds to the value you determined experimentally for your sample.
- 2) Write a general equation for the neutralisation of a monocarboxylic acid with:
  - i) potassium ethoxide,
  - ii) potassium hydroxide.
- 3) During the titration of some weak carboxylic (fatty) acids, similar to the titration that you have carried out, turbidity or cloudiness is observed. Suggest an explanation for this turbidity.
- 4) How would you produce 1 dm<sup>3</sup> of a standard solution of 0.1 M potassium ethoxide? Which compound would you use, as a standard solution?
- 5) Why are the titrations of weak acids carried out in non-aqueous media?
- 6) Name another solvent which is suitable for use in the titration of weak acids.
- 7) How would you recover the organic solvent used in your experiment?
- 8) Sketch a schematic titration curve (pH as a function of volume) for the titration of 20 ml of a 0.1 M aqueous solution of a weak monobasic acid with a standard aqueous solution of 0.1 M potassium hydroxide.
- 9) Calculate the pH of 0.1 M aqueous solution of an acid which has a dissociation constant of  $1 \times 10^{-7}$ .

**18<sup>th</sup>**



**International Chemistry Olympiad**

**7 theoretical problems  
2 practical problems**

# THE EIGHTEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 6–15 JULY 1986, LEIDEN, NETHERLANDS

## THEORETICAL PROBLEMS

### PROBLEM 1

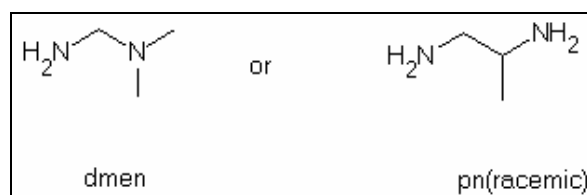
Compounds containing divalent platinum with the general formula  $\text{PtX}_2(\text{amine})_2$  ( $X = \text{Cl}_2, \text{SO}_4^{2-}, \text{malonate}, \text{etc.}$ ) have met a lot of scientific interest because of their biological activity, particularly in view of their properties in the treatment of tumours. The best known compound used clinically is  $\text{PtCl}_2(\text{NH}_3)_2$ . This compound, in which platinum is coordinated in a planar square, has two geometrical isomers of which only one shows the antitumour activity.

- 1.1 Sketch the spatial structures of the two possible isomers.  
1.2 How many isomers has  $\text{PtBrCl}(\text{NH}_3)_2$ ? Sketch all of them.

It is possible to replace the amine ligands by one ligand containing two donor atoms (N). Then one obtains a chelating ligand, such as 1,2-diaminoethane (en).

- 1.3 Show graphically that  $\text{PtBrCl}(\text{en})$  has only one stable structure.

The ligand en can be substituted via methylation to form dmen or pn (racemic).



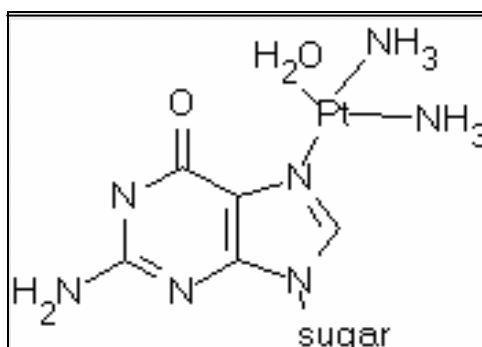
- 1.4 Give spatial structures of all isomers of the following compounds:  $\text{PtCl}_2(\text{dmen})$ ,  $\text{PtCl}_2(\text{pn})$ ,  $\text{PtBrCl}(\text{dmen})$  and  $\text{PtBrCl}(\text{pn})$ .

These compounds can isomerise in aqueous solution through dissociation of a ligand and transient replacement of the stronger ligands by the weak ligand water.  $\text{Cl}^-$  and  $\text{Br}^-$  are

replaced relatively easily, but it is more difficult to replace the amine ligands, which usually requires heating.

- 1.5** Considering each of the isomers in the previous questions a-d, indicate which isomers can be converted to another at room temperature. Give both the original molecule and the products.
- 1.6**  $\text{PtCl}_2(\text{en})$  reacts with  $\text{Br}^-$  in a molar proportion of 1:2 at room temperature. Which compound would you expect to form in what proportion? You can assume that the Pt-Br and Pt-Cl bonds are equally strong and that there is no perturbing influence from hydrolysis.
- 1.7** Using the equation to express chemical equilibrium, show that hydrolysis hardly ever occurs in blood but that it does occur in the cells. Note:  $\text{PtCl}_2(\text{NH}_3)_2$  hydrolyses to and 2  $\text{Cl}^-$ . In cells the  $\text{Cl}^-$  concentration is low; in blood it is fairly high.

After hydrolysis in the tumour cell a reactive platinum ion is formed to which two  $\text{NH}_3$  groups are still bound, as it was found in the urine of patients treated with this compound. The reactive platinum ion appears to be bound to cellular DNA, where the bonding occurs via guanine to one of the N-atoms.

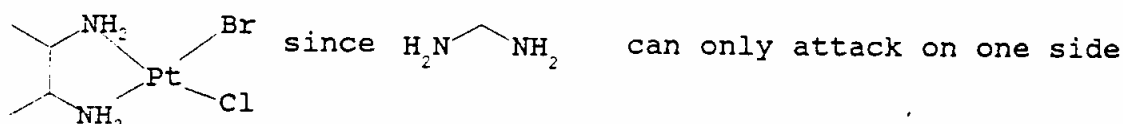
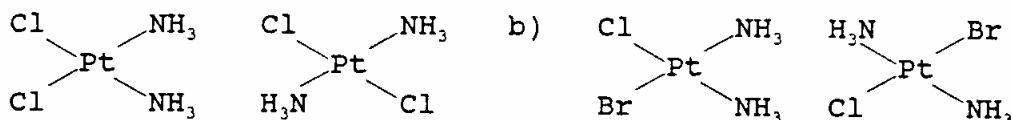


As a result of the two reactive sites of platinum and the two unreactive  $\text{NH}_3$  ligands, it can form additionally a second bond to DNA. Research has shown that this happens in particular with a second guanine base from the same strand of DNA.

- 1.8** Show by calculations which of the two isomers in question a) can form this bond. (Note: Pt-N distance = 210 pm, DNA base distance = 320 pm).

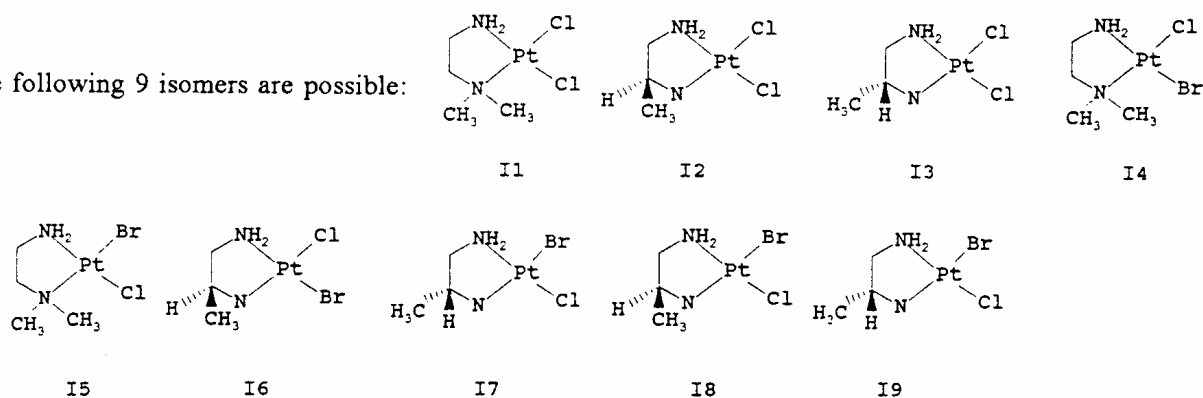
## SOLUTION

1.1 - 1.3 The isomers are:



1.4

d) The following 9 isomers are possible:



1.5 In a-c) there is no change possible;

in d) I4 and I5, I6 and I7, I8 and I9 transform one into another. Via this isomerization also  $\text{PtCl}_2(\text{dmen})$ ,  $\text{PtBr}_2(\text{dmen})$ ,  $\text{PtCl}_2(\text{pn})$  and  $\text{PtBr}_2(\text{pn})$  can be formed, even though they are not isomers.

1.6  $\text{PtCl}_2(\text{en}) : \text{PtBr}_2(\text{en}) : \text{PtBrCl}(\text{en}) = 1 : 1 : 2$

1.7  $\text{PtCl}_2(\text{NH}_3)_2 \rightleftharpoons (\text{PtCl}(\text{H}_2\text{O})(\text{NH}_3)_2)^+ \rightleftharpoons \text{Pt}(\text{H}_2\text{O})_2(\text{NH}_3)_2^{2+}$

In blood the hydrolysis does not occur, because the concentration of  $\text{Cl}^-$  is rather high and the equilibrium is shifted to the left side.

1.8 The bond is formed by the cis-isomer, because in that case the distance between the bases (320 pm) has to change only to  $210\sqrt{2} = 297$  nm, whereas in the case of the trans-compound the distant would be  $210 \times 2 = 420$  nm.



**PROBLEM 2**

The compound  $\text{Na}_5\text{P}_3\text{O}_{10}$  is used as an additive for detergents to bind the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in water in order to prevent the precipitation of their fatty acid salts on the laundry.

- 2.1 Draw the structure of the ions  $(\text{P}_3\text{O}_{10})^{5-}$  and  $(\text{P}_3\text{O}_9)^{3-}$  assuming that P-P bonds do not occur.
- 2.2 Assuming an octahedral coordination of the  $\text{Mg}^{2+}$  ion give a drawing of the  $\text{Mg}(\text{P}_3\text{O}_{10})(\text{H}_2\text{O})_n^{3-}$  ion also indicating the value for n.

The complex ions of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and triphosphate are well soluble in water. They are, among other things, responsible for the wild growth of algae in surface waters. They could be removed by precipitation as an insoluble compound.

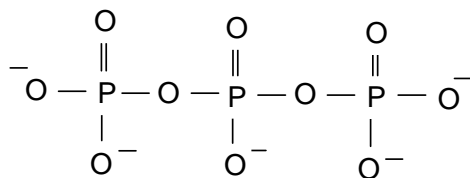
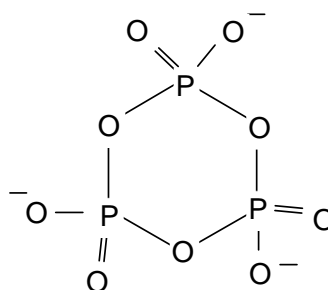
- 2.3 Give some possibilities (ions) to precipitate the triphosphates bound to  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ .
- 2.4 Calculate the mass of  $\text{Na}_5\text{P}_3\text{O}_{10}$  (in grams) necessary in a washing machine to reduce the amount of  $\text{Ca}^{2+}$  in 20 litres of city water (0.225 g/l) to an acceptable maximum of 0.02 g/l. Effects of pH, the precipitation of  $\text{Ca}(\text{OH})_2$ , and possible effects by other positive ions, can be neglected. The following data is given:

$$K_1 = \frac{[\text{Ca}^{2+}][\text{P}_3\text{O}_{10}^{5-}]}{[\text{CaP}_3\text{O}_{10}^{3-}]} = 1.0 \times 10^{-6}$$

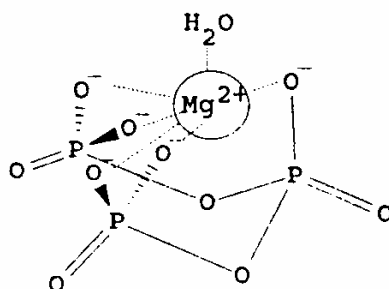
Molar mass of  $\text{Na}_5\text{P}_3\text{O}_{10}$  is  $366 \text{ g mol}^{-1}$ , the molar mass of Ca is  $40 \text{ g mol}^{-1}$ .

**SOLUTION**

- 2.1 The structures are:


 $\text{P}_3\text{O}_{10}^{5-}$ 

 $\text{P}_3\text{O}_9^{3-}$

2.2 Since  $\text{Mg}^{2+}$  has the coordination number 6, one water molecule serves as the sixth ligand among the five  $\text{O}^-$  ligands already present in the  $[\text{P}_3\text{O}_{10}]^{5-}$  - ligand:



2.3 Possible ions are  $\text{Al}^{3+}$  or  $\text{Fe}^{2+}$  because of their equal charge and similar size. The triphosphates are not soluble in water.

$$2.4 \quad [\text{Ca}^{2+}] + [\text{CaP}_3\text{O}_{10}]^{3-} = \frac{0.225}{40} \text{ mol dm}^{-3};$$

$$[\text{Ca}^{2+}] = \frac{0.020}{40} \text{ mol dm}^{-3} \Rightarrow [\text{CaP}_3\text{O}_{10}^{3-}] = \frac{0.205}{40} \text{ mol dm}^{-3}$$

$$[\text{P}_3\text{O}_{10}^{5-}] = \frac{K_1[\text{CaP}_3\text{O}_{10}^{3-}]}{[\text{Ca}^{2+}]} = 1.025 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\text{CaP}_3\text{O}_{10}^{3-}] + [\text{P}_3\text{O}_{10}^{5-}] = 5.135 \times 10^{-3} \text{ mol dm}^{-3} \equiv 37.6 \text{ g Na}_3\text{P}_3\text{O}_{10} \text{ in } 20 \text{ dm}^3 \text{ H}_2\text{O}$$

### PROBLEM 3

In order to explain why dyes are coloured, they can be considered as rod-like, one-dimensional molecules over which the electrons are distributed. The wave lengths of the electrons should fit to the available space which is the length  $l$ . When absorbing light, an electron makes a transition from a lower to a higher energy state. The energy difference is given by:

$$\Delta E = h \times \text{cover} \lambda \text{ where } \lambda = \frac{h}{p}$$

- 3.1 Give a general expression for possible wavelengths of the electron as a function of the length  $l$ .

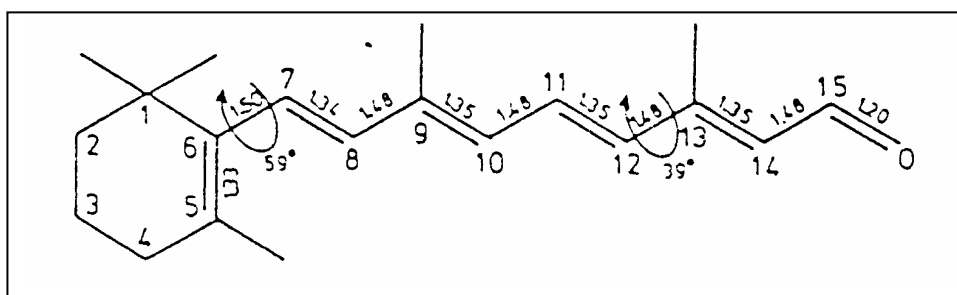
In the 'particle in the box' model, only the variations in the kinetic energy of the electrons are considered.

- 3.2 Give an expression for the possible energies that electrons in the molecule can have (as a function of  $l$ ).
- 3.3 Show that for a chain of length  $l$  with  $k$  electrons, the longest wavelength absorption occurs at:

$$\lambda = \frac{8mc l^2}{h(k+1)}$$

- 3.4 Derive an expression for the wavelength of the first electronic transition as a function of the number of C-atoms for even values of  $n$ .
- 3.5 Calculate the minimum number of C-atoms (conjugated systems) to obtain a visible colour. C-C bond length is 142 pm.

The retina in the human eye contains rhodopsin, a light absorbent.



The molecule in the part of C-atoms 7 through 12 is planar. The angle between the bonds C5-C6, C7-C8, C11-C12 and C13-C14 is about 39°. According to the 'particle in the box' theory fragment C7 through C12 should absorb at about 213 nm. In reality the absorption of retinal occurs at 308 nm.

- 3.6 Give a reason for the longer wavelength that is observed in practice using the above mentioned theories.
- 3.7 When retinal is bound to opsin to form rhodopsin, the absorption occurs around 600 nm. Which atoms must be forced into one plane by the protein? Show by calculation that it's true.

## SOLUTION

3.1  $\lambda = c\nu = 2l/n$  with  $n = 1, 2, 3, \dots$

3.2  $E = \frac{hc}{\lambda} = \frac{mv^2}{2} = \frac{p^2}{2m}; p = \frac{h}{\lambda} = \frac{hn}{2l} \Rightarrow \Delta E_n = \frac{h^2 n^2}{8mI^2} = \frac{h^2}{8mI^2} \times (n_{\text{homo}}^2 - n_{\text{lumo}}^2)$

- 3.3 For  $k$  electrons and  $k \equiv 0 \pmod{2}$ ,  $k/2$  orbitals are possible, so  $n_{\text{homo}} = k/2$  and  $n_{\text{lumo}} = k/2 + 1$

$$\Delta E_n = \frac{h^2}{8mI^2} [(1/2k + 1)^2 - 1/2k^2] = \frac{h^2}{8mI^2} \times (k + 1) \Rightarrow \lambda = \frac{hc}{\Delta E} = \frac{8mcI^2}{h(k + 1)}$$

- 3.4 If  $N$  is the number of C-atoms,  $N$  is equal to  $k+1$  for even number of electrons  $k$ , so

$$\lambda = \frac{8mcI^2}{Nh} = \frac{8mcI^2}{h(k + 1)}$$

for even  $N$ 's, the length of the box would be  $a(N-1)$  with  $k = N$  electrons, so

$$\lambda = \frac{8mc(N1)^2 a^2}{h(N+1)}$$

- 3.5 For a conjugated system  $N$  has to be even. To obtain a visible colour, the wavelength should be greater than 400 nm. Therefore:

$$\frac{8mc(N1)^2 a^2}{h(N+1)} \geq 4 \times 10^7 \text{ so accordingly : } \frac{(N1)^2}{N+1} \geq 6.02$$

The equation  $N^2 - 6.02 N - 6.02 > 0$  derived from the equation above has the only positive solution  $N = 8.60$ . Since  $N$  must be even, the minimum number of C-Atoms is 10.

**3.6** The angles between 5-6 and 7-8, as well as between 11-12 and 13-14 are smaller than  $90^\circ$  and therefore the effect of the double bonds between C5 and C6, C13, C14 and O cannot be neglected. They overlap to a small extent with the conjugated system C7 through C12 and enlarge the box significantly. A larger  $l$  leads to a larger  $\lambda$ , causing a shift towards a longer wavelength.

**3.7** Obviously, the box must be much larger when bound to opsin. For  $\lambda = 600$  nm the atoms C5 to O at the end of the chain must be forced into the plane:

$$l = 0.133 + 0.150 + 4(0.134 + 0.148) + 0.120 = 1.54 \text{ nm}; \quad k = 12;$$

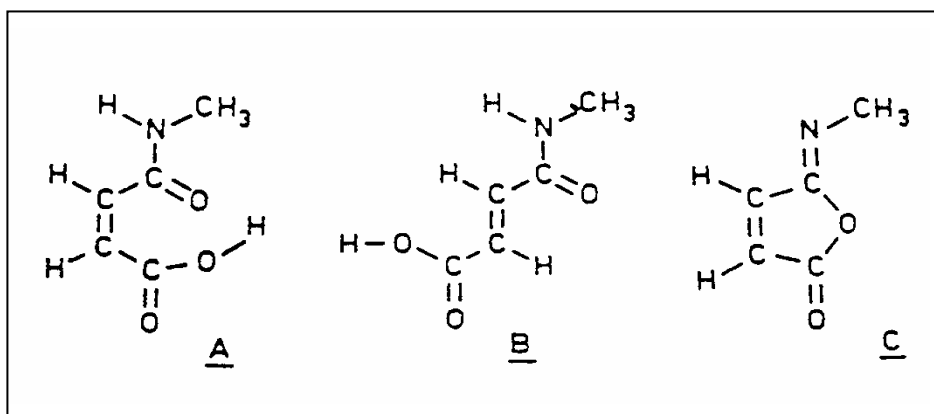
$$\lambda = 3.30 \times 10^{12} l^2 / (k + 1) = \underline{602 \text{ nm}}$$

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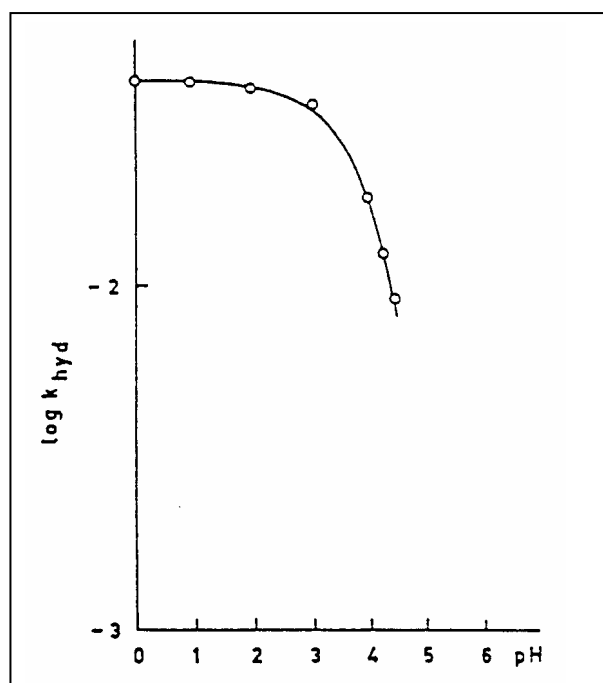
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**PROBLEM 4**

The high efficiency of catalysis by enzymes is mainly due to an enzyme-reactant complex in which the reacting group is placed in a favourable position for the reaction with respect to the catalyzing groups of the enzyme. Studies are carried out with model compounds in which a catalyzing group has been introduced in the proximity of the reaction centre of the molecule. As an example we consider the hydrolysis of the amide bond in compound **A**. This reaction proceeds in water at 39 °C and pH = 2 more than a million times faster than the hydrolysis of compound **B**.



The relation between the rate constant  $k_{\text{hyd}}$  and pH for the hydrolysis of **A** at 39 °C is shown in figure below.



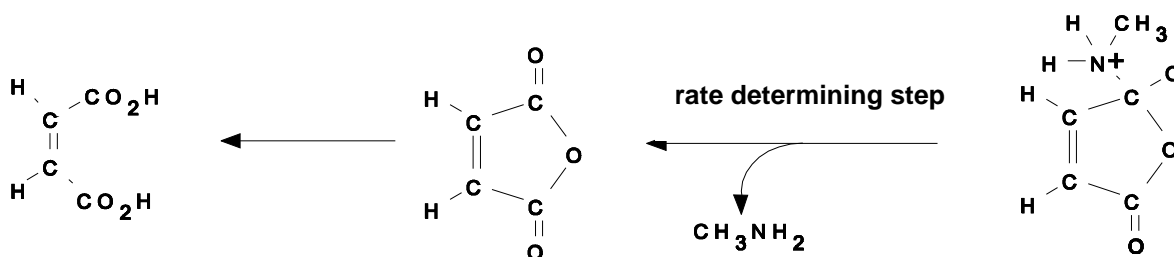
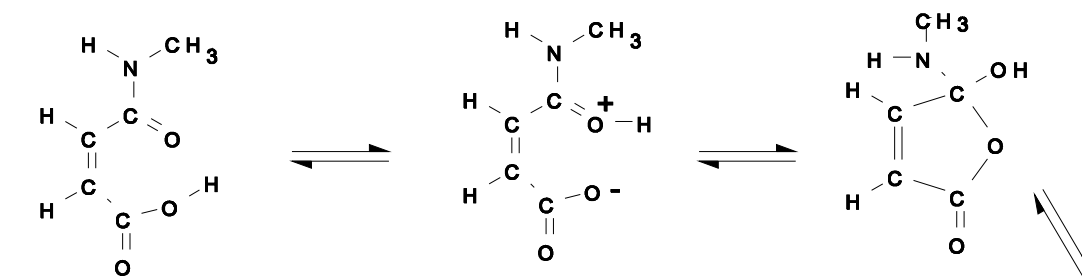
Further observation:

Addition of water to the iso-imide **C** gives a rapid reaction, which initially yields **A**. Subsequently, hydrolysis of **A** occurs. The amid carbonyl group in **A** is labelled with <sup>13</sup>C and the hydrolysis is allowed to take place in H<sub>2</sub><sup>18</sup>O at pH = 2 and 39 °C. The diacid formed upon hydrolysis is isolated, converted into a disilver salt and completely decarboxylated with bromine in an anhydrous reaction medium. The carbon dioxide formed is a mixture of particles of masses 44, 45, 46 and 47 which are formed in equal amounts.

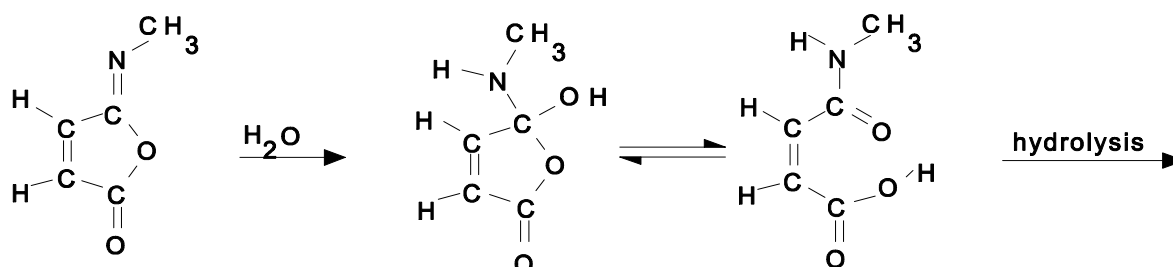
- 4.1 Why is the hydrolysis of **A** so much faster than that of **B**?
- 4.2 Explain why the rate of hydrolysis of **A** is independent on pH in the range between pH = 0 to pH = 2.
- 4.3 Why does  $k_{\text{hyd}}$  decrease so rapidly at pH values higher than 3.
- 4.4 Give a detailed reaction mechanism for the hydrolysis of **A**. Indicate which step in the reaction is rate determining.
- 4.5 Show that the observations further made are consistent with the reaction mechanism given under d.

## SOLUTION

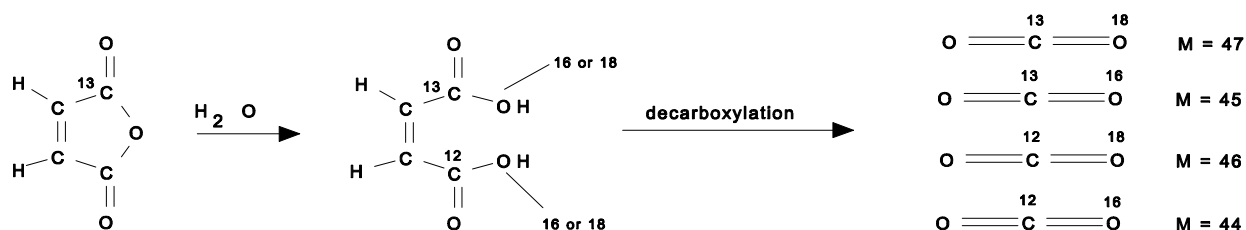
- 4.1 The high rate of hydrolysis of **A** is caused by intramolecular catalysis of the COOH group in the cis-position. In **B** the COOH group is situated in the trans-position with respect to the amide group and therefore too far away for intramolecular catalysis.
- 4.2 For  $0 < \text{pH} < 2$  the COOH group is not ionized and therefore, it can act as an intramolecular catalyser. If the hydrolysis in that pH-range is only the result of catalysis by the COOH-group and not competing with H<sub>3</sub>O<sup>+</sup> the rate constant in that range is pH independent.
- 4.3 At pH > 3 the COOH group deprotonates giving COO<sup>-</sup>. Intramolecular acid catalysis, in which proton transfer plays an important role, is then not possible anymore.
- 4.4 The mechanism of hydrolysis is indicated below:



4.5



With the observation given, the rate determining step can be identified.





**PROBLEM 5**

Bacterial conversion of saccharose leads to (S)-(+)-2-hydroxypropanoic acid (L-(+)-lactic acid), which forms a cyclic ester out of two molecules. This dilactide can be polymerized to a polylactide, which is used in surgery.

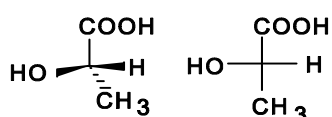
- 5.1 Give the spatial structures and Fischer projection of L-(+)-lactic acid and its dilactide.
- 5.2 Sketch the structure of the polylactide discussed above (at least three units). What is its tacticity (iso-, syndio- or atactic)?
- 5.3 Draw the isomeric dilactides formed out of racemic lactic acid. Show the configuration of the chiral centres.

L-(+)-lactic acid is used for the preparation of the herbicide Barnon that is used against wild oats. In this case (+)-lactic acid is esterified with 2-propanol and then the hydroxyl group is treated with methanesulfonyl chloride. The product is then submitted to a  $S_N2$ -reaction with 3-fluoro-4-chloro-phenylamine, where the methanesulfonate group leaves as  $\text{CH}_3\text{SO}_3^-$ . Finally a benzoyl group is introduced with the help of benzoyl chloride.

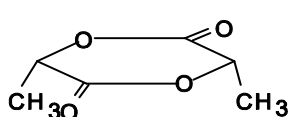
- 5.4 Draw the Fischer projection of the various consecutive reaction products.

**SOLUTION**

5.1

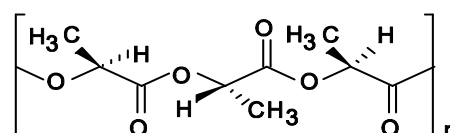


L-(+)-lactic acid and its Fischer projection



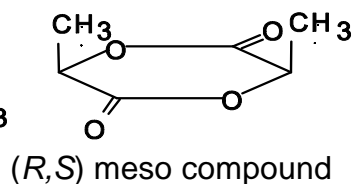
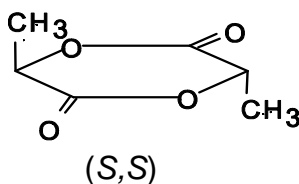
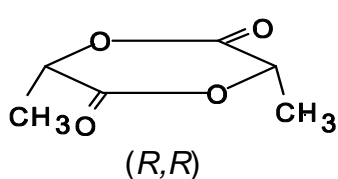
Dilactide of L-(+)-lactic acid - spatial formula

5.2

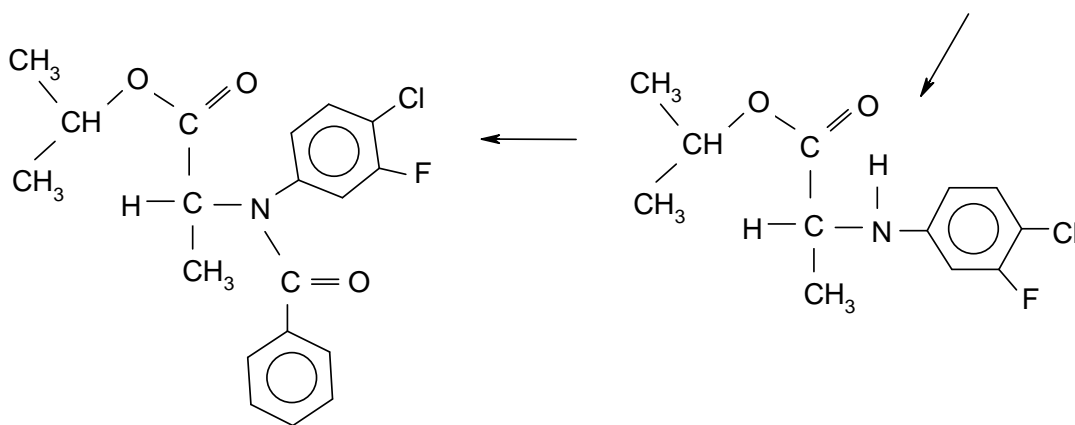
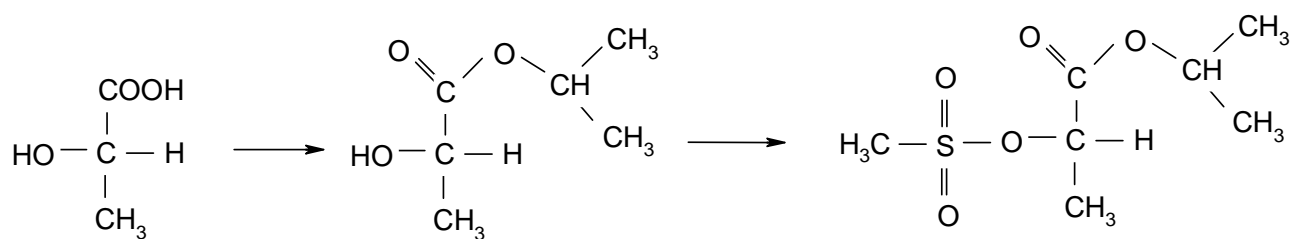


Polylactide of L-(+)-lactic acid

- 5.3 Dilactides of racemic lactic acid with the following configurations:



## 5.4

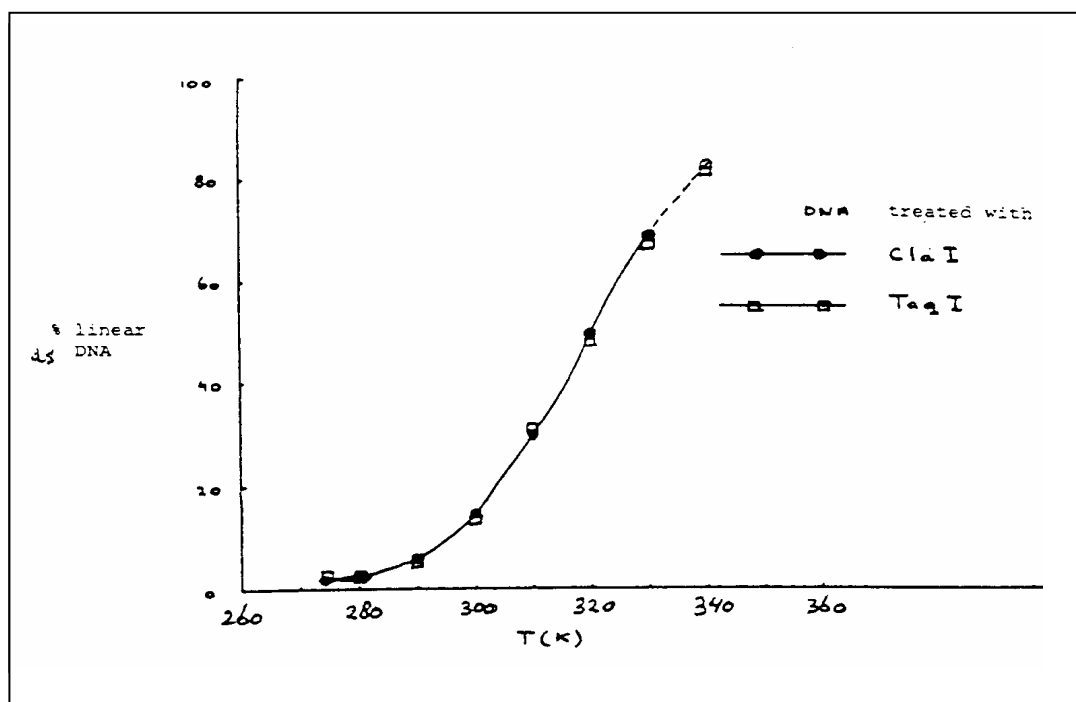
**Barnon**

## PROBLEM 6

In recombinant DNA technology specific endonucleases can recognize and hydrolyse the phosphoric ester bound in each of both strands. Cla I for example hydrolyses the bond between two nucleotides in the sequence:



- 6.1 Give the base sequence of the complementary strand in the 5' - 3' direction and indicate with arrows the location where the hydrolysis by Cla I would occur.
- 6.2 How often on average will this sequence occur in one strand of DNA molecule of  $10^5$  base pairs? You can assume that the four bases occur equally often and that they randomly distribute in the two chains.



Taq I hydrolyses a long double strand DNA molecule into fragments which are on average 256 base pairs long. The 3' end of these fragments treated by cleavage turns out to be a thymine(T)- and the 5' end a cytosine(C) -end.

- 6.3 How long is the sequence recognized by Taq I?
- 6.4 Give the two possible base sequences (in the direction 5' - 3') which form the recognition pattern for Taq I (must obviously have some symmetry).

The DNA of a phage which occurs as a close circle contains only 5'-pApTpCpGpApT-3' sequence in each of the two strands. After treatment with ClaI equilibrium is established: circular DNA  $\rightleftharpoons$  linear DNA.

**6.5** Give a schematic drawing of the circular and linear molecules. Indicate the bases adjacent to the cleaving site in both strands. Indicate also the 3' and 5' ends.

In Fig. 1 the percentage of linear DNA is given as a function of temperature, measured in a solution of 0.15 M NaCl buffered with citrate at pH = 6.5. With Taq I as cleavage enzyme, the same curve is obtained.

**6.6** Is the reaction as written endothermic or exothermic? Explain your answer.

**6.7** Show, considering the information given, which of the two base sequences of the answer to **6.4** is the correct one.

**6.8** What would look the curve for Taq I like if the recognition pattern would have been the other possibility of d)?

A large DNA molecule is cut into fragments with the aid of Cla I. One fragment is isolated, purified and mixed in the ratio of 1:1 with phage DNA which was also cleaved with Cla I. Thereby recombinant molecules can be formed through the reaction:



**6.9** Would the enthalpy of this reaction be positive, negative or about zero? Explain your answer.

**6.10** Which combination of temperature, DNA concentration and ionic strength (high or low in each case) will give the maximum percentage of recombinant molecules?

## SOLUTION

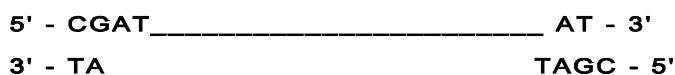
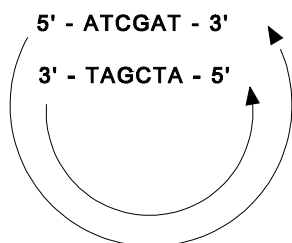
**6.1** 5' - pTpApGpCpT \pC

**6.2** The probability of the sequence given is  $(1/4)^6 = 1/4096$ . Thus, this specific sequence may occur in the DNA  $10^5/4096 = 24.4$  times on average

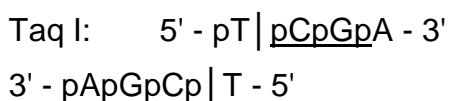
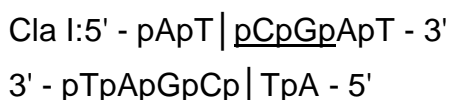
**6.3** The sequence recognized by Taq I is 2 base pairs, that is 4 bases.

**6.4** The sequence is 5' - pTpCpGpA - 3' or 5' - pGpApTpC - 3'

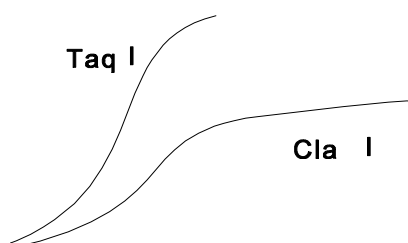
## 6.5



- 6.6** The reaction is endothermic. The reaction has a positive enthalpy, since the hydrogen bonds between the bases G and C in the complementary strands are broken.
- 6.7** The two relations show the same dependence on temperature. Therefore, the enthalpy of the two reactions is roughly the same. Then the interaction of the double helix must be identical and therefore we must choose TCGA for the first recognition sequence of question **6.4**. The cleavage in the two cases mentioned in d) occurs as follows:



- 6.8** The following curve would be obtained:



**6.9**  $\Delta H$  is negative.

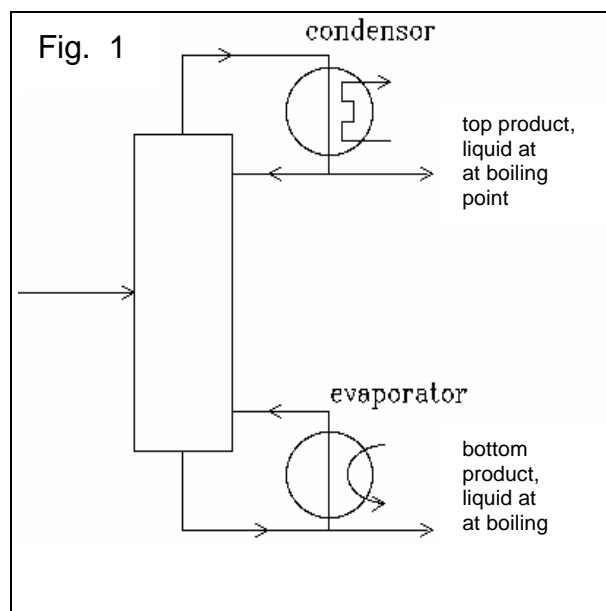
**6.10** Low temperature, low DNA concentration and high ionic strength will give the maximum percentage of recombinant molecules.

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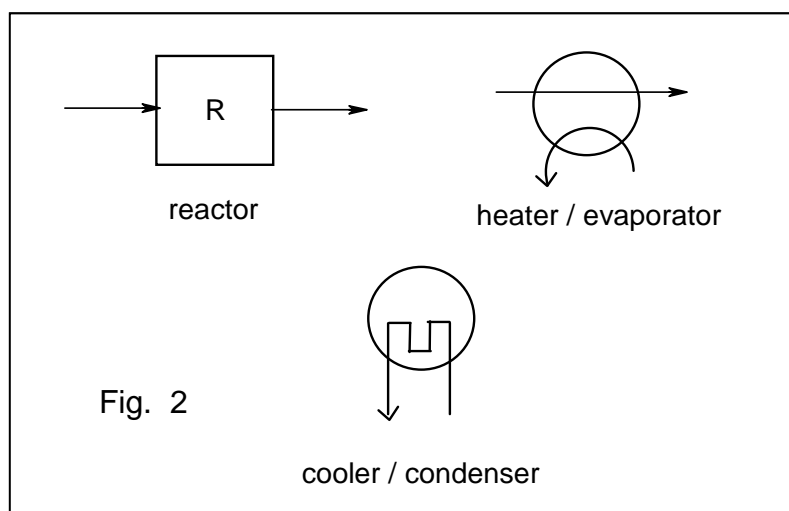
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**PROBLEM 7**

The equilibrium constant of the reaction  $A_{(g)} + 2 B_{(g)} \rightleftharpoons 2 C_{(g)}$  is  $K_p = 10.0 \text{ MPa}^{-1}$ . The starting materials are supplied at 25 °C and heated to 100 °C where complete equilibration takes place. Below 100 °C the reaction rate is negligibly small. The whole process is executed continuously in a stationary state. The boiling points at 0.1 MPa of **A**, **B**, and **C** are 40 °C, 80 °C, and 60 °C, respectively. The three compounds have the same heat of evaporation:  $q \text{ J mol}^{-1}$ . The heat capacities of **A**, **B**, and **C** may be neglected. A schematic diagram of a distillation is shown below (Fig. 1).



The total heat used at each of the two distillations is  $3q \text{ J mol}^{-1}$  (of the top product). Apart from distillation columns (each with its own evaporator and condenser) the pieces of apparatus shown of Fig. 2 are available.

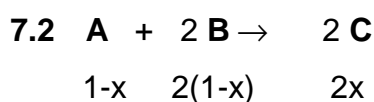
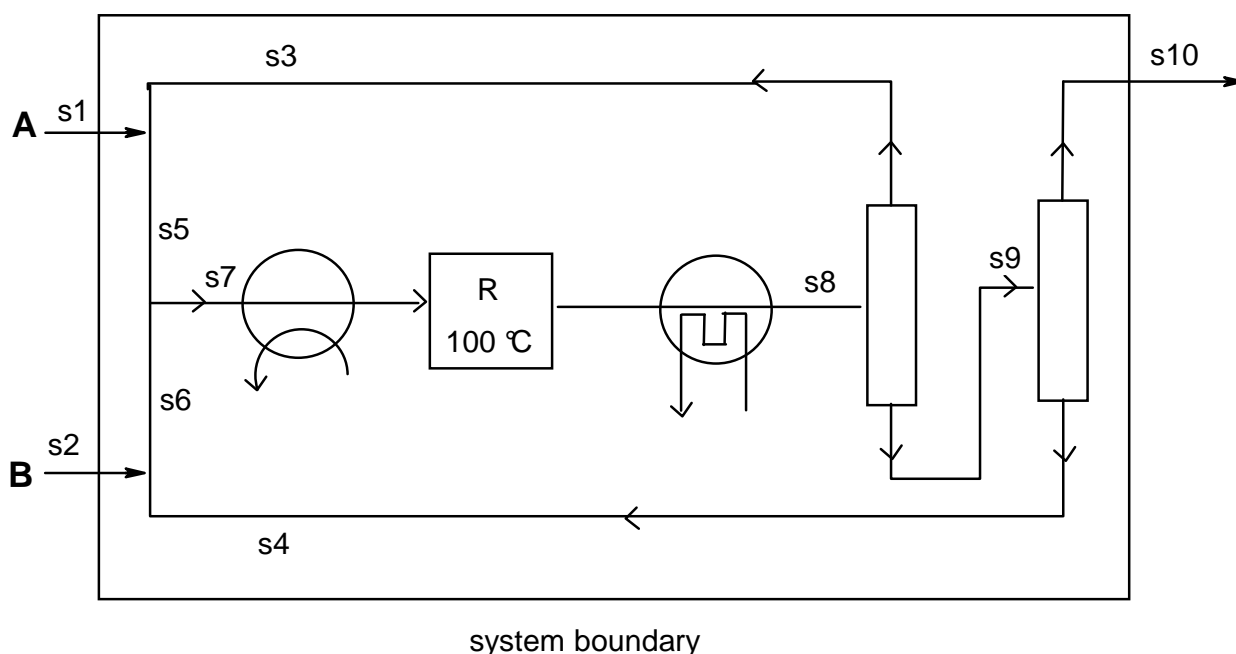


**7.1** Draw a flow diagram of the process in which all flows are given (flow sheet) and in which the starting materials are used as efficiently as possible using as few pieces of apparatus as possible.

- 7.2 Express the equilibrium constant in terms of the degree of conversion and of total pressure for the case that the feed to the reactor is stoichiometric. What is the value of the degree of conversion when total pressure is 0.100 MPa?
- 7.3 Number all flows. Calculate the composition of each flow in mol s<sup>-1</sup> for a rate of production of 1 mole of **C** per second under the conditions of part b.
- 7.4 In what respect can the reaction conditions influence the composition of the mixture that leaves the reactor? (Refer to question b.)
- 7.5 The process requires energy. For the conditions of b explain where energy should be supplied in the flow diagram drawn in part a. Derive an expression for the total energy needed.

## SOLUTION

- 7.1 In order to minimize the pieces of apparatus, the liquids A and B should evaporate together. For complete consumption of the starting materials, A and B are recirculated as feed for the reactor. The scheme of figure depicts the solution.





In total  $3-x$  mol gases are present after conversion. Supposing that the input of **A** is a mol (S5) and the input of **B**  $b$  mol (S6) we can write for the equilibrium:

$$K_p = \frac{p_C^2}{p_A \times p_B^2} = 10.0$$

If  $x$  mol of **A** are converted, S8 contains  $(a - x)$  mol of **A**,  $(b - 2x)$  mol of **B** and  $2x$  mol of **C**. Therefore S8 contains  $(a - x) + (b - 2x) + 2x = (a + b - x)$  moles and we can write for the partial pressures of A and B:

$$p_A = \frac{a - x}{a + b - x} P \quad p_B = \frac{b - 2x}{a + b - x} P \quad p_C = \frac{2x}{a + b - x} P$$

Therefore the equilibrium can be written as

$$K_p = \frac{(2x)^2}{(a - x)(b - 2x)^2} \times \frac{a + b - x}{P} = 10$$

**7.3** For  $P = 0.10$  we obtain:  $4x^2a + 4x^2b - 4x^3 = ab^2 - 4abx + 4ax^2 - xb^2 + 4x^2b - 4x^3$  and wherefrom:

$$0 = ab^2 - 4abx - xb^2 \text{ and since } b \neq 0: \quad 0 = ab - 4ax - bx$$

With a total inflow of  $0.5 \text{ mol s}^{-1}$  **A** (S1) and  $1 \text{ mol s}^{-1}$  **B** (S2), the amount of **C** leaving the reactor (S10) is  $1 \text{ mol s}^{-1}$ . So  $2x = 1$  and  $x = 0.5$ . The relation between  $a$  and  $b$  can be written as:  $a = b / (2b - 4)$ . Since the feed is stoichiometric  $a : b = 1 : 2$ . This leads to  $b = 3$  and  $a = 1.5$ .

All flows (mol/s) can be calculated now:

$$s_1 = 0.5 \text{ mol s}^{-1} \text{ A}$$

$$s_2 = 1 \text{ mol s}^{-1} \text{ B}$$

$$s_3 = 1.5 - 0.5 = 1 \text{ mol s}^{-1} \text{ A}$$

$$s_4 = 3 - 1 = 2 \text{ mol s}^{-1} \text{ B}$$

$$s_5 = a = 1.5 \text{ mol s}^{-1} \text{ A}$$

$$s_6 = b = 3 \text{ mol s}^{-1} \text{ B}$$

$$s_7 = 1.5 \text{ mol s}^{-1} \text{ A} + 3 \text{ mol s}^{-1} \text{ B}$$

$$s_8 = 1 \text{ mol s}^{-1} \text{ A} + 2 \text{ mol s}^{-1} \text{ B} + 1 \text{ mol s}^{-1} \text{ C}$$

$$s_{10} = 1 \text{ mol C}$$

$$s_{9_1} = 2 \text{ mol B} + 1 \text{ mol C}; \quad s_{9_2} = 1 \text{ mol A} + 1 \text{ mol C}$$

**7.4** By increasing the pressure, the equilibrium is pushed towards the side with the smallest number of molecules that means to the right side. Another possibility is changing the ratio of the feed. i. e.  $a : b$ . According to  $a = b / (2b - 4)$ ,  $b$  will be larger

if  $a$  decreases and vice versa. Because the net enthalpy change is 0, temperature has no effect.

**7.5** Energy must be supplied for heating the evaporator and for the two distillation columns. The total energy consumed of the flow in scheme can be calculated as follows:

$$Q_1 = q \cdot S_7 + 3q \cdot S_3 + 3q \cdot S_{10} = 10.5 q$$

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## PRACTICAL PROBLEMS

Introduction:

The experimental assignment consists of the synthesis and subsequently, the analysis of amminenickel(II) chloride:  $\text{NiCl}_x(\text{NH}_3)_y$ .

The synthesis proceeds in three steps:

- Preparation of a solution of nickel nitrate from nickel and concentrated nitric acid (green solution), time required about 20 min.
- Preparation of amminenickel(II) nitrate (blue crystals)
- Preparation of amminenickel(II) chloride (blue-violet crystals)

The analysis encompasses the determination of the percentages of the three components (ammonia, nickel and chlorine) of the salt, according to the instructions given in 2.

### PROBLEM 1 (practical)

Synthesis of the nickel(II) salt:

All work on the synthesis must be carried out in the fume hood. Use of (safety) glasses is obligatory. If necessary use other safety equipment, such as rubber gloves and pipetting balloons.

- Put a "dubbeltje" (Dutch coin of 10 c, containing 1.5 g of nickel), in a 100 ml conical flask (Erlenmeyer flask) and add 10 ml of concentrated nitric acid (65 %). Fit the flask with an "air cooled" condenser (no water) and heat the contents on a hot plate until a violent reaction occurs. Continue heating carefully until all metal is dissolved. Cool the green solution in an ice-water mixture.

Write in the report form the equation of the chemical reaction that has occurred.

- Add, under continuous cooling, in small portions 25 ml of ammonia solution (25 %) to the ice cold solution. As soon as about 15 ml has been added, salt crystals start to precipitate. Having added all ammonia solution, filter the cold solution through a sintered glass filtering crucible by applying a vacuum with an aspirator. Wash the crystals three times with small portions of a cold ammonia solution (25 %). Remove as much liquid as possible from the crystalline mass by maintaining the vacuum.

- c) Dissolve the moist crystalline mass in 10 ml of hydrochloric acid (18 %). Cool the blue solution in an ice-water mixture and then add slowly 30 ml of a solution of 30 g ammonium chloride in 100 ml of ammonia solution (25 %). This yields a blue-violet coloured crystalline mass. Cool the mixture and filter as in b). Wash with ammonia solution (25 %), then with ethanol and finally with diethyl ether. Leave the crystals on air until all ether has evaporated. Determine the mass of the dry product and record this on the report form.
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**PROBLEM 2 (practical)**Analysis of the Nickel Salt:

For the analysis of the salt, only one sample solution is prepared. The determination of the components is achieved by titrating each time 25 ml of the sample solution in duplicate.

For the determination of the ammonia and chlorine content a back titration is carried out. For that purpose a certain amount of reagent is added in excess. The total amount of reagent, available for the sample, is determined by following the same procedure for 25 ml of a blank solution. This titration should not be carried out in duplicate.

Prepare the following solutions:

A) Sample solution:

Pipette 25.0 ml of 1.6 M nitric acid into a volumetric flask of 250 ml. Add a sample of about 1.2 g of the ammonienickel(II) chloride and dilute with water to a volume of 250 ml.

B) Blank solution:

Pipette 25.0 ml of the same 1.6 M nitric acid and dilute it with water to a volume of 250 ml.

Note:

- 1) For the chlorine determination use conical (Erlenmeyer) flasks with a ground glass stopper.
- 2) The nitric acid contains a small amount of hydrochloric acid. The total acid content is 1.6 M.

a) *Determination of the ammonia content*

Titrate the solutions with a standard solution of NaOH (about 0.1 M). Indicator: methylred, 0.1 % solution in ethanol.

Calculate the percentage of ammonia in the salt.

b) *Determination of the nickel content*

Add about 100 ml of water, 2 ml of ammonia solution (25 %) and 5 drops of murexide solution to the nickel solution, which now should have a yellow colour. Titrate the solution with a standard solution of EDTA (about 0.025 M) until a sharp colour change from yellow to violet is observed. Calculate the percentage of nickel in the salt.

c) *Determination of the chlorine content*

Execute the titration as quickly as possible after the addition of the reagent!

Add to each solution 25 ml of 0.1 M silver nitrate solution. Add about 5 ml of toluene, shake vigorously, add indicator and titrate with the standard solution of ammonium thiocyanate (-rhodanide, about 0.05 M) until a permanent colour change to red is observed. At the end of the titration, shake vigorously again. The red coloration should persist.

Indicator: 1 ml of a saturated solution of iron(III) sulphate.

Calculate the percentage of chlorine in the salt.

Data: Relative atomic masses: H = 1, Cl = 35.5, Ni = 58.7, N = 14.

## Questions:

Calculate from the results obtained the molar ratio of the components to two decimal points and enter this on the report form in the format: Ni : Cl : NH<sub>3</sub> = 1.00 : x : y.

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**19<sup>th</sup>**



**5 theoretical problems  
3 practical problems**

# THE NINETEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 6–15 JULY 1987, VESZPRÉM – BUDAPEST, HUNGARY

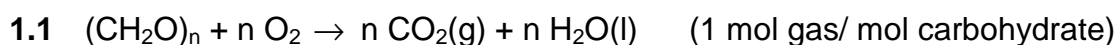
## THEORETICAL PROBLEMS

### PROBLEM 1

Treating waste water in a sewage plant, 45 % of its carbohydrate  $(\text{CH}_2\text{O})_n$  is completely oxidized, 10 % undergoes anaerobic decomposition by fermentation (two components) and the rest remains in the sludge. The total gas formation is  $16 \text{ m}^3$  per day ( $25 \text{ }^\circ\text{C}$ ,  $100 \text{ kPa}$ ).

- 1.1 What is the amount of carbohydrate remaining in the sludge measured in kg per day?
- 1.2 Using the heat of combustion of methane ( $-882 \text{ kJ mol}^{-1}$ ), calculate the amount of energy that can be produced by combustion of the methane formed per day.
- 1.3 Knowing that the concentration of the carbohydrate in the waste water is  $250 \text{ mg dm}^{-3}$ , calculate the daily amount of waste water processed in the plant in  $\text{m}^3$  of water per day.

### SOLUTION



For  $16 \text{ m}^3$  of gases:  $n(\text{gas}) = \frac{pV}{RT} = 646 \text{ mol}$  (55 %) with the rest (45 %) therefore

being in the sludge.

The amount in the sludge is  $\frac{45}{55} \times 646 = 528 \text{ mol}$ , that is 15.85 kg/day.

$$1.2 \quad n(\text{CH}_4) = \frac{5}{55} \times 646 = 58.71 \text{ mol}$$

$$\Delta H = -882 \times 58.71 = -5.178 \times 10^4 \text{ kJ/day}$$



1.3 The sum of CH<sub>2</sub>O is  $\frac{646}{0.55} = 1174$  mol. Since  $250 \text{ mg dm}^{-3} = 0.25 \text{ kg m}^{-3}$ , the daily

amount of water is:  $V = \frac{1174 \times 30}{0.25 \times 10^3} = \underline{140.9 \text{ m}^3/\text{day}}$

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**PROBLEM 2**

500 mg of a hydrated sodium salt of phosphoric acid are dissolved in 50.0 cm<sup>3</sup> of 0.1 molar sulphuric acid. This solution is diluted with distilled water to 100.0 cm<sup>3</sup> and 20.0 cm<sup>3</sup> of it are titrated with 0.100 molar NaOH solution using thymolphthalein as indicator. The average of the burette reading is 26.53 cm<sup>3</sup>. The pH at the end-point is 10.00.

Problems:

- 2.1 Calculate the percentage distribution by moles of all protonated H<sub>n</sub>PO<sub>4</sub><sup>n-3</sup> species at the end-point.
- 2.2 What is the stoichiometric formula of the salt?

The cumulative protonation constants are given by

$$\beta_n = \frac{[\text{H}_n\text{PO}_4^{n-3}]}{[\text{PO}_4^{3-}][\text{H}^+]^n}$$

where  $\log\beta_1 = 11.70$ ;  $\log\beta_2 = 18.6$ ;  $\log\beta_3 = 20.6$ .

The relative atomic masses are: Na = 23.0; P = 31.0; H = 1.0; O = 16.0.

**SOLUTION**

2.1  $[\text{H}_3\text{PO}_4] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{PO}_4^{3-}] = T_{\text{konst}}$ ;  $[\text{H}^+] = 10^{-10} \text{ mol dm}^{-3}$

$$[\text{H}_3\text{PO}_4] = 1 \text{ mol dm}^{-3}$$

$$[\text{HPO}_4^{2-}] = \beta_1[\text{PO}_4^{3-}][\text{H}^+] = 1.25 \times 10^{10} \text{ mol dm}^{-3} = 97.97 \%$$

$$[\text{H}_2\text{PO}_4^-] = \beta_2[\text{PO}_4^{3-}][\text{H}^+]^2 = 1 \times 10^8 \text{ mol dm}^{-3} = 0.078 \%$$

$$[\text{PO}_4^{3-}] = (\beta_3[\text{H}^+]^3)^{-1} = 2.5 \times 10^9 \text{ mol dm}^{-3} = 1.955 \%$$

2.2 A general formula of the salt:  $\text{Na}_{3-n}(\text{H}_n\text{PO}_4) \times m \text{ H}_2\text{O}$  ( $n = 0, 1, 2$ )

The titrated solution contains 100 mg ( $y$  mol) of the salt and 1.00 mmol of sulphuric acid. The reacted protons (in mmol) can be calculated using the results of a):

$$2 + (n - 0.9797 - 2 \times 0.00078) y = 2.653$$

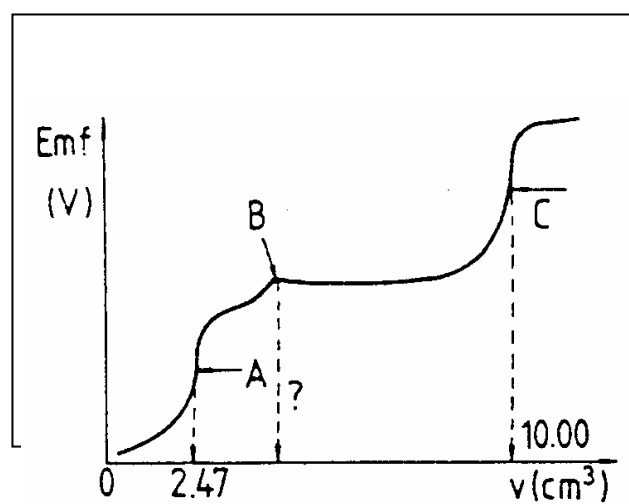
Since  $y = 100/M$  (in mmol) but  $M \geq 120 \text{ g mol}^{-1}$ , the only real solution is  $n = 2$ .

Therefore  $M = 156 \text{ g mol}^{-1}$ ,  $m$  is  $(156-120)/18 = 2 \Rightarrow \underline{\text{NaH}_2\text{PO}_4 \cdot 2 \text{ H}_2\text{O}}$

**PROBLEM 3**

25.00 cm<sup>3</sup> of a neutral solution containing potassium chloride and potassium cyanide are potentiometrically titrated with a standard 0.1000 molar silver nitrate solution at 25 °C using a silver electrode and a normal calomel half-cell with KNO<sub>3</sub> - salt bridge. The protonation of cyanide ions is negligible. The potentiometric curve obtained (emf (V)) vs. burette readings (in cm<sup>3</sup>) is shown in Fig. 1.

Fig. 1



- 3.1 The end points of the reactions taking place during the titration, are marked with A, B and C. Write the balanced ionic equation for each reaction.
- 3.2 What volume of the titrant is required to reach point B?
- 3.3 Calculate the concentrations of KCl and KCN (in mol dm<sup>-3</sup>) in the sample solution.
- 3.4 Calculate the emf readings at the points A and C in volts.
- 3.5 What is the molar ratio Cl<sup>-</sup>/CN<sup>-</sup> in the solution and in the precipitate at point C?

Data:

$$E^{\circ}(\text{Ag}^+/\text{Ag}) = 0.800 \text{ V}$$

$$E^{\circ}(\text{Calomel}) = 0.285 \text{ V}$$

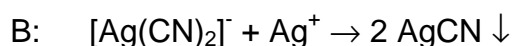
$$K_{\text{sp}}(\text{AgCN}) = 10^{-15.8}$$

$$K_{\text{sp}}(\text{AgCl}) = 10^{-9.75}$$

$$\beta_2 = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 10^{21.1}$$

**SOLUTION**

3.1  $\beta_2$  indicates that the complexation of  $\text{Ag}^+$  with  $\text{CN}^-$  occurs easily. Thus A denotes the point where all  $\text{Ag}^+$  is present in the complex form, having a higher potential than  $\text{Ag}^+$ , B shows the point where the precipitation of  $\text{AgCN}$  starts, thus leading to a constant  $\text{Ag}^+$  concentration until all  $\text{CN}^-$  is precipitated. Now at point C the precipitation of the more soluble  $\text{AgCl}$  begins:



$$3.2 \quad 2 \times 2.47 \text{ cm}^3 = \underline{4.94 \text{ cm}^3}$$

$$3.3 \quad [\text{CN}^-] = (4.94 \times 0.1 \times 40) / 1000 \text{ mol dm}^{-3} = 1.98 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{Cl}^-] = ((10 - 4.94) \times 0.1 \times 40) / 1000 \text{ mol dm}^{-3} = 2.02 \times 10^{-2} \text{ mol dm}^{-3}$$

3.4 For the system  $\text{Ag}/\text{Ag}^+$  at point A:  $E = E_o + 0.059 \log[\text{Ag}^+]$ .

The following equations are derived from the equilibrium conditions:

$$[\text{Ag}^+] = \frac{[\text{Ag}(\text{CN}^-)_2]}{[\text{CN}^-]^2 \beta_2}$$

$$[\text{Ag}^+] + [\text{Ag}(\text{CN}^-)_2] = \frac{2.47 \times 0.1}{25 + 2.47}$$

$$[\text{CN}^-] = 2 [\text{Ag}^+]$$

It yields an equation of third degree in  $[\text{Ag}^+]$ :

$$4\beta_2[\text{Ag}^+]^3 + [\text{Ag}(\text{CN}^-)_2] = 0$$

$[\text{Ag}(\text{CN}^-)_2]$  can be assumed to be  $(2.47 \times 0.1) / 27.47 \text{ mol dm}^{-3}$ , and therefore  $[\text{Ag}^+]$  equals  $1.213 \times 10^{-8} \text{ mol dm}^{-3}$ .

$$\text{The emf will be: } E = 0.8 + 0.059 \log[\text{Ag}^+] - 0.285 = \underline{0.048 \text{ V}}$$

At point C:  $[\text{Ag}^+] = \sqrt{K_{sp}(\text{AgCl})} = 1.333 \times 10^{-5}$  and

$$E = 0.8 + 0.059 \log[\text{Ag}^+] - 0.285 = \underline{0.227 \text{ V}}$$

**3.5** Since both AgCN and AgCl are present as the precipitate, the solution must be saturated:

$$\text{In the solution: } [\text{Cl}^-]/[\text{CN}^-] = K_{sp}(\text{AgCl})/K_{sp}(\text{AgCN}) = 10^{6.05} = \underline{1.222 \times 10^6}$$

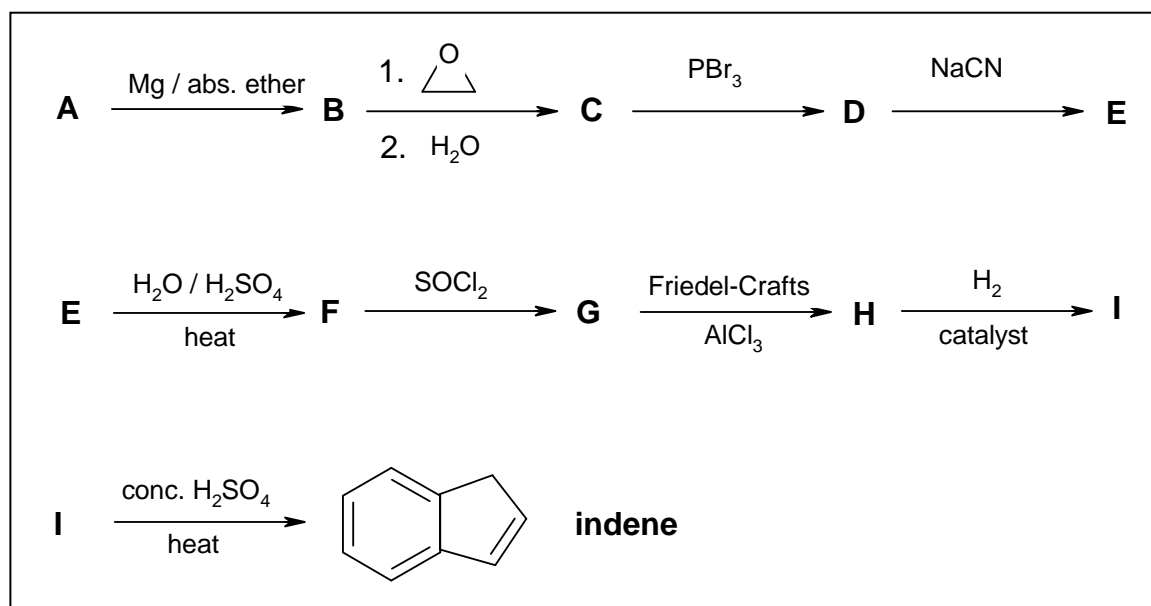
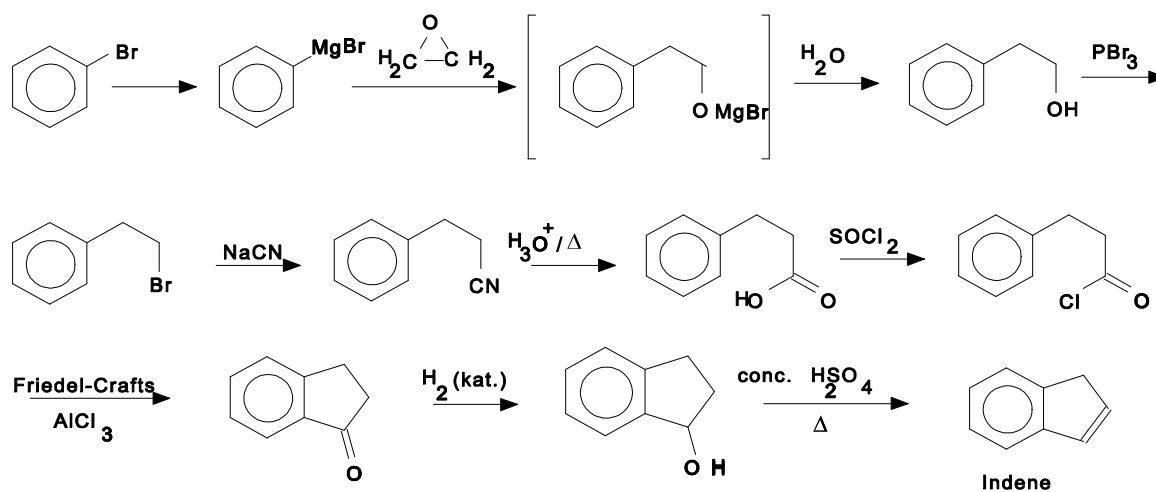
$$\text{In the precipitate: } n(\text{AgCl}) / n(\text{AgCN}) = 2.02 / 1.98 = \underline{1.02}$$

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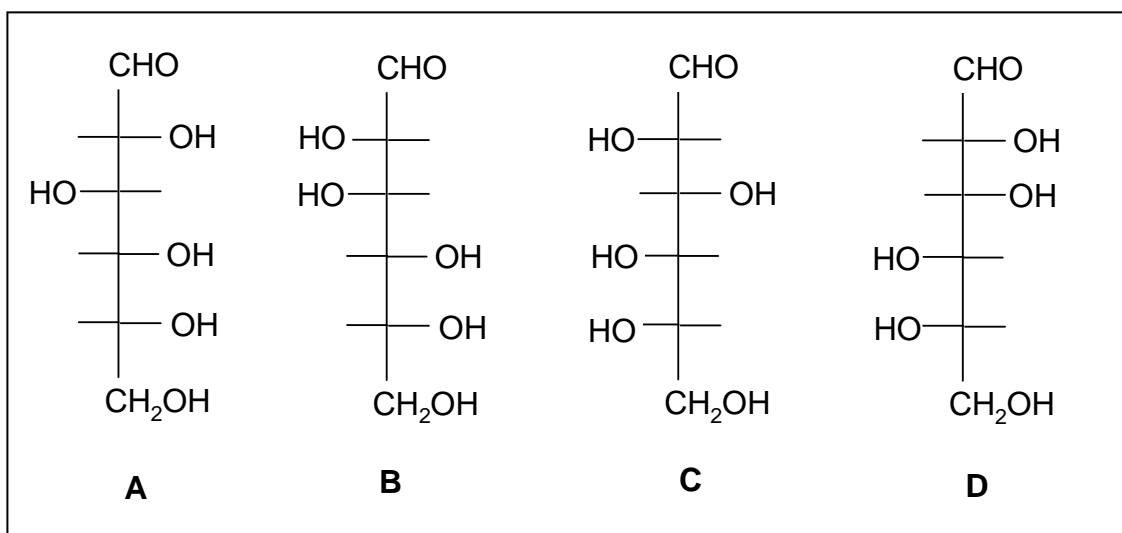
**PROBLEM 4**

Write the structural formulae of the compounds **A** to **I** in the following reaction sequence.

**SOLUTION**

**PROBLEM 5**

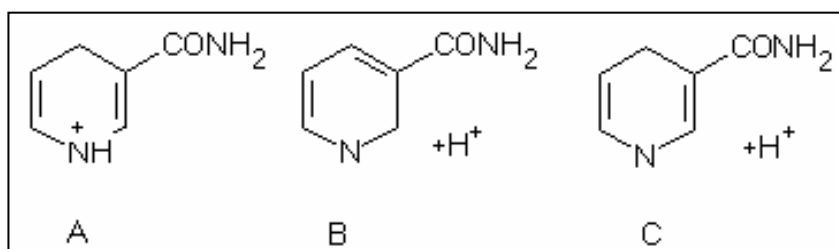
- 5.1** What ratio of primary / secondary / tertiary products can statistically be expected in the high temperature chlorination of methyl butane? Assume that the reaction rate of the substitution is equal for all C-H bonds.
- 5.2** Which of the following alcohols: pentan-1-ol, pentan-2-ol and 2-methyl-butan-2-ol react with the following reagents listed below?  
1) cold, concentrated sulphuric acid; 2)  $\text{CrO}_3 / \text{H}_2\text{SO}_4$ ; 3)  $\text{ZnCl}_2 / \text{HCl}$ ; 4)  $\text{I}_2 / \text{NaOH}$
- 5.3** Which of the following aldohexose structures are:  
1) enantiomer pairs, 2) diastereomer pairs?



- 5.4** Two hydrocarbon compounds of the same molecular formula,  $\text{C}_4\text{H}_8$ , easily react with hydrogen in the presence of a platinum catalyst. During ozonolysis only ethanal (acetaldehyde) is formed in both cases. The  $^1\text{H-NMR}$  spectra of the two compounds show two types of protons in a ratio of 3 to 1. Draw the structures of the described compounds.
- 5.5** Select the components of the group listed below that can be obtained during complete hydrolysis of lecithin (a phospholipid): serine, phosphoric acid, sphingosine, choline, glycerol, myo-inositol, phosphatidic acid and fatty acids).
- 5.6** Which of the following carboxylic acid can be formed in the tricarboxylic acid cycle (Krebs' citric acid cycle):

maleic acid (cis-butenedioic acid), mandelic acid (α-hydroxy-phenylethanoic acid), malic acid (2-hydroxy-butanedioic acid), tricarballylic acid (propane-1,2,3-tricarboxylic acid), oxalacetic acid (2-oxo-butanedioic acid), keto-glutaric acid (2-oxo-pentanedioic acid), fumaric acid (trans-butenedioic acid) and acetoacetic acid (3-oxo-butanonic acid).

- 5.7 To which structures is the nicotinamide moiety (part) of NAD<sup>+</sup> converted during the uptake of hydrogen to form NADH (A, B or C)?



## SOLUTION

- 5.1 The ratio of primary, secondary and tertiary products will be 9 : 2 : 1.

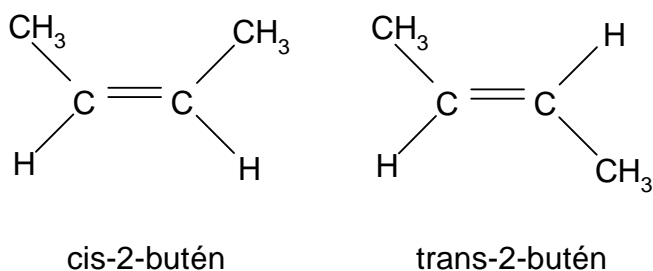
- 5.2 1-Pentanol reacts with 1) cold conc. sulphuric acid (elimination) and with 2) CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (oxidation).

2-Pentanol reacts with 1) under elimination, with 2) under oxidation, with 3) under reduction and with 4) (haloform oxidation).

2-Methyl-2-butanol reacts with 1) under elimination and with 3) under reduction.

- 5.3 a/c and b/d are enantiomers, a/b, a/d, b/c and c/d are diastereomers.

- 5.4





- 5.5** Glycerol, choline, phosphoric acid and fatty acids can be found during complete hydrolysis of lecithin.
- 5.6** maleic acid, oxalacetic acid, ketoglutaric acid, fumaric acid
- 5.7** c) is correct since the  $\text{NAD}^+$  is converted into  $\text{NADH}/\text{H}^+$
- 
-

**PRACTICAL PROBLEMS****PROBLEM 1 (practical)**

You are required to investigate seven inorganic compounds.

Your test-tube rack is numbered 1 to 9. Two of the positions are empty. Each of the seven test-tubes provided contains only one compound in aqueous solution. Using only these solutions, pH indicator paper, and test-tubes, you are to identify as many of the ions present as you are able.

For your information, record in the table the observations you make on mixing the solutions. Use the following symbols:

elimination reactions: ↓ precipitate; ↑ gaseous product;

↓<sub>s</sub> precipitate soluble in the excess of a precipitating agent.

colours: w - white or colourless, b - blue, g - green, y - yellow, p - pink, r - red, br - brown.

pH: a - acidic, b - alkaline, n - neutral.

Equipment:

A home-made rack contained 9 test-tubes with the unknown solutions, 30 empty Wassermann-tubes and one small beaker containing the pH indicator paper. Into each solution a dropper was inserted, and thus, the test-tubes need not to be removed from the rack while handling them. According to the original plan the following nine unknown solutions were expected to be given to the participants:  $\text{CoCl}_2$ ,  $\text{Fe}(\text{SCN})_3$ ,  $\text{NH}_4\text{OH}$ ,  $\text{KI}$ ,  $\text{AgNO}_3$ ,  $\text{Na}_2\text{HAsO}_4$ ,  $\text{HgCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ .

During the discussion of the International Jury it became known that in some countries the corresponding laws forbid the pupils in secondary schools to handle mercury and arsenic compounds. For this reason these two compounds were removed from the rack and consequently the number of ions to be detected - and the marks available - were reduced to 12 (from the original 15). (Under these conditions the alkali and nitrate ions cannot be detected.)

The order of the test-tubes varied individually, but the first two contained invariably red solutions ( $\text{CoCl}_2$  and  $\text{Fe}(\text{SCN})_3$ ), while the last two were the green  $\text{NiCl}_2$  and  $\text{CuCl}_2$  symbolizing the Hungarian national colours, red-white-green.

**SOLUTION**

The ions of the remaining seven solutions can easily be identified by mutual reactions. Out of the 21 possible reactions, 12 are common positive reactions. Additional information is available from the colour of 4, and the smell of one solution.

AgNO<sub>3</sub>: reacts with all the six compounds;

NH<sub>3</sub>: with the exception of iodide it gives a characteristic reaction with all the others salts;

Fe(SCN)<sub>3</sub>: its colour and reaction with NH<sub>3</sub>, I<sup>-</sup>, Ag<sup>+</sup> are characteristic;

CoCl<sub>2</sub>: can be detected from its colour and by adding NH<sub>3</sub> or Ag<sup>+</sup>;

KI: can be identified by its reaction with Ag<sup>+</sup> and from the evolution of I<sub>2</sub> due to an addition of Fe<sup>3+</sup> or Cu<sup>2+</sup>;

CuCl<sub>2</sub>: can be detected from its colour and reaction with NH<sub>3</sub>, I<sup>-</sup> and Ag<sup>+</sup>;

NiCl<sub>2</sub>: has a characteristic colour and reacts with NH<sub>3</sub> and Ag<sup>+</sup>.

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**PROBLEM 2 (practical)**

You are required to estimate the heat (enthalpy) change on mixing a series of 5 liquids to produce equimolar mixtures and to explain the temperature changes.

Procedure:

1. A mixture of trichloromethane (chloroform) and propanone (acetone)

Measure 0.5 mol of trichloromethane in the measuring cylinder labelled A<sub>1</sub> and measure its temperature. Dry the thermometer with a piece of tissue paper. Measure 0.5 mol of propanone using measuring cylinder B<sub>1</sub>, pour it into a beaker and measure its temperature. Record the average of the two temperatures as temperature  $t_1$  (to 0.1 °C). Leave the thermometer in the beaker. Add the trichloromethane to the propanone, stir the mixture carefully and follow the temperature changes until a maximum or minimum is reached. Record this extreme temperature as temperature  $t_2$ . Dispose the mixture into a special bottle labelled "waste solution", dry the reaction beaker and the thermometer and proceed to the next part of the experiment.

2. A mixture of methanol and propanone (acetone)

Measure 0.5 mol of propanone in measuring cylinder B<sub>1</sub> and 0.5 mol of methanol in measuring cylinder A<sub>2</sub>, and continue as in part 1.

3. A mixture of methanol and n-hexane

Measure 0.5 mol of methanol into measuring cylinder A<sub>2</sub> and 0.5 mol of hexane into measuring cylinder B<sub>2</sub>, and continue as in part 1.

4. A mixture of methanol and water

Measure 0.5 mol of methanol into measuring cylinder A<sub>2</sub>, measure its temperature and pour it into the beaker. Rinse the cylinder thoroughly with distilled water and then measure 0.5 mole of water using this measuring cylinder. Continue as instructed in the above part 1.

## Tasks:

Calculate the enthalpy (heat) changes involved in the mixings on the basis of the temperature changes observed. In your calculations you should neglect heat exchanges with the surroundings as well as the heat capacity of the beaker and thermometer. Briefly explain your results in terms of the molecular interactions in the pure liquids and in the mixture, preferably using sketches.

## Data:

Substance	Relative molecular mass	Density (g cm <sup>-3</sup> )	Molar heat capacity (J K <sup>-1</sup> mol <sup>-1</sup> )
methanol	32.04	0.79	80.61
chloroform	119.38	1.49	114.94
acetone	58.08	0.79	124.96
n-hexane	86.18	0.66	190.10
water	18.02	1.00	75.35

**PROBLEM 3 (practical)**

You are required to determine the concentrations of hydrochloric acid and potassium iodate in the diluted solution containing both.

Procedure:

A solution containing potassium iodate and hydrochloric acid has already been measured into the volumetric flask provided. Fill the flask to the mark with distilled water using the wash bottle, close it with a stopper and shake it thoroughly. Fill the burette with the standard sodium thiosulphate solution using one of the beakers provided. (The exact concentration of the thiosulphate is given on the label of the bottle.)

a) First titration

Pipette a 10.00 cm<sup>3</sup> aliquot (portion) of the solution from the volumetric flask into a glass stoppered conical flask. Dilute it with 10 cm<sup>3</sup> of distilled water, add 1 g (a small spatula end-full) of potassium iodide and acidify with 10 cm<sup>3</sup> of 10 % sulphuric acid using a measuring cylinder. Titrate immediately the iodine formed with the standard sodium thiosulphate solution until the solution in the flask is pale yellow. Add with a pipette 1 cm<sup>3</sup> of starch indicator solution and continue the titration to completion. Repeat the titration twice more and record your readings on the result sheet.

b) Second titration

Pipette a 10.00 cm<sup>3</sup> aliquot of the solution into another glass stoppered conical flask, dilute with 10 cm<sup>3</sup> of distilled water, add 1 g of solid potassium iodide, and leave to stand for 10 minutes. Then titrate the iodine formed using the standard sodium thiosulphate solution, adding 1 cm<sup>3</sup> of starch indicator solution when the mixture is pale yellow. Repeat the titration twice more, recording your readings on the result sheet.

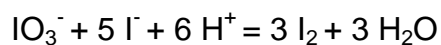
Task:

Calculate the concentration of the HCl and the KIO<sub>3</sub> in the solution that you prepared by dilution (in mol dm<sup>-3</sup>).

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**SOLUTION**

The reaction:



occurs to be quantitative both with respect to  $\text{IO}_3^-$  and  $\text{H}^+$ . Consequently the first titration (in the presence of sulphuric acid) is suitable for the determination of iodate, while the second one for the determination of the hydrochloric acid content.

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**20<sup>th</sup>**



**International Chemistry Olympiad**

**6 theoretical problems  
2 practical problems**



# THE TWENTIETH INTERNATIONAL CHEMISTRY OLYMPIAD 2–9 JULY 1988, ESPOO, FINLAND

## THEORETICAL PROBLEMS

### PROBLEM 1

The periodic system of the elements in our three-dimensional world is based on the four electron quantum numbers  $n = 1, 2, 3, \dots$ ;  $l = 0, 1, \dots, n - 1$ ,  $m = 0, \pm 1, \pm 2, \dots, \pm l$ ; and  $s = \pm 1/2$ . In Flatlandia, a two-dimensional world, the periodic system is thus based on three electron quantum numbers:  $n = 1, 2, 3, \dots$ ;  $m_l = 0, \pm 1, \pm 2, \dots, \pm (n-1)$ ; and  $s = \pm 1/2$  where  $m_l$  plays the combined role of  $l$  and  $m_l$  of the three dimensional world. The following tasks relate to this two-dimensional world, where the chemical and physical experience obtained from our world is supposed to be still applicable.

- 1.1 Draw the first four periods of the Flatlandian periodic table of the elements. Number them according to their nuclear charge. Use the atomic numbers ( $Z$ ) as symbols of the specific element. Write the electron configuration for each element.
- 1.2 Draw the hybrid orbitals of the elements with  $n = 2$ . Which element is the basis for the organic chemistry in Flatlandia? Find the Flatlandian analogous for ethane, ethene and cyclohexane. What kind of aromatic ring compounds are possible?
- 1.3 Which rules in Flatlandia correspond to the octet and the 18-electron rules in the three dimensional world?
- 1.4 Predict graphically the trends in the first ionization energies of the Flatlandian elements with  $n = 2$ . Show graphically how the electronegativities of the elements increase in the Flatlandian periodic table.
- 1.5 Draw the molecular orbital energy diagrams of the neutral homonuclear diatomic molecules of the elements with  $n = 2$ . Which of these molecules are stable in Flatlandia?
- 1.6 Consider simple binary compounds of the elements ( $n = 2$ ) with  $Z = 1$ . Draw their Lewis structure, predict their geometries and propose analogues for them in the three dimensional world.

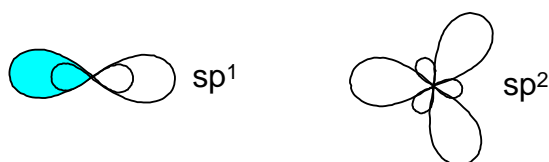
1.7 Consider elements with  $n \leq 3$ . Propose an analogue and write the chemical symbol from our world for each of these Flatlandian elements. On the basis of this chemical and physical analogue predict which two-dimensional elements are solid, liquid or gaseous at normal pressure and temperature.

## SOLUTION

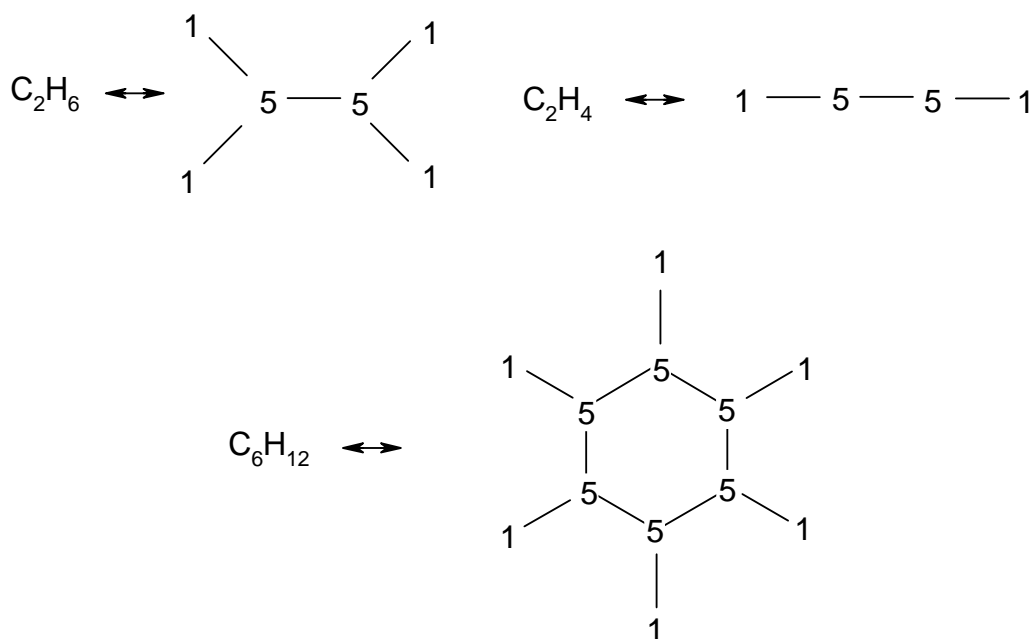
1.1 In the two dimensional world and the electron quantum numbers given, we obtain the following Flatlandian periodic table:

<b>1</b> 1s <sup>1</sup>								<b>2</b> 1s <sup>2</sup>	
<b>3</b> [ ]2s <sup>1</sup>	<b>4</b> [ ]2s <sup>2</sup>					<b>5</b> [ ]2s <sup>2</sup> 2p <sup>1</sup>	<b>6</b> [ ]2s <sup>2</sup> 2p <sup>2</sup>	<b>7</b> [ ]2s <sup>2</sup> 2p <sup>3</sup>	<b>8</b> [ ]2s <sup>2</sup> 2p <sup>4</sup>
<b>9</b> [ ]3s <sup>1</sup>	<b>10</b> [ ]3s <sup>2</sup>					<b>11</b> [ ]3s <sup>2</sup> 3p <sup>1</sup>	<b>12</b> [ ]3s <sup>2</sup> 3p <sup>2</sup>	<b>13</b> [ ]3s <sup>2</sup> 3p <sup>3</sup>	<b>14</b> [ ]3s <sup>2</sup> 3p <sup>4</sup>
<b>15</b> [ ]4s <sup>1</sup>	<b>16</b> [ ]4s <sup>2</sup>	<b>17</b> [ ]4s <sup>2</sup> 3d <sup>1</sup>	<b>18</b> [ ]4s <sup>2</sup> 3d <sup>2</sup>	<b>19</b> [ ]4s <sup>2</sup> 3d <sup>3</sup>	<b>20</b> [ ]4s <sup>2</sup> 3d <sup>4</sup>	<b>21</b> [ ]4s <sup>2</sup> 3d <sup>4</sup> 4p <sup>1</sup>	<b>22</b> [ ]4s <sup>2</sup> 3d <sup>4</sup> 4p <sup>2</sup>	<b>23</b> [ ]4s <sup>2</sup> 3d <sup>4</sup> 4p <sup>3</sup>	<b>24</b> [ ]4s <sup>2</sup> 3d <sup>4</sup> 4p <sup>4</sup>

1.2  $sp^1$  and  $sp^2$  hybrid orbitals are possible:



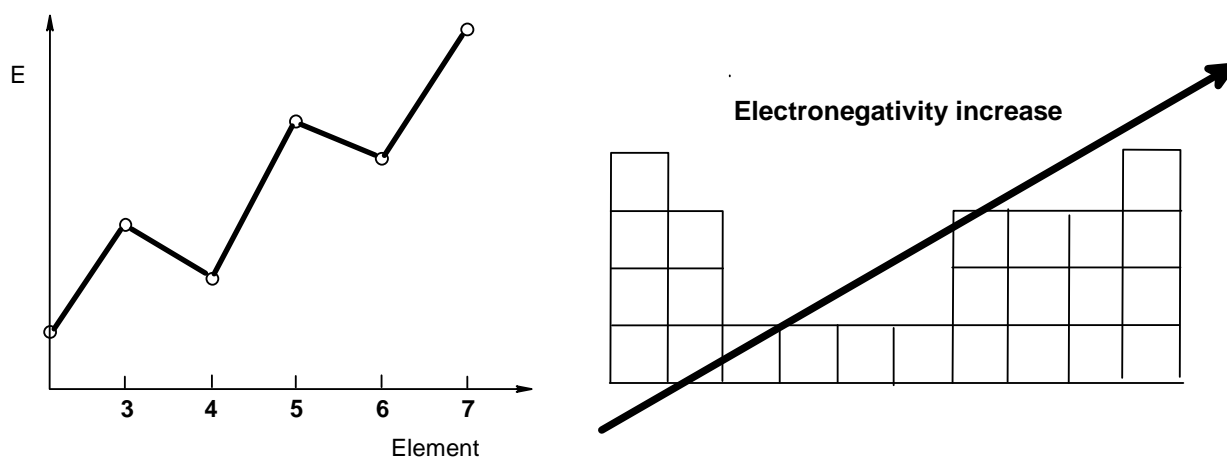
The element of life is the element with  $Z = 5$ . The corresponding compounds of ethane, ethene and cyclohexane are:



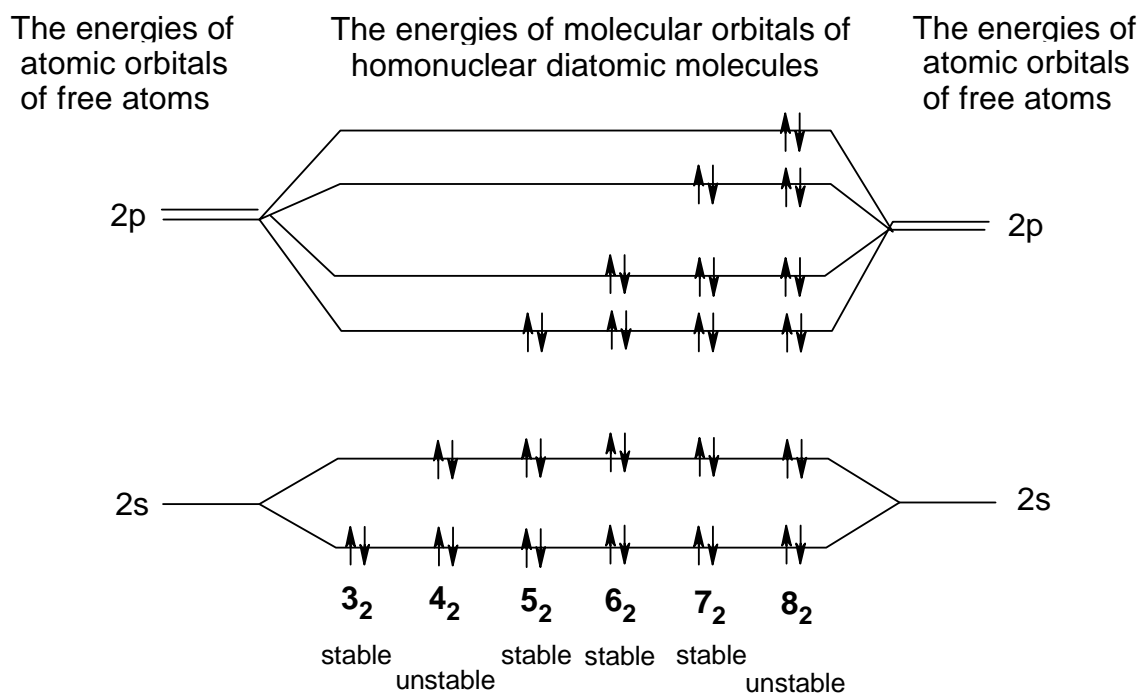
Aromatic ring compounds are not possible since there are no electron orbitals left that may overlap in the case of  $sp^2$ .

**1.3** The Octet rule is changed to a Sextet rule, the 18-electron rule corresponds to a 10-electron rule.

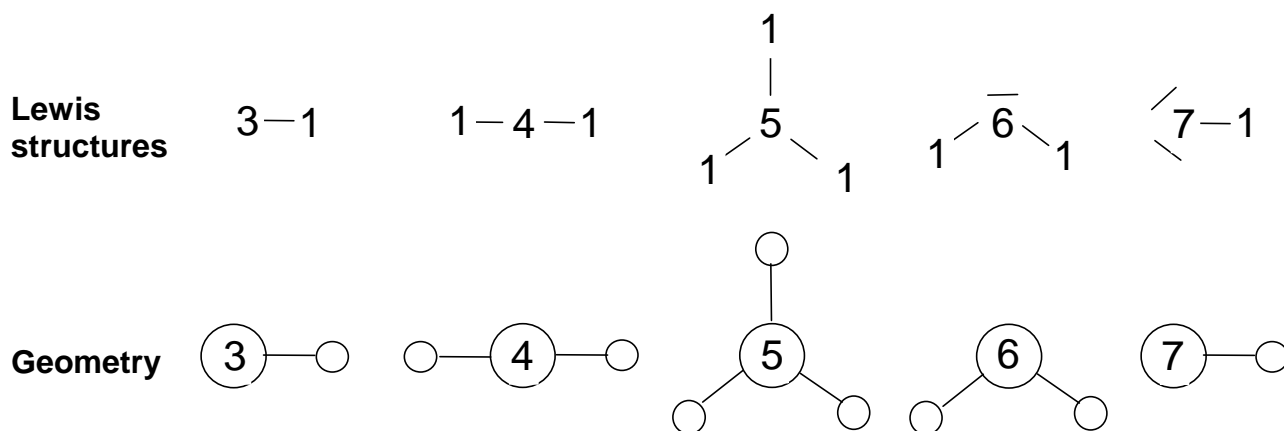
**1.4** The ionization energies and the trends in electronegativity



**1.5** The molecular orbital diagram of the homonuclear  $X_2$  molecules:



### 1.6 The Lewis structures and geometries:

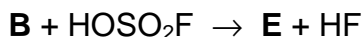


### 1.7 The three-dimensional analogues of Flatlandian elements are:

1: H, gas	5: B or C, solid	9: Na, solid	13: Cl, gas
2: He, gas	6: N or O, gas	10: Mg, solid	14: Ar, gas
3: Li, solid	7: F, gas	11: Al or Si, solid	
4: Be, solid	8: Ne, gas	12: P or S, solid	

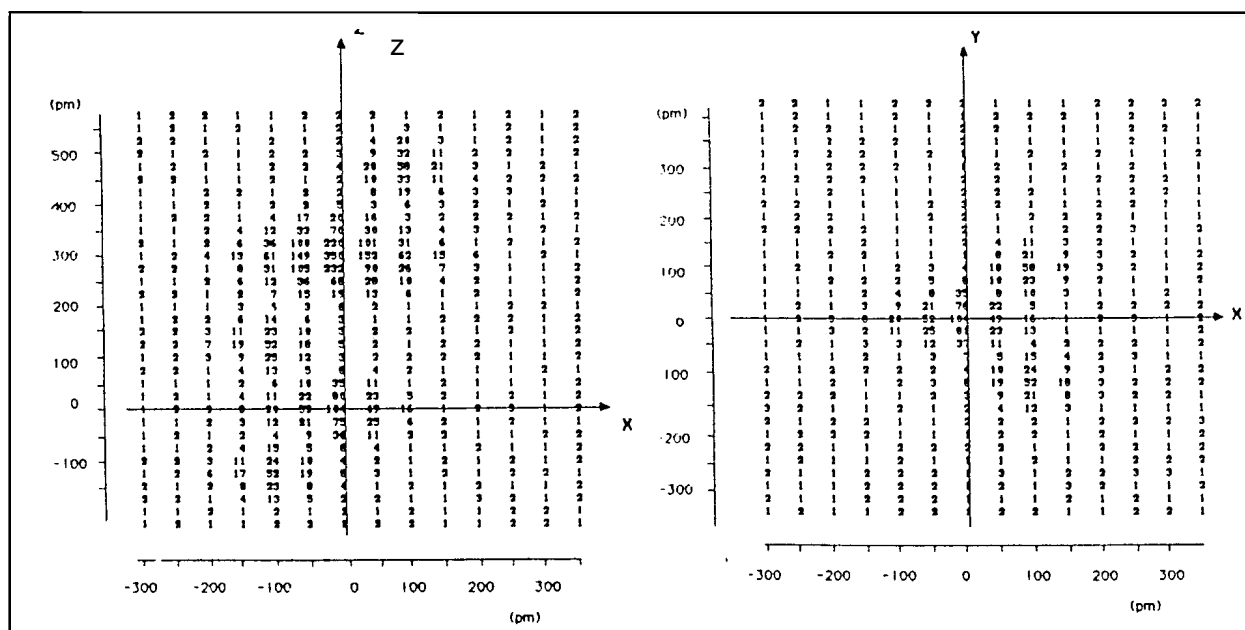
## PROBLEM 2

Upon heating of a mixture of **A** and fluorine (molar ratio 1 : 9, pressure approximately 1 MPa) to 900 °C three compounds (**B**, **C** and **D**) are formed. All three products are crystalline solids at ambient temperature with melting points below 150 °C. The fluorine content of **C** is found to be 36.7 % and that of **D** 46.5 % (by weight). When **B** is treated with anhydrous HOSO<sub>2</sub>F at -75 °C a compound **E** is formed:



**E** is a solid which is stable for weeks at 0 °C, but decomposes in days at room temperature. The electron density distribution of **E** obtained through X-ray diffraction studies is shown on two intersecting, mutually perpendicular planes (see Fig. 1).

Fig. 1



The numbers indicated on the maps relate to the electron density in the neighbourhood of the atoms of **E** as a function of the spatial coordinates. The maxima found in these maps coincide with the locations of the atoms and the values are approximately proportional to the number of electrons in the atom in question.

**2.1** Show where the maxima lie by drawing the contour curves around the maxima, connecting points of equal electron densities. Label each maximum to show the identities of the atoms in **E**.

- 2.2** When 450.0 mg of **C** was treated with an excess of mercury, 53.25 ml of **A** was liberated at a pressure of 101.0 kPa and a temperature of 25 °C. Calculate the relative atomic mass of **A**.
- 2.3** Identify **A**, **B**, **C**, **D** and **E**.
- 2.4** Use the valence-shell electron-pair repulsion theory (VSEPR) to propose electron-pair geometries for **B** and **C**. Using the two electron density maps, sketch the molecular geometry of **E**.

The original mixture was hydrolysed in water. **B** reacts to **A** while liberating oxygen and producing aqueous hydrogen fluoride. Hydrolysis of **C** leads to **A** and oxygen (in molar ratio of 4 : 3) and yields an aqueous solution of  $\text{AO}_3$  and hydrogen fluoride. **D** hydrolyses to an aqueous solution of  $\text{AO}_3$  and hydrogen fluoride.

- 2.5** Write the equations for the three hydrolysis reactions.
- 2.6** Quantitative hydrolysis of a mixture of **B**, **C** and **D** gives 60.2 ml of gas (measured at 290 K and 100 kPa). The oxygen content of this gas is 40.0% (by volume). The amount of  $\text{AO}_3$  dissolved in water is titrated with an aqueous 0.1 molar  $\text{FeSO}_4$  solution and 36.0 ml used thereby. During the titration  $\text{Fe}^{2+}$  is oxidized to  $\text{Fe}^{3+}$  and  $\text{AO}_3$  is reduced to **A**. Calculate the composition (% by moles) of the original mixture of **B**, **C** and **D**.

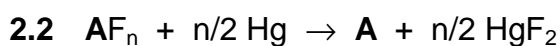
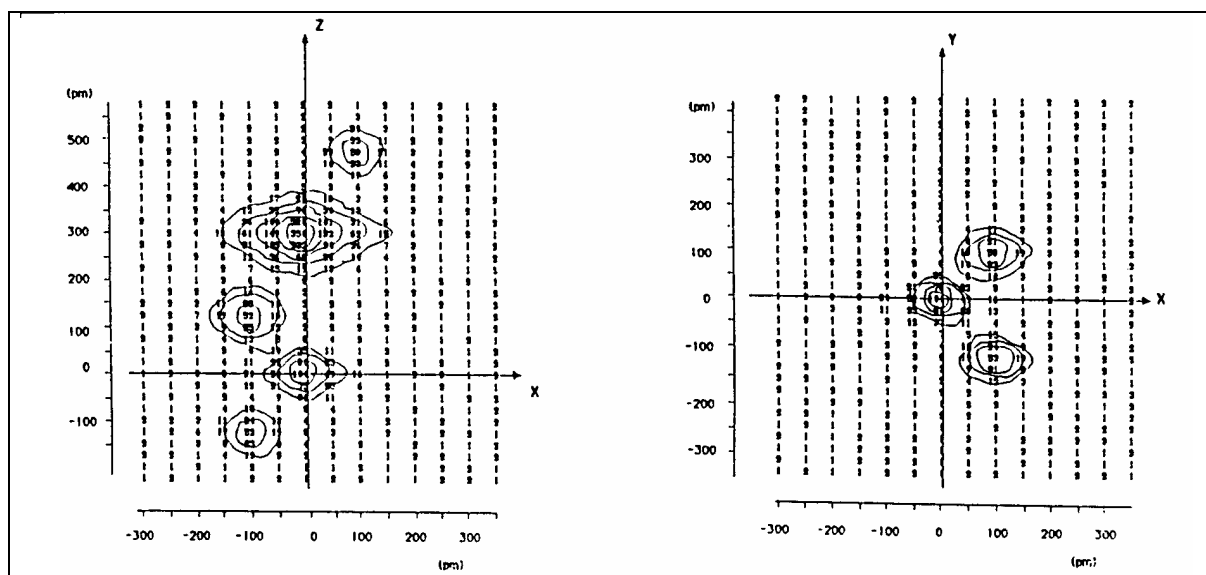
## SOLUTION

- 2.1** Fig. 2 shows the electron densities with maxima 52, 58, 104, and 350. Since compound **E** is supposed to contain the atoms of fluorine, oxygen, sulphur, and **A**, the above maxima can be assign to particular atoms as follows:

Maximum	Element	Atomic number
52	O	8
58	F	9
104	S	16
350	<b>A</b>	?

The atomic number of **A** is 54. Thus, the element **A** is xenon.

Fig. 2



$$n_{\text{gas}} = \frac{pV}{RT} = \frac{101\,000 \text{ Pa} \times 53.25 \times 10^{-6} \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 2.17 \times 10^{-3} \text{ mol} = n(\text{A}) = n(\text{AF}_n)$$

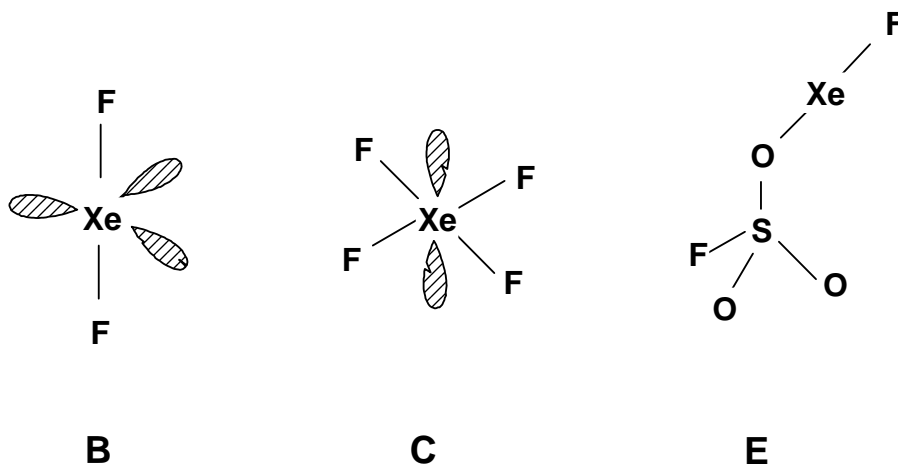
$$\underline{M(\text{AF}_n)} = \frac{0.45}{2.17 \times 10^{-3}} = \underline{207.4 \text{ g mol}^{-1}} = M(\text{A}) + n M(\text{F})$$

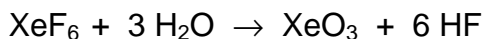
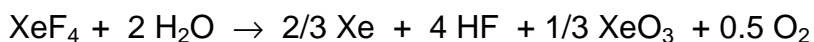
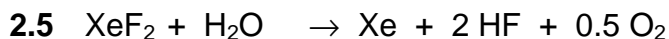
$$n M(\text{F}) = 0.367 M(\text{AF}_n) \Rightarrow n = \frac{207 \times 0.367}{19} = 4.0055 \Rightarrow \underline{\text{AF}_4};$$

$$\underline{M(\text{A})} = M(\text{AF}_n) - n M(\text{F}) = 207.4 - 76.1 = \underline{131.3 \text{ g mol}^{-1}}$$



2.4





2.6 
$$n_{\text{gas}} = \frac{pV}{RT} = \frac{100\,000 \text{ Pa} \times 60.2 \times 10^{-6} \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 290 \text{ K}} = 2.50 \times 10^{-3} \text{ mol}$$

$n(\text{O}_2) = 0.4 \times n_{\text{gas}} = 1.00 \times 10^{-3} \text{ mol}$

$n(\text{Xe}) = 1.50 \times 10^{-3} \text{ mol}$

Assume  $n(\text{XeF}_2) = a$ ;  $n(\text{XeF}_4) = b$ ;  $n(\text{XeF}_6) = c$

$n(\text{Xe}) = a + 2/3 b$ ;

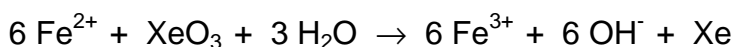
$n(\text{O}_2) = 1/2 a + 1/2 b$ ;

$n_{\text{gas}} = n(\text{Xe}) + n(\text{O}_2) = 3/2 a + 7/6 b = 2.50 \times 10^{-3} \text{ mol}$

$n(\text{O}_2) = 1/2 a + 1/2 b = 1.00 \times 10^{-3} \text{ mol}$

Solution of the equations:

$a = 0.5 \times 10^{-3} \text{ mol}$ ;  $b = 1.5 \times 10^{-3} \text{ mol}$



$$n(\text{XeO}_3) = 1/6 n(\text{Fe}^{2+}) = 1/6 [c(\text{Fe}^{2+}) V(\text{Fe}^{2+})] = 1/6 \times 0.100 \times 36.0 \times 10^{-3} \text{ mol} =$$
  

$$= 6.00 \times 10^{-4} \text{ mol} = 1/3 b + c$$

$c = 0.6 \times 10^{-3} - 0.5 \times 10^{-3} = 1 \times 10^{-4}$

<u>molar composition:</u>	$\text{XeF}_2$ :	$0.5 \times 10^{-3} \text{ mol}$	(23.8 %)
	$\text{XeF}_4$ :	$1.5 \times 10^{-3} \text{ mol}$	(71.4 %)
	$\text{XeF}_6$ :	$1 \times 10^{-4} \text{ mol}$	(4.8 %)



**PROBLEM 3**

A typical family car has four cylinders with a total cylinder volume of 1600 cm<sup>3</sup> and a fuel consumption of 7.0 l per 100 km when driving at a speed of 90 km/h. During one second each cylinder goes through 25 burn cycles and consumes 0.4 g of fuel. Assume that fuel consists of 2,2,4-trimethylpentane, C<sub>8</sub>H<sub>18</sub>. The compression ratio of the cylinder is 1:8.

- 3.1** Calculate the air intake of the engine (m<sup>3</sup>/s). The gasified fuel and air are introduced into the cylinder when its volume is largest until the pressure is 101.0 kPa. Temperature of both incoming air and fuel are 100 °C. Air contains 21.0 % (by volume) of O<sub>2</sub> and 79.0 % of N<sub>2</sub>. It is assumed that 10.0 % of the carbon forms CO upon combustion and that nitrogen remains inert.
- 3.2** The gasified fuel and the air are compressed until the volume in the cylinder is at its smallest and then ignited. Calculate the composition (% by volume) and the temperature of the exhaust gases immediately after the combustion (exhaust gases have not yet started to expand). The following data is given:

Compound	$\Delta H_f$ (kJ/mol)	$C_p$ (J/mol K)
O <sub>2</sub> (g)	0.0	29.36
N <sub>2</sub> (g)	0.0	29.13
CO(g)	-110.53	29.14
CO <sub>2</sub> (g)	-395.51	37.11
H <sub>2</sub> O(g)	-241.82	33.58
2,2,4-trimethylpentane	-187.82	

- 3.3** Calculate the final temperature of the leaving gases assuming that the piston has moved to expand the gases to the maximum volume of the cylinder and that the final gas pressure in the cylinder is 200 kPa.
- 3.4** To convert CO(g) into CO<sub>2</sub>(g) the exhaust gases are led through a bed of catalysts with the following work function:

$$\frac{n(\text{CO})}{n(\text{CO}_2)} = \frac{1}{4} k \left[ \frac{n(\text{CO})}{n(\text{CO}_2)} \right]_1 v e^{-\frac{T}{T_0}}$$

where  $[n(\text{CO}) / n(\text{CO}_2)]_1$  is the molar ratio before the catalyst,  $v$  is the flow rate in

mol/s and  $T$  the temperature of the gases entering the catalyst (the same as the temperature of the leaving exhaust gases).  $T_0$  is a reference temperature (373 K) and  $k$  is equal to 3.141 s/mol. Calculate the composition (% by volume) of the exhaust gases leaving the catalyst.

## SOLUTION

3.1  $M_r(\text{C}_8\text{H}_{18}) = 114.0,$

Cylinder volume ( $V_0$ ) =  $4.00 \times 10^{-4} \text{ m}^3$ ,  $p_0 = 101\,000 \text{ Nm}^{-2}$ ,  $T_0 = 373 \text{ K}$

Considering one cylinder during one burn cycle one obtains (f = fuel):

$$m_f = 0.400 / 25 \text{ g} = 0.0160 \text{ g}, \quad n_f = 1.4004 \times 10^{-4} \text{ mol}$$

( $m_f$  = mass of fuel,  $n_f$  = amount of substance of fuel)

$$n_G = n_f + n_A = p_0 V_0 / (RT_0) = 0.0130 \text{ mol}$$

( $n_G$  = number of moles of gases,  $n_A$  = moles of air)

$$\Rightarrow n_A = 0.0129 \text{ mol}$$

$\Rightarrow$  Air intake of one cylinder during 25 burn cycles:

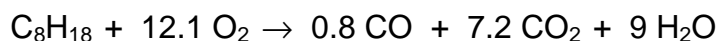
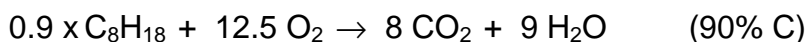
$$V_A = 25 n_A R T_0 / p_0 = 9.902 \times 10^{-3} \text{ m}^3/\text{s}$$

$\Rightarrow$  The air intake of the whole engine is therefore:  $V_{\text{total}} = 4 V_A = 0.0396 \text{ m}^3/\text{s}$

3.2 The composition of the exhaust gases of one cylinder during one burn cycle is considered:

before:  $n_{\text{O}_2} = 0.21 n_A = 2.709 \text{ mmol}$

$$n_{\text{N}_2} = 0.79 n_A = 10.191 \text{ mmol}$$



Amounts of substances (in mol) before and after combustion:

	$\text{C}_8\text{H}_{18}$	$\text{O}_2$	$\text{CO}$	$\text{CO}_2$	$\text{H}_2\text{O}$
before	$1.404 \times 10^{-4}$	$2.709 \times 10^{-3}$	0	0	0
after	0	$10.10 \times 10^{-4}$	$1.123 \times 10^{-4}$	$10.11 \times 10^{-4}$	$12.63 \times 10^{-4}$

The composition of the gas after combustion is therefore:

Component	N <sub>2</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	Total
mol × 10 <sup>4</sup>	101.91	10.10	1.12	10.11	12.63	135.87
%	75.0	7.4	0.8	7.5	9.3	100

From thermodynamics the relation between the enthalpy and temperature change is given by

$$\Delta H = \int_{T_1}^{T_2} \sum_{i=1}^{i=k} c_{pi} n_i dT = \sum_{i=1}^{i=k} c_{pi} n_i (T_2 - T_1)$$

$$\Delta H = n_f [0.8 \Delta H_f(\text{CO}) + 7.2 \Delta H_f(\text{CO}_2) + 9 \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_8\text{H}_{18})] = -0.6914 \text{ kJ}$$

This yields to:  $691.4 = 0.4097 (T_2 - 373)$  and  $T_2 = \underline{2060 \text{ }^\circ\text{C}}$

**3.3** The final temperature of the leaving gases from one cylinder:

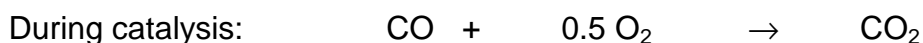
$$p_2 = 200\,000 \text{ Pa}, V_0 = 4.00 \times 10^{-4} \text{ m}^3,$$

$$n_G = \text{moles of exhaust gases in one cylinder} = 0.01359 \text{ mol}$$

$$T_2 = \frac{p_2 V_0}{n_G R} = \underline{708 \text{ K}}$$

**3.4** The flow from all four cylinders is given:  $v = 4 \times 25 \times n_G = 1.359 \text{ mol/s}$ , so that

$$\frac{n(\text{CO})}{n(\text{CO}_2)_2} = 0.25 \times 3.141 \times \frac{1.12 \times 10^4}{10.11 \times 10^4} \times 1.359 \times e^{\frac{708}{373}} = 0.01772$$



moles × 10<sup>4</sup> (4 cylinders):

initial	4.48	40.40	40.44
final	4.48 - x	40.40 - 0.5 x	40.44 + x

$$0.01772 (40.44 + x) = 4.48 + x \Rightarrow x = 3.70$$

Thus, the composition of the gas after the catalyst is:

Component	N <sub>2</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	Total
mol × 10 <sup>4</sup>	407.64	40.40 - 0.5x	4.48 - x	40.44 + x	50.52	541.63
		38.55	0.78	44.14		
%	75.26	7.12	0.15	8.14	9.33	100

**PROBLEM 4**

Chloride ions are analytically determined by precipitating them with silver nitrate. The precipitate is undergoing decomposition in presence of light and forms elemental silver and chlorine. In aqueous solution the latter disproportionates to chlorate(V) and chloride. With excess of silver ions, the chloride ions formed are precipitated whereas chlorate(V) ions are not.

- 4.1** Write the balanced equations of the reactions mentioned above.
- 4.2** The gravimetric determination yielded a precipitate of which 12 % by mass was decomposed by light. Determine the size and direction of the error caused by this decomposition.
- 4.3** Consider a solution containing two weak acids HA and HL, 0.020 molar and 0.010 molar solutions, respectively. The acid constants are  $1 \times 10^{-4}$  for HA and  $1 \times 10^{-7}$  for HL. Calculate the pH of the solution.
- 4.4** M forms a complex ML with the acid H<sub>2</sub>L with the formation constant  $K_1$ . The solution contains another metal ion N that forms a complex NHL with the acid H<sub>2</sub>L. Determine the conditional equilibrium constant,  $K'_1$  for the complex ML in terms of  $[H^+]$  and  $K$  values.

$$K_1 = \frac{[ML]}{[M][L]}$$

$$K'_1 = \frac{[ML]}{[M'][L']}$$

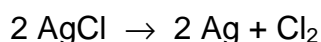
$[M']$  = total concentration of M not bound in ML

$[L']$  = the sum of the concentrations of all species containing L except ML

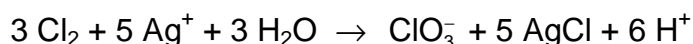
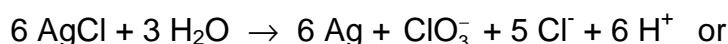
In addition to  $K_1$ , the acid constants  $K_{a1}$  and  $K_{a2}$  of H<sub>2</sub>L as well as the formation constant  $K_{NHL}$  of NHL are known.

$$K_{NHL} = \frac{[NHL]}{[N][L][H^+]}$$

You may assume that the equilibrium concentration  $[H^+]$  and  $[N]$  are known, too.

**SOLUTION**

Total:



4.2 From 100 g AgCl 12 g decompose and 88 g remain. 12 g equals 0.0837 mol and therefore, 0.04185 mol Cl<sub>2</sub> are liberated. Out of that  $(12 \times 107.9) / 143.3 = 9.03$  g Ag remain in the precipitate.  $5/6 \times 0.837$  mol AgCl are newly formed (= 10.0 g), so that the total mass of precipitate (A) yields:

$$A = 88 \text{ g} + 9.03 \text{ g} + 10.0 \text{ g} = \underline{107.03 \text{ g}}; \text{ relative error} = \underline{7.03 \%}$$



$$[\text{HA}] + [\text{A}^-] = 0.02 \text{ mol dm}^{-3} \quad \text{p}K(\text{HA}) = \text{pH} + \text{p}[\text{A}^-] - \text{p}[\text{HA}] = 4$$

$$[\text{HL}] + [\text{L}^-] = 0.01 \text{ mol dm}^{-3} \quad \text{p}K(\text{HL}) = \text{pH} + \text{p}[\text{L}^-] - \text{p}[\text{HL}] = 7$$

For problems like these, where no formal algebraic solution is found, only simplifications lead to a good approximation of the desired result, e.g.

1.  $[\text{H}^+] = [\text{A}^-]$  (since HA is a much stronger acid than HL then  $[\text{A}^-] \gg [\text{L}^-] + [\text{OH}^-]$ )

$$[\text{H}^+]^2 + K_{(\text{HA})}[\text{H}^+] - K_{(\text{HA})}0.02 = 0$$

$$[\text{H}^+] = 1.365 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = \underline{2.865}$$

2. Linear combination of the equations

$$[\text{H}^+] = K_{(\text{HA})} \frac{[\text{HA}]}{[\text{A}^-]} = K_{(\text{HL})} \frac{[\text{HL}]}{[\text{L}^-]};$$

$$[\text{HA}] = 0.02 - [\text{A}^-];$$

$$[\text{HL}] = 0.01 - [\text{L}^-];$$

$$[\text{H}^+] = [\text{A}^-] + [\text{L}^-] + [\text{OH}^-]$$

yields:

$$[A] = \frac{0.02 \times K_{(HA)}}{[H^+] + K_{(HA)}}$$

$$[L] = \frac{0.01 \times K_{(HL)}}{[H^+] + K_{(HL)}}$$

$$[H^+] = \frac{0.02 \times K_{(HA)}}{[H^+] + K_{(HA)}} + \frac{0.01 \times K_{(HL)}}{[H^+] + K_{(HL)}} + \frac{K_w}{[H^+]}$$

The equation above can only be solved by numerical approximation methods. The result is  $\text{pH} = 2.865$ . We see that it is not necessary to consider all equations. Simplifications can be made here without loss of accuracy. Obviously it is quite difficult to see the effects of a simplification - but being aware of the fact that already the so-called exact solution is not really an exact one (e.g. activities are not being considered), simple assumption often lead to a very accurate result.

#### 4.4

$$K_1 = \frac{[ML]}{[M]([L] + [HL] + [NHL] + [H_2L])} = \frac{K_1 [L]}{([L] + [HL] + [NHL] + [H_2L])}$$

$$[HL] = \frac{K_{a1} [H_2L]}{[H]}$$

$$[HL] = \frac{[L] [H]}{K_{a2}}$$

$$[L] = \frac{K_{a2} [HL]}{[H]} = \frac{K_{a1} K_{a2} [H_2L]}{[H]^2}$$

$$[NHL] = K_{NHL} [N] [L] [H]$$

$$K_1 = \frac{K_1}{\left[ 1 + \frac{[H]}{K_{a1}} + \frac{[H]^2}{K_{a1} K_{a2}} + K_{NHL} [N] [H] \right]}$$

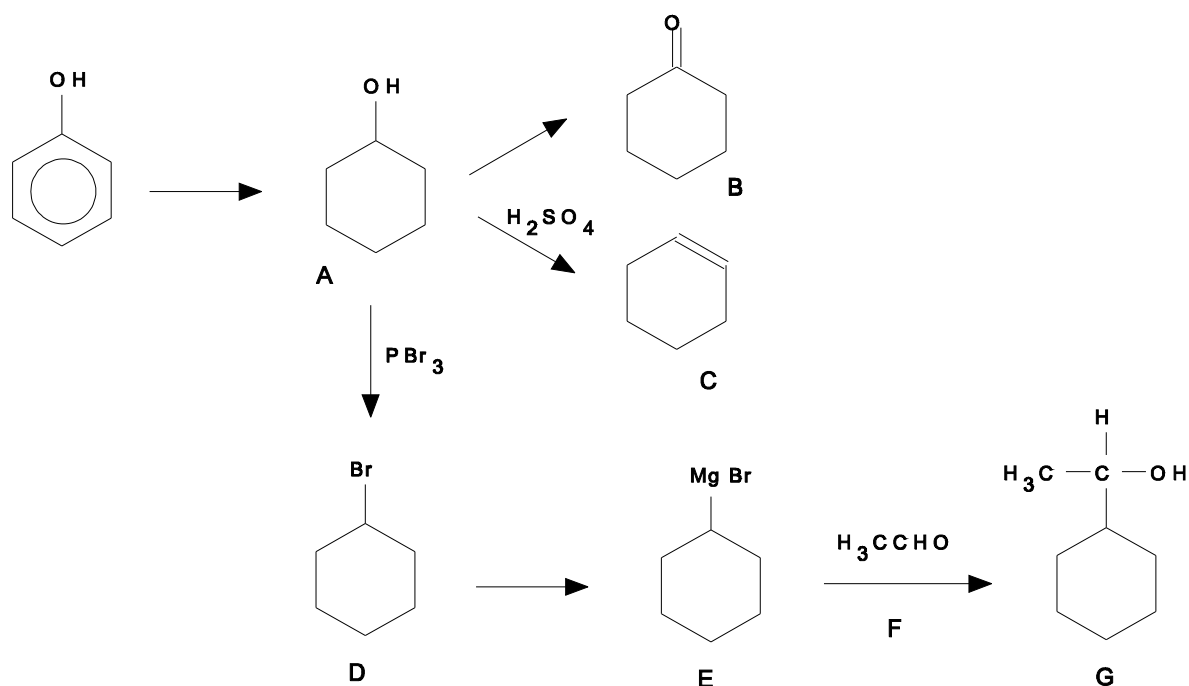
**PROBLEM 5**

A common compound **A** is prepared from phenol and oxidized to compound **B**. Dehydration of **A** with  $\text{H}_2\text{SO}_4$  leads to compound **C** and treatment of **A** with  $\text{PBr}_3$  gives **D**. In the mass spectrum of **D** there is a very strong peak at  $m/e = 83$  (base peak) and two molecular ion peaks at  $m/e = 162$  and  $164$ . The ratio of intensities of the peaks 162 and 164 is 1.02. Compound **D** can be converted to an organomagnesium compound **E** that reacts with a carbonyl compound **F** in dry ether to give **G** after hydrolysis. **G** is a secondary alcohol with the molecular formula  $\text{C}_8\text{H}_{16}\text{O}$ .

- 5.1 Outline all steps in the synthesis of **G** and draw the structural formulae of the compounds **A – G**.
- 5.2 Which of the products **A – G** consist of configurational stereoisomeric pairs?
- 5.3 Identify the three ions in the mass spectrum considering isotopic abundances given in the text.

**SOLUTION**

5.1



**5.2** **G** has two stereoisomeric pairs since it has a chiral carbon.

**5.3** The base peak at  $m/e = 83$  is due to the cyclohexyl-cation,  $C_6H_{11}^+$ , the peaks at  $m/e = 162$  and  $164$  show the same ratio as the abundance of the two bromine isotopes. Therefore, they are the molecular peaks of bromocyclohexane.

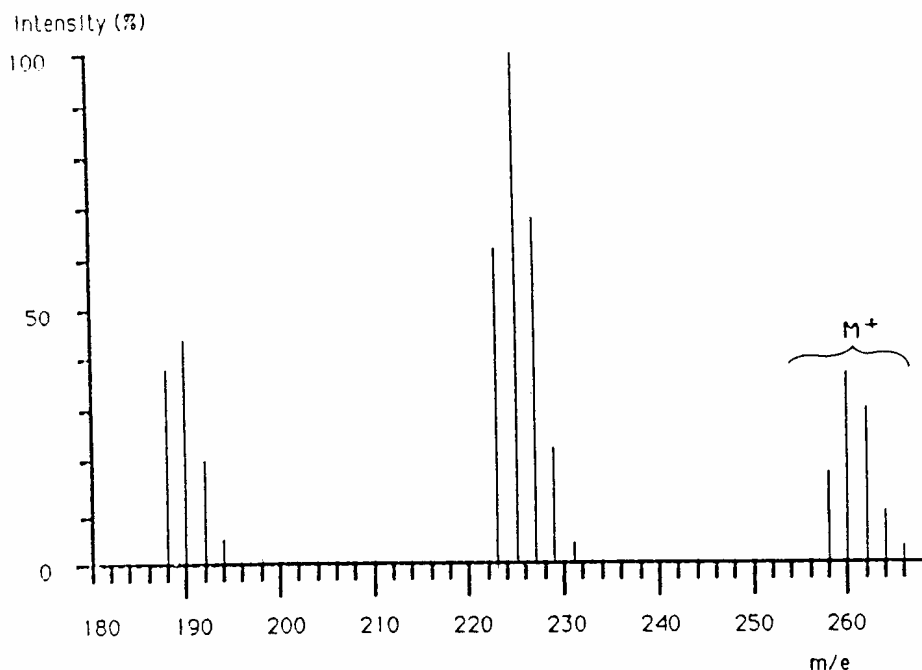
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## PROBLEM 6

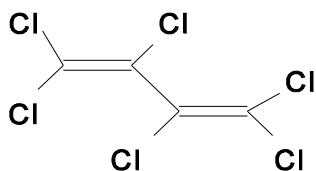
Upon analyzing sea mussels a new bio-accumulated pollutant **X** was found as determined by mass spectroscopy coupled to a gas chromatograph. The mass spectrum is illustrated in figure. Determine the structural formula of **X** assuming that it is produced out of synthetic rubber used as insulation in electrolysis cells that are used for the production of chlorine. Give the name of the compound **X**. The isotopic abundances of the pertinent elements are shown in the figure and table below. Intensities of the ions  $m/e = 196, 233, 268$  and  $270$  are very low and thus omitted. Peaks of the  $^{13}\text{C}$  containing ions are omitted for simplicity.



Element	Mass	Norm.abundanc	Mass	Norm.abundanc	Mass	Norm.abundanc
H	1	100.0	2	0.015		
C	12	100.0	13	1.1		
N	14	100.0	15	0.37		
O	16	100.0	17	0.04	18	0.20
P	31	100.0				
S	32	100.0	33	0.80	34	4.4
Cl	35	100.0			37	32.5
Br	79	100.0			81	98.0

**SOLUTION**

The molecule **X** is hexachlorobutadiene. Butadiene is the monomer of synthetic rubber and freed by decomposition:



**PRACTICAL PROBLEMS****PROBLEM 1 (practical)**Synthesis of a derivative (NaHX) of the sodium salt of an organic acid*Apparatus:*

1 beaker (250 cm<sup>3</sup>), 2 beakers (50 cm<sup>3</sup>), 1 pipette (10 cm<sup>3</sup>; graduated at intervals of 0.1 cm<sup>3</sup>), 1 measuring cylinder (50 cm<sup>3</sup>), 1 capillary pipette (Pasteur pipette), 1 thermometer, 1 filter crucible (G4), apparatus for suction filtering, 1 glass rod.

*Reagents:*

Sodium salt of 1-naphtol-4-sulfonic acid (S), (sodium 1-naphtol-4-sulfonate), ( $M = 246.22 \text{ g mol}^{-1}$ ), sodium nitrite ( $M = 69.00 \text{ g mol}^{-1}$ ), aqueous solution of HCl (2 mol dm<sup>-3</sup>), deionised water, absolute ethanol.

*Procedure:*

Mix the given lot of technical grade starting material, labelled I, (contains 1.50 g of sodium 1-naphtol-4-sulfonate, S) and 0.6 g of NaNO<sub>2</sub> with about 10 cm<sup>3</sup> of water in 50 cm<sup>3</sup> beaker. Cool in ice bath (a 250 cm<sup>3</sup> beaker) to the temperature 0 – 5 °C. Keeping the temperature in the 0 – 5 °C range, add dropwise 5 cm<sup>3</sup> of 2 M HCl (aq) to the reaction mixture. Stir for ten more minutes in an ice bath to effect the complete precipitation of the yellow-orange salt NaHX · n H<sub>2</sub>O. Weigh the filter crucible accurately (± 0.5 mg). Filter the product with suction in the crucible and wash with a small amount (ca. 5 cm<sup>3</sup>) of cold water and then twice (about 10 cm<sup>3</sup>) with ethanol. Dry the product in the filter crucible at 110 °C for 30 minutes. Weigh the air-cooled anhydrous material together with the crucible and present it to the supervisor.

Calculate the percentage yield of NaHX ( $M = 275.20 \text{ g mol}^{-1}$ ).

The purity of the product NaHX influences your results in Problem 2!

*Question:*

Write the reaction equation using structural formulae.

**PROBLEM 2 (practical)**

The spectrophotometric determination of the concentration, acid constant  $K_{a2}$  and  $pK_{a2}$  of  $H_2X$

*Apparatus:*

7 volumetric flasks (100 cm<sup>3</sup>), 2 beakers (50 cm<sup>3</sup>), 1 capillary pipette (Pasteur), 1 pipette (10 cm<sup>3</sup>; graduated in intervals of 0.1 cm<sup>3</sup>), 1 washing bottle, 1 glass rod, 1 container for waste materials, funnel.

*Reagents:*

Compound NaHX, aqueous stock solution of Na<sub>2</sub>X (0.00100 mol dm<sup>-3</sup>), aqueous solution of sodium perchlorate (1.00 mol dm<sup>-3</sup>), aqueous solution of HCl (0.1 mol dm<sup>-3</sup>), aqueous solution of NaOH (0.1 mol dm<sup>-3</sup>).

*Procedure:*

- a) Weigh accurately  $183.5 \pm 0.5$  mg of NaHX and dissolve it in water in a volumetric flask and dilute up to the 100 cm<sup>3</sup> mark. Pipette 15.0 cm<sup>3</sup> of this solution into another 100 cm<sup>3</sup> volumetric flask and fill up to the mark with water to obtain the stock solution of NaHX. If you do not use your own material, you will get the NaHX from the service desk.
- b) Prepare 5 solutions, numbered 1-5, in the remaining five 100 cm<sup>3</sup> volumetric flasks. These solutions have to fulfil the following requirements:
  - The total concentration of ( $[X^{2-}] + [HX^-]$ ) in each solution must be exactly 0.000100 mol dm<sup>-3</sup>.
  - The concentration of sodium perchlorate in each solution must be 0.100 mol dm<sup>-3</sup> to maintain constant ionic strength. The solutions are prepared by pipetting into each volumetric flask 1-5 the accurate volumes of the NaHX and Na<sub>2</sub>X stock solutions, adding a required volume of sodium perchlorate solution and filling up to the mark with water.
  - Solution 1 is prepared by pipetting the required amount of the stock solution of NaHX. Add ca. 3 cm<sup>3</sup> of HCl (aq) with the pipette to ensure that the anion is completely in the form  $HX^-$ , before adding the sodium perchlorate solution.

- Solution 5 is prepared by pipetting the required amount of the stock solution of Na<sub>2</sub>X which is provided for you. Add ca. 3 cm<sup>3</sup> of the NaOH(aq) to ensure that the anion is completely in the form X<sup>2-</sup>, before adding the sodium perchlorate solution.
- The three remaining solutions 2-4 are prepared by pipetting the stock solutions of NaHX and Na<sub>2</sub>X in the following ratios before adding the sodium perchlorate solution:

Solution No.	Ratio NaHX(aq) : Na <sub>2</sub> X(aq)
2	7 : 3
3	1 : 1
4	3 : 7

- c) Take the five volumetric flasks to the service centre where their UV-vis spectra will be recorded in the region 300-500 nm for you. In another service centre the accurate pH of each solution will be recorded. You may observe the measurements.
- d) From the plot of absorbance vs. wavelength, select the wavelength most appropriate for the determination of  $pK_{a2}$  of H<sub>2</sub>X, and measure the corresponding absorbance of each solution.
- e) Calculate the  $pK_{a2}$  of H<sub>2</sub>X from the pH-absorbance data when the ionic strength  $I = 0.1$  and the temperature is assumed to be ambient (25 °C). Note that:

$$K_{a2} = \frac{[H^+][X^-]}{[HX^-]} = \frac{c_{H^+} \times c_{X^{2-}}}{c_{HX^-}}$$

$$K_{a2} = \frac{(A - A_{HX^-})[H^+]}{(A_{X^{2-}} - A)} \quad \text{or} \quad A = A_{X^{2-}} - (A - A_{HX^-}) \frac{[H^+]}{K_{a2}}$$

$$pf_{H^+} = \frac{0.509 \times \sqrt{I}}{1 + \sqrt{I}}$$

- f) Which of your prepared solutions shows the largest buffer capacity? Calculate this buffer capacity,  $P$ , by any suitable method. You may use the equations given:

$$P = 2.3 \times \left( [OH^-] + [H^+] + \frac{K_a [H^+] C}{(K_a + [H^+])^2} \right)$$

$$P = 2.3 \times \left( \frac{K_w}{[H^+]} + [H^+] + \frac{[X^{2-}][HX^-]}{C} \right)$$

C is the total concentration of the acid.

$K_w = 2.0 \times 10^{-14}$  at  $I = 0.1$  and  $25\text{ }^\circ\text{C}$ .

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