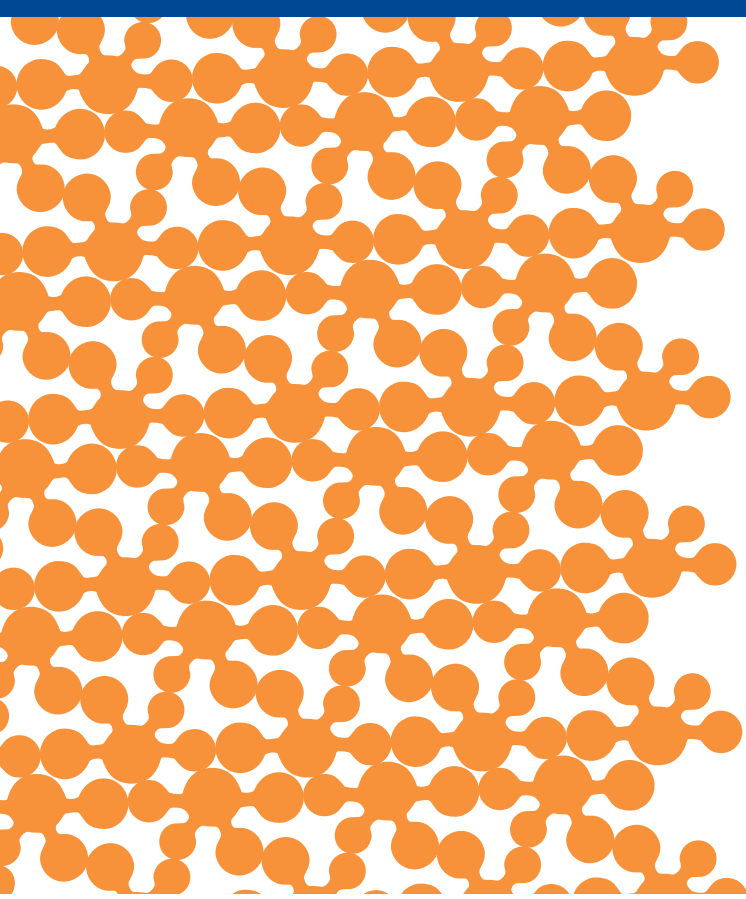


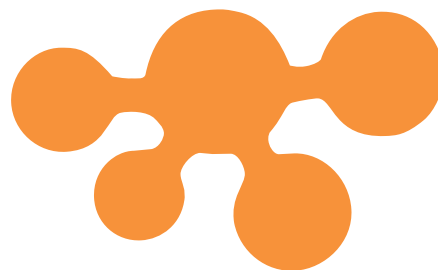
# Preparatory Problems



**ICHO34**  
**2002**

**GRONINGEN**  
The Netherlands

5 - 14 JULY



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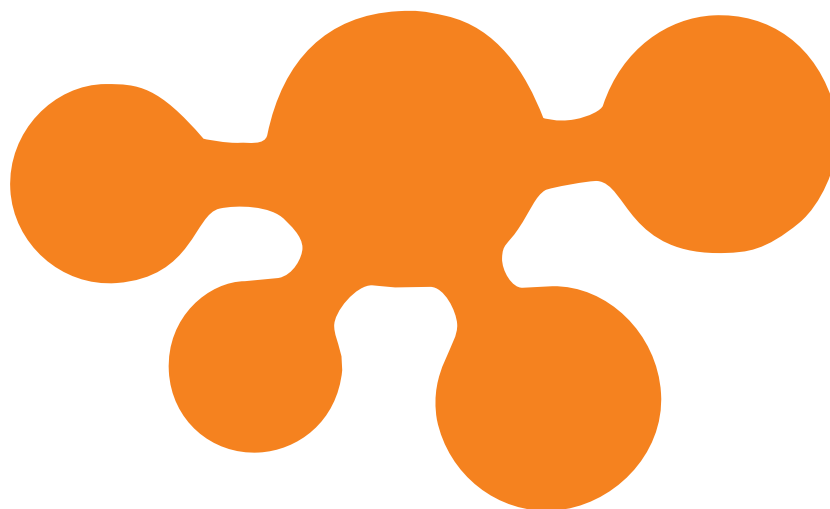
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**Preparatory Problems**

34th International Chemistry Olympiad

Editors: Binne Zwanenburg and René Ruinaard

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# Preface

This booklet contains a series of preparatory problems for the International Chemistry Olympiad in 2002. Most of the problems refer to level 3 mentioned in the Syllabus of the International Chemistry Olympiad. Topics from various areas of chemistry are covered. The scientific committee selected problems which reflect the relevance of modern chemistry and which receive current interest. Of course, problems concerning the understanding of chemistry in qualitative and quantitative terms are included as well.

While working on the problems students will encounter, for example, the chemistry of lactose, which is the by-product of Dutch cheese making, how whales manage to stay under water for a considerable length of time, how the color of Delft blue pottery can be understood, how a bio-compatible polymer can be made from lactic acid, how modern spectroscopy is applied, how the structure of the natural product carvone can be unravelled, how aspects of green chemistry can be treated more quantitatively, how detergents aggregate to give micelles, how a hard coating can be made, and how fuel cells can produce electricity.

In the practical problems microscale equipment will be used. The synthesis of some organic compounds, the use of thin-layer chromatography, the quantitative analysis using spectroscopic methods and the use of enzymes are illustrative for this section.

We recommend that students try to withstand the temptation to look too early at the answers which are included in this booklet. Students will benefit most from these preparatory problems when they try to solve the problems on their own.

It should be emphasized that in answering the questions concise but clear answers must be given. During the Olympiad answer boxes will be provided and the students must give the answers in that box. For two problems such answer boxes have been included in this booklet.

We hope that students and their teachers will consider the problems described in this booklet as a stimulus for the preparation for the competition during the Olympiad in July 2002.

We wish you good luck and hope to welcome you in Groningen.

## Acknowledgement

We thank the members of the Scientific Committee for their invaluable contribution in making suitable and relevant problems for the Olympiad in The Netherlands. The contents of this booklet is the result of real teamwork. We owe a special word of thanks to Peter de Groot, Dolf Witte, Ton van Weerd and Wout Davids who served as consulting members of the committee. Their critical comments and constructive remarks were highly appreciated. We also thank Dr. Gordon J.F. Chittenden for proof-reading the manuscript and correcting the English.

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René Ruinaard  
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# Syllabus of the International Chemistry Olympiad

**Level 1:** These topics are included in the overwhelming majority of secondary school chemistry programs and need not to be mentioned in the preparatory problems.

**Level 2:** These topics are included in a substantial number of secondary school programs and maybe used without exemplification in the preparatory problems.

**Level 3:** These topics are not included in the majority of secondary school programs and can only be used in the competition if examples are given in the preparatory problems.

## 1 INORGANIC CHEMISTRY

### 1.1 Electronic configuration of atoms and ions

|       |                                |   |
|-------|--------------------------------|---|
| 1.1.1 | main groups                    | 1 |
| 1.1.2 | transition metals              | 2 |
| 1.1.3 | lanthanide and actinide metals | 3 |
| 1.1.4 | Pauli exclusion principle      | 1 |
| 1.1.5 | Hund's rule                    | 1 |

### 1.2 Trends in the periodic table (main groups)

|       |                          |   |
|-------|--------------------------|---|
| 1.2.1 | electronegativity        | 1 |
| 1.2.2 | electron affinity        | 2 |
| 1.2.3 | first ionisation energy  | 2 |
| 1.2.4 | atomic size              | 1 |
| 1.2.5 | ionic size               | 2 |
| 1.2.6 | highest oxidation number | 1 |

### 1.3 Trends in physical properties (main groups)

|       |                         |   |
|-------|-------------------------|---|
| 1.3.1 | melting point           | 1 |
| 1.3.2 | boiling point           | 1 |
| 1.3.3 | metal character         | 1 |
| 1.3.4 | magnetic properties     | 2 |
| 1.3.5 | thermal properties      | 3 |
| 1.3.6 | law of Dulong and Petit | 1 |
| 1.3.7 | electrical conductivity | 3 |

### 1.4 Structures

|       |  |   |
|-------|--|---|
| 1.4.1 | simple molecular structures  | 2 |
| 1.4.2 | simple molecular structures with a central atom exceeding the octet rule | 3 |
| 1.4.3 | ionic crystal structures   | 3 |
| 1.4.4 | metal structures   | 3 |
| 1.4.5 | stereochemistry  | 3 |

### 1.5 Nomenclature

|       |                             |   |
|-------|-----------------------------|---|
| 1.5.1 | oxidation number            | 1 |
| 1.5.2 | main group compounds        | 1 |
| 1.5.3 | transition metal compounds  | 1 |
| 1.5.4 | simple metal complexes      | 2 |
| 1.5.5 | multicenter metal complexes | 3 |

### 1.6 Chemical calculations

|       |                             |   |
|-------|-----------------------------|---|
| 1.6.1 | balancing equations         | 1 |
| 1.6.2 | stoichiometric calculations | 1 |
| 1.6.3 | mass and volume relations   | 1 |
| 1.6.4 | empirical formula           | 1 |
| 1.6.5 | Avogadro's number           | 1 |
| 1.6.6 | concentration calculations  | 1 |

### 1.7 Isotopes

|       |  |   |
|-------|--|---|
| 1.7.1 | counting of nucleons                             | 1 |
| 1.7.2 | radioactive decay                                | 1 |
| 1.7.3 | nuclear reactions (alpha, beta, gamma, neutrino) | 2 |

### 1.8 Natural cycles

|       |          |   |
|-------|----------|---|
| 1.8.1 | nitrogen | 2 |
| 1.8.2 | oxygen   | 2 |
| 1.8.3 | carbon   | 2 |

### 1.9 s-Block

|         |   |   |
|---------|---|---|
| 1.9.1   | Products of reactions of group I and II metals  |   |
| 1.9.1.1 | with water, basicity of the products  | 1 |
| 1.9.1.2 | with halogens   | 1 |
| 1.9.1.3 | with oxygen   | 2 |
| 1.9.2   | heavier s-block elements are more reactive  | 1 |
| 1.9.3   | lithium combines with H <sub>2</sub> and N <sub>2</sub> forming LiH and Li <sub>3</sub> N | 2 |

### 1.10 p-Block

|        |   |   |
|--------|---|---|
| 1.10.1 | stoichiometry of simplest non-metal hydrides  | 1 |
| 1.10.2 | properties of metal hydrides  | 3 |
| 1.10.3 | acid-base properties of CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O, H <sub>2</sub> S, and hydrogen halides HX | 1 |
| 1.10.4 | NO reacts with O <sub>2</sub> to form NO <sub>2</sub>   | 1 |
| 1.10.5 | equilibrium between NO <sub>2</sub> and N <sub>2</sub> O <sub>4</sub>   | 1 |

|                                |  |   |  |   |   |
|--------------------------------|--|---|--|---|---|
| 1.10.6                         | products of reaction of $\text{NO}_2$ with water   | 1 | 2.1.3  | chemical equilibria expressed in terms of partial pressures   | 2 |
| 1.10.7                         | $\text{HNO}_2$ and its salts are reductants  | 1 | 2.1.4  | the relationship between equilibrium constants for ideal gases expressed in different ways (concentration, pressure, mole fraction) | 3 |
| 1.10.8                         | $\text{HNO}_3$ and its salts are oxidants  | 1 | 2.1.5  | relation of equilibrium constant and standard Gibbs energy  | 3 |
| 1.10.9                         | $\text{N}_2\text{H}_4$ is a liquid and reluctant   | 3 |  |   |   |
| 1.10.10                        | existence of acids like $\text{H}_2\text{N}_2\text{O}_2$ , $\text{HN}_3$   | 3 |  |   |   |
| 1.10.11                        | reactions of $\text{HNO}_3$ with different metals and reductants   | 3 |  |   |   |
| 1.10.12                        | reaction of $\text{Na}_2\text{S}_2\text{O}_3$ with iodine  | 2 |  |   |   |
| 1.10.13                        | other thioacids, polyacids, peroxyacids  | 3 |  |   |   |
| 1.10.14                        | B(III), Al(III), Si(IV), P(V), S(IV), S(VI), O(-II), F(-I), Cl(-I), Cl(I), Cl(III), Cl(V), Cl(VII) are normal oxidation states of 2nd and 3rd row elements in compounds with halogens and in oxoanions | 1 | <b>2.2 Ionic equilibria</b>                  |   |   |
| 1.10.15                        | compounds of non-metals with other oxidation states  | 3 | 2.2.1  | Arrhenius theory of acids and bases   | 1 |
| 1.10.16                        | the preferred oxidation states are Sn(II), Pb(II) and Bi(III)  | 2 | 2.2.2  | Broensted-Lowry theory, conjugated acids and bases  | 1 |
| 1.10.17                        | products of reactions of non-metal oxides with water and stoichiometry of resulting acids  | 1 | 2.2.3  | definition of pH  | 1 |
| 1.10.18                        | reactions of halogens with water   | 2 | 2.2.4  | ionic product of water  | 1 |
| 1.10.19                        | reactivity and oxidizing power of halogens decrease from $\text{F}_2$ to $\text{I}_2$  | 1 | 2.2.5  | relation between $K_a$ and $K_b$ for conjugated acids and bases   | 1 |
| 1.10.20                        | differences of chemistry between row 4 and row 3 elements  | 3 | 2.2.6  | hydrolysis of salts   | 1 |
|                                |  |   | 2.2.7  | solubility product - definition   | 1 |
|                                |  |   | 2.2.8  | calculation of solubility (in water) from solubility product  | 1 |
|                                |  |   | 2.2.9  | calculation of pH for weak acids from $K_a$   | 1 |
|                                |  |   | 2.2.10                                       | calculation of pH for $10^{-7}$ mol $\text{dm}^{-3}$ HCl solution   | 2 |
|                                |  |   | 2.2.11                                       | calculation of pH for multiprotic acids   | 2 |
|                                |  |   | 2.2.12                                       | calculation of pH for weak acid mixtures  | 3 |
|                                |  |   | 2.2.13                                       | definition of activity coefficient  | 2 |
|                                |  |   | 2.2.14                                       | definition of ionic strength  | 3 |
|                                |  |   | 2.2.15                                       | Debye-Hückel formula  | 3 |
| <b>1.11 d-Block</b>            |  |   | <b>2.3 Electrode equilibria</b>              |   |   |
| 1.11.1                         | common oxidation states of the common d-block metals are Cr(III), Cr(VI), Mn(II), Mn(IV), Mn(VII), Fe(II), Fe(III), Co(II), Ni(II), Cu(I), Cu(II), Ag(I), Zn(II), Hg(I), and Hg(II)                    | 1 | 2.3.1  | electromotive force (definition)  | 1 |
| 1.11.2                         | colors of the listed common ions in aqueous solutions  | 2 | 2.3.2  | first kind electrodes   | 1 |
| 1.11.3                         | other oxidation states and chemistry of other d-block elements   | 3 | 2.3.3  | standard electrode potential  | 1 |
| 1.11.4                         | Cr, Mn, Fe, Co, Ni, Zn dissolve in dilute HCl; Cu, Ag, Hg do not dissolve  | 1 | 2.3.4  | Nernst equation   | 2 |
| 1.11.5                         | products of dissolution are (2+) cations   | 2 | 2.3.5  | second kind electrodes  | 2 |
| 1.11.6                         | passivation of Cr, Fe (and also Al)  | 2 | 2.3.6  | relation between $\Delta G$ and electromotive force   | 3 |
| 1.11.7                         | $\text{Cr}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$ are amphoteric, other common hydroxides are not  | 1 | <b>2.4 Kinetics of homogeneous reactions</b> |   |   |
| 1.11.8                         | $\text{MnO}_4^-$ , $\text{CrO}_4^{2-}$ , $\text{Cr}_2\text{O}_7^{2-}$ are strong oxidants  | 1 | 2.4.1  | factors influencing reaction rate   | 1 |
| 1.11.9                         | products of reduction of $\text{MnO}_4^-$ depending on pH  | 2 | 2.4.2  | rate equation   | 1 |
| 1.11.10                        | polyanions other than $\text{Cr}_2\text{O}_7^{2-}$   | 3 | 2.4.3  | rate constant   | 1 |
|                                |  |   | 2.4.4  | order of reactions  | 2 |
|                                |  |   | 2.4.5  | 1st order reactions: time dependence of concentration   | 2 |
|                                |  |   | 2.4.6  | 1st order reactions: half life  | 2 |
|                                |  |   | 2.4.7  | 1st order reactions: relation between half-life and rate constant   | 2 |
|                                |  |   | 2.4.8  | rate-determining step   | 2 |
|                                |  |   | 2.4.9  | molecularity  | 2 |
|                                |  |   | 2.4.10                                       | Arrhenius equation, activation energy (definition)  | 2 |
|                                |  |   | 2.4.11                                       | calculation of rate constant for 1st order reaction   | 2 |
|                                |  |   | 2.4.12                                       | calculation of rate constant for second and third order reactions   | 3 |
|                                |  |   | 2.4.13                                       | calculation of activation energy from experimental data   | 3 |
|                                |  |   | 2.4.14                                       | basic concepts of collision theory  | 3 |
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| 2.1.2                          | chemical equilibria expressed in terms of relative concentrations  | 1 |  |   |   |

|   |   |  |   |
|---|---|--|---|
| theory  | 3 | <b>3.2 Cycloalkanes</b>  |   |
| 2.4.16 opposing, parallel and consecutive reactions                           | 3 | 3.2.1 names  | 1 |
|   |   | 3.2.2 strain in small rings  | 2 |
|   |   | 3.2.3 chair/boat conformation  | 2 |
| <b>2.5 Thermodynamics (First law)</b>   |   | <b>3.3 Alkenes</b>   |   |
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| 2.5.2 energy, heat and work   | 2 | 3.3.2 <i>E/Z (cis-trans)</i> isomerism                               | 1 |
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| 2.5.11 bond energies - definition and uses                                    | 2 | 3.4.2 acidity  | 2 |
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| 2.7.3 definition of partial pressure  | 1 | 3.5.9 effect of first substituent on direction of substitution       | 2 |
| 2.7.4 temperature dependence of the vapor pressure of liquid                  | 2 | 3.5.10 explanation of substituent effects                            | 3 |
| 2.7.5 Clausius-Clapeyron equation   | 3 | <b>3.6 Halogen compounds</b>   |   |
| 2.7.6 reading phase diagrams: triple point                                    | 3 | 3.6.1 hydrolytic reactions   | 2 |
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| 2.7.8 liquid-vapor system (diagram)   | 3 | 3.6.3 reactivity (primary vs secondary vs tertiary)                  | 2 |
| 2.7.9 liquid-vapor: ideal and non-ideal systems                               | 3 | 3.6.4 ionic mechanism of substitution                                | 2 |
| 2.7.10 liquid-vapor: use in fractional distillation                           | 3 | 3.6.5 side products (elimination)                                    | 2 |
| 2.7.11 Henry's law  | 2 | 3.6.6 reactivity (aliphatic vs aromatic)                             | 2 |
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| 2.7.13 deviations from Raoult's law   | 3 | 3.6.8 halogen derivatives and pollution                              | 3 |
| 2.7.14 boiling point elevation law  | 2 | <b>3.7 Alcohols and phenols</b>                                      |   |
| 2.7.15 freezing point depression, determination of molar mass                 | 2 | 3.7.1 hydrogen bonding - alcohols vs ethers                          | 1 |
| 2.7.16 osmotic pressure   | 2 | 3.7.2 acidity of alcohols vs phenols                                 | 2 |
| 2.7.17 partition coefficient  | 3 | 3.7.3 dehydration to alkenes   | 1 |
| 2.7.18 solvent extraction   | 3 | 3.7.4 dehydration to ethers  | 2 |
| 2.7.19 basic principles of chromatography                                     | 2 | 3.7.5 esters with inorganic acids                                    | 2 |
|   |   | 3.7.6 iodoform reaction  | 2 |
|   |   | 3.7.7 reactions of primary/secondary/tertiary: Lucas reagent         | 2 |
|   |   | 3.7.8 formula of glycerol  | 1 |
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| <b>3.1 Alkanes</b>  |   | 3.8.1 nomenclature   | 1 |
| 3.1.1 isomers of butane   | 1 | 3.8.2 keto/enol tautomerism  | 2 |
| 3.1.2 naming (IUPAC)  | 1 | 3.8.3 Preparation of carbonyl compounds                              |   |
| 3.1.3 trends in physical properties   | 1 | 3.8.3.1 oxidation of alcohols  | 1 |
| 3.1.4 Substitution (e.g. with Cl <sub>2</sub> )                               |   | 3.8.3.2 from carbon monoxide   | 3 |
| 3.1.4.1 products  | 1 |  |   |
| 3.1.4.2 free radicals   | 2 |  |   |
| 3.1.4.3 initiation/termination of the chain reaction                          | 2 |  |   |

|                                |  |   |                                     |   |   |
|--------------------------------|--|---|-------------------------------------|---|---|
| 3.8.4                          | Reaction of carbonyl compounds   |   | 3.10.11                             | nitro compounds : aci/nitro tautomerism                             | 3 |
| 3.8.4.1                        | oxidation of aldehydes   | 1 | 3.10.12                             | Beckmann (oxime - amide) rearrangements                             | 3 |
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| 3.8.4.3                        | addition of HCN  | 2 | <b>3.11 Some large molecules</b>    |   |   |
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| 3.8.4.5                        | addition of NH <sub>2</sub> OH   | 2 | 3.11.2                              | micelle structure   | 3 |
| 3.8.4.6                        | aldol condensation   | 3 | 3.11.3                              | preparation of soaps  | 1 |
| 3.8.4.7                        | preparation of acetates  | 2 |                                     | products of polymerization of:                                      |   |
| 3.8.4.8                        | Cannizzaro (PhCHO disproportionation)                                    | 3 | 3.11.4                              | - styrene   | 2 |
| 3.8.4.9                        | Grignard reaction  | 2 | 3.11.5                              | - ethene  | 1 |
| 3.8.4.10                       | Fehling (Cu <sub>2</sub> O) and Tollens (Ag mirror) reagents             | 2 | 3.11.6                              | - polyamides  | 3 |
|                                |  |   | 3.11.7                              | - phenol + aldehydes  | 3 |
| <b>3.9 Carboxylic acids</b>    |  |   | 3.11.8                              | - polyurethanes   | 3 |
| 3.9.1                          | inductive effect and strength  | 2 | 3.11.9                              | polymer cross linking   | 3 |
| 3.9.2                          | equivalence of oxygen atoms in anions                                    | 2 | 3.11.10                             | chain mechanism of polymer formation                                | 2 |
| 3.9.3                          | Preparation and reactions of carboxylic acids                            |   | 3.11.11                             | rubber composition  | 3 |
| 3.9.3.1                        | preparation from esters  | 2 |                                     |   |   |
| 3.9.3.2                        | preparation from nitriles  | 2 | <b>4. BIOCHEMISTRY</b>              |   |   |
| 3.9.3.3                        | products of reaction with alcohols (esters)                              | 3 | <b>4.1 Amino acids and peptides</b> |   |   |
| 3.9.3.4                        | mechanism of esterification  | 2 | 4.1.1                               | ionic structure of amino acids                                      | 1 |
| 3.9.3.5                        | isotopes in mechanism elucidation  | 3 | 4.1.2                               | isoelectric point   | 2 |
| 3.9.3.6                        | nomenclature of acid halides   | 2 | 4.1.3                               | 20 amino acids (classification in groups)                           | 2 |
| 3.9.3.7                        | preparation of acid chlorides  | 2 | 4.1.4                               | 20 amino acids (names and structures)                               | 3 |
| 3.9.3.8                        | preparation of amides from acid chlorides                                | 2 | 4.1.5                               | ninhydrin reaction (including equation)                             | 3 |
| 3.9.3.9                        | preparation of nitriles from acid chlorides                              | 3 | 4.1.6                               | separation by chromatography  | 3 |
| 3.9.3.10                       | properties and preparation of anhydrides                                 | 2 | 4.1.7                               | separation by electrophoresis                                       | 3 |
| 3.9.3.11                       | oxalic acid, name and formula  | 1 | 4.1.8                               | peptide linkage   | 1 |
| 3.9.3.12                       | multifunctional acids (e.g. hydroxy acids, keto acids)                   | 2 | <b>4.2 Proteins</b>                 |   |   |
| 3.9.3.13                       | polycarboxylic acids   | 2 | 4.2.1                               | primary structure of proteins                                       | 1 |
| 3.9.3.14                       | optical activity (e.g. lactic acid)                                      | 2 | 4.2.2                               | -S-S- bridges   | 3 |
| 3.9.3.15                       | R/S nomenclature   | 3 | 4.2.3                               | sequence analysis   | 3 |
| 3.9.3.16                       | plant and animal fats, differences                                       | 2 | 4.2.4                               | secondary structures  | 3 |
|                                |  |   | 4.2.5                               | details of alpha-helix structure                                    | 3 |
| <b>3.10 Nitrogen compounds</b> |  |   | 4.2.6                               | tertiary structure  | 3 |
| 3.10.1                         | basicity of amines   | 1 | 4.2.7                               | denaturation reaction by change of pH, temperature, metals, ethanol | 2 |
| 3.10.2                         | comparing aliphatic vs. aromatic   | 2 | 4.2.8                               | quaternary structure  | 3 |
| 3.10.3                         | names: primary, secondary, tertiary, quaternary amines                   | 2 | 4.2.9                               | separation of proteins (molecule size and solubility)               | 3 |
| 3.10.4                         | identification of primary/sec./tert./quaternary amines in the laboratory | 3 | 4.2.10                              | metabolism of proteins (general)                                    | 3 |
| 3.10.5                         | Preparation of amines  |   | 4.2.11                              | proteolysis   | 3 |
| 3.10.5.1                       | from halogen compounds   | 2 | 4.2.12                              | transamination  | 3 |
| 3.10.5.2                       | from nitro compounds (e.g. PhNH <sub>2</sub> from PhNO <sub>2</sub> )    | 3 | 4.2.13                              | four pathways of catabolism of amino acids                          | 3 |
| 3.10.5.3                       | from amides (Hoffmann)   | 3 | 4.2.14                              | decarboxylation of amino acids                                      | 3 |
| 3.10.6                         | mechanism of Hoffmann rearrangement in acidic/basic medium               | 3 | 4.2.15                              | urea cycle (only results)   | 3 |
| 3.10.7                         | basicity amines vs. amides   | 2 | <b>4.3 Fatty acids and fats</b>     |   |   |
| 3.10.8                         | diazotation products of aliphatic amines                                 | 3 | 4.3.1                               | IUPAC names from C <sub>4</sub> to C <sub>18</sub>                  | 2 |
| 3.10.9                         | diazotation products of aromatic amines                                  | 3 | 4.3.2                               | trivial names of most important (ca. 5) fatty acids                 | 2 |
| 3.10.10                        | dyes: color vs. structure (chromophore groups)                           | 3 | 4.3.3                               | general metabolism of fats  | 2 |
|                                |  |   | 4.3.4                               | beta-oxidation of fatty acids (formulae and ATP balance)            | 3 |
|                                |  |   | 4.3.5                               | fatty acids and fats anabolism                                      | 3 |
|                                |  |   | 4.3.6                               | phosphoglycerides   | 3 |

|  |   |   |                                 |   |   |
|--|---|---|---------------------------------|---|---|
| 4.3.7  | membranes   | 3 | 4.8.4                           | mineral metabolism (no details)   | 3 |
| 4.3.8  | active transport  | 3 | 4.8.5                           | ions in blood   | 3 |
| <b>4.4 Enzymes</b>                             |   |   | 4.8.6                           | buffers in blood  | 3 |
| 4.4.1  | general properties, active centres                          | 2 | 4.8.7                           | haemoglobin; function and skeleton  | 3 |
| 4.4.2  | nomenclature, kinetics, coenzymes, function of ATP, etc.    | 3 | 4.8.8                           | haemoglobin; diagram of oxygen absorption   | 3 |
| <b>4.5 Saccharides</b>                         |   |   | 4.8.9                           | steps in clotting the blood   | 3 |
| 4.5  | Glucose and fructose:                                       |   | 4.8.10                          | antigens and antibodies   | 3 |
| 4.5.1  | - chain formulas  | 2 | 4.8.11                          | blood groups  | 3 |
| 4.5.2  | - Fischer projections                                       | 2 | 4.8.12                          | acetyl choline, structure and functions   | 3 |
| 4.5.3  | - Haworth formulas  | 3 | <b>OTHER PROBLEMS</b>           |   |   |
| 4.5.4  | osazones  | 3 | <b>5. Analytical chemistry</b>  |   |   |
| 4.5.5  | maltose as reducing sugar                                   | 2 | 5.1                             | choice of indicators for acidimetry   | 1 |
| 4.5.6  | difference between starch and cellulose                     | 2 | 5.2                             | titration curve; pH (strong and weak acid)  | 2 |
| 4.5.7  | difference between alpha- and beta-D glucose                | 2 | 5.3                             | EMF (redox titration)   | 2 |
| 4.5.8  | metabolism from starch to acetyl-CoA                        | 3 | 5.4                             | calculation of pH of simple buffer solution   | 2 |
| 4.5.9  | pathway to lactic acid or to ethanol; catabolism of glucose | 3 | 5.5                             | identification of $\text{Ag}^+$ , $\text{Ba}^{2+}$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$   | 1 |
| 4.5.10   | ATP balance for the above pathways                          | 3 | 5.6                             | identification of $\text{Al}^{3+}$ , $\text{NO}_2^-$ , $\text{NO}_3^-$ , $\text{Bi}^{3+}$ | 2 |
| 4.5.11   | photosynthesis (products only)                              | 2 | 5.7                             | identification of $\text{VO}_3^-$ , $\text{ClO}_3^-$ , $\text{Ti}^{4+}$                   | 3 |
| 4.5.12   | light and dark reaction                                     | 3 | 5.8                             | use of flame tests for identification of K, Ca and Sr                                     | 1 |
| 4.5.13   | detailed Calvin cycle                                       | 3 | 5.9                             | Lambert -Beer law   | 2 |
| <b>4.6 Krebs cycle and respiration chain</b>   |   |   | <b>6. Complexes</b>             |   |   |
| 4.6.1  | formation of $\text{CO}_2$ in the cycle (no details)        | 3 | 6.1                             | writing down complexation reactions   | 1 |
| 4.6.2  | intermediate compounds in the cycle                         | 3 | 6.2                             | definition of coordination number   | 1 |
| 4.6.3  | formation of water and ATP (no details)                     | 3 | 6.3                             | prediction of coordination number of complex ions and molecules                           | 3 |
| 4.6.4  | FMN and cytochromes   | 3 | 6.4                             | complex formation constants (definition)  | 2 |
| 4.6.5  | calculation of ATP amount for 1 mole of glucose             | 3 | 6.5                             | $E_g$ and $T_{2g}$ terms: high and low spin octahedral complexes                          | 3 |
| <b>4.7 Nucleic acids and protein synthesis</b> |   |   | 6.6                             | calculation of solubility of AgCl in $\text{NH}_3$ (from $K_s$ and constants $\beta$ )    | 3 |
| 4.7.1  | pyrimidines, purines  | 2 | 6.7                             | <i>cis</i> and <i>trans</i> forms   | 3 |
| 4.7.2  | nucleosides and nucleotides                                 | 3 | <b>7. Theoretical chemistry</b> |   |   |
| 4.7.3  | formulae of all pyrimidine and purine bases                 | 3 | 7.1                             | energy levels of hydrogen atom (formula)  | 2 |
| 4.7.4  | difference between ribose and 2-deoxyribose                 | 3 | 7.2                             | square of the wave function and probability   | 3 |
| 4.7.5  | base combination CG and AT                                  | 3 | 7.3                             | understanding the simplest Schrödinger equation   | 3 |
| 4.7.6  | base combination CG and AT (hydrogen bonding structure)     | 3 | 7.4                             | n, l, m quantum numbers   | 2 |
| 4.7.7  | difference between DNA and RNA                              | 3 | 7.5                             | shape of p-orbitals   | 2 |
| 4.7.8  | difference between mRNA and tRNA                            | 3 | 7.6                             | d-orbital stereoconfiguration   | 3 |
| 4.7.9  | hydrolysis of nucleic acids                                 | 3 | 7.7                             | molecular orbital diagram: $\text{H}_2$ molecule  | 2 |
| 4.7.10   | semiconservative replication of DNA                         | 3 | 7.8                             | molecular orbital diagram: $\text{N}_2$ and $\text{O}_2$ molecules                        | 3 |
| 4.7.11   | DNA-ligase  | 3 | 7.9                             | bond orders in $\text{O}_2$ , $\text{O}_2^+$ , $\text{O}_2^-$                             | 3 |
| 4.7.12   | RNA synthesis (transcription) without details               | 3 | 7.10                            | unpaired electrons and paramagnetism  | 2 |
| 4.7.13   | reverse transcriptase                                       | 3 | 7.11                            | Hückel theory for aromatic compounds  | 3 |
| 4.7.14   | use of genetic code   | 3 | 7.12                            | Lewis acids and bases   | 2 |
| 4.7.15   | start and stop codons                                       | 3 | 7.13                            | hard and soft Lewis acids   | 3 |
| 4.7.16   | translation steps   | 3 |                                 |   |   |
| <b>4.8 Other biochemical problems</b>          |   |   |                                 |   |   |
| 4.8.1  | hormones, regulation  | 3 |                                 |   |   |
| 4.8.2  | hormones, feedback  | 3 |                                 |   |   |
| 4.8.3  | insulin, glucagon, adrenaline                               | 3 |                                 |   |   |

## 8. Instrumental methods of determining structure

### 8.1 UV-VIS spectroscopy

|       |                                     |   |
|-------|-------------------------------------|---|
| 8.1.1 | identification of aromatic compound | 3 |
| 8.1.2 | identification of chromophores      | 3 |

### 8.2 Mass spectra

|       |                                      |   |
|-------|--------------------------------------|---|
| 8.2   | recognition of:                      |   |
| 8.2.1 | - molecular ions                     | 3 |
| 8.2.2 | - fragments with the help of a table | 3 |
| 8.2.3 | typical isotope distribution         | 3 |

### 8.3 Infrared spectra

|       |   |   |
|-------|---|---|
| 8.3.1 | interpretation using a table of group frequencies | 3 |
| 8.3.2 | recognition of hydrogen bonds                     | 3 |
| 8.3.3 | Raman spectroscopy                                | 3 |

### 8.4 NMR

|       |                                     |  |
|-------|-------------------------------------|--|
| 8.4.1 | interpretation of a simple spectrum |  |
|-------|-------------------------------------|--|

|       |  |   |
|-------|--|---|
|       | (like ethanol)   | 3 |
| 8.4.2 | spin-spin coupling   | 3 |
| 8.4.3 | coupling constants   | 3 |
| 8.4.4 | identification of <i>o</i> - and <i>p</i> -substituted benzene | 3 |
| 8.4.5 | <sup>13</sup> C- NMR   | 3 |

### 8.5 X-rays

|       |  |   |
|-------|--|---|
| 8.5.1 | Bragg's law  | 3 |
| 8.5.2 | electron density diagram                             | 3 |
| 8.5.3 | coordination number                                  | 3 |
| 8.5.4 | unit cell structures:                                | 3 |
| 8.5.5 | - of NaCl  | 3 |
| 8.5.6 | - of CsCl  | 3 |
| 8.5.7 | - close-packed (2 types)                             | 3 |
| 8.5.8 | determining of the Avogadro constant from X-ray data | 3 |

### 8.6 Polarimetry

|       |  |   |
|-------|--|---|
| 8.6.1 | calculation of specific rotation angle | 3 |
|-------|--|---|

## Syllabus for the experimental part of the IChO competition

**Level 1** is assigned to the basic experimental activities which are supposed to be mastered very well by competitors.

**Level 2** is assigned to the activities which are parts of school experimental exercises in developed countries and the authors of IChO tasks may incorporate them into the tasks without being bound to mention it in advance.

**Level 3** is assigned to such activities which are not in the chemistry syllabus in the majority of participating countries and the authors are obliged to mention them in the set of preparatory tasks.

## 1. Synthesis of inorganic and organic compounds

|      |  |   |
|------|--|---|
| 1.1  | heating with burners and hotplates                                     | 1 |
| 1.2  | heating of liquids   | 1 |
| 1.3  | handling of inflammable substances and materials                       | 1 |
| 1.4  | measuring of masses (analytical balance)                               | 1 |
| 1.5  | measuring of volumes of liquids (measuring cylinder, pipette, burette) | 1 |
| 1.6  | preparation of solutions from a solid compound and solvent             | 1 |
| 1.7  | mixing and dilution of solutions                                       | 1 |
| 1.8  | mixing and stirring of liquids   | 1 |
| 1.9  | using mixer and magnetic stirrer                                       | 2 |
| 1.10 | using a dropping funnel  | 1 |
| 1.11 | syntheses in flat bottom vessels - general principles                  | 1 |
| 1.12 | syntheses in round bottom vessels - general principles                 | 1 |
| 1.13 | syntheses in a closed apparatus - general principles                   | 1 |
| 1.14 | using micro scale equipment for synthesis                              | 3 |
| 1.15 | apparatus for heating of a reaction mixture under reflux               | 2 |
| 1.16 | apparatus for distillation of liquids at                               |   |

|      |   |   |
|------|---|---|
| 1.17 | normal pressure apparatus for distillation of liquids at reduced pressure       | 2 |
| 1.18 | apparatus for steam distillation  | 3 |
| 1.19 | filtration through flat paper filter  | 1 |
| 1.20 | filtration through a folded paper filter  | 1 |
| 1.21 | handling a water vacuum pump  | 1 |
| 1.22 | filtration through a Büchner funnel   | 1 |
| 1.23 | suction through a glass filter  | 1 |
| 1.24 | washing of precipitates by decantation  | 1 |
| 1.25 | washing of precipitates on a filter   | 2 |
| 1.26 | drying of precipitates on a filter with appropriate solvents                    | 2 |
| 1.27 | recrystallization of substances from aqueous solution                           | 1 |
| 1.28 | recrystallization of substances from a known organic solvent                    | 2 |
| 1.29 | practical choice of an appropriate solvent for recrystallization of a substance | 3 |
| 1.30 | drying of substances in a drying box  | 2 |
| 1.31 | drying of substances in a desiccator  | 2 |
| 1.32 | connecting and using a gas washing bottle                                       | 2 |
| 1.33 | extraction with an immiscible solvent   | 1 |

**2. Identification of inorganic and organic compounds - general principles**

|      |  |   |
|------|--|---|
| 2.1  | test-tube reactions  | 1 |
| 2.2  | technique of reactions performed in a dot dish and on a filter paper   | 1 |
| 2.3  | group reactions of some cations and anions specified by the organizer  | 2 |
| 2.4  | selective reactions of some cations and anions specified by the organizer                                    | 2 |
| 2.5  | specific reactions of some cations and anions specified by the organizer                                     | 3 |
| 2.6  | identification of elements by flame coloration (using a platinum wire/ MgO rod, Co-glass)                    | 2 |
| 2.7  | using a hand spectroscope/Bunsen spectroscope  | 3 |
| 2.8  | melting point determination with Kofler or similar type of apparatus   | 3 |
| 2.9  | qualitative evidence of basic functional groups of organic substances specified by the organizer             | 2 |
| 2.10 | exploitation of some specific reactions for identification of organic compounds (specified by the organizer) | 3 |

**3. Determination of some inorganic and organic compounds - general principles**

|     |   |   |
|-----|---|---|
| 3.1 | quantitative determinations using precipitation reactions | 2 |
| 3.2 | igniting of a precipitate in a crucible                   | 1 |
| 3.3 | quantitative volumetric determinations                    | 1 |
| 3.4 | rules of titrations                                       | 1 |
| 3.5 | use of a pipetting ball                                   | 1 |
| 3.6 | preparation of a standard solution                        | 2 |
| 3.7 | alkalimetric and acidimetric                              |   |

|      |  |   |
|------|--|---|
|      | determinations   | 2 |
| 3.8  | color transitions of indicators at alkalimetric and acidimetric determinations | 2 |
| 3.9  | direct and indirect determinations (back titration)                            | 3 |
| 3.10 | manganometric determinations   | 3 |
| 3.11 | iodometric determinations  | 3 |
| 3.12 | other types of determinations on basis of redox reactions                      | 3 |
| 3.13 | complexometric determinations  | 3 |
| 3.14 | color transitions of solutions at complexometric determinations                | 3 |
| 3.15 | volumetric determinations on basis of precipitation reactions                  | 3 |
| 3.16 | thermometric titration   | 3 |

**4. Special measurements and procedures**

|     |  |   |
|-----|--|---|
| 4.1 | measuring with a pH-meter                                  | 2 |
| 4.2 | chromatography on thin layers                              | 3 |
| 4.3 | column chromatography                                      | 3 |
| 4.4 | separation on ion exchanger                                | 3 |
| 4.5 | measuring of UV-VIS absorbances with a spectral photometer | 3 |
| 4.6 | performing of conductivity measurements                    | 3 |

**5. Evaluation of results**

|     |   |   |
|-----|---|---|
| 5.1 | Estimation of experimental errors (significant figures, plots scales) | 1 |
|-----|---|---|

**6. If the organizer wants to apply a technique which is not mentioned in the above syllabus, this technique is set to level 3 automatically.**



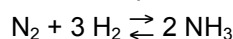
# Theoretical Problems

## Important general remark:

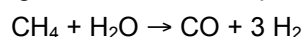
The task "calculate" implies that equation(s), formula(s), number(s), etc., and the way that has been followed to arrive at the answer, must be given!

### Problem 1 Production of Ammonia

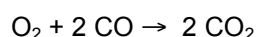
Ammonia is an important commodity chemical used for the manufacture of the fertilizer urea and many other products. The production of ammonia takes place according to the equilibrium reaction:



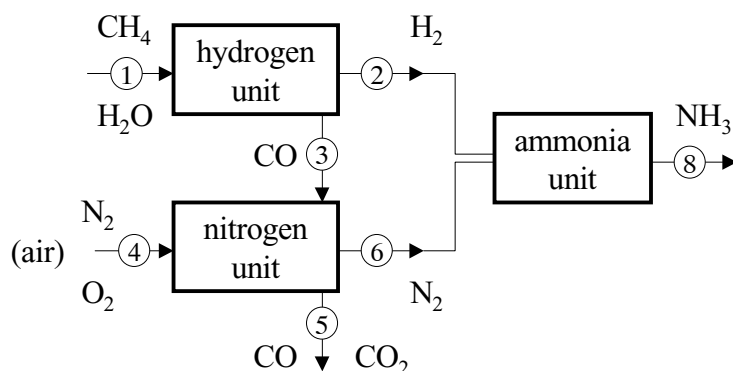
The hydrogen in the ammonia plant is obtained from methane and water by the reaction:



Nitrogen is taken from air, whereby oxygen is removed by the reaction with CO as follows:



In air the nitrogen content is 80%. The reactions are performed in a catalytic reactor, the diagram of which is shown below. The respective flows are numbered in the arrows.



Assume that the reactants are converted completely. Take as flow for ammonia at position ⑧:

$$n[\text{NH}_3, \textcircled{8}] = 1000 \text{ mol s}^{-1}$$

1-1 Calculate the following flows in the plant in  $\text{mol s}^{-1}$

$n[\text{H}_2, \textcircled{2}]$ , for hydrogen at position ②

$n[\text{N}_2, \textcircled{6}]$ , for nitrogen at position ⑥

$n[\text{CH}_4, \textcircled{1}]$ , for methane at position ①

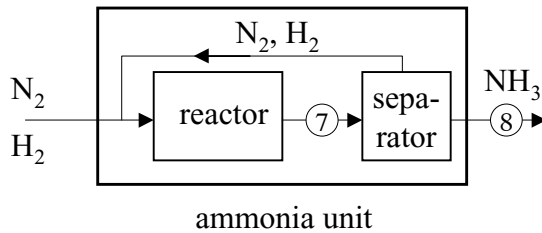
$n[\text{H}_2\text{O}, \textcircled{1}]$ , for water at position ①

$n[\text{CO}, \textcircled{3}]$ , for CO at position ③

$n[\text{O}_2, \textcircled{4}]$ , for oxygen at position ④

$n[\text{CO}, \textcircled{5}]$ , for CO at position ⑤

In real practice the ammonia formation is an equilibrium reaction, converting only a part of the reactants. The ammonia unit thus must be equipped with a separator and a recycle unit, as shown below.



Suppose the recycle of  $N_2 + H_2$  that leaves the separator is two times the  $NH_3$  flow.

**1-2** Calculate the flow of  $N_2$  at position ⑦ and the flow of  $H_2$  at position ⑦.

At a temperature  $T = 800$  K, the Gibbs energies of the three gases are:

$$\begin{aligned} G(N_2) &= -8.3 \times 10^3 \text{ J mol}^{-1} \\ G(H_2) &= -8.3 \times 10^3 \text{ J mol}^{-1} \\ G(NH_3) &= 24.4 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

**1-3** Calculate the change in the Gibbs energy ( $\Delta G_r$ ) for the conversion of one mole of  $N_2$ .

**1-4** Calculate the equilibrium constant  $K_r$  for the  $NH_3$  formation, using  $\Delta G_r$  (see 1-3).  
The gas constant equals to:  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

Equilibrium constants can also be expressed in partial pressures of the reactants, thus:

$$K_r = \frac{p_{NH_3}^2 p_0^2}{p_{N_2} p_{H_2}^3}$$

The partial pressure of ammonia at position ⑦ is a fraction  $x$  of the total pressure:

$$p_{NH_3} = x p_{tot}, \text{ whereby } x \text{ is also expressed by the flow ratio } n_{NH_3} / n_{tot}$$

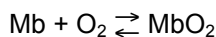
**1-5** Derive the equations for the partial pressures  $p_{N_2}$  and  $p_{H_2}$  at position ⑦.

**1-6** Insert the partial pressures in  $K_r$  and simplify the formula thus obtained as much as possible.

**1-7** Calculate  $x$  when  $p_0 = 0.1$  Mpa and  $p_{tot} = 30$  Mpa. (Hint:  $K_r$  has been calculated in 1-4)

## Problem 2 Myoglobin for Oxygen Storage

Myoglobin (Mb) is a protein containing a heme (iron) group. Myoglobin is an enzyme that allows storage of oxygen. Each myoglobin molecule can reversibly bind one oxygen molecule according to the equation:



This oxygen storage is important for diving animals such as whales. We are going to investigate how whales use it.

The fraction of Mb that is bound to oxygen increases with the oxygen concentration as:

$$Y = \frac{c_{O_2}}{c_{O_2} + K_c}, \text{ wherein } K_c \text{ is a constant}$$

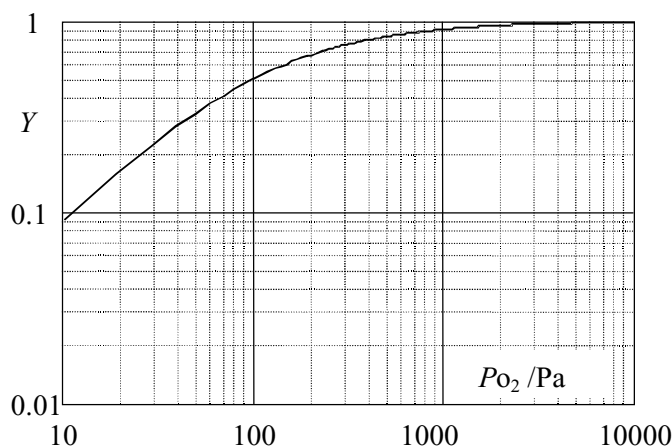
Oxygen is only slightly soluble in water: the amount that dissolves is proportional to the oxygen pressure:

$$c_{O_2} \propto p_{O_2}$$

The fraction of Mb bound is then related to the oxygen pressure by:

$$Y = \frac{p_{O_2}}{p_{O_2} + K_p}, \text{ wherein } K_p \text{ is a constant}$$

The graph below is showing this relation (the scale of the graph is logarithmic!)



2-1 Determine the value and the unit of the constant  $K_p$  in the formula above (use the graph).

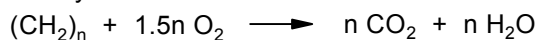
The Mb molecule has the dimensions of  $4.5 \times 3.5 \times 2.5$  nm meaning that Mb fits in a box with these dimensions. Because the molecule is roughly elliptical in shape it will have a volume of about one half of the volume of the box. Proteins have a density of about  $1400 \text{ kg m}^{-3}$ . The Avogadro number is  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ .

2-2 Estimate the molar mass of Mb.

Whales obtain their oxygen by breathing air. They can stay under water for a long time using their oxygen storage. Assume that 20% of the mass of their muscular tissues consists of myoglobin.

2-3 Calculate how many moles of oxygen the whale can store per kilogram of tissue.

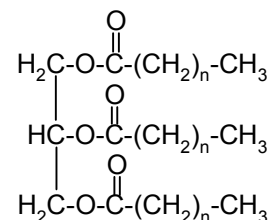
Oxygen is used to produce energy (heat and motion) by burning fat. The overall equation can be approximated by:



The energy released by this type of reaction is about 400 kJ per mole of oxygen. A large animal, such as a whale, needs to dissipate about 0.5 W per kg of mass of muscle tissue to stay warm and keep moving.

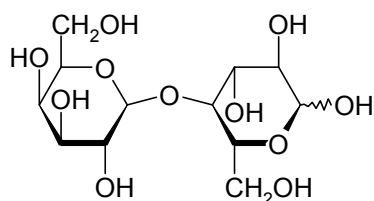
2-4 Calculate how long the whale can stay under water.

2-5 Give the equation for the burning of a real fat molecule:



### Problem 3 Lactose Chemistry

Lactose (milk sugar) is produced on a fairly large scale in The Netherlands starting from whey (a by-product of cheese manufacture). Lactose is applied in baby food and in pharmaceutical tablets. It is a disaccharide composed of the monosaccharides D-galactose and D-glucose. The structure is shown below (Haworth projection). The left hand monosaccharide unit is D-galactose.

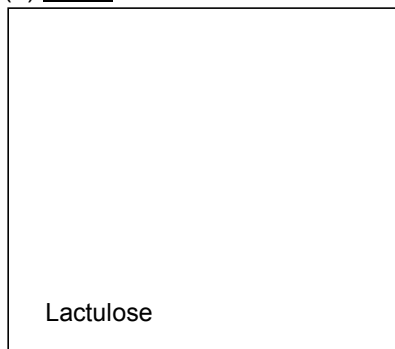


**Lactose**

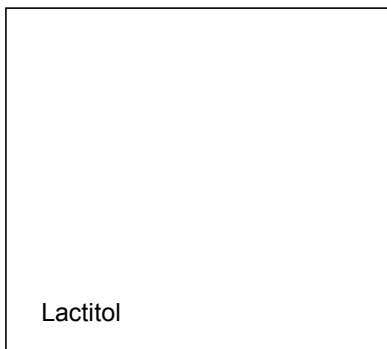
3-1 Draw the Fischer projection of D-galactose and D-glucose.



- 3-4 (a) Draw the Haworth structure of lactulose.  
(Hint: the glucose part of lactose has been isomerised to the keto-sugar fructose).  
(b) Draw the Haworth structure of lactitol.



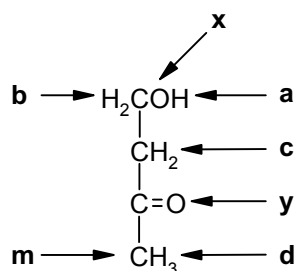
Answer box (a)



Answer box (b)

### Problem 4 Atom Mobility (Dynamics) in Organic Compounds

For the study of reaction mechanisms in organic chemistry isotopic labelling, e.g. with  $^2\text{H}$  or  $^{17}\text{O}$ , can give valuable information. Modern NMR techniques are able to 'see' deuterium  $^2\text{H}$  and the oxygen isotope  $^{17}\text{O}$ . As an example, the introduction of isotopic labels in 4-hydroxybutan-2-one is considered.



a, b, c, d are hydrogen atoms, x, y are oxygen atoms and m is a carbon atom.

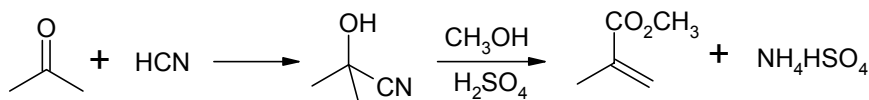
- 4-1 The substrate is treated with  $^2\text{H}_2\text{O}$  at pH = 10. Rank the order of exchange (introduction) of deuterium atoms ( $^2\text{H}$ ) from first to last.  
First     last.
- 4-2 Similarly, the substrate is treated with  $\text{H}_2^{17}\text{O}$  at pH = 10. Rank the order of introduction of  $^{17}\text{O}$  from first to last.  
First   last.
- 4-3 Do you consider the exchange method appropriate for the introduction of a  $^{13}\text{C}$  at position m, yes or no?

### Problem 5 Towards Green Chemistry: The E-factor

The well being of modern society is unimaginable without the myriad of products of industrial organic synthesis, from pharmaceuticals combating diseases or relieving pain, to synthetic dyestuffs for aesthetic appeal. The flip side of the coin is that many of these processes generate substantial amounts of waste. The solution is not less chemistry but alternative, cleaner technologies that minimize waste. In order to evaluate the environmental (un)friendliness of a process, the terms "atom utilization" and "the E-factor" were introduced. The atom utilization is obtained by dividing the molar mass of the desired product by the sum of the molar masses of all substances produced according to the reaction equations. The E-factor is the amount (in kg) of by-products per kg of product.

Methyl methacrylate is an important monomer for transparent materials (Plexiglas).

### Classical route



### Modern route

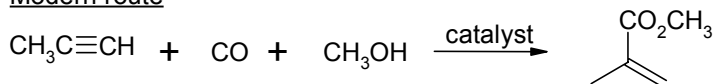
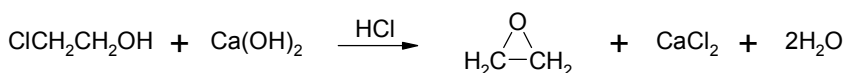
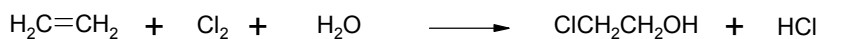


Figure 1: Methyl methacrylate synthesis

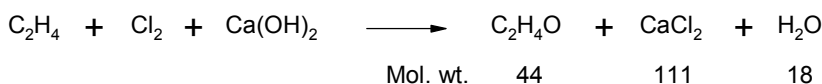
- 5-1 Calculate the atom utilization and the *E*-factor for both processes. The classical and a modern process for methyl methacrylate manufacture are shown in Figure 1.

Another example is the manufacture of ethene oxide (see Figure 2). The classical route produces calcium chloride. Moreover, 10% of the ethene is converted into 1,2-ethanediol by hydrolysis. In the modern direct route a silver catalyst is applied. Here, 15% of the ethene is oxidized to carbon dioxide and water.

### Classical chlorohydrin route



Overall:



### Modern petrochemical route

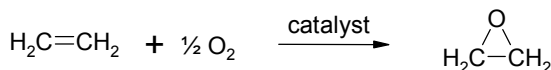


Figure 2: Ethene oxide synthesis

- 5-2 Calculate the atom utilization and *E*-factor for both processes.

## Problem 6 Selective Solubility

Solubility is an important factor for the measurement of the environmental pollution of salts. The solubility of a substance is defined as the amount that dissolves in a given quantity of solvent to form a saturated solution. This solubility varies greatly with the nature of the solute and the solvent, and the experimental conditions, such as temperature and pressure. The pH and the complex formation also may have influence on the solubility.

An aqueous solution contains  $\text{BaCl}_2$  and  $\text{SrCl}_2$  both in a concentration of 0.01 M. The question is whether it will be possible to separate this mixture completely by adding a saturated solution of sodium sulfate. The criterion is that at least 99.9% of the  $\text{Ba}^{2+}$  has precipitated as  $\text{BaSO}_4$  and that  $\text{SrSO}_4$  may be contaminated with no more than 0.1 %  $\text{BaSO}_4$ . The solubility product constants are as follows:  $K_{\text{sp}}(\text{BaSO}_4) = 1 \times 10^{-10}$  and  $K_{\text{sp}}(\text{SrSO}_4) = 3 \times 10^{-7}$ .

- 6-1 Give the relevant equations.  
Calculate the residual concentration of  $\text{Ba}^{2+}$ .  
Calculate the percentage of  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  in the separated substances.

Complex formation may have a profound effect on the solubility. A complex is a charged species consisting of a central metal ion bonded to one of more ligands. For example  $\text{Ag}(\text{NH}_3)_2^+$  is a complex containing  $\text{Ag}^+$  as the central ion and two  $\text{NH}_3$  molecules as ligands.

The solubility of  $\text{AgCl}$  in water is  $1.3 \times 10^{-5} \text{ M}$ .

The solubility product constant of  $\text{AgCl}$  is  $1.7 \times 10^{-10}$ .

The equilibrium constant for the formation of the complex ( $K_f$ ) has a value of  $1.5 \times 10^{+7}$ .

- 6-2 Show by calculation that the solubility of  $\text{AgCl}$  in 1.0 M aqueous ammonia is higher than in pure water.

## Problem 7 UV-spectrometry as an Analytical Tool

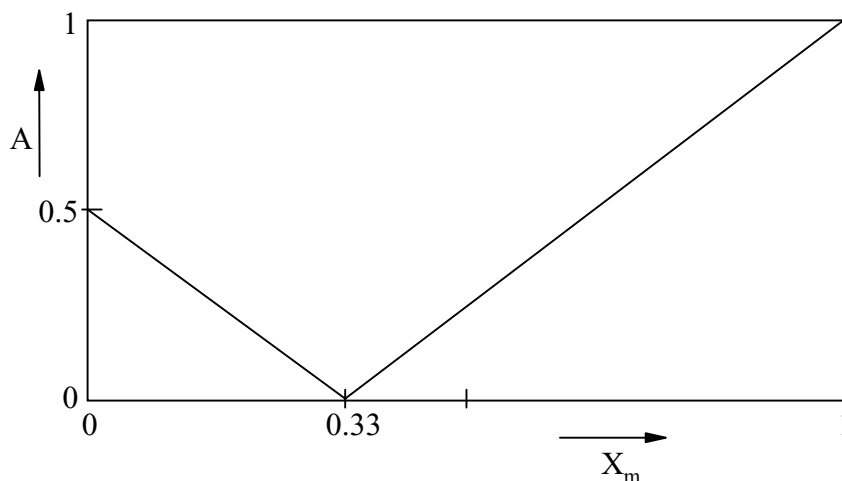
UV-spectrometry is frequently used to determine the concentration of a substance in solution by measuring the UV absorbance at a certain wavelength of either visible or ultraviolet light. The law of Lambert and Beer states that the absorbance is directly proportional to the concentration in moles per litre at a given wavelength:  $A = \epsilon c l$  ( $\epsilon$  is the molar absorptivity or the extinction coefficient in  $\text{L mol}^{-1} \text{ cm}^{-1}$ , the path length in cm,  $A = {}^{10}\log I_0/I$ ).

Here the maximal and minimal concentration that can be measured for the redox concentration  $\text{Fe(II)}$  ferrioxalate (ferriox) will be considered. ( $\lambda_{\text{max}} = 512 \text{ nm}$ ,  $\epsilon = 10500 \text{ L mol}^{-1} \text{ cm}^{-1}$ ).

- 7-1 Calculate the lowest concentration of ferriox that can be measured in a 1 cm cuvet at 512 nm, if a 2% difference in light intensity still can be measured.

- 7-2 Calculate the highest concentration of ferriox that can be measured in a 1 cm cuvet at 512 nm, if at least 2% of the incident light must reach the detector.

The composition of a complex between a metal M and a ligand L can also be determined spectrometrically, using the method of Continuous Variation, also known as Job's method, whereby the sum of the molar concentrations of M and L is kept constant as their ratio is varied. The following graph of absorbance vs. mol fraction for a complex is given, whereby the mol fraction  $x_M = c_M / (c_M + c_L)$  is varied. (measurement at 552 nm).



- 7-3 Determine the composition of the complex and show your calculation.

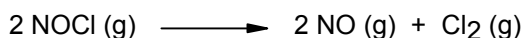
- 7-4 Which compounds absorb at  $x_M = 0$  ?  
Which compounds absorb at  $x_M = 1$  ?  
Show how you derive your answer.

- 7-5 Calculate the ratio of the extinction coefficients of M and L.

- 7-6 Calculate the percentage of the incident light that has been transmitted through the solutions belonging to  $x_M = 0$  and  $x_M = 1$ , respectively.

## Problem 8 Reaction Kinetics

The study of reaction kinetics provides essential information about details of chemical reactions. Here the formation of NO and its reaction with oxygen is considered. The formation of NO takes place according to the equation:



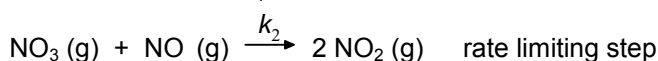
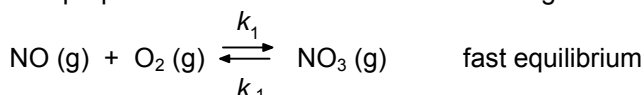
The rate constant  $k$  is  $2.6 \times 10^{-8} \text{ L mol}^{-1} \text{ s}^{-1}$  at 300K and  $4.9 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$  at 400K.

The gas constant  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

**8-1** Calculate the activation energy for the NO formation using the Arrhenius equation.

The reaction of NO with oxygen is as follows:  $2 \text{NO (g)} + \text{O}_2 \text{(g)} \longrightarrow 2 \text{NO}_2 \text{(g)}$ .

The proposed mechanism for this reaction is given below.



**8-2** Give the rate equation for the  $\text{NO}_2$  formation on basis of this mechanism.

Experimentally, the rate equation reads  $s = k [\text{NO}]^2 [\text{O}_2]$ .

**8-3** Which conclusion do you draw:

- The proposed mechanism is incorrect.
- The proposed mechanism is correct.
- The experiment is non-conclusive.

(Mark the correct answer).

## Problem 9 Bonding and Bond Energies

A number of processes with salts and crystals can be understood by estimating the energies involved with a simple ionic model in which the ions have a specific radius and a charge equal to an integer number times the elementary charge. This model is used to describe the dissociation of ionic molecules in the gas phase. Such dissociations usually lead directly to neutral atoms, but the dissociation energy can be calculated by assuming a hypothetical reaction path which involves dissociation to free ions, followed by neutralization of the ions. This is the Born-Haber cycle.

The bonding energies, electron affinity and ionisation energies of the following diatomic species have been measured:

|                     |                              |                                      |                              |
|---------------------|------------------------------|--------------------------------------|------------------------------|
| Bonding energy NaCl | = - 464 kJ mol <sup>-1</sup> | Electron affinity Cl                 | = - 360 kJ mol <sup>-1</sup> |
| Bonding energy KCl  | = - 423 kJ mol <sup>-1</sup> | Ionisation energy Na                 | = 496 kJ mol <sup>-1</sup>   |
| Bonding energy MgCl | = - 406 kJ mol <sup>-1</sup> | 1 <sup>st</sup> Ionisation energy Ca | = 592 kJ mol <sup>-1</sup>   |
| Bonding energy CaCl | = - 429 kJ mol <sup>-1</sup> | 2 <sup>nd</sup> Ionisation energy Ca | = 1148 kJ mol <sup>-1</sup>  |

**9-1** Design a Born-Haber cycle for the dissociation of NaCl into neutral atoms and calculate the dissociation energy of NaCl. Assume that the bonding is completely (100%) ionic in nature.

**9-2** Design a Born-Haber cycle for the dissociation of  $\text{CaCl}_2$  into three neutral atoms and calculate the dissociation energy of  $\text{CaCl}_2$ , assuming that the bond length in the triatomic species is 9% shorter than in the diatomic species.

## 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,  $^{31}\text{P}$ -NMR spectra can provide valuable information of P containing products. A characteristic feature of  $^{31}\text{P}$ -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  $^1\text{H}$ -decoupled  $^{31}\text{P}$ -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  $(\text{RO})_2\text{P-OH}$ .

- 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**.

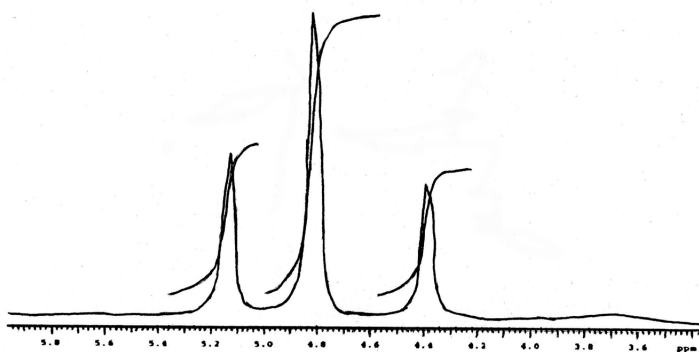


Figure: The  $^{31}\text{P}$ -NMR spectrum of **A** ( $^1\text{H}$ -decoupled).

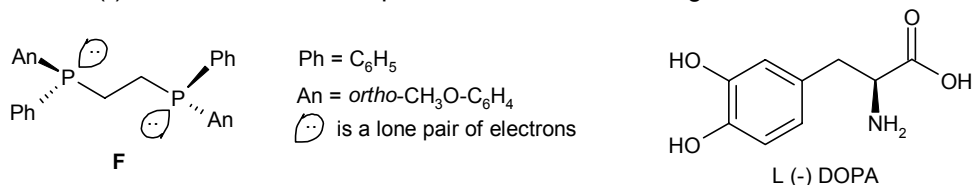
Compound **C** is a dialkyl phosphite derived from methanol.

Compound **D** is a dialkyl phosphite derived from propan-2-ol.

Compound **E** is a dialkyl phosphite derived from racemic 1-phenylethanol.

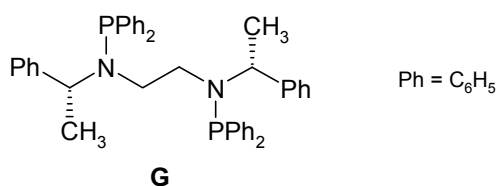
- 10-2** How many signals are present in the  $^{31}\text{P}$ -NMR spectra of the compounds **C**, **D** and **E**? If there is more than one signal, then indicate also the relative peak areas.
- 10-3** Sketch the  $^1\text{H}$ -NMR spectrum of **A** (assume that there is no overlap of signals). Show 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.



- 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.

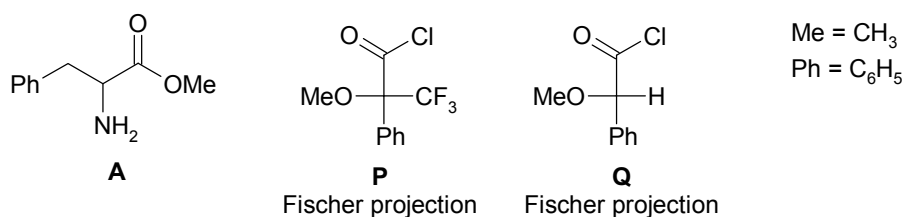
Later the ligand **G** was developed for the same purpose.



- 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  $^{31}\text{P}$ -NMR spectrum of ligand **G**? If there is more than one signal then indicate also the relative peak areas.

## Problem 11 Optical Purity

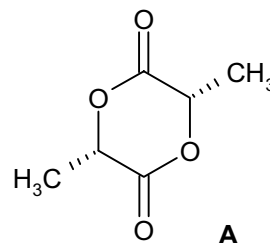
Antipodes (enantiomers) of optically active compounds have different physiological properties, e.g. the *R*-enantiomer of asparagine tastes sweet, whereas the *S*-enantiomer is bitter. In modern drug design utmost attention is paid to the optical purity of active ingredients. Phenylalanine is an amino 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,  $(\text{C}_2\text{H}_5)_3\text{N}$ .



- 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  $^1\text{H}$ -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  $^{19}\text{F}$ -NMR signal(s) for the derivative from **P**.

## Problem 12 Poly(lactic Acid)

Poly(lactic 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**.



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

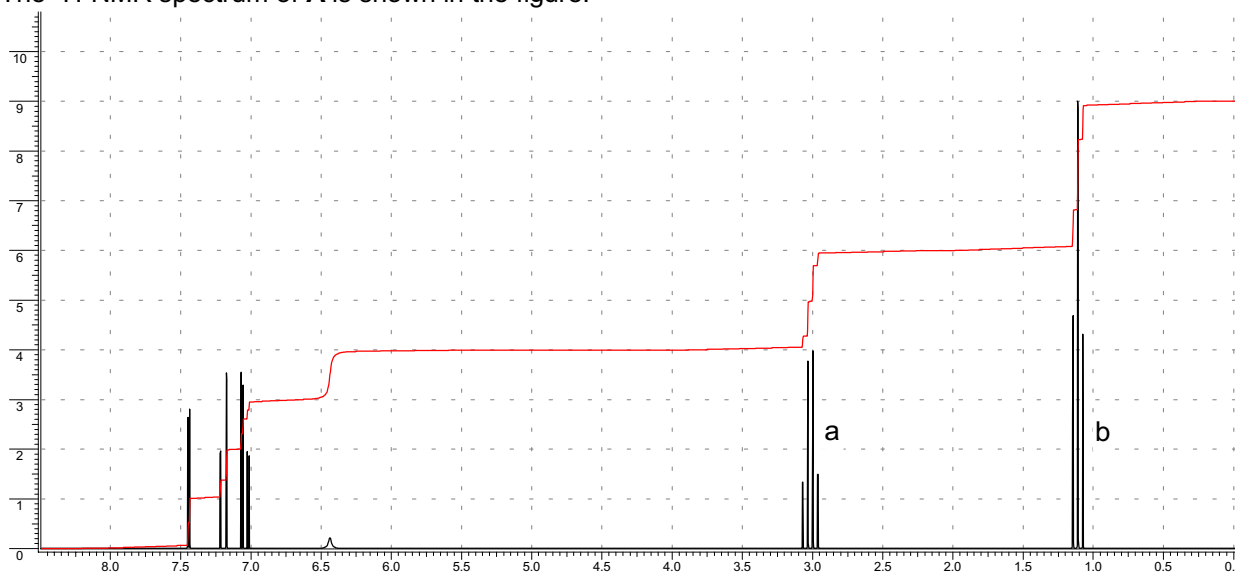
Compound **A** with the formula  $C_8H_9N_2O_2Cl$  is insoluble in water and base. Compound **A** slowly dissolves in a dilute solution of hydrochloric acid.

**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  $^1H$ -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.

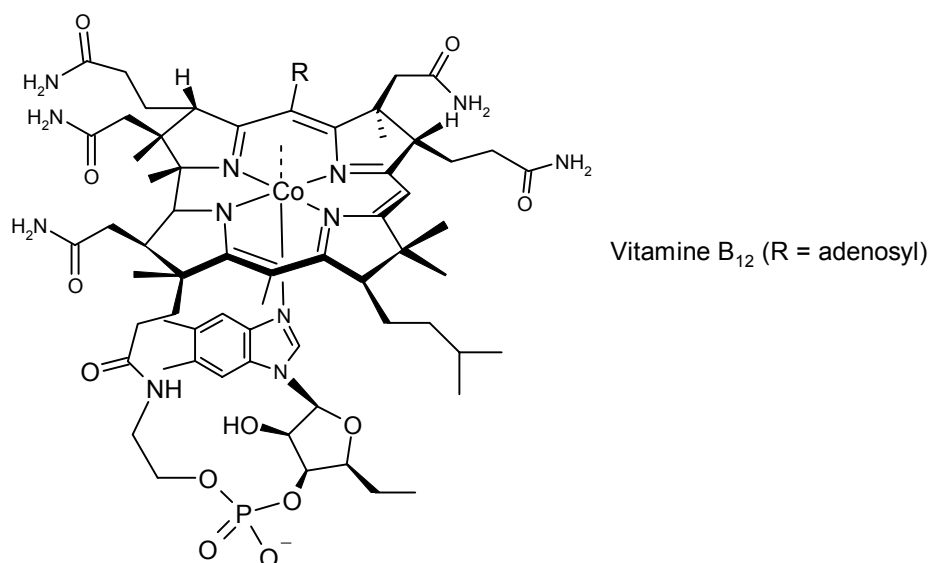
Answer box

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 vitamin B<sub>12</sub>. 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 vitamin B<sub>12</sub> also Co<sup>+</sup> is possible.



**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 <sup>+</sup>  | yes / no |
| Co <sup>2+</sup> | yes / no |
| Co <sup>3+</sup> | 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 vitamin B<sub>12</sub> complex? (mark the correct answer)

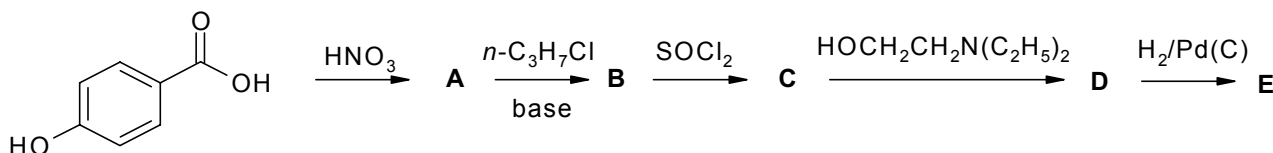
|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|

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*- $\text{C}_4\text{H}_9\text{Cl}$  is used in the second step instead of *n*- $\text{C}_3\text{H}_7\text{Cl}$ , this will lead to:

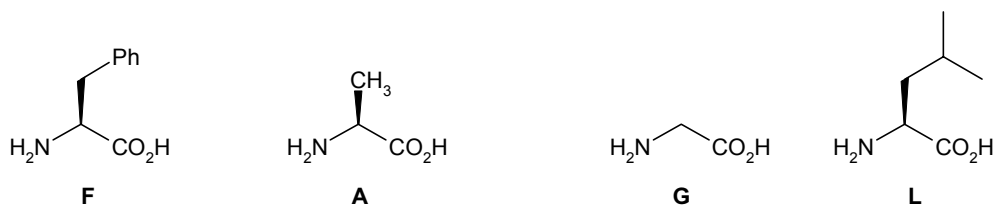
- A similar product as **B**, if so give the structure.
- No reaction at all.
- Decomposition of the *tert*- $\text{C}_4\text{H}_9\text{Cl}$ .
- An aromatic substitution reaction.

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  $\alpha$ -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  $\text{NH}_2$  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.

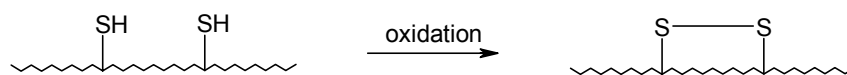
16-2 Which reaction takes place with Sanger's reagent (for reason of simplicity write the *N*-terminal side of the peptide as  $\text{H}_2\text{NR}$ ). Give the equation.

The *C*-terminal residue, which contains the free  $\text{CO}_2\text{H}$  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**.

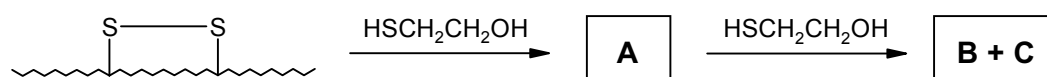
16-3 Deduce the possible structure(s) of this tetrapeptide. Give the structure(s).

## 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° 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.

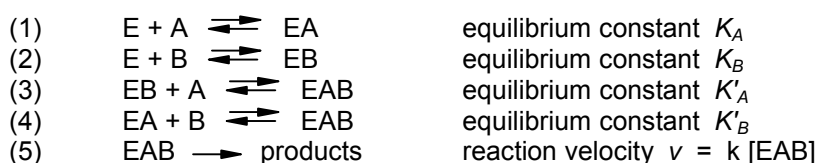
Treatment of ribonuclease A with 8 M urea  $\text{H}_2\text{NC(=O)NH}_2$  in the presence of 0.01 M 2-mercaptoethanol results in a complete disappearance of the enzymatic activity by disruption of S-S bridges. Slow removal of the urea and 2-mercaptoethanol by means of dialysis together with re-oxidation 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):

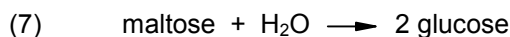


When the rate constant is small, the equilibria (1)-(4) are hardly shifted due to the reaction (5). This leads to expression (6) in which  $V_{\max}$  is the maximal velocity of the reaction, that is reached when the enzyme is saturated with the substrates (all enzyme is bound to A and B).

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

**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  $\alpha$ -glucosidase from yeast.



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  $[A] \longrightarrow 0$ .

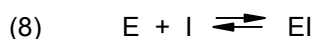
**18-4** (a) Simplify the Michaelis-Menten equation by taking [A] as very high, thus  $[A] \longrightarrow \infty$ , which is the case when the enzyme is completely saturated with substrate.

(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:



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-competitive 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  $\alpha$ -glucosidase the model substrate *p*-nitrophenyl- $\alpha$ -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:

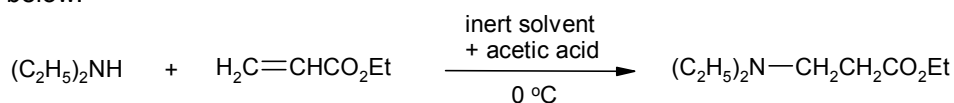
- The maltose does not influence the rate of release of *p*-nitrophenol.
- Maltose functions as a competitive inhibitor.
- Maltose functions as a non-competitive inhibitor.

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  $[\text{maltose}] = K_{\text{maltose}}$ . Insert the graph made in question 18-6. Mark the points  $V_{\max}$  en  $\frac{1}{2} V_{\max}$ .

## 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)  $\text{NH}_3$  is treated exhaustively with an excess of acrylonitrile ( $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N}$ ) to give a product that contains 3 cyanide groups.
- (2) This product is reduced catalytically with  $\text{H}_2$  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  $\text{H}_2$  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  $\text{NH}_3$ , 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.

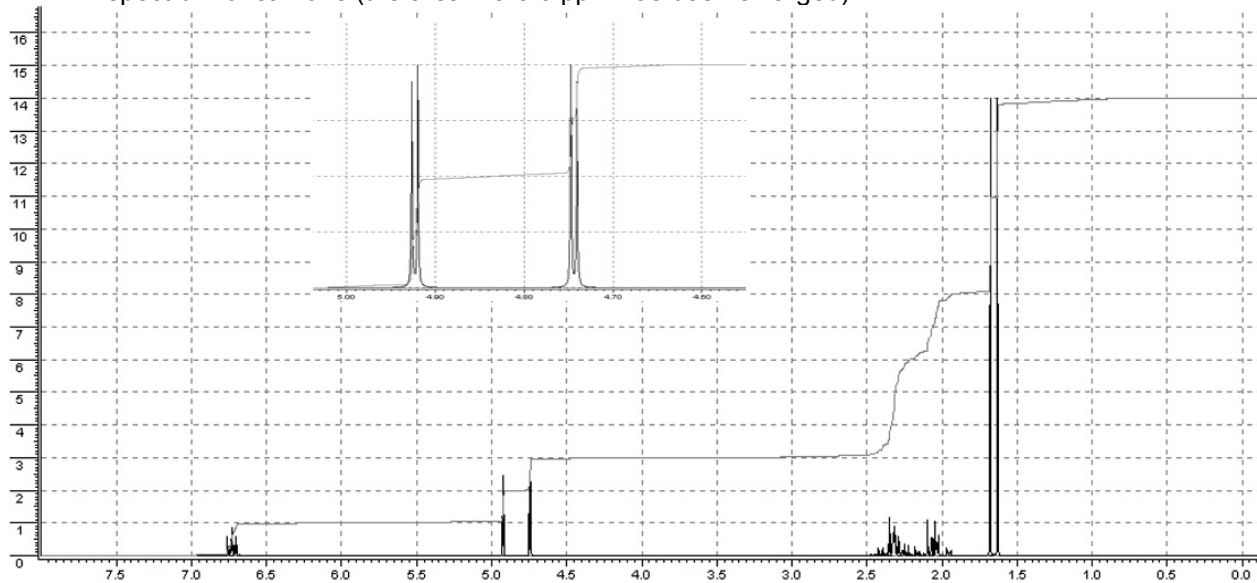
- 20-1** Calculate the molecular formula of carvone.
- 20-2** Calculate the number of unsaturation of carvone.
- 20-3** Which functional group is responsible for the strong absorption at  $1680\text{ cm}^{-1}$  in the IR spectrum?
- 20-4** In the IR-spectrum there is no absorption above  $3000\text{ cm}^{-1}$ . Indicate which type of functional group is absent in carvone.

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

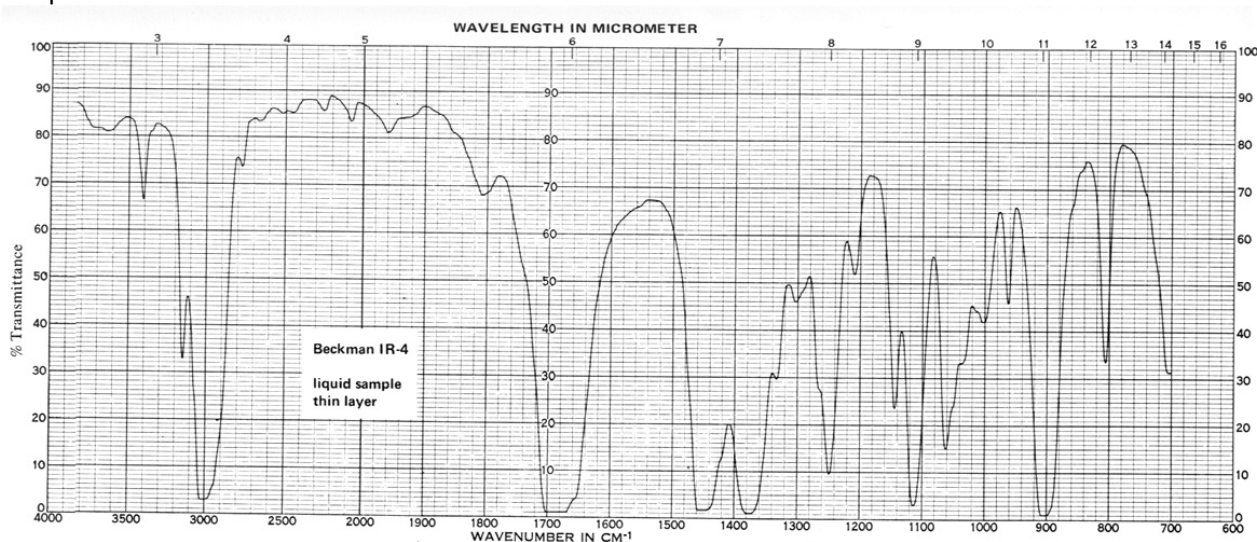
| $\delta$ (ppm) | Type                   | Integration |
|----------------|------------------------|-------------|
| 1.63           | singlet                | 3           |
| 1.68           | singlet                | 3           |
| 1.9-2.2        | multiplet              | 2           |
| 2.2-2.5        | 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  $\text{CH}_2$  signal).

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

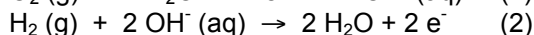
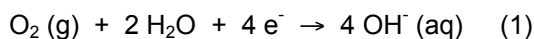


IR spectrum of carvone:

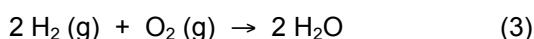


## Problem 21 Electrochemical Energy Conversion

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:



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



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.

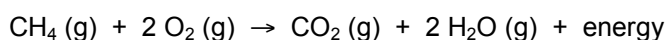
The change of the Gibbs energy  $\Delta G_0$  is a measure of the driving force of a reaction. The change of energy is given by:

$$\Delta G_0 = - n F E$$

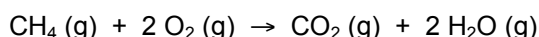
where  $n$  is the number of electrons transferred in the reaction and  $F$  is the Faraday constant (96487 C). The standard electrode potential for  $\text{O}_2(\text{g})$  at 25 °C is + 1.23 V.

**21-4** Calculate the  $\Delta G_0$  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:



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:



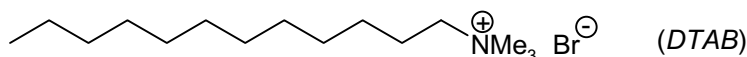
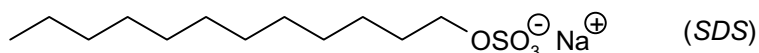
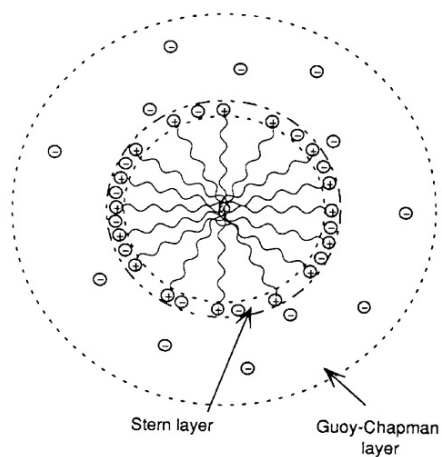
**21-5** Give the reactions at the anode and the cathode.

Another high-temperature fuel cell utilizes molten carbonate as the ionically conducting electrolyte. Hydrogen is used as fuel, oxygen is mixed with  $\text{CO}_2$ .

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

## Problem 22 Micelles

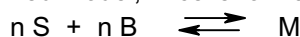
Biomembranes fulfil many important functions in the living cell. Membranes in plant and animal cells contain 40-50% lipids and 50-60% proteins. Phospholipids, which are key constituents in biomembranes, have hydrophobic fatty acid tails and polar hydrophilic head groups. Such structures are commonly 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*-dodecyltrimethylammonium 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.



| Amphiphile  | CMC (mmol L <sup>-1</sup> ) | Relative micelle mass (g mol <sup>-1</sup> × 10 <sup>3</sup> ) |
|-------------|-----------------------------|--|
| <i>SDS</i>  | 8.1                         | 18.0   |
| <i>DTAB</i> | 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:



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<sup>-1</sup> K<sup>-1</sup>).

**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  $\text{kg m}^{-3}$  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-Landé formula given below can be used to calculate the lattice energy:

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

The factor  $f e^2$  amounts to 1390 when the ionic radii  $r_+$  and  $r_-$  are given in Å. The Madelung constant is 1.638. The Born exponent  $n$  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, °C | [BBr <sub>3</sub> ], mol L <sup>-1</sup> | [PBr <sub>3</sub> ], mol L <sup>-1</sup> | [H <sub>2</sub> ], mol L <sup>-1</sup> | $r$ , mol s <sup>-1</sup> |
|-----------------|--|--|--|---------------------------|
| 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                                  | $4.60 \times 10^{-8}$     |
| 880             | $2.25 \times 10^{-6}$                    | $9.00 \times 10^{-6}$                    | 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 °C.
- 23-10** Calculate the activation energy for the formation of BP.