## Problem 10 The Nature of Phosphorus

Phosphorus is an important element in naturally occurring as well as in man-made products. Typical examples are phospholipids, nucleic acids and ligands for efficient catalysts. Furthermore, $^{31}$P-NMR spectra can provide valuable information of P containing products. A characteristic feature of $^{31}$P-NMR spectra (interaction with protons is removed by decoupling) is the rather large chemical shift differences for structurally related structures. (Note: optical antipodes = enantiomers do not show a difference in NMR-spectra).

The dialkyl phosphite **A** is derived from racemic butan-2-ol and dialkyl phosphite **B** from enantiomerically (optically) pure (*S*)-butan-2-ol. The $^{1}$H-decoupled $^{31}$P-spectrum of **A** is shown in the figure. The spectrum of **B** shows only one peak and that has the same chemical shift as one of the signals of **A**.
Note: A dialkylphosphite has the formula $(RO)_2P\text{-}OH$.

**10-1** Draw the spatial structures and the corresponding Fischer projections of the stereoisomers that can account for the spectrum of **A** (Figure 1).
Draw the spatial structures and the Fischer projections of compound **B**.

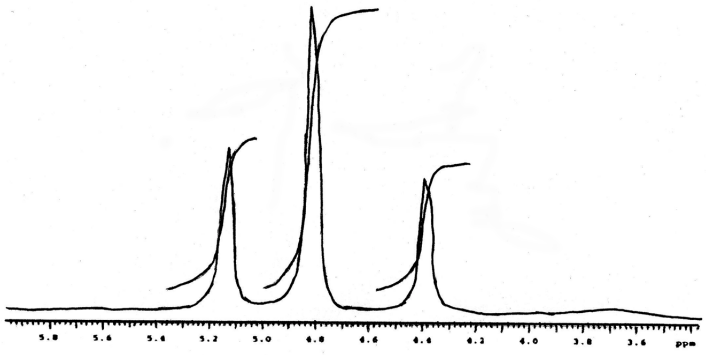


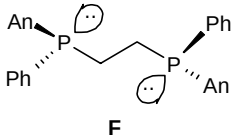
Figure: The $^{31}$P-NMR spectrum of **A** ($^{1}$H-decoupled).

Compound **C** is a dialkyl phosphite derived from methanol.
Compound **D** is a dialkyl phosphite derived from propan-2-ol.
Compound **E** is a dialkyl phosphite derived from racemic 1-phenylethanol.

**10-2** How many signals are present in the $^{31}$P-NMR spectra of the compounds **C**, **D** and **E**? If there is more than one signal, then indicate also the relative peak areas.

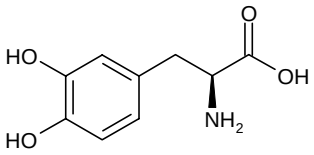
**10-3** Sketch the $^{1}$H-NMR spectrum of **A** (assume that there is no overlap of signals). Show the relative peak heights also for the splitting pattern of the signals.

William S. Knowles (Nobel prize 2001) used a rhodium catalyst containing the phosphorus-ligand **F** for the synthesis of L(-) DOPA which is an important anti-Parkinson drug.




**F**

Ph = $C_6H_5$
An = *ortho*-$CH_3O\text{-}C_6H_4$
is a lone pair of electrons




L (-) DOPA

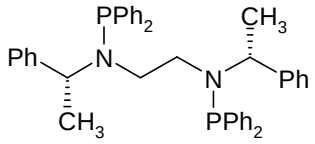
**10-4** Draw the spatial structures of all possible stereoisomers of compound **F** and indicate which of them would be suitable in an asymmetric synthesis of either L(-) or D(+) DOPA. (Use spatial structures as shown for **F**).

**10-5** In compound **F** phosphorus is pyramidal. This is:

- ❑ Absolutely essential for compound **F** to serve as a chiral ligand.
- ❑ Not essential at all.
- ❑ Only true when there is no pyramidal inversion.
- ❑ Only true at very high temperatures.

More than one correct answer is possible.

Later the ligand **G** was developed for the same purpose.




**G**

Ph = $C_6H_5$

**10-6** Draw the spatial structures of all possible stereoisomers of ligand **G** and indicate which of them would be suitable in an asymmetric synthesis of either L(-) or D(+) DOPA. (Use spatial structures as in the figure above).

**10-7** In ligand **G** phosphorus is pyramidal. This is:

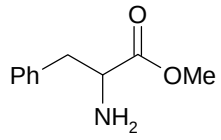
- ❑ Absolutely essential for compound **G** to serve as a chiral ligand.
- ❑ Not essential.
- ❑ Only true when there is pyramidal inversion.
- ❑ Only true at very high temperature.

More than one correct answer is possible.

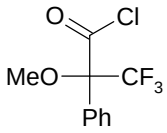
**10-8** How many signals will be present in the $^{31}$P-NMR spectrum of ligand **G**? If there is more than one signal then indicate also the relative peak areas.

## Problem 11 Optical Purity

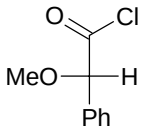
Antipodes (enantiomers) of optically active compounds have different physiological properties, e.g. the *R*-enantiomer of asparagine tastes sweet, whereas the *S*-enantiomer is bitter. In modern drug design utmost attention is paid to the optical purity of active ingredients. Phenylalanine is an amino acid that is a building block for pharmaceuticals. Enantiomers do not show different signals in the NMR-analysis. However, when suitable derivatives are made, different NMR signals may be possible. For this purpose, phenylalanine methyl ester **A**, which has an optical purity of 75%, is treated with optically pure Mosher's reagent **P** and optically pure reagent **Q** derived from mandelic acid in the presence of triethylamine, $(C_2H_5)_3N$.




**A**




**P**
Fischer projection




**Q**
Fischer projection

Me = $CH_3$
Ph = $C_6H_5$

**11-1** Draw the formulas of the derivatives which are obtained from compound **A** with reagent **P** and reagent **Q**.

**11-2** What is the function of triethylamine in this derivatization reaction? (Mark the correct answer)

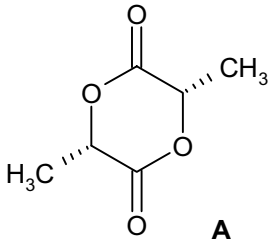
- ❑ To prevent racemization of ester **A**.
- ❑ To neutralize the hydrogen chloride formed.
- ❑ To activate ester **A**.
- ❑ To form a complex with excess reagent **P** or **Q**.

**11-3** Sketch the $^1$H-NMR signals for the following protons in the derivatives made in **11-1**.
(Note: Compound **A** has an optical purity of 75 %)
(a) The methoxy protons of the derivative from P.
(b) The methoxy protons of the derivative from Q.

**11-4** Sketch the $^{19}$F-NMR signal(s) for the derivative from P.

## Problem 12 Polylactic Acid

Polylactic acid (PLA) is an important biocompatible polymer. It is produced on a rather large scale in The Netherlands. The building block is (+)-lactic acid, which is obtained from sugar by fermentation. An attractive feature of PLA is its biodegradability. PLA is used in medical applications, e.g. medical implants and controlled drug delivery. High-molecular weight PLA can be obtained from either lactic acid or its cyclic dilactone **A**.




**A**

Cyclic dilactone of (+)-lactic acid

**12-1** Give the equation for the formation of the tetramer of PLA starting from lactic acid.

**12-2** Give the equation for the formation of the tetramer of PLA starting from cyclic dilactone **A**.

It is assumed that during the polymerisation of lactic acid the reaction volume does not change and that the equilibrium constant $K$ for the ester formation equals 4. The progress of polymerisation is $p$. The average polymer chain length $P = 1/(1-p)$. The polymerisation starts with U mol lactic acid.

**12-3** Calculate the maximal attainable average number of monomer units per chain when no water is removed.

**12-4** Calculate how much water has to be removed in the production of PLA from lactic acid to obtain an average number of monomer units per chain of 100, starting from 10 moles of lactic acid.

## Problem 13 A Chemical Puzzle

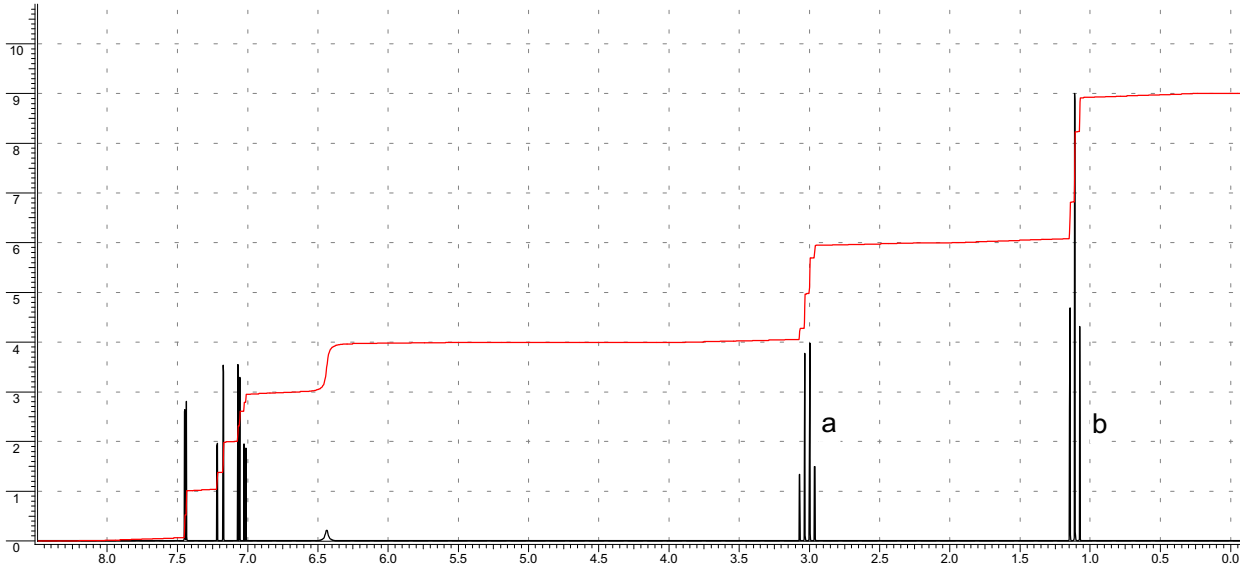
Compound **A** with the formula $C_8H_9N_2O_2Cl$ is insoluble in water and base. Compound **A** slowly dissolves in a dilute solution of hydrochloric acid.

**13-1** Which atom of **A** is involved in the reaction with HCl?

Compound **A** readily reacts with acetyl chloride yielding a product which is insoluble in acid and base.

**13-2** Which functional group(s) in **A** can account for this reaction with acetyl chloride?

The $^1$H-NMR spectrum of **A** is shown in the figure:




**13-3** Which groups can account for the signals a and b?

Compound **A** reacts with Sn/HCl to give, after work-up, compound **B** with the formula $C_8H_{11}N_2Cl$.

**13-4** Which functional group is involved in this reaction with Sn/HCl?

**13-5** Draw the structure(s) of **A** that can be deduced on the basis of the information given. (Hint: Compound **A** does not react with a solution of silver nitrate, even not on heating).

## Problem 14 Delft Blue and Vitamin B 12

The typical blue color of the famous Delft pottery originates from the absorption of red and green light by $Co^{2+}$ ions which are incorporated in the thin layer of glaze on the pottery. The glaze is made by mixing a cobalt salt with the glass forming components, e.g. silicate, borate and sodium. Upon heating, a thin glass layer is formed which contains $Co^{2+}$ ions. The $Co^{2+}$ ion is a transition metal ion which has a partially filled 3d orbital. The color of the 3d transition metal ions is caused by electronic transitions between lower and higher energy 3d orbitals which are split by the crystal field.

**14-1** What is the full electron configuration of $Co^{2+}$ ?
(atomic number of Cobalt = 27)

Answer box

**14-2** Sketch the shape of the five 3d orbitals. Draw also the *x*-, *y*- and *z*-axes.

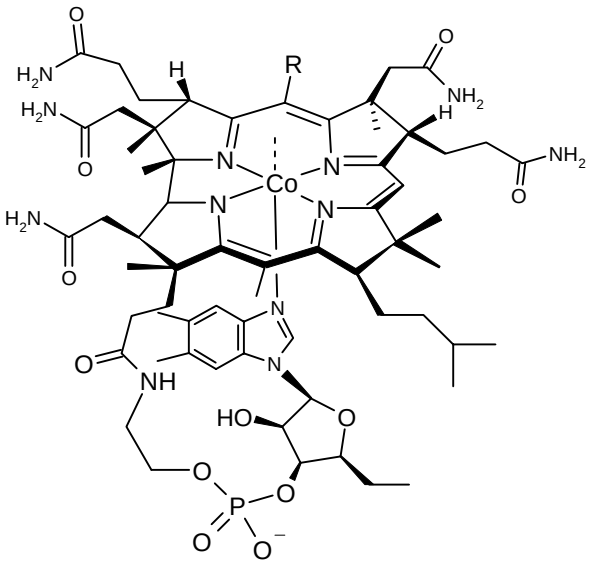
Answer box

The transitions between 3d orbitals are not very strong. The molar absorption coefficient for $Co^{2+}$ in the green and red is about 20 $M^{-1}cm^{-1}$. For an intense blue color about 90% of the red and green light needs to be absorbed.

**14-3** Calculate the concentration of $Co^{2+}$ in the glaze if the thickness of the glaze layer is 1 mm. (Hint: Use the Lambert-Beer law).

Answer box

In the body trace amounts of Co ions are present, mainly incorporated in vitamine $B_{12}$. The total amount of Co in a human body of 70 kg is about 3 mg. In 1964 Dorothy Crowfoot-Hodgkin received the Nobel Prize for the structure determination of this vitamin. The structure is shown below. The oxidation state of Co can vary. Common oxidation states are 2+ or 3+, but in the vitamine $B_{12}$ also $Co^{+}$ is possible.



Vitamine $B_{12}$ (R = adenosyl)

**14-4** Arrange the Co ions in order of increasing ionic radii for the three different oxidation states.

| |
|---|
| |

Answer box

**14-5** For which oxidation states of Co ions (1+, 2+, 3+) do you expect to see a signal in an EPR (Electron Paramagnetic Resonance) spectrum? Assume a high-spin configuration in all oxidation states.

| | |
|---|---|
| $Co^{+}$ | yes / no |
| $Co^{2+}$ | yes / no |
| $Co^{3+}$ | yes / no |

Answer box

**14-6** Calculate how many Co ions are present in a human body of 70 kg.
(Atomic mass of Co = 58.93.)

| |
|---|
| |

Answer box

**14-7** What is the coordination number of cobalt in the vitamine $B_{12}$ complex?
(mark the correct answer)

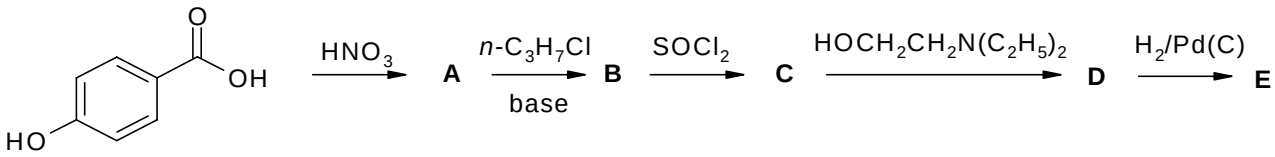
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|

Answer box

## Problem 15 Synthesis of a Local Anaesthetic

The development of new pharmaceutical drugs depends heavily on organic synthesis. Molecular fine-tuning is often required to obtain the desired properties. Here the synthesis of the local anaesthetic proparacaine (also called proxymetacaine), which is used in treatment of eye problems, is considered.

**15-1** Complete the synthetic scheme by drawing the structures **A**, **B**, **C**, **D**, and **E**.




It may be assumed that all products are properly isolated.

**15-2** Which nitration product(s) will be obtained when *meta*-hydroxybenzoic acid is taken as the starting material? Draw the structure(s).

**15-3** When *tert*-$C_4H_9Cl$ is used in the second step instead of *n*-$C_3H_7Cl$, this will lead to:

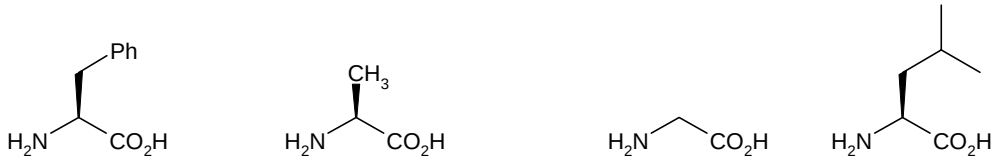
- ❑ A similar product as **B**, if so give the structure.
- ❑ No reaction at all.
- ❑ Decomposition of the *tert*-$C_4H_9Cl$.
- ❑ An aromatic substitution reaction.

Mark the correct answer.

## Problem 16 Structure of Peptides

Proteins are present in all living cells and fulfil numerous functions in the chemistry of life. They are composed of α-aminocarboxylic acids. Peptides are 'small' proteins with a relative small number of amino acids. The peptide bond, is an amide bond formed by interaction of the amino group of an amino acid with the carboxylic acid group of its neighbour.

**16-1** Which dipeptides can be derived from phenylalanine F and alanine A? Give the structures.




In the structure analysis of peptides the *N*-terminal and *C*-terminal residues play an important role. Sanger's method for the determination of the *N*-terminal residue (this is the amino acid unit in the peptide with the free $NH_2$ group) involves treatment with 2,4-dinitrofluorobenzene under mild alkaline conditions, followed by a total acid hydrolysis of all peptide linkages. The *N*-terminal amino acid then has a yellow tag which can readily be spotted in the paper chromatographic analysis. Sanger received the Nobel prize in 1958 and 1980.

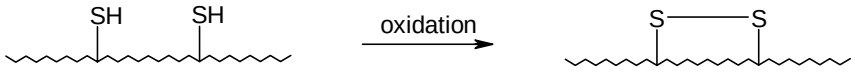
**16-2** Which reaction takes place with Sanger's reagent (for reason of simplicity write the *N*-terminal side of the peptide as $H_2NR$). Give the equation.

The *C*-terminal residue, which contains the free $CO_2H$ group in the peptide, is performed by a selective enzymatic hydrolysis of the *C*-terminal amino acid unit by carboxypeptidase (from the pancreas). For a tetrapeptide composed of the amino acids F, A, glycine G and Leucine L the *C*-terminal residue was identified as F. Sanger's method indicated that the *N*-terminal unit is G.

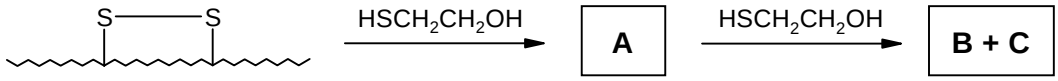
**16-3** Deduce the possible structure(s) of this tetrapeptide. Give the structure(s).

## Problem 17 Ribonuclease

Bovine pancreatic ribonuclease A is an enzyme that digests RNA. It is very stable. It retains its activity after heating in water at $100^{o}$ C and pH 7, while practically all other enzymes are inactivated by that treatment. The stability of ribonuclease A is attributed to an unusually stable 3D-structure kept together by four S-S bridges between its eight cysteine residues. The S-S bridges are formed by oxidation of the thiol groups present in the cysteine residues, according to the equation:




**17-1** Reducing agents such as 2-mercaptoethanol can cleave the S-S bridges. Complete the equation for this cleavage using two equivalents of 2-mercaptoethanol. Draw the structures **A**, **B** and **C**.




**17-2** Which other factors are known to determine the 3D structure of a protein?

- ❑ High proline content
- ❑ Atmospheric pressure
- ❑ Electrostatic forces
- ❑ Gravity
- ❑ Hydrogen bonds
- ❑ Magnetic forces
- ❑ The size of the organism (large animals have more stable proteins)
- ❑ van der Waals forces.

Mark your answer, more than one answer may be correct.

Treatment of ribonuclease A with 8 M urea $H_2NC(=O)NH_2$ in the presence of 0.01 M 2-mercaptoethanol results in a complete disappearance of the enzymatic activity by disruption of S-S bridges. Slow removal of the urea and 2-mercaptoethanol by means of dialysis together with re-oxidation in the presence of oxygen restores the enzymatic activity. This classical experiment carried out by Christian Anfinsen nearly fifty years ago was interpreted as the proof that proteins spontaneously fold into their native, biologically active, 3D-conformation. In a modified experiment Anfinsen only removed the 2-mercaptoethanol and brought it, still in the presence of 8 M urea, in contact with oxygen. Now S-S bridges were formed at random. Subsequent removal of urea led to the restoration of approximately 1 % of the enzymatic activity.

Assume that only one specific set of S-S bridges out all possible combinations renders the protein enzymatically active. Assume also that every possible combination of S-S bridges has an equal probability of being formed under the experimental conditions described.

**17-3** Calculate the resulting fraction of enzymatically active ribonuclease A.

## Problem 18 Enzyme Kinetics

Reactions with enzymes play an important role in chemistry. Kinetic analyses of these reactions help to understand the typical behaviour of enzymes. An enzymatic reaction of substrates A and B with an enzyme E can be described by the equations (1)-(5):

| | | |
|---|---|---|
| (1) | $E + A \rightleftharpoons EA$ | equilibrium constant $K_A$ |
| (2) | $E + B \rightleftharpoons EB$ | equilibrium constant $K_B$ |
| (3) | $EB + A \rightleftharpoons EAB$ | equilibrium constant $K'_A$ |
| (4) | $EA + B \rightleftharpoons EAB$ | equilibrium constant $K'_B$ |
| (5) | $EAB \longrightarrow$ products | reaction velocity $v = k\,[EAB]$ |

When the rate constant is small, the equillibria (1)-(4) are hardly shifted due to the reaction (5). This leads to expression (6) in which $V_{max}$ is the maximal velocity of the reaction, that is reached when the enzyme is saturated with the substrates (all enzyme is bound to A and B).

$$(6) \qquad v = \frac{V_{max}}{1 + K_A/[A] + K_B/[B] + K_A K'_B/[A][B]}$$

**18-1** Give the equilibrium constant $K_A$, $K_B$, $K'_A$ and $K'_B$ in terms of the respective concentrations.

Consider the enzymatic hydrolysis of maltose by the enzyme α-glucosidase from yeast.

$$(7) \qquad \text{maltose} + H_2O \longrightarrow 2\ \text{glucose}$$

The substrate maltose is usually present in concentrations ranging from $10^{-4}$ to $10^{-1}$ M. Water is the solvent, thus its concentration is practically constant at 55.6 M. Expression (6) can now be simplified by letting [B] approach infinity.

**18-2** Give the simplified expression. NB: This simplified expression is the famous Michaelis-Menten equation for an enzymatic reaction with one substrate.

**18-3** (a) Simplify the Michaelis-Menten equation further by taking [A] as very small (thus approaching zero).
(b) The order n of a reaction is defined by $v = k\ c^n$. Thus, for n=1 the kinetics are first order. What is the n of the reaction [A] $\longrightarrow$ 0.

**18-4** (a) Simplify the Michaelis-Menten equation by taking [A] as very high, thus [A] $\longrightarrow \infty$, which is the case when the enzyme is completely saturated with substrate.
(b) What is the order n of the reaction for [A] $\longrightarrow \infty$.

**18-5** The constant $K_A$ is a measure for the affinity of an enzyme for its substrate. Does a high affinity correspond with a high or low value for $K_A$? At which velocity is [A] = $K$?

**18-6** Draw a graph of v versus [A] (take [A] at the x-axis). Indicate $V_{max}$ and $K_A$ in this graph.

An enzymatic reaction can be strongly retarded or blocked by an inhibitor I according to the equation:

$$(8) \qquad E + I \rightleftharpoons EI$$

with equilibrium constant $K_I$. For competitive inhibition the inhibitor competes with the substrate at the binding side of the enzyme, thus the reaction is slowed down but leaving $V_{max}$ unaffected. In the Michaelis-Menten equation $K_A$ is then multiplied by a factor $(1+[I]/K_i)$, which equals 1 for [I] = 0 and is large when [I] is large. For non-competitve inhibition I does not compete with A; $K_A$ is not affected, $V_{max}$ is lowered. In the Michaelis-Menten equation $V_{max}$ is then divided by the factor $(1+[I]/K_I)$. In order to investigate the hydrolysis by α-glucosidase the model substrate *p*-nitrophenyl- α-D-glucoside (PNPG) is used instead of maltose, whereby the release of the yellow *p*-nitrophenol is monitored spectrophotometrically. The following experiment is carried out: PNPG is used in the presence of maltose to measure the activity of glucosidase.

**18-7** Which situation applies:

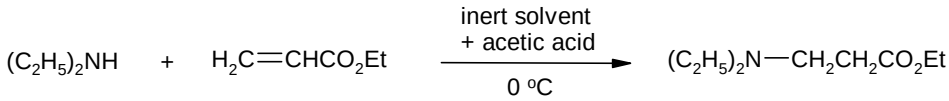
- ❑ The maltose does not influence the rate of release of *p*-nitrophenol.
- ❑ Maltose functions as a competitive inhibitor.
- ❑ Maltose functions as a non-competitive inhibitor.

Mark the correct answer.

**18-8** Draw a graph of $V$ versus [A] (take [A] at the x-axis) for the release of *p*-nitrophenol in the presence of maltose for [maltose] $= K_{maltose}$. Insert the graph made in question **18-6**. Mark the points $V_{max}$ en ½ $V_{max}$.

## Problem 19 Dendrimers: Tree-like Macromolecules

Dendrimers are fascinating highly branched macromolecules with tree-like structures. One method of preparation of these compounds makes use of the Michael addition reaction, a simple example of which is shown below:




A dendrimer can be obtained by the following sequence of reactions:
(1) $NH_3$ is treated exhaustively with an excess of acrylonitrile ($H_2C$=CH-C≡N) to give a product that contains 3 cyanide groups.
(2) This product is reduced catalytically with $H_2$ and a catalyst to produce a molecule with three primary amines.
(3) This primary amine is treated again with an excess of acrylonitrile.
(4) The product of step (3) is again hydrogenated with $H_2$ and a catalyst to give a hexa-amine. This is the beginning of a branched macromolecule.

**19-1** (a) Give the equation of the reaction of step (1).
(b) Give the equation of the reaction of step (2).
(c) Give the structure of the product from step (3).
(d) Give the structure of the hydrogenated product from step (4).

The sequence of treatment with acrylonitrile and subsequent reduction of the cyanide group can be repeated several times, leading finally to a spherical type of molecule, with primary amine groups on the surface.

**19-2** Calculate how many primary amine end-groups are present in the dendrimer after 5 full cycles (the first cycle consists of steps 1 + 2).

**19-3** (a) Calculate the amount of hydrogen in moles per mole $NH_3$, needed for 5 cycles.
(b) Calculate the number of moles of acrylonitrile needed for 5 cycles.
(c) The dendrimer increases in diameter by about 10 Å per cycle. Calculate the volume of the dendrimer after 5 cycles.

## Problem 20 Carvone

The natural compound *l*-carvone is found in spearmint and gingergrass oil. *l*-Carvone has a negative optical rotation. Its enantiomer *d*-carvone which has a positive optical rotation is present in caraway seeds. Carvone has been analysed and consists of 80.00% carbon, 9.33% hydrogen and 10.67% oxygen. Mass spectrometry indicates that the molecular mass of carvone = 150. The NMR and IR spectra of carvone are shown below. In the UV spectrum of carvone there is a strong absorption maximum at 238 nm.

**20-1** Calculate the molecular formula of carvone.

**20-2** Calculate the number of unsaturation of carvone.

**20-3** Which functional group is responsible for the strong absorption at 1680 $cm^{-1}$ in the IR spectrum?

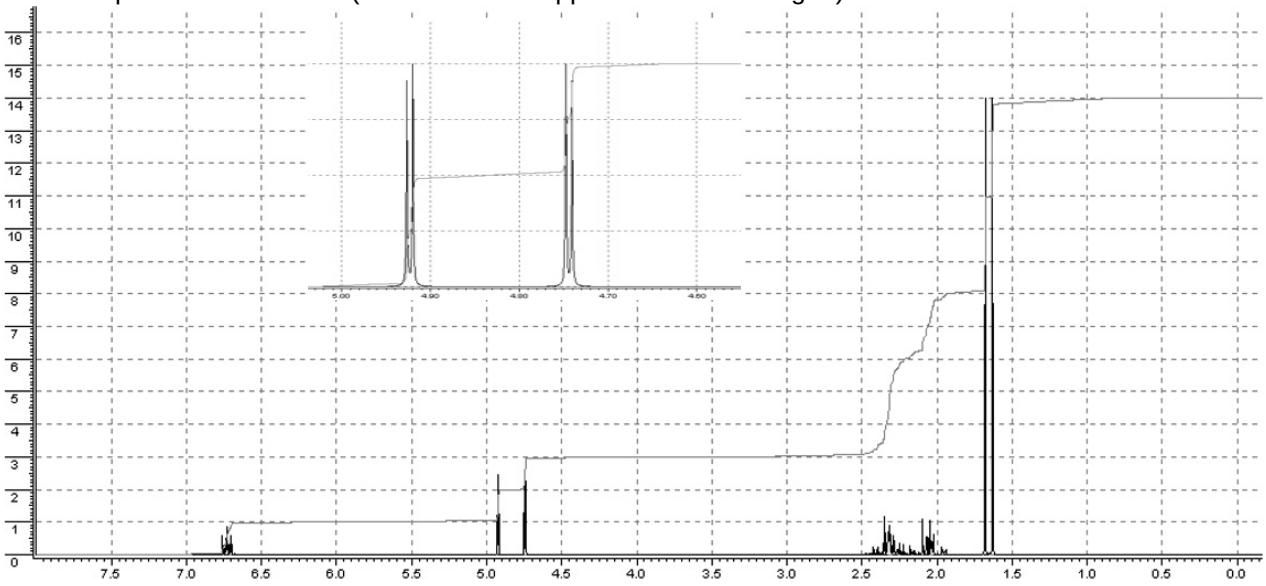
**20-4** In the IR-spectrum there is no absorption above 3000 $cm^{-1}$. Indicate which type of functional group is absent in carvone.

In the 200 MHz $^1$H-NMR spectrum the type of the signals is as follows (we do not consider long range couplings).

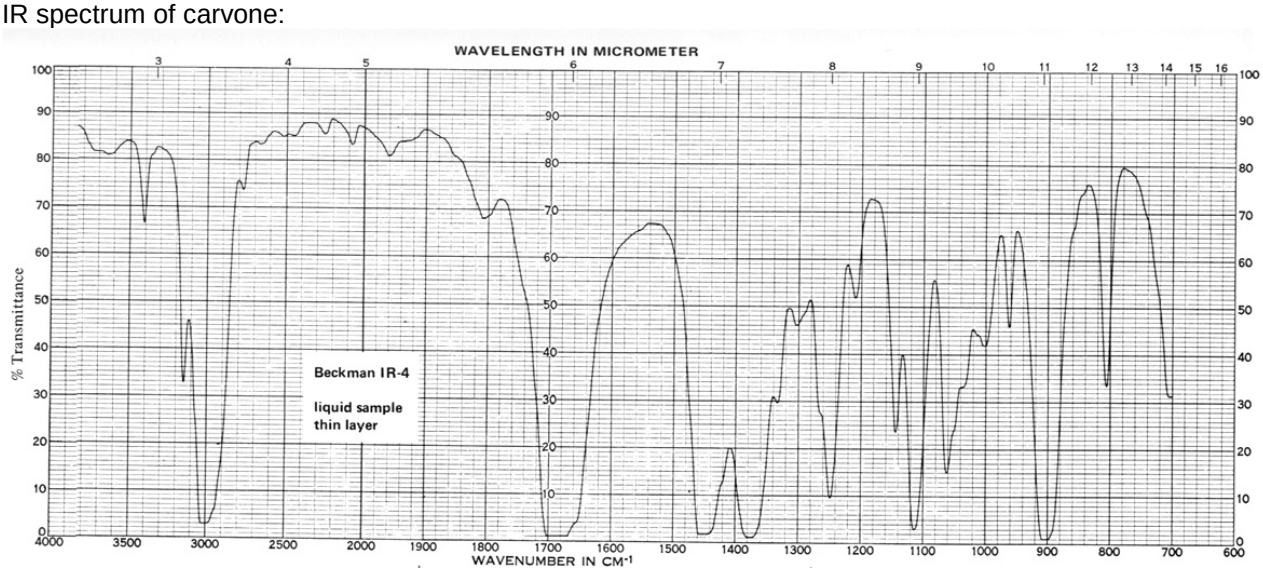
| δ (ppm) | Type | Integration |
|---|---|---|
| 1.63 | singlet | 3 |
| 1.68 | singlet | 3 |
| 1.9-2.2 | multiplet | 2 |
| 2.2-2.5 | overlapping multiplets | 3 |
| 4.75 | doublet | 1 |
| 4.93 | doublet | 1 |
| 6.73 | triplet | 1 |

**20-5** Propose the most likely structure for carvone when it is given that it is a 1,2,4 trisubstituted 6-membered ring system. (The overlapping multiplets consist of a CH and a $CH_2$ signal).

$^1$H-NMR spectrum of carvone (the area 4.5-5.0 ppm has been enlarged)



IR spectrum of carvone:



## Problem 21 Electrochemical Energy Conversion

Mobility is of vital importance for our modern society. Electric cars are under active development to ensure our future needs of transportation. One of the major problems for electrically driven vehicles is the supply of a suitable source of electricity. Batteries have the drawback that they must be recharged, thus the action radius is limited. The in situ generation of electricity in fuel cells is an attractive alternative. A fuel cell, or flow battery, is a galvanic cell for which the reactants are continuously supplied. Fuel cells utilize combustion reactions to produce electricity. The reactants undergo half-reactions at the electrodes, and the electrons are transferred through an external circuit. The electrodes are separated by an ionically conducting liquid or a molten or solid electrolyte. The electrode half-reactions for a hydrogen-oxygen fuel cell with a concentrated potassiumhydroxide electrolyte are:

$$O_2\,(g) + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-\,(aq) \quad (1)$$
$$H_2\,(g) + 2\,OH^-\,(aq) \rightarrow 2\,H_2O + 2\,e^- \quad (2)$$

The fuel-cell reaction, after making electron loss equal to electron gain, is:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O \quad (3)$$

The reaction product is water! and the efficiency is about 50-60%.

**21-1** Which reaction occurs at the cathode.

**21-2** Which reaction occurs at the anode.

**21-3** Give the electrode reactions when the electrolyte is phosphoric acid.

The change of the Gibbs energy $\Delta G_o$ is a measure of the driving force of a reaction. The change of energy is given by:

$$\Delta G_o = - n\,F\,E$$

where $n$ is the number of electrons transferred in the reaction and $F$ is the Faraday constant (96487 $C$). The standard electrode potential for $O_2$ (g) at 25 °C is + 1.23 V.

**21-4** Calculate the $\Delta G_o$ of the fuel-cell reaction under acidic conditions (see **21-3**).

The production of usable energy by combustion of fuels is an extremely inefficient process. In The Netherlands natural gas is a highly attractive energy source as it is abundantly available. Modern electric power plants are able to furnish only 35-40% of the energy theoretically available from natural gas. The exothermic reaction of natural gas (methane) with oxygen is:

$$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g) + \text{energy}$$

Usually, the energy released from this reaction is used indirectly to heat houses or to run machines. However, in a high-temperature ceramic fuel cell based on a solid oxide-ion conducting electrolyte, natural gas can be utilized directly, without a catalyst and with a high efficiency of conversion (75%). The net fuel-cell reaction is:

$$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

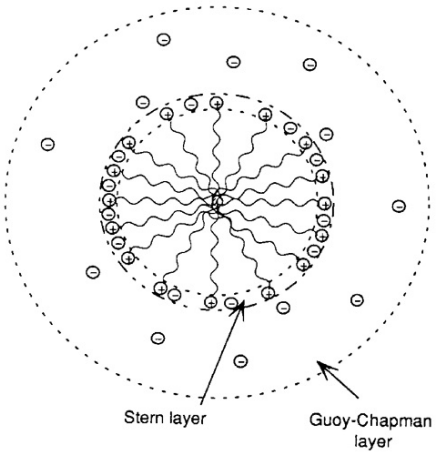
**21-5** Give the reactions at the anode and the cathode.

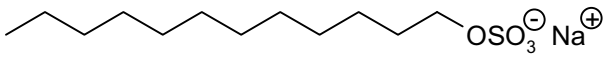
Another high-temperature fuel cell utilizes molten carbonate as the ionically conducting electroyte. Hydrogen is used as fuel, oxygen is mixed with $CO_2$.

**21-6** Give the half-reactions at the anode and cathode, and the net fuel-cell reaction.

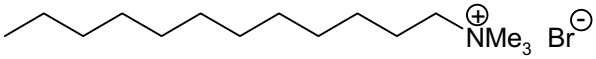
## Problem 22 Micelles

Biomembranes fulfil many important functions in the living cell. Membranes in plant and animal cells contain 40-50% lipids and 50-60% proteins. Phospholipids, which are key constituents in biomembranes, have hydrophobic fatty acid tails and polar hydrophilic head groups. Such structures are commonly called amphiphiles. Knowledge of membranes is obtained from studies of the aggregation behavior of amphiphiles with a simple(r) molecular structure. Typical aggregates are micelles, mono- and bilayer structures and vesicles (liposomes). Single-tailed surfactant molecules like sodium *n*-dodecylsulfate (*SDS*) and *n*-dodecyl-trimethylammonium bromide (*DTAB*) cooperatively form micelles upon dissolution in water above the critical micelle concentration (CMC). The structure of micelles is pictured in the figure. In these micelles, a central hydrophobic core can be recognized and a layer containing head groups and some counter ions (Stern layer) and an outer shell with hydrated counter ions (Guoy-Chapman layer). For micelles of *SDS* the central core has a radius of 16.6 Å and the Stern layer has a thickness of 4.6 Å.




(*SDS*)




(*DTAB*)

| Amphiphile | CMC (mmol $L^{-1}$) | Relative micelle mass (g $mol^{-1}$ x $10^3$) |
|---|---|---|
| *SDS* | 8.1 | 18.0 |
| *DTAB* | 14.4 | 15.0 |

**22-1** Calculate the volume of the Stern-layer in this micelle of *SDS*.

In a simplified model, micelle formation can be expressed by the equilibrium:

$$n\,S + n\,B \rightleftharpoons M$$

wherein S is the amphiphile, B is the counter ion and n is the number of molecules involved. The standard Gibbs energy of micelle formation per S is expressed by:

$$\Delta G_M = -\frac{RT}{n} \ln K_M$$

$K_M$ is the equilibrium constant. At the critical micelle concentration [M] = 0. Furthermore, assume that [S] is approximately equal to [B]. $R$ is the gas constant (8.314 J $mol^{-1}$ $K^{-1}$).

**22-2** Calculate $\Delta G_M$ for the micelle formation of *SDS* and of *DTAB*.

**22-3** Calculate the number of amphiphile molecules in the micelles of *SDS* and of *DTAB.*

## Problem 23 A Ceramic Hard Coating

BP (boron phosphide) is a valuable wear-resistant hard coating that is produced by the reaction of boron tribromide and phosphorus tribromide under a hydrogen atmosphere at high temperature (>750°C). This ceramic material is used as a protecting thin film on metal surfaces. BP crystallizes in a cubic-close-packed structure with tetrahedral surrounding.

**23-1** Give the equation for the formation of BP.

**23-2** Draw the Lewis structures of boron tribromide and phosphorus tribromide.

**23-3** Draw the structure of BP in the crystalline state.

**23-4** Give the overall composition of the unit cell corresponding with the formula BP.

**23-5** Calculate the density of BP in $kg \cdot m^{-3}$ when the lattice parameter of the unit cell is 4.78 Å.

**23-6** Calculate the distance between a boron and a phosphorus atom in BP.

The Born-Lande formula given below can be used to calculate the lattice energy:

$$U_{lattice} = -f \frac{Z_+ Z_- Ae^2}{r_+ + r_-} \left(1 - \frac{1}{n}\right)$$

The factor $fe^2$ amounts to 1390 when the ionic radii $r_+$ and $r_-$ are given in Å. The Madelung constant is 1.638. The Born exponent is n is 7. The charges of the ions $Z_+$ and $Z_-$ are integer numbers.

**23-7** Calculate the lattice energy of BP.

The rate (r) of formation of BP depends on the concentration of the reactants as given in the table

| Temperature, $^oC$ | $[BBr_3]$ mol $L^{-1}$ | $[PBr_3]$, mol $L^{-1}$ | $[H_2]$, mol $L^{-1}$ | r, mol $s^{-1}$ |
|---|---|---|---|---|
| 800 | $2.25 \times 10^{-6}$ | $9.00 \times 10^{-6}$ | 0.070 | $4.60 \times 10^{-8}$ |
| 800 | $4{,}50 \times 10^{-6}$ | $9.00 \times 10^{-6}$ | 0.070 | $9.20 \times 10^{-8}$ |
| 800 | $9.00 \times 10^{-6}$ | $9.00 \times 10^{-6}$ | 0.070 | $18.4 \times 10^{-8}$ |
| 800 | $2.25 \times 10^{-6}$ | $2.25 \times 10^{-6}$ | 0.070 | $1.15 \times 10^{-8}$ |
| 800 | $2.25 \times 10^{-6}$ | $4{,}50 \times 10^{-6}$ | 0.070 | $2.30 \times 10^{-8}$ |
| 800 | $2.25 \times 10^{-6}$ | $9.00 \times 10^{-6}$ | 0.035 | $4.60 \times 10^{-8}$ |
| 800 | $2.25 \times 10^{-6}$ | $9.00 \times 10^{-6}$ | 0.070 | $19.6 \times 10^{-8}$ |

**23-8** Determine the order of the reaction leading to BP and give the equation.

**23-9** Calculate the rate constants at 800 and 880 $^oC$.

**23-10** Calculate the activation energy for the formation of BP.