Preparatory Problems

IChO34
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The Netherlands

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34th International Chemistry Olympiad

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Contents

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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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_2 and N_2 forming LiH and Li_3N	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_4, NH_3, H_2O, H_2S, and hydrogen halides HX	1
1.10.4	NO reacts with O_2 to form NO_2	1
1.10.5	equilibrium between NO_2 and N_2O_4	1

1.10.6 products of reaction of NO_2 with water 1
1.10.7 HNO_2 and its salts are reductants 1
1.10.8 HNO_3 and its salts are oxidants 1
1.10.9 N_2H_4 is a liquid and reluctant 3
1.10.10 existence of acids like $H_2N_2O_2$, HN_3 3
1.10.11 reactions of HNO_3 with different metals and reductants 3
1.10.12 reaction of $Na_2S_2O_3$ with iodine 2
1.10.13 other thioacids, polyacids, peroxoacids 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
1.10.15 compounds of non-metals with other oxidation states 3
1.10.16 the preferred oxidation states are Sn(II), Pb(II) and Bi(III) 2
1.10.17 products of reactions of non-metal oxides with water and stoichiometry of resulting acids 1
1.10.18 reactions of halogens with water 2
1.10.19 reactivity and oxidizing power of halogens decrease from F_2 to I_2 1
1.10.20 differences of chemistry between row 4 and row 3 elements 3

1.11 d-Block

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
1.11.2 colors of the listed common ions in aqueous solutions 2
1.11.3 other oxidation states and chemistry of other d-block elements 3
1.11.4 Cr, Mn, Fe, Co, Ni, Zn dissolve in dilute HCl; Cu, Ag, Hg do not dissolve 1
1.11.5 products of dissolution are (2+) cations 2
1.11.6 passivation of Cr, Fe (and also Al) 2
1.11.7 $Cr(OH)_3$ and $Zn(OH)_2$ are amphoteric, other common hydroxides are not 1
1.11.8 MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$ are strong oxidants 1
1.11.9 products of reduction of MnO_4^- depending on pH 2
1.11.10 polyanions other than $Cr_2O_7^{2-}$ 3

1.12 Other inorganic problems

1.12.1 industrial production of H_2SO_4, NH_3, Na_2CO_3, Na, Cl_2, NaOH, 1
1.12.2 chemistry of lanthanides and actinides 3
1.12.3 chemistry of noble gases 3

2. PHYSICAL CHEMISTRY

2.1 Chemical equilibria

2.1.1 dynamical model of chemical equilibria 1
2.1.2 chemical equilibria expressed in terms of relative concentrations 1
2.1.3 chemical equilibria expressed in terms of partial pressures 2
2.1.4 the relationship between equilibrium constants for ideal gases expressed in different ways (concentration, pressure, mole fraction) 3
2.1.5 relation of equilibrium constant and standard Gibbs energy 3

2.2 Ionic equilibria

2.2.1 Arrhenius theory of acids and bases 1
2.2.2 Broensted-Lowry theory, conjugated acids and bases 1
2.2.3 definition of pH 1
2.2.4 ionic product of water 1
2.2.5 relation between K_a and K_b for conjugated acids and bases 1
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 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

2.3 Electrode equilibria

2.3.1 electromotive force (definition) 1
2.3.2 first kind electrodes 1
2.3.3 standard electrode potential 1
2.3.4 Nernst equation 2
2.3.5 second kind electrodes 2
2.3.6 relation between ΔG and electromotive force 3

2.4 Kinetics of homogeneous reactions

2.4.1 factors influencing reaction rate 1
2.4.2 rate equation 1
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
2.4.15 basic concepts of transition state

	theory	3
2.4.16	opposing, parallel and consecutive reactions	3

2.5 Thermodynamics (First law)

2.5.1	system and its surroundings	2
2.5.2	energy, heat and work	2
2.5.3	relation between enthalpy and energy	2
2.5.4	heat capacity - definition	2
2.5.5	difference between C_p and C_v (ideal gas only)	2
2.5.6	Hess law	2
2.5.7	Born-Haber cycle for ionic compounds	3
2.5.8	lattice energies - approximate calculations (e.g. Kapustinski equation)	3
2.5.9	use of standard formation enthalpies	2
2.5.10	heats of solution and solvation	2
2.5.11	bond energies - definition and uses	2

2.6 Thermodynamics (Second law)

2.6.1	entropy, definition (q/T)	2
2.6.2	entropy and disorder	2
2.6.3	relation $S = k \ln W$	3
2.6.4	relation $\Delta G = \Delta H - T\Delta S$	2
2.6.5	ΔG and directionality of changes	2

2.7 Phase systems

2.7.1	ideal gas law	1
2.7.2	van der Waals gas law	3
2.7.3	definition of partial pressure	1
2.7.4	temperature dependence of the vapor pressure of liquid	2
2.7.5	Clausius-Clapeyron equation	3
2.7.6	reading phase diagrams: triple point	3
2.7.7	phase diagrams: critical temperature	3
2.7.8	liquid-vapor system (diagram)	3
2.7.9	liquid-vapor: ideal and non-ideal systems	3
2.7.10	liquid-vapor: use in fractional distillation	3
2.7.11	Henry's law	2
2.7.12	Raoult's law	2
2.7.13	deviations from Raoult's law	3
2.7.14	boiling point elevation law	2
2.7.15	freezing point depression, determination of molar mass	2
2.7.16	osmotic pressure	2
2.7.17	partition coefficient	3
2.7.18	solvent extraction	3
2.7.19	basic principles of chromatography	2

3. ORGANIC CHEMISTRY

3.1 Alkanes

3.1.1	isomers of butane	1
3.1.2	naming (IUPAC)	1
3.1.3	trends in physical properties	1
3.1.4	Substitution (e.g. with Cl_2)	
3.1.4.1	products	1
3.1.4.2	free radicals	2
3.1.4.3	initiation/termination of the chain reaction	2

3.2 Cycloalkanes

3.2.1	names	1
3.2.2	strain in small rings	2
3.2.3	chair/boat conformation	2

3.3 Alkenes

3.3.1	planarity	1
3.3.2	*E/Z* (*cis-trans*) isomerism	1
3.3.3	Addition of Br_2 and HBr	
3.3.3.1	products	1
3.3.3.2	Markovnikov's rule	2
3.3.3.3	carbonium ions in addition reactions	3
3.3.3.4	relative stability of carbonium ions	3
3.3.3.5	1,4-addition to alkadienes	3

3.4 Alkynes

3.4.1	linear geometry	1
3.4.2	acidity	2
3.4.3	differences in chemical properties between alkenes and alkynes	3

3.5 Arenes and heterocycles

3.5.1	formula of benzene	1
3.5.2	delocalization of electrons	1
3.5.3	stabilization by resonance	1
3.5.4	Hückel (4n + 2) rule	3
3.5.5	aromaticity of heterocycles	3
3.5.6	nomenclature of heterocycles (IUPAC)	3
3.5.7	polycyclic aromatic compounds	3
3.5.8	effect of first substituent on reactivity	2
3.5.9	effect of first substituent on direction of substitution	2
3.5.10	explanation of substituent effects	3

3.6 Halogen compounds

3.6.1	hydrolytic reactions	2
3.6.2	exchange of halogens	3
3.6.3	reactivity (primary vs secondary vs tertiary)	2
3.6.4	ionic mechanism of substitution	2
3.6.5	side products (elimination)	2
3.6.6	reactivity (aliphatic vs aromatic)	2
3.6.7	Wurtz (RX + Na) reaction	3
3.6.8	halogen derivatives and pollution	3

3.7 Alcohols and phenols

3.7.1	hydrogen bonding - alcohols vs ethers	1
3.7.2	acidity of alcohols vs phenols	2
3.7.3	dehydration to alkenes	1
3.7.4	dehydration to ethers	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

3.8 Carbonyl compounds

3.8.1	nomenclature	1
3.8.2	keto/enol tautomerism	2
3.8.3	Preparation of carbonyl compounds	
3.8.3.1	oxidation of alcohols	1
3.8.3.2	from carbon monoxide	3

3.8.4	Reaction of carbonyl compounds	
3.8.4.1	oxidation of aldehydes	1
3.8.4.2	reduction with Zn metal	2
3.8.4.3	addition of HCN	2
3.8.4.4	addition of $NaHSO_3$	2
3.8.4.5	addition of NH_2OH	2
3.8.4.6	aldol condensation	3
3.8.4.7	preparation of acetates	2
3.8.4.8	Cannizzaro (PhCHO disproportionation)	3
3.8.4.9	Grignard reaction	2
3.8.4.10	Fehling (Cu_2O) and Tollens (Ag mirror) reagents	2

3.9 Carboxylic acids

3.9.1	inductive effect and strength	2
3.9.2	equivalence of oxygen atoms in anions	2
3.9.3	Preparation and reactions of carboxylic acids	
3.9.3.1	preparation from esters	2
3.9.3.2	preparation from nitriles	2
3.9.3.3	products of reaction with alcohols (esters)	3
3.9.3.4	mechanism of esterification	2
3.9.3.5	isotopes in mechanism elucidation	3
3.9.3.6	nomenclature of acid halides	2
3.9.3.7	preparation of acid chlorides	2
3.9.3.8	preparation of amides from acid chlorides	2
3.9.3.9	preparation of nitriles from acid chlorides	3
3.9.3.10	properties and preparation of anhydrides	2
3.9.3.11	oxalic acid, name and formula	1
3.9.3.12	multifunctional acids (e.g. hydroxy acids, keto acids)	2
3.9.3.13	polycarboxylic acids	2
3.9.3.14	optical activity (e.g. lactic acid)	2
3.9.3.15	*R/S* nomenclature	3
3.9.3.16	plant and animal fats, differences	2

3.10 Nitrogen compounds

3.10.1	basicity of amines	1
3.10.2	comparing aliphatic vs. aromatic	2
3.10.3	names: primary, secondary, tertiary, quaternary amines	2
3.10.4	identification of primary/sec./tert./ quaternary amines in the laboratory	3
3.10.5	Preparation of amines	
3.10.5.1	from halogen compounds	2
3.10.5.2	from nitro compounds (e.g. $PhNH_2$ from $PhNO_2$)	3
3.10.5.3	from amides (Hoffmann)	3
3.10.6	mechanism of Hoffmann rearrangement in acidic/basic medium	3
3.10.7	basicity amines vs. amides	2
3.10.8	diazotation products of aliphatic amines	3
3.10.9	diazotation products of aromatic amines	3
3.10.10	dyes: color vs. structure (chromophore groups)	3
3.10.11	nitro compounds : aci/nitro tautomerism	3
3.10.12	Beckmann (oxime - amide) rearrangements	3

3.11 Some large molecules

3.11.1	hydrophilic/hydrophobic groups	2
3.11.2	micelle structure	3
3.11.3	preparation of soaps	1
	products of polymerization of:	
3.11.4	- styrene	2
3.11.5	- ethene	1
3.11.6	- polyamides	3
3.11.7	- phenol + aldehydes	3
3.11.8	- polyurethanes	3
3.11.9	polymer cross linking	3
3.11.10	chain mechanism of polymer formation	2
3.11.11	rubber composition	3

4. BIOCHEMISTRY

4.1 Amino acids and peptides

4.1.1	ionic structure of amino acids	1
4.1.2	isoelectric point	2
4.1.3	20 amino acids (classification in groups)	2
4.1.4	20 amino acids (names and structures)	3
4.1.5	ninhydrin reaction (including equation)	3
4.1.6	separation by chromatography	3
4.1.7	separation by electrophoresis	3
4.1.8	peptide linkage	1

4.2 Proteins

4.2.1	primary structure of proteins	1
4.2.2	-S-S- bridges	3
4.2.3	sequence analysis	3
4.2.4	secondary structures	3
4.2.5	details of alpha-helix structure	3
4.2.6	tertiary structure	3
4.2.7	denaturation reaction by change of pH, temperature, metals, ethanol	2
4.2.8	quaternary structure	3
4.2.9	separation of proteins (molecule size and solubility)	3
4.2.10	metabolism of proteins (general)	3
4.2.11	proteolysis	3
4.2.12	transamination	3
4.2.13	four pathways of catabolism of amino acids	3
4.2.14	decarboxylation of amino acids	3
4.2.15	urea cycle (only results)	3

4.3 Fatty acids and fats

4.3.1	IUPAC names from C_4 to C_{18}	2
4.3.2	trivial names of most important (ca. 5) fatty acids	2
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
4.3.8	active transport	3

4.4 Enzymes

4.4.1	general properties, active centres	2
4.4.2	nomenclature, kinetics, coenzymes, function of ATP, etc.	3

4.5 Saccharides

4.5	Glucose and fructose:	
4.5.1	- chain formulas	2
4.5.2	- Fischer projections	2
4.5.3	- Haworth formulas	3
4.5.4	osazones	3
4.5.5	maltose as reducing sugar	2
4.5.6	difference between starch and cellulose	2
4.5.7	difference between alpha- and beta-D glucose	2
4.5.8	metabolism from starch to acetyl-CoA	3
4.5.9	pathway to lactic acid or to ethanol; catabolism of glucose	3
4.5.10	ATP balance for the above pathways	3
4.5.11	photosynthesis (products only)	2
4.5.12	light and dark reaction	3
4.5.13	detailed Calvin cycle	3

4.6 Krebs cycle and respiration chain

4.6.1	formation of CO_2 in the cycle (no details)	3
4.6.2	intermediate compounds in the cycle	3
4.6.3	formation of water and ATP (no details)	3
4.6.4	FMN and cytochromes	3
4.6.5	calculation of ATP amount for 1 mole of glucose	3

4.7 Nucleic acids and protein synthesis

4.7.1	pyrimidines, purines	2
4.7.2	nucleosides and nucleotides	3
4.7.3	formulae of all pyrimidine and purine bases	3
4.7.4	difference between ribose and 2-deoxyribose	3
4.7.5	base combination CG and AT	3
4.7.6	base combination CG and AT (hydrogen bonding structure)	3
4.7.7	difference between DNA and RNA	3
4.7.8	difference between mRNA and tRNA	3
4.7.9	hydrolysis of nucleic acids	3
4.7.10	semiconservative replication of DNA	3
4.7.11	DNA-ligase	3
4.7.12	RNA synthesis (transcription) without details	3
4.7.13	reverse transcriptase	3
4.7.14	use of genetic code	3
4.7.15	start and stop codons	3
4.7.16	translation steps	3

4.8 Other biochemical problems

4.8.1	hormones, regulation	3
4.8.2	hormones, feedback	3
4.8.3	insulin, glucagon, adrenaline	3
4.8.4	mineral metabolism (no details)	3
4.8.5	ions in blood	3
4.8.6	buffers in blood	3
4.8.7	haemoglobin; function and skeleton	3
4.8.8	haemoglobin; diagram of oxygen absorption	3
4.8.9	steps in clotting the blood	3
4.8.10	antigens and antibodies	3
4.8.11	blood groups	3
4.8.12	acetyl choline, structure and functions	3

OTHER PROBLEMS

5. Analytical chemistry

5.1	choice of indicators for acidimetry	1
5.2	titration curve; pH (strong and weak acid)	2
5.3	EMF (redox titration)	2
5.4	calculation of pH of simple buffer solution	2
5.5	identification of Ag^+, Ba^{2+}, Cl^-, SO_4^{2-}	1
5.6	identification of Al^{3+}, NO_2^-, NO_3^-, Bi^{3+}	2
5.7	identification of VO_3^-, ClO_3^-, Ti^{4+}	3
5.8	use of flame tests for identification of K, Ca and Sr	1
5.9	Lambert -Beer law	2

6. Complexes

6.1	writing down complexation reactions	1
6.2	definition of coordination number	1
6.3	prediction of coordination number of complex ions and molecules	3
6.4	complex formation constants (definition)	2
6.5	E_g and T_{2g} terms: high and low spin octahedral complexes	3
6.6	calculation of solubility of AgCl in NH_3 (from K_s and constants β)	3
6.7	*cis* and *trans* forms	3

7. Theoretical chemistry

7.1	energy levels of hydrogen atom (formula)	2
7.2	square of the wave function and probability	3
7.3	understanding the simplest Schrödinger equation	3
7.4	n, l, m quantum numbers	2
7.5	shape of p-orbitals	2
7.6	d-orbital stereoconfiguration	3
7.7	molecular orbital diagram: H_2 molecule	2
7.8	molecular orbital diagram: N_2 and O_2 molecules	3
7.9	bond orders in O_2, O_2^+, O_2^-	3
7.10	unpaired electrons and paramagnetism	2
7.11	Hückel theory for aromatic compounds	3
7.12	Lewis acids and bases	2
7.13	hard and soft Lewis acids	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 *o*- and *p*- substituted benzene	3
8.4.5	^{13}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	3
	structures:	
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 normal pressure	2
1.17	apparatus for distillation of liquids at reduced pressure	3
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 alkali-metric 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:

$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$

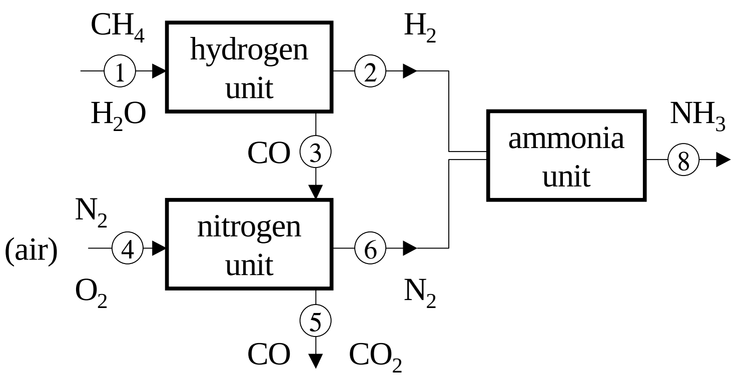
The hydrogen in the ammonia plant is obtained from methane and water by the reaction:

$CH_4 + H_2O \rightarrow CO + 3\ H_2$

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

$O_2 + 2\ CO \rightarrow 2\ CO_2$

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.



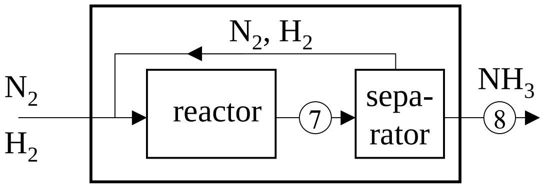
Assume that the reactants are converted completely. Take as flow for ammonia at position ⑧:

n [NH_3, ⑧] = 1000 mol s^{-1}.

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

n[H_2,②], for hydrogen at position ②
n[N_2,⑥], for nitrogen at position ⑥
n[CH_4,①], for methane at position ①
n[H_2O,①], for water at position①
n[CO,③], for CO at position ③
n[O_2,④], for oxygen at position ④
n[CO,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.



ammonia unit

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:

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

1-3 Calculate the change in the Gibbs energy (ΔG_r) for the conversion of one mole of N_2.

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

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

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

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

$p_{NH_3} = x\, p_{tot}$, whereby x 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:

$Mb + O_2 \rightleftarrows MbO_2$

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:

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

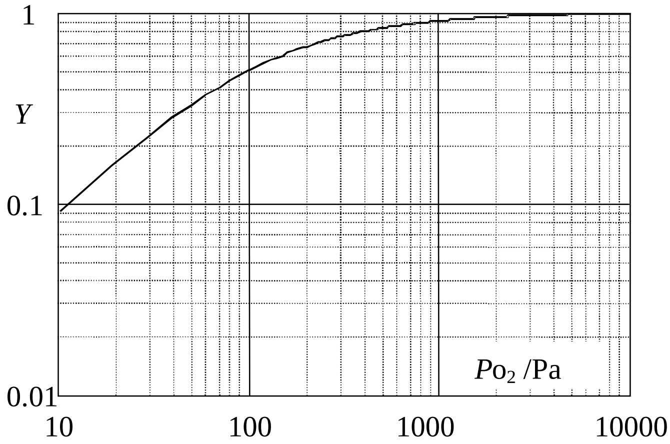
Oxygen is only slightly soluble in water: the amount that dissolves is proportional to the oxygen pressure:

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

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

$$Y = \frac{p_{O_2}}{p_{O_2} + K_p}$$, wherein K_p 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 kg m^{-3}. The Avogadro number is $N_A = 6.02 \times 10^{23}$ 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.

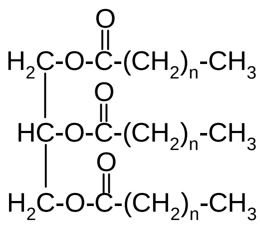
Oxygen is used to produce energy (heat and motion) by burning fat. The overall equation can be approximated by:

$$(CH_2)_n + 1.5n\ O_2 \longrightarrow n\ CO_2 + n\ H_2O$$

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.

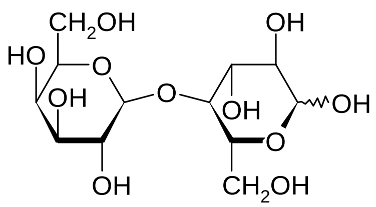
2-4 Calculate how long the whale can stay under water.

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.

D-galactose

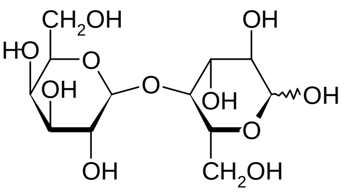
Answer box

D-glucose

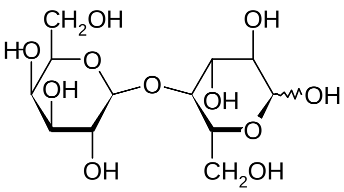
Answer box

The acid-catalysed hydrolysis of lactose gives D-galactose and D-glucose.

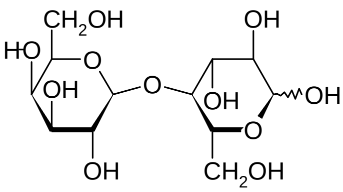
3-2 Indicate with an arrow in the formula of lactose:
(a) To which oxygen atom a proton will be attached in order to effect hydrolysis.
(b) Which carbon-oxygen bond will be cleaved during the hydrolysis reaction.
(c) Which carbon atom will be involved in the reaction with Fehling's reagent (this reagent is used to detect reducing sugars).



Answer box (a)



Answer box (b)



Answer box (c)

The hydrolysis of lactose can be coupled with hydrogenation using a metal catalyst which leads to the polyalcohols sorbitol and galactitol, also known as glucitol and dulcitol, respectively.

3-3 Draw Fischer projections of sorbitol and galactitol.
Indicate whether these compounds are optically active or inactive.

Sorbitol

Optically active: yes / no

Answer box

Galactitol

Optically active: yes / no

Answer box

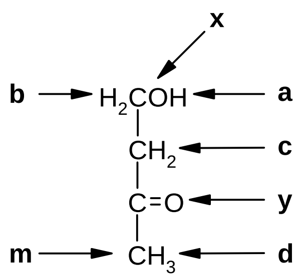
In industrial processes lactose is isomerised to lactulose, which is an intestinal pharmaceutical. Hydrogenation of lactose leads to lactitol, a C_{12}-polyol which is a low-calorific sweetener. Both processes are executed in The Netherlands.

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.

Lactulose	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}H or ^{17}O, can give valuable information. Modern NMR techniques are able to 'see' deuterium ^{2}H and the oxygen isotope ^{17}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 $^{2}H_2O$ at pH = 10. Rank the order of exchange (introduction) of deuterium atoms (^{2}H) from first to last.
First ☐ ☐ ☐ ☐ last.

4-2 Similarly, the substrate is treated with $H_2{}^{17}O$ at pH = 10. Rank the order of introduction of ^{17}O from first to last.
First ☐ ☐ last.

4-3 Do you consider the exchange method appropriate for the introduction of a ^{13}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).

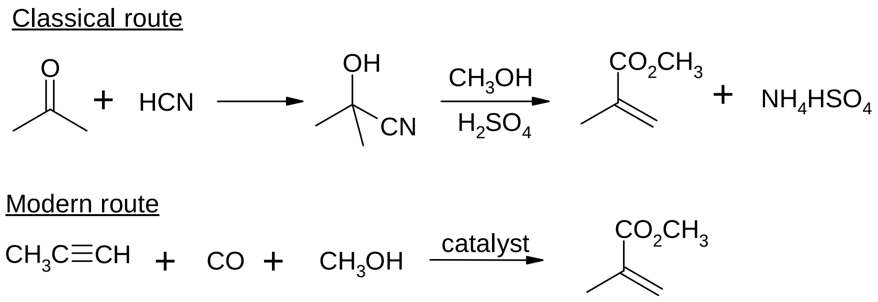


Figure 1: Methyl methacrylate synthesis

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.

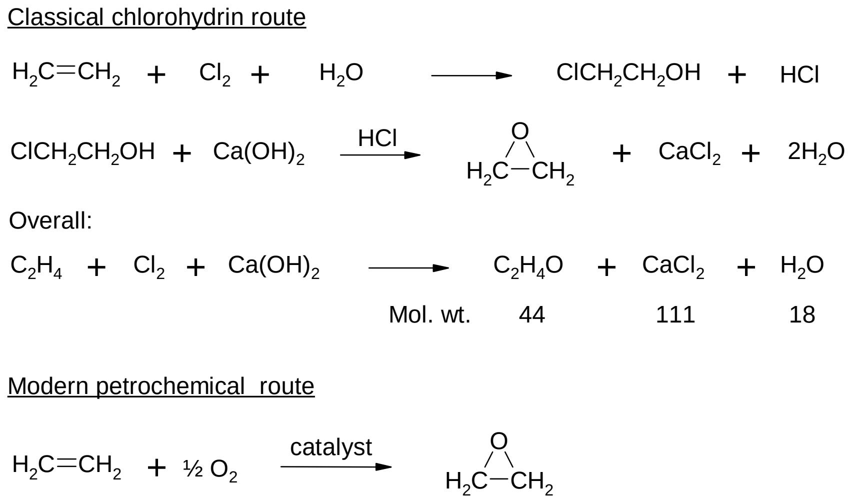


Figure 2: Ethene oxide synthesis

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 $BaCl_2$ and $SrCl_2$ 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 Ba^{2+} has precipitated as $BaSO_4$ and that $SrSO_4$ may be contaminated with no more than 0.1 % $BaSO_4$. The solubility product constants are as follows:
$K_{sp}(BaSO_4) = 1 \times 10^{-10}$ and $K_{sp}(SrSO_4) = 3 \times 10^{-7}$.

6-1 Give the relevant equations.
Calculate the residual concentration of Ba^{2+}.
Calculate the percentage of Ba^{2+} and 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 $Ag(NH_3)_2^+$ is a complex containing Ag^+ as the central ion and two NH_3 molecules as ligands.
The solubility of AgCl in water is 1.3×10^{-5} M.
The solubility product constant of AgCl is 1.7×10^{-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 AgCl in 1.0 M aqueous ammonia is higher than in pure water.

Problem 7 UV-spectrometry as an Analytical Tool

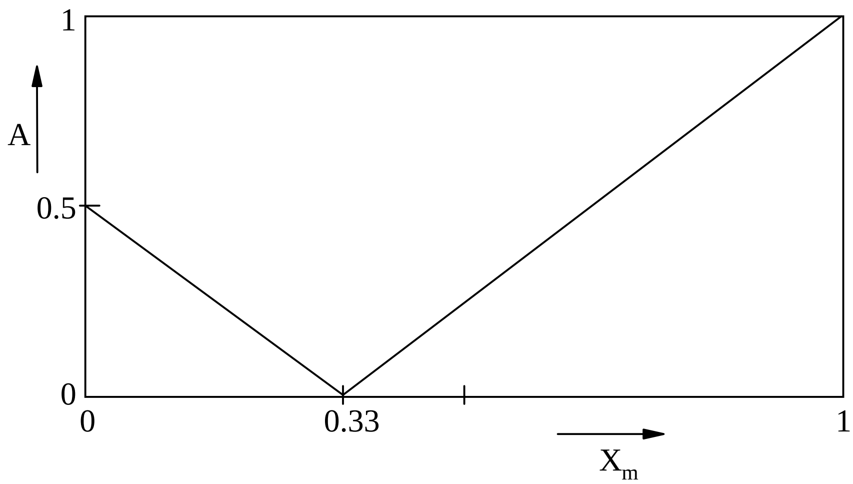
UV-spectrometry is frequently used to determine the concentration of a substance in solution by measuring the UV absorbance at a certain wavelength of either visible or ultraviolet light. The law of Lambert and Beer states that the absorbance is directly proportional to the concentration in moles per litre at a given wavelength: $A = \varepsilon\, c\, l$ (ε is the molar absorptivity or the extinction coefficient in L mol^{-1} 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 Fe(II) fenanthroline (ferroin) will be considered. (λ_{max}= 512 nm, ε = 10500 L mol^{-1} cm^{-1}).

7-1 Calculate the lowest concentration of ferroin 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 ferroin 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:

$$2\ NOCl\ (g) \longrightarrow 2\ NO\ (g) + Cl_2\ (g)$$

The rate constant k is 2.6 x 10^{-8} L mol^{-1} s^{-1} at 300K and 4.9 x 10^{-4} L mol^{-1} s^{-1} at 400K.
The gas constant R = 8.314 J mol^{-1} 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: $2\ NO\ (g) + O_2\ (g) \longrightarrow 2\ NO_2\ (g)$.
The proposed mechanism for this reaction is given below.

$$NO\ (g) + O_2\ (g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3\ (g) \qquad \text{fast equilibrium}$$

$$NO_3\ (g) + NO\ (g) \xrightarrow{k_2} 2\ NO_2\ (g) \qquad \text{rate limiting step}$$

8-2 Give the rate equation for the NO_2 formation on basis of this mechanism.

Experimentally, the rate equation reads $s = k\,[NO]^2\,[O_2]$.

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^{-1}	Electron affinity Cl	= - 360 kJ mol^{-1}
Bonding energy KCl	= - 423 kJ mol^{-1}	Ionisation energy Na	= 496 kJ mol^{-1}
Bonding energy MgCl	= - 406 kJ mol^{-1}	1st Ionisation energy Ca	= 592 kJ mol^{-1}
Bonding energy CaCl	= - 429 kJ mol^{-1}	2nd Ionisation energy Ca	= 1148 kJ mol^{-1}

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 $CaCl_2$ into three neutral atoms and calculate the dissociation energy of $CaCl_2$, assuming that the bond length in the triatomic species is 9% shorter than in the diatomic species.