Preparatory Problems

2 - 11 July 2000
Copenhagen

32nd IChO

Denmark

32nd International
Chemistry Olympiad

Preparatory Problems

2 - 11 July 2000
Copenhagen

32nd IChO

2000

Denmark

32nd International
Chemistry Olympiad

Edited by Henrik Parbo

The Association of Upper Secondary Chemistry Teachers

Kemi Forlaget

Preparatory Problems
32nd International Chemistry Olympiad

Edited by Henrik Parbo

ISBN 87-89782-14-3

Printed and bound in Denmark by TL · Offset

Kemi Forlaget
LMFK-Sekretariatet
Slotsgade 2, 3.
DK - 2200 København N

Contents

Preface

The aim of the scientific committee has been that as many as possible of the preparatory problems should take their starting point in issues of general chemical, public or environmental interest. Therefore some of the problems cover several topics from the International Chemistry Olympiad.

We have also endeavoured to apply the IUPAC nomenclature in this collection of problems. For the solutions of physical chemistry problems the units of the equilibrium constant, depending on the particular circumstances, have to be specified. If the constant appears in thermodynamic equations, the equilibrium constant (K_a) is dimensionless and its value depends on the choice of standard state.

We hope that your students will learn a considerable amount of chemistry from these worked solutions without your continual assistance, and that the publication will be of general interest among chemistry teachers.

We have tried to highlight the safety precautions that need to be taken during the laboratory work, but our warnings cannot be comprehensive. We have included some details regarding handling or disposal of the products of these lab exercises. Students should of course also make themselves aware of any hazards associated with the chemicals that they will be using in any exercise, and we encourage you to bring these to their attention.

Acknowledgement
I would like to thank the members of the scientific committee for inspiring teamwork, profitable discussions and enormous amount of work. Furthermore, I am indebted to my colleague lecturer Poul Thulstrup for his unremitting contribution to solving computer problems. I would also like to thank Martin Hancock for his assistance in proof-reading of the committee's UK English.

Funding for printing of this publication was generously provided by the chemistry teachers' publishing company (Kemi Forlaget) and the Association of Upper Secondary Chemistry Teachers (Kemilærerforeningen). I would also like to thank the TL·Offset for an extremely high production rate and excellent co-operation.

I hope you will be successful in your preparations and we are looking forward to meeting you in Copenhagen.

Aarhus
December 1999

Henrik Parbo
Chairman, 32nd IChO Scientific Committee

The Preparatory Problems page on the WWW is
http://www.icho2000.gymfag.dk

Scientific Committee of the 32nd International Chemistry Olympiad

Prof. Mikael Begtrup	Royal Danish School of Pharmacy
Assoc. Prof. Frode Galsbøl	University of Copenhagen
Assoc. Prof. Anders Hammershøi	University of Copenhagen
Prof. Poul Erik Hansen1)	Roskilde University Centre
Assoc. Prof. Kim K Mortensen	University of Aarhus
Lecturer Helge Mygind	Varde Upper Secondary School
Assoc. Prof. Lene Mønsted	Royal Veterinary and Agricultural University
Lecturer Henrik Parbo (chairman)	Aarhus Cathedral School
Assoc. Prof. Inger Søtofte	Technical University of Denmark
Assoc. Prof. Niels Thorup	Technical University of Denmark
Assoc. Prof. Palle W Jensen	University of Southern Denmark, Odense

1) Retired from the committee December 1999

Draft Syllabus for the International Chemistry Olympiad

Classification of the chemical topics

Group 1: These topics are included in the overwhelming majority of secondary school chemistry programs.

Group 2: These topics are included in a substantial number of secondary school programs; however, if not covered, it would be expected that the Olympiad level students from every country would have been introduced to these topics.

Group 3: These topics are not included in the majority of secondary school programs.

It is no longer necessary to have preparatory problems on Group 1 and Group 2 topics, although, in the latter case, a listing of the specific topics of that Group which might be part of the Olympiad Examination is to be given by the host nation. Any topics in Group 3 which might appear on the Olympiad Examination must be covered in the preparatory problems.

INORGANIC CHEMISTRY

ELECTRONIC CONFIGURATION

1	main groups	1
2	transition metals	2
3	lanthanide and actinide metals	3
4	Pauli exclusion Principle	1
5	Hund's Rule	1

TRENDS IN THE PERIODIC TABLE (MAIN GROUPS)

6	electronegativity	1
7	electron affinity	2
8	first ionization energy	2
9	atomic size	1
10	ionic size	2
11	highest oxidation number	1

TRENDS IN PHYSICAL PROPERTIES (MAIN GROUPS)

12	melting point	1
13	boiling point	1
14	metal character	1
15	magnetic properties	2
16	thermal properties	3

STRUCTURES

17	metal structures	3
18	ionic crystal structures. Simple molecular structures with central atom	3
19	exceeding the octet rule	3
20	stereochemistry	3

NOMENCLATURE

21	main group compounds	1
22	transition metal compounds	1
23	simple metal complexes	2
24	multicenter metal complexes	3
25	coordination number	1

STOICHIOMETRY

26	balancing equations	1
27	mass and volume relationships	1
28	empirical formula	1
29	Avogadro's number	1
30	concentration calculations	1

ISOTOPES

31	counting of nucleons	1
32	radioactive decay	1
33	nuclear reaction (alpha, beta, gamma, neutrino)	2

NATURAL CYCLES

34	nitrogen	2
35	oxygen	2
36	carbon	2

s-BLOCK

	products of reaction of group I and II metals	
37	with water, basicity of the products	1
38	products of reaction of the metals with halogens	1
39	products of reaction of the metals with oxygen	2
40	heavier elements are more reactive	1
41	Li combine with H_2 and N_2, forming LiH and Li_3N	2

p-BLOCK

42	stoichiometry of simplest nonmetal hydrides	1
43	properties of metal hydrides	3
44	acid/base properties of CH_4, NH_3, H_2S, H_2O, HX	1
45	NO reaction with O_2 to form NO_2	1
46	equilibrium between NO_2 and N_2O_4	1
47	products of reaction of NO_2 with water	1
48	HNO_2 and its salts are reductants	1
49	HNO_3 and its salts are oxidants	1
50	N_2H_4 is a liquid and reductant	3
51	there exist acids such like $H_2N_2O_2$, HN_3	3
52	to remember, what are products of reduction of nitrates or HNO_3 with different metals and reductors	3
53	reaction of $Na_2S_2O_3$ with iodine	2
54	other thioacids polyacids, peroxoacids	3
	B(III), Al(III), Si(IV), P(V) S(IV), S(VI), O(II), F(I), Cl(I), Cl(III), Cl(V) and Cl(VIII) are normal oxidation states of 2nd and 3rd row elements in compounds	
55	with halogens and in oxoanions	1
56	compounds of nonmetals with other oxidation states	3
57	the preferred oxidation states are Sn(II), Pb(II), Bi(III)	2
58	products of reactions of nonmetal oxides with water, and stoichiometry of resulting acids	1
59	reactions of halogens with water	2
60	reactivity and oxidizing power of halogens decrease from F_2 to I_2	1
61	differences in chemistry between row 4 and row 3 elements	3

d-BLOCK

62	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), Hg(II)	1
63	colors of the listed common ions in aqueous solution	2
64	other oxidation stales and chemistry of other d-block elements	3
65	Cr, Mn, Fe, Ni, Co, Zn dissolve in dil. HCl; Cu, Ag, Hg do not dissolve	1
66	products of the dissolution are (2+) cations	2
67	passivation of Cr, Fe (and also Al)	2
	$Cr(OH)_3$ and $Zn(OH)_2$ are amphoteric, other common hydroxides are not	1
68	MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$ are strong oxidants	1
69	products of reduction of MnO_4^- depending on pH	2
70	polyanions other than $Cr_2O_7^{2-}$	3

OTHER INORGANIC PROBLEMS

71	industrial production of H_2SO_4, NH_3, Na_2CO_3, Na, Cl_2, NaOH	1
72	chemistry of lanthanides and actinides	3
73	chemistry of noble gases	3

ORGANIC CHEMISTRY

ALKANES

74	isomers of butane	1
75	naming (IUPAC)	1
76	trends in physical properties	1
	substitution (eg with Cl_2)	
77	- products	1
78	- free radicals	2
79	- initiation/termination of the chain reaction	2
	cycloalkanes	
80	- names	1
81	- strain in small rings	2
82	- chair/boat conformation	2

ALKENES

83	planarity	1
84	*E/Z* (*cis/trans*) isomerism	1
85	addition of Br_2, HBr - products	1
86	- Markovnikoff rule	2
87	- carbonium ions in addition reaction	3
88	- relative stability of carbonium ions	3
89	- 1,4-addition to alkadiene	3

ALKYNES

90	linear geometry	1
91	acidity	2

ARENES

92	formula of benzene	1
93	delocalization of electrons	1
94	stabilisation by resonance	1
95	Huckel ($4n+2$) rule	3
96	aromaticity of heterocycles	3
97	nomenclature (IUPAC) of heterocycles	3
98	polycyclic aromatic compounds	3
99	effect of first substituent: - on reactivity	2
100	- on direction of substitution	2
101	explanation of substituent effects	2

HALOGEN COMPOUNDS

102	hydrolysis reactions	2
103	exchange of halogens	3
104	reactivity (primary vs secondary vs tertiary)	2
105	ionic mechanism	2
106	side products (elimination)	2
107	reactivity (aliphatic vs aromatic)	2
108	Wurtz (RX + Na) reaction	3
109	halogen derivatives & pollution	3

ALCOHOLS, PHENOLS

110	hydrogen bonding - alcohols vs ethers	1
111	acidity of alcohols vs phenols	2
112	dehydration to alkenes	1
113	dehydration to ethers	2
114	esters with inorganic acids	2
115	iodoform reaction	2
116	reactions of primary/sec./tert: Lucas reagent	2
117	formula of glycerol	1

CARBONYL COMPOUNDS

118	nomenclature	1
119	keto/enol tautomerism	2
120	preparation - oxidation of alcohols	1
121	- from carbon monoxide	3
122	reactions: - oxidation of aldehydes	1
123	- reduction with Zn metal	2
124	- addition of HCN	2
125	of $NaHSO_3$	2
126	of NH_2OH	2
127	- aldol condensation	3
128	- Cannizzaro ($PhCH_2OH$ disproportionation)	3
129	- Grignard reaction	2
130	- Fehling (Cu_2O) and Tollens (Ag mirror)	2

CARBOXYLIC ACIDS

131	inductive effect and strength	2
132	equivalence of oxygen atoms in anions	2
133	preparation: - from esters	2
134	- from nitriles	2
134	products of reaction with alcohols (esters)	1
136	mechanism of esterification	2
137	isotopes in mechanism elucidation	3
138	nomenclature: acid halides	2
139	preparation of acid chlorides	2
140	amides from acid chlorides	2
141	nitriles from acid chlorides	3
142	properties & preparation of anhydrides	2
143	oxalic acid: name and formula	1
144	multifunctional acids	2
145	optical activity (e.g. lactic acid)	2
146	*R/S* nomenclature	3
147	plant vs animal fats - differences	2

NITROGEN COMPOUNDS

148	amines are basic	1
149	comparing aliphatic vs aromatic	2
150	names: primary, secondary, tertiary, quaternary	2
151	identification of primary/sec/tert/quatern. in lab.	3
	preparation of amines	
152	- from halogen compounds	2
153	- from nitro compounds ($PhNH_2$ from $PhNO_2$)	3
154	- from amides (Hoffmann)	3
155	mechanism of Hoffmann reaction in acidic/basic medium	3
156	basicity of amines vs amides	2
	diazoization products	
157	- of aliphatic amines	3
158	- of aromatic amines	3
159	dyes: color vs structure (chromophore groups)	3
160	nitro compounds: aci/nitro tautomerism	3
161	Beckmann (oxime-amide) rearrangements	3

SOME LARGE MOLECULES

162	hydrophilic/hydrophobic groups	2
163	micelle structure	3
164	preparation of soaps	1
	products of polymerization of	
165	- styrene	2
166	- ethene	1
167	- polyamides	3
168	- phenol + aldehydes	3
169	- polyurethanes	3
170	polymers - cross-linking	3
171	- structures (isotactic etc)	3
172	- chain mechanism of formation	2
173	rubber composition	3

BIOCHEMISTRY

AMINO ACIDS AND PEPTIDES

174	ionic structure of amino acids	1
175	isoelectric point	2
176	20 amino acids (classification in groups)	2
177	20 amino acids (all structures)	3

178	ninhydrin reaction (incl. equation)	3
179	separation by chromatography	3
180	separation by electrophoresis	3
181	peptide linkage	1

PROTEINS

182	primary structure of proteins	1
183	-S-S- bridges	3
184	sequence analysis	3
185	secondary structures	3
186	details of alpha-helix structure	3
187	tertiary structure	3
188	denaturation by change of pH, temp., metals, EtOH	2
189	quaternary structure	3
190	separation of proteins (molecule size and solubility)	3
191	metabolism of proteins (general)	3
192	proteolysis	3
193	transamination	3
194	four pathways of catabolism of amino acids	3
195	decarboxylation of amino acids	3
196	urea cycle (results only)	3

FATTY ACIDS AND FATS

197	IUPAC names from C_4 to C_{18}	2
198	trivial names of most important (ca 5) f.acids	2
199	general metabolism of fats	3
200	beta-oxidation of fatty acids (formulas & ATP balance)	3
201	fatty acids & fats anabolism	3
202	phosphoglycerides	3
203	membranes	3
204	active transport	3

ENZYMES

205	general properties, active centres	2
206	nomenclature, kinetics, coenzymes, function of ATP etc	3

CARBOHYDRATES

207	glucose and fructose: chain formulas	2
208	- Fischer projections	2
209	- Haworth formulas	3
210	osazones	3
211	maltose as reducing sugar	2
212	difference between starch & cellulose	2
213	difference between alpha- and beta-D glucose	2
214	metabolism from starch to acetyl-CoA	3
	pathway to lactic acid or to ethanol;	
215	catabolism of glucose	3
216	ATP balance for these pathways	3
217	photosynthesis (products only)	2
218	light and dark reaction	3
219	detailed Calvin cycle	3

KREBS CYCLE AND RESPIRATION CHAIN

220	formation of CO_2 in the cycle (no details)	3
221	intermediate compounds in the cycle	3
222	formation of water and ATP (no details)	3
223	FMN and cytochromes	3
224	calculation of ATP amount for 1 mol glucose	3

NUCLEIC ACIDS AND PROTEIN SYNTHESES

225	pyrimidine, purine	2
226	nucleosides, nucleotides	3
227	formulas of all pyrimidine and purine bases	3
228	difference between ribose and 2-deoxyribose	3
229	base combination CG and AT	3
230	- “- (hydrogen bonding structures)	3
231	difference between DNA and RNA	3
232	difference between mRNA and tRNA	3
233	hydrolysis of nucleic acids	3
234	semiconservative replication of DNA	3
235	DNA-ligase	3
236	RNA synthesis (transcription) without details	3
237	reverse transcriptase	3
238	use of genetic code	3
239	start and stop codons	3
240	translation steps	3

OTHER BIOCHEMISTRY

241	hormones, regulation	3
242	hormone feedback	3
243	insulin, glucagon, adrenaline	3
244	mineral metabolism (no details)	3
245	ions in blood	3
246	buffers in blood	3
247	haemoglobin: function & skeleton	3
248	- diagram of oxygen absorption	3
249	steps in clotting of blood	3
250	antigens and antibodies	3
251	blood groups	3
252	acetylcholine structure and functions	3

INSTRUMENTAL METHODS OF DETERMINING STRUCTURE

UV-VIS SPECTROSCOPY

253	identification of aromatic compound	3
254	identification of chromophore	3

MASS SPECTRA

255	recognition of: - molecular ion	3
256	- fragments with the help of a table	3
257	- typical isotope distribution	3

IR

258	interpretation using a table of group frequencies	3
259	recognition of hydrogen bonds	3
260	Raman spectroscopy	3

NMR

261	interpret. of a simple spectrum (such as of ethanol)	3
262	spin-spin coupling	3
263	coupling constants	3
264	identification of *o*- and *p*-substituted benzene	3
265	^{13}C-NMR	3

X-RAYS

266	Bragg law	3
267	electron density diagrams	3
268	coordination number	3
269	unit cell	3
	structures of:	
270	- NaCl	3
271	- CsCl	3
272	- close-packing (2 types)	3
273	determination of the Avogadro constant from X-ray data	3

POLARIMETRY

274	calculation of specific rotation angle	3

PHYSICAL CHEMISTRY

CHEMICAL EQUILIBRIA

275	dynamic model of chemical equilibrium	1
	chemical equilibrium expressed in terms of	
276	- relative concentration	1
277	- relative partial pressures	2
278	the relationship between the equilibrium constant for ideal gases expressed in different ways (concentrations, pressures, mole fractions)	2
279	relation between equilibrium constant and standard Gibbs energy	3

IONIC EQUILIBRIA

280	Arrhenius theory of acids and bases	1
281	Brønsted-Lowry theory, conjugate acids & bases	1
282	definition of pH	1
283	ionic product of water	1
284	relationship between K_a and K_b for conjugate acids & bases	1
285	hydrolysis of salts	1
286	solubility product - definition	1
287	calculation of solubility (in water) from solubility product	1
288	calculation of pH for weak acid from K_a	1
289	calculation of pH for 10^{-7} mol/dm^3 HCI	2
290	calculation of pH for multiprotic acids	2
291	definition of activity coefficient	2
292	definition of ionic strength	3
293	Debye-Hueckel formula	3

ELECTRODE EQUILIBRIA

294	electromotive force (definition)	1
295	first kind electrodes	1
296	standard electrode potential	1
297	Nernst equation	2
298	second kind electrodes	2
299	relation between ΔG and electromotive force	3

KINETICS OF HOMOGENEOUS REACTION

300	factors influencing reaction rate	1
301	rate equation	1
302	rate constant	1
303	order of reaction	2
304	1st order reactions: time dependence of concentration	2
305	- half-life	2
306	- relation between half-life and rate constant	2
307	rate-determining step	2
308	molecularity	2
309	Arrhenius equation, activation energy (defin.)	2
310	calculation of rate constant for 1st order reactions	2
311	calculation of rate constant for 2nd, 3rd order reactions	3
312	calculation of activation energy from experimental data.	3

313	basic concepts of collision theory	3
314	basic concepts of transition state theory	3
315	opposing, parallel and consecutive reactions	3

THERMODYNAMICS

316	system and its surroundings	2
317	energy, heat and work	2
318	relationship between enthalpy and energy	2
319	heat capacity - definition	2
320	difference between C_p and C_v	3
321	Hess' law	2
322	Born-Haber cycle for ionic compounds	3
323	lattice energies - approximate calculations (e.g. Kapustinski equation)	3
324	use of standard formation enthalpies	2
325	heats of solution and solvation	2
326	bond energies - DEFINITION and uses	2

SECOND LAW

327	Entropy - definition (q/T)	2
328	entropy and disorder	2
329	relation $S = k \ln W$	3
330	relation $G = H - T S$	2
331	ΔG and directionality of changes	2

PHASE SYSTEMS

332	ideal gas law	1
333	van der Waals gas law	3
334	definition of partial pressure	1
335	Temp. dependence of the vapour pressure of a liquid	2
336	Clausius-Clapeyron equation	3
337	reading a phase diagram: triple point	3
338	- critical temperature	3
339	liquid-vapour system (diagram)	3
340	- ideal and non-ideal systems	3
341	- use in fractional distillation	3
342	Henry's law	2
343	Raoult's law	2
344	deviations from Raoult's law	3
345	Boiling point elevation law	2
346	freezing-point depression, determination of molar mass	2
347	osmotic pressure	2
348	partition coefficient	3
349	solvent extraction	2
350	basic principles of chromatography	2

OTHER PROBLEMS

ANALYTICAL CHEMISTRY

351	using a pipette	1
352	using a burette	1
353	choice of indicators for acidimetry	1
354	titration curve: pH (strong AND weak acid)	2
355	- EMF (redox titration)	2
356	calculation of pH of simple buffer solution	2
357	identification of: Ag^+, Ba^{2+}, Cl^-, SO_4^{2-} ions	1
358	- of Al^{3+}, NO_2^-, NO_3^-, Bi^{3+} ions	2
359	- of VO_3^-, ClO_3^-, Ti^{4+} ions	3
360	- using flame test for K, Ca, Sr	1
361	Lambert-Beer Law	2

COMPLEXES

362	writing equations for complexation reactions	1
363	complex formation constants (definition)	2
364	E_g and T_{2g} terms: high- and low-spin octahedral	3
365	calculation of solubility of AgCl in NH_3 (from K_{sp} and β's)	3
366	*cis* and *trans* forms	3

THEORETICAL CHEMISTRY

367	n, l, m quantum numbers	2
368	energy levels of hydrogen atom (formula)	2
369	shape of p-orbitals	2
370	d-orbital stereo-configuration	3
371	molecular orbital diagram: H_2 molecule	3
372	- N_2 or O_2 molecule	3
373	bond orders in O_2 or O_2^+ or O_2^-	3
374	Hückel theory for aromatic compounds	3
375	Lewis acids and bases	2
376	hard and soft Lewis acids	3
377	unpaired electrons and paramagnetism	2
378	square of the wave function and probability	3
379	understanding the simplest Schrödinger equation	3

Theoretical Problems

Problem 1 Acid Rain

1908 1966
The effect of ‘acid rain’

The pH value for pure water is 7.0, whereas natural rainwater is weakly acidic. This is caused by dissolution of atmospheric carbon dioxide. In many areas, however, rainwater is more acidic. This has several causes, some of which are natural and some of which derive from human activity. In the atmosphere, sulphur dioxide and nitrogen monoxide are oxidized to sulphur trioxide and nitrogen dioxide, respectively, which react with water to give sulphuric acid and nitric acid. The resulting so-called “acid rain” has an average pH value of 4.5. Values as low as 1.7 have, however, been measured.
Sulphur dioxide, SO_2, is a diprotic acid in aqueous solution. At 25 °C the acidity constants are:

$$SO_2(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H^+(aq) \qquad K_{a1} = 10^{-1.92}\ \text{M}$$

$$HSO_3^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H^+(aq) \qquad K_{a2} = 10^{-7.18}\ \text{M}$$

All the following questions refer to 25 °C.

a. The solubility of sulphur dioxide gas is 33.9 litre in 1 litre of water at a sulphur dioxide partial pressure of 1 bar.

i. Calculate the total concentration of sulphur dioxide in water saturated with sulphur dioxide gas (the change of volume caused by dissolution of SO_2 may be ignored).

ii. Calculate the percentage of hydrogen sulphite ions.

iii. Calculate pH in the solution.

b. Calculate the concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium sulphite.

c. The dominant equilibrium in an aqueous solution of sodium hydrogen sulphite is:

$$2\ HSO_3^-(aq) \rightleftharpoons SO_2(aq) + SO_3^{2-}(aq) + H_2O(l)$$

i. Calculate the equilibrium constant for this equilibrium.

ii. Calculate the concentration of sulphur dioxide in a 0.0100 M aqueous solution of sodium hydrogen sulphite taking only this equilibrium into consideration.

d. The solubility of barium sulphite in water is 0.016 g/100 mL.

i. Calculate the concentration of barium ions in a saturated solution.

ii. Calculate the concentration of sulphite ions in a saturated solution.

iii. Calculate the solubility product constant of barium sulphite.

The solubility product constant of silver sulphite is $10^{-13.82}$ M^3.

e. Calculate the silver ion concentration in a saturated aqueous solution of silver sulphite (the basicity of the sulphite ion may be ignored).

The solubility product constant of calcium sulphite is $10^{-7.17}$ M^2.

f. Calculate the equilibrium constant for the reaction:

$$Ca^{2+}(aq) + Ag_2SO_3(s) \rightleftharpoons CaSO_3(s) + 2\,Ag^+(aq)$$

Bromine in excess is added dropwise to a 0.0100 M solution of sulphur dioxide. All sulphur dioxide is oxidized to sulphate(VI). Excess of bromine is removed by flushing with gaseous nitrogen.

g. Write a reaction equation for the process and calculate the hydrogen ion concentration in the resulting solution. All chemical processes and all manipulations are assumed to take place without change of volume. pK_a for the hydrogen sulphate ion is 1.99.

h. After a volcanic eruption the pH value in rainwater was measured to 3.2. Calculate the total concentration of sulphuric acid in the rainwater assuming that the acidification is due only to sulphuric acid. The first proton of sulphuric acid may be regarded as being fully dissociated.

Problem 2 Potassium Chlorate

Chlorates and perchlorates are used in the manufacture of, for instance matches, fireworks and explosives.
The first step in production of potassium chlorate involves electrolysis of an aqueous solution of potassium chloride.

a. Write the reaction equation for the two electrode reactions. Cl_2 is formed at the anode and OH^- formed at the cathode.

b. The chlorine formed reacts with the hydroxide ions to form chlorate ions.
Write the reaction equation.

c. Calculate the mass of potassium chloride and the electric charge (in A h) needed to produce 100 g of potassium chlorate.

Problem 3 Sugar Inversion

Table sugar is pure sucrose, which is found in sugar beets and sugar cane. In solution, sucrose is slowly hydrolysed to give a solution of D-glucose and D-fructose. This is called invert sugar. The hydrolysis reaction may be followed by polarimetry. The sucrose solution is dextrorotatary, ($[\alpha]_D^{20} = +66.53$ deg cm^3 g^{-1} dm^{-1}), whereas the solution of invert sugar is laevorotatary ($[\alpha]_D^{20}$ of glucose = +52.7 deg cm^3 g^{-1} dm^{-1} and $[\alpha]_D^{20}$ of fructose = –92.4 deg cm^3 g^{-1} dm^{-1}). The rate of the hydrolysis is strongly dependent on the hydrogen ion concentration.

a. Write the reaction equation (the reaction scheme) for hydrolysis of sucrose using Haworth formulas for the reactant and the reaction products.

b. The inversion of sucrose was followed at 25 °C. The following values of the angle of rotation, α_t, as a function of time, t, were found:

t/min:	0	10	20	40	80	180	300	∞
α_t / °:	6.60	6.17	5.79	5.00	3.71	1.40	–0.24	–1.98

α_∞ corresponds to complete transformation. Thus $\alpha_t - \alpha_\infty$ is a measure of the concentration of sucrose. Use the values given above to show that the reaction is first order in the concentration of sucrose, and calculate the rate constant.

c. In 0.1 M HCl the rate is doubled by increasing the temperature from 25 to 30 °C. Calculate the activation energy.

Problem 4 Humus

In most Danish soils both manganese and iron originate mainly from enzymes in dead organic material. Under acidic, reducing conditions these elements are present as Mn^{II} and Fe^{II}.
In places where the ground water comes to the surface as a spring, the ions are oxidized by the oxygen of the atmosphere.

a. Write the reaction equation for oxidation in manganese(II) to manganese(IV) oxide by dioxygen.

b. Calculate $\Delta G_1^\ominus$ at 25 °C for the reaction in question **a** using the data given below:

2. $MnO_2(s) + 4\ H^+(aq) + 2\ e^- \rightarrow Mn^{2+}(aq) + 2\ H_2O(l)$, $E_2^\ominus = 1.21$ V

3. $O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(l)$, $E_3^\ominus = 1.23$ V

c. Calculate the equilibrium constant, K_1, at 25 °C for the reaction in question **a**.

It is assumed that manganese(II) forms complexes with organic material in soil containing humus. It is further assumed that the formation constant for the manganese(II) humus complex is $10^5\ \text{M}^{-1}$ and that the concentration of the ligand is 10^{-4} M.

d. Calculate the equilibrium constant for the reaction:

$$2\ Mn(hum)^{2+}(aq) + O_2(g) + 2\ H_2O(l) \rightleftharpoons 2\ MnO_2(s) + 2\ hum(aq) + 4\ H^+(aq)$$

An acidic soil may have a pH value of 5, and an alkaline soil may have a pH value of 8.

e. Calculate from the theoretical data given above the concentration of $Mn(hum)^{2+}$ at pH value of 5 and pH value of 8, respectively. $p(O_2)$ is 0.2 bar and the soil contains an excess of MnO_2.

f. Manganese is absorbed by the plants via the humus complexes. Which type of cultivated soil gives problems with deficiency of manganese in spite of the presence of large quantities of manganese in the soil?

Problem 5 Brønsted Acids and Bases

1.00 g NH_4Cl and 1.00 g $Ba(OH)_2{\cdot}8H_2O$ are added to 80 mL water and dissolved. The resulting solution is diluted to 100 mL with water at 25 °C.

a. Calculate the pH of the solution ($pK_a(NH_4^+) = 9.24$).

b. Calculate the concentrations of all ions in the solution.

c. Calculate pH after the addition of 10.0 mL 1.00 M HCl to the above solution.

d. Calculate $[NH_3]$ of the new solution.

Problem 6 Magnesium Hydroxide

A student prepares a saturated solution of magnesium hydroxide in pure water at 25 °C. A measurement shows that the saturated solution has a pH of 10.5.

a. Use this result to calculate the solubility of magnesium hydroxide in water. The solubility should be calculated in mol L^{-1} as well as in g/100 mL.

b. Calculate the solubility product constant of magnesium hydroxide.

c. Calculate the solubility of magnesium hydroxide in 0.010 M NaOH at 25 °C.

A mixture of 10 g $Mg(OH)_2$ and 100 mL 0.100 M HCl is stirred magnetically for some time at 25°C.

d. Calculate the pH of the liquid phase when the system has reached equilibrium.

Problem 7 An Unstable Solid

Ammonium hydrogen sulphide, $NH_4HS(s)$, is an unstable compound which easily decomposes to $NH_3(g)$ and $H_2S(g)$:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

The following thermodynamic data at 25 °C are given:

Compound	$H^\ominus$/(kJ mol^{-1})	$S^\ominus$/(J K^{-1} mol^{-1})
$NH_4HS(s)$	–156.9	113.4
$NH_3(g)$	–45.9	192.6
$H_2S(g)$	–20.4	205.6

a. Calculate $\Delta H^\ominus$, $\Delta S^\ominus$ and $\Delta G^\ominus$ at 25 °C for the above reaction.

b. Calculate the equilibrium constant K_p at 25 °C for the above reaction.

c. Calculate the equilibrium constant K_p at 35 °C for the above reaction assuming that both $\Delta H^\ominus$ and $\Delta S^\ominus$ are independent of temperature.

Suppose an amount of 1.00 mol $NH_4HS(s)$ is introduced into an empty 25.00 L container.

d. Calculate the total pressure in the container when the decomposition reaction has reached equilibrium at 25 °C. The volume of $NH_4HS(s)$ may be neglected.

e. Calculate the resultant total pressure in the container if the volume of the container is changed to 100.00 L in the above experiment.

Problem 8 Electrochemistry

Electrochemical techniques are often used to determine solubilities of sparingly soluble salts. As the electromotive force is a linear function of the logarithm of the concentration, very small concentrations can be determined.
This problem deals with an electrochemical cell consisting of two half-cells separated by a salt bridge. The left-hand side (referring to the cell diagram) is a Zn(s) rod immersed in a 0.200 M $Zn(NO_3)_2(aq)$ solution, and the right-hand side is an Ag(s) rod immersed in a 0.100 M $AgNO_3(aq)$ solution. Each solution has a volume of 1.00 L and a temperature of 25 °C.

a. Write the cell diagram for this cell and write the corresponding cell reaction.

b. Calculate the electromotive force of the cell and write the reaction which takes place during discharge of the cell.

Suppose the cell is allowed to discharge completely and that Zn(s) is present in excess.

c. Calculate the total transported electric charge (in coulomb) in the course of discharge.

In another experiment KCl(s) has been added to the $AgNO_3$ solution on the right-hand side of the original cell. This is accompanied by precipitation of AgCl(s) and a change in electromotive force. After the addition, the electromotive force is 1.04 V and $[K^+]$ is 0.300 M.

d. Calculate $[Ag^+]$ at equilibrium.

e. Calculate $[Cl^-]$ at equilibrium as well as the solubility product constant of AgCl.

Standard reduction potentials (at 25 °C) are as follows:

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E^\ominus = -0.76\ \text{V}$$

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E^\ominus = 0.80\ \text{V}$$

Problem 9 Cyanide in Waste

Cadmium is one of the most toxic metals and is found in high concentration in wastes from zinc smelting, electroplating, and sewage treatment. Inhalation of cadmium particles rapidly affects the respiratory tract and later the kidneys. Cadmium appears to compete with zinc at the active sites of enzymes.

Cadmium forms the slightly insoluble hydroxide, $Cd(OH)_2$.

a. Calculate the solubility of $Cd(OH)_2$ in pure water (the autoprotolysis equilibrium can be ignored).

b. Calculate the solubility of $Cd(OH)_2$ in a 0.010 M NaOH(aq) solution.

The Cd^{2+} ion has a high affinity for CN^- ions:

$$Cd^{2+}(aq) + CN^-(aq) \rightleftharpoons Cd(CN)^+(aq) \qquad K_1 = 10^{5.48}\ \text{M}^{-1}$$

$$Cd(CN)^+(aq) + CN^-(aq) \rightleftharpoons Cd(CN)_2(aq) \qquad K_2 = 10^{5.12}\ \text{M}^{-1}$$

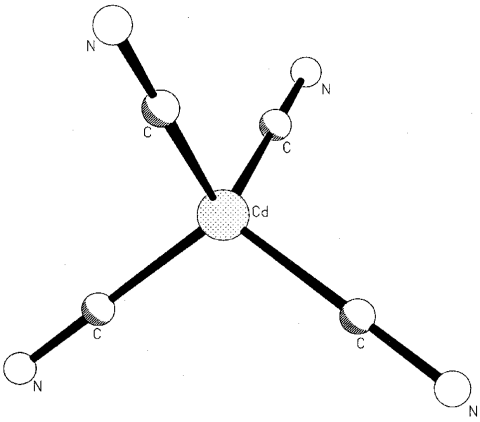
$$Cd(CN)_2(aq) + CN^-(aq) \rightleftharpoons Cd(CN)_3^-(aq) \qquad K_3 = 10^{4.63}\ \text{M}^{-1}$$

$$Cd(CN)_3^-(aq) + CN^-(aq) \rightleftharpoons Cd(CN)_3^{2-}(aq) \qquad K_4 = 10^{3.65}\ \text{M}^{-1}$$

c. Calculate the solubility of $Cd(OH)_2$ in water containing CN^- ions. The equilibrium concentration is

$[CN^-] = 1.00 \times 10^{-3}$ M

d. Assume that only the complex ion $Cd(CN)_4^{2-}$ is formed and calculate the percentage deviation of the solubility from the solubility found in **c**.



The formation constant, $\beta_n = \dfrac{[Cd(CN)_n^{2-n}]}{[Cd^{2+}][CN^-]^n}$

The solubility product constant of $Cd(OH)_2(s)$ is: $K_{sp} = 5.9 \times 10^{-15}$ M^3.

Problem 10 Age of Greenland Rock

Some of the world's oldest rock formations are found in the Isua region of Greenland. Their age was determined from their content of radioactive and stable isotopes in specific mineral grains.

The radioactive uranium isotope ^{238}U decays with a halflife of 4.468 Ga to the stable ^{206}Pb isotope through a series of much less stable isotopes. In contrast to ^{206}Pb, the ^{204}Pb isotope is not a product of radioactive decay and, therefore, $n(^{204}Pb)$ can be taken as constant with time in a given piece of mineral. At the time ($t = 0$) when a mineral crystallized these isotopes may have been incorporated as pollutants. The initial amounts of the isotopes ($n_0(^{238}U)$, $n_0(^{206}Pb)$ and $n(^{204}Pb)$) of such incorporation may differ for different pieces of mineral. However, the initial ratio of isotopes of the same element, e.g. the $n_0(^{206}Pb)/n(^{204}Pb)$ ratio, would be expected to be the same for all pieces of mineral crystallized as part of the same rock formation.

a. Write the relationship expressing $n_t(^{206}Pb)$ as a function of $n_t(^{238}U)$, $n_0(^{206}Pb)$, k and t, with t representing the time elapsed after a given mineral specimen crystallized and k being the radioactive decay constant of ^{238}U.

Different pieces of mineral contain different initial amounts of the pollutant isotopes ^{238}U and ^{206}Pb. Therefore, the age of a given piece of mineral cannot be deduced from measurements of $n_t(^{238}U)$ and $n_t(^{206}Pb)$, alone. However, $n(^{204}Pb)$ is proportional to the initial amount of lead in a given piece of mineral, and thus also proportional to $n_0(^{206}Pb)$.

Sets of related values of $n_t(^{238}U)$, $n_t(^{206}Pb)$ and $n(^{204}Pb)$ for different pieces of mineral originating from the same rock may be determined by mass spectrometry. Each such set would represent a separate point in a diagram with abcissa $n_t(^{238}U)/n(^{204}Pb)$ and ordinate $n_t(^{206}Pb)/n(^{204}Pb)$. Taken together, the points of several such sets ideally describe a straight line, denoted an isochron, and the age of the rock may be derived from the slope.

The following sets of isotopic ratios were recently obtained for minerals of an Isua rock:

$n(^{238}U)/n(^{204}Pb)$	$n(^{206}Pb)/n(^{204}Pb)$
1.106	12.098
1.883	12.733
2.632	13.305
2.859	13.567
2.896	13.488
3.390	13.815

b. Calculate the age of the Isua rock.

c. What is the significance of the y-axis intercept in the above-mentioned diagram?

Problem 11 Lead Poisoning

Environmental exposure to lead remains a major problem. In humans, toxic levels of lead in blood may be reduced through “chelation therapy” by administering ligands that potentially form stable Pb^{2+} complexes which are excretable through the kidneys. The $edta^{4-}$ ligand is used for this purpose owing to formation of the very stable $[Pb(edta)]^{2-}$ complex (stability constant, $K(Pb) = 10^{18.0}\ \mathrm{M}^{-1}$). The ligand is administered by infusion of a solution of $Na_2[Ca(edta)]$, the sodium salt of the comparatively less stable calcium complex $[Ca(edta)]^{2-}$ (stability constant, $K(Ca) = 10^{10.7}\ \mathrm{M}^{-1}$). In the bloodstream, exchange of calcium for lead in the complex takes place, essentially.

a. The level of lead in a patient’s blood was found to be 83 μg/dL. Calculate the molar concentration of lead in the patient’s blood.

b. In a model experiment an aqueous solution was prepared by dissolving amounts of $Ca(NO_3)_2{\cdot}4H_2O$ and $Na_2[Ca(edta)]$ resulting in formula concentrations of each substance of 2.5 mM and 1.0 mM, respectively. Solid $Pb(NO_3)_2$ was added to the solution so as to yield a total lead concentration corresponding to that in the above-mentioned patient's blood. Calculate an approximate value for the $[Pb(edta)^{2-}]/[Pb^{2+}]$ ratio at equilibrium in the resulting solution. Acid-base properties of relevant species and any volume change may be ignored.

c. The excretion of $[Pb(edta)]^{2-}$ complex through the kidneys is essentially a first-order process with respect to the $[Pb(edta)]^{2-}$ complex concentration in the blood. After a period of 2 hours the blood concentration of $[Pb(edta)]^{2-}$ complex is typically lowered by 60 % in most patients. Calculate the "biological half-life" of the $[Pb(edta)]^{2-}$ complex.

Problem 12 Nickel Enzyme

Urease is a nickel-containing enzyme that catalyzes the hydrolysis of urea (H_2NCONH_2) to ammonium ion and carbamate ion (H_2NCOO^-). The carbamate ion is subsequently hydrolyzed further in a spontaneous process which is not catalyzed by urease.

a. Write the equation for the hydrolysis reaction of carbamate ion.

b. Each protein subunit of the urease tertiary structure contains two nickel(II) ions. These metal ions are coordinated to relevant donor atoms of the side chains of amino acids of the protein primary structure. Draw structural formulas for the side chains of aspartate and histidine, respectively, and circle potential donor atoms of each side chain.

c. The two nickel(II) centres of urease are also linked by a bridging carboxylate group and a bridging water molecule. The bridging carboxylate group belongs to a lysine side chain which has been modified into a carbamate derivative. Draw the structural formula for the lysine side chain carbamate derivative.

d. Write the electronic configuration of the nickel(II) ion.

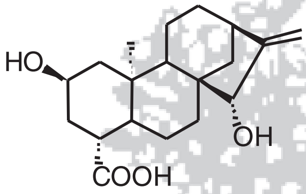
e. A number of coordination geometries are known for nickel(II) complexes. In octahedral coordination geometry the d orbitals are distributed between two energy levels. Indicate which of the five d orbitals (d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz} and d_{yz}) in octahedral geometry occupy the higher and lower energy levels, respectively. Give a qualitative explanation for your answer based on a comparison of the d orbital spatial distributions.

f. Certain nickel(II) complexes also display square planar coordination geometry, which is the dominant geometry of complexes of the palladium(II) and platinum(II) metal ions. Draw the two isomers of square planar $[Ni(SCH_2CH_2NH_2)_2]$ and label each isomer as *cis* or *trans*.

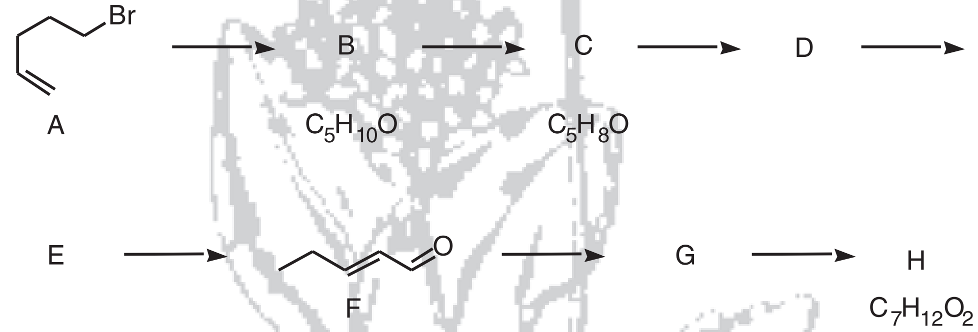
g. Draw all geometrical isomers of square planar $[Pt(NH_3)(pyridine)ClBr]$.

Problem 13 Killer Thistle for use in Medical Treatment ?

(-)-Atractyligenin is a biologically active compound which has been isolated from the so-called killer thistle. It has been used by the Zulu's in treatment of diseases, but frequently with fatal results. In order to be able to develop less toxic analogues independent chemical syntheses have now been developed.



(-)-Atractyligenine



In the synthesis of (-)-atractyligenin analogues, compound **A** can be used as a starting material. Compound **A** was first treated with aqueous sodium hydroxide to give **B** ($C_5H_{10}O$).

a. Draw the structural formula of compound **B**.

Compound **B** upon treatment with potassium dichromate in aqueous sulphuric acid produced **C** (C_5H_8O).

b. Draw the structural formula of compound **C**

Compound **C** was dissolved in toluene, and gaseous hydrogen bromide was passed through the solution until all **C** had been consumed. This gave compound **D**.

c. Draw the structure of compound **D**.

d. Do stereoisomers of compound **D** exist ?
If yes, give the number of stereoisomers. ☐

Compound **D** was then treated with a solution of sodium hydroxide in ethanol to give compound **E,** which upon heating rearranged to compound **F**.

e. Draw the structure of compound **E**.

f. Do stereoisomers of compound **F** exist ?
If yes, give the number of stereoisomers. ☐

A solution of compound **F** was treated with potassium permanganate to give compound **G**. Finally, compound **G** was heated to reflux with an excess of ethanol in the presence of a catalytic amount of sulphuric acid to give compound **H**.

g. Set a cross in the box corresponding to the IUPAC name of compound **H**:

Ethyl pentanoate ☐
Ethyl (*E*)-3-pentenoate ☐
(*E*)-1-pentenoyloxyethane ☐
1-Ethoxy (*Z*)-2,4-pentadienol ☐
Ethyl (*E*)-2-pentenoate ☐
Ethyl (*E*)-2-butenoate ☐
Ethoxy (*E*)-2,4-pentadienal ☐

Compound **F** was treated with 2-methyl-butylmagnesiumbromide. After acidification a mixture of isomeric products **I** was obtained.

h. Draw the structure of product **I** (without considering isomers).

i. Answer the following questions by setting a cross beneath your choice in the appropriate box:

I. The number of isolated stereoisomers of product **I** is:

2	4	6	8

II. All isolated stereoisomers of product **I** are formed in equal amounts ☐

Some of the isolated stereoisomers of **I** are formed in unequal amounts ☐

All stereoisomers are formed in unequal amounts ☐

III. Of the isolated stereoisomers of product **I**:

All have the same melting point ☐

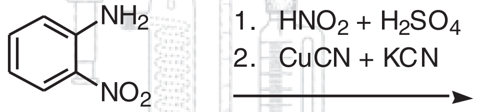
All have different melting points ☐

Some have the same melting point ☐

Problem 14 Application of Organic Synthesis

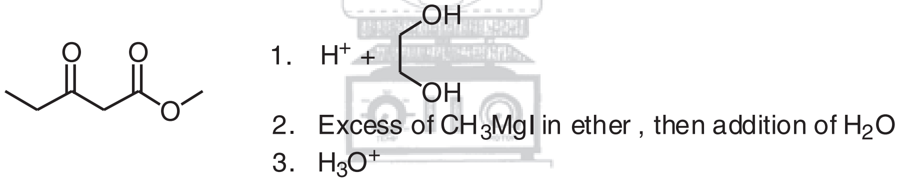
During preparation of a pharmaceutical substance three intermediates were prepared in the separate reactions described below.

a. Draw the formula and give the IUPAC name of the product obtained in the following reaction:



b. Draw the formula in a stereochemically unambiguous manner and give the full IUPAC name of the product obtained when (2*S*)-2-Chlorobutane reacts with sodium methoxide in a S_N2 type reaction.

c. Draw the formulas of the products obtained in the following three reaction steps and give the number of stereoisomers obtained in the final step.



Problem 15 Cayenne

A natural product **A** is isolated from a cayenne pepper. **A** is a colourless compound with a sharp taste.

An elementary analysis reveals the following composition:

Atom	**Percentage mass**
C	70.8 %
H	8.9 %
N	4.6 %
O	15.7 %

No other types of atoms were detected.

a. Give the empirical formula of **A**.

After acid hydrolysis with aqueous hydrochloric acid two products could be isolated: **B** and **C**. Product **C** is an isomer of decanoic acid: (*E*)-8-methyl-6-nonenoic acid.

b. Draw a structural formula of **C**.

B was characterised in the following way:

The ^{1}H NMR spectrum at 60 MHz is given in Figure 1. A mixed solvent consisting of $CDCl_3$ and dimethyl sulphoxide-d_6 was used (note that a calculated spectrum is given in Figure 2).

It could be shown that addition of a drop of D_2O causes the resonances at δ 9.1 and 8.55 ppm (referring to Figure 1) to disappear.

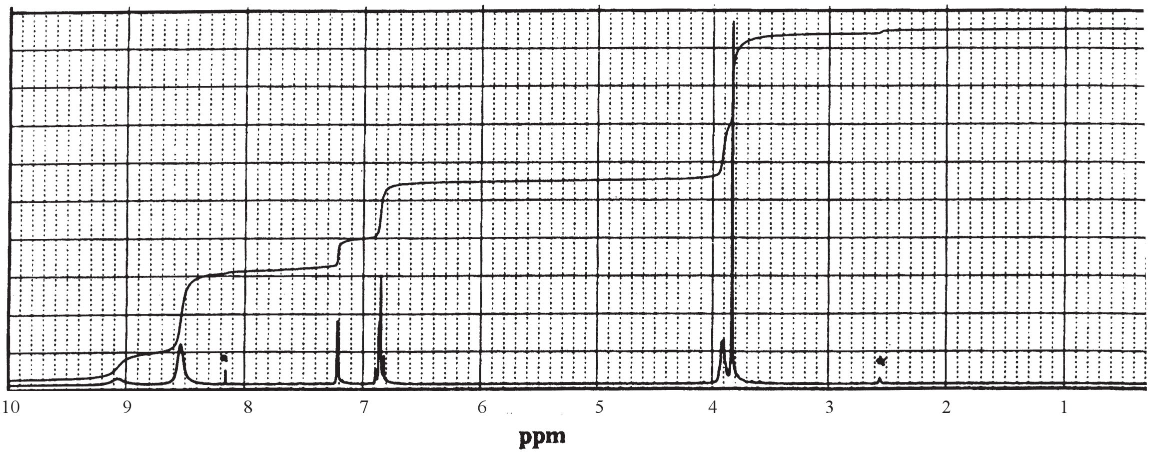


Figure 1 ^{1}H NMR spectrum

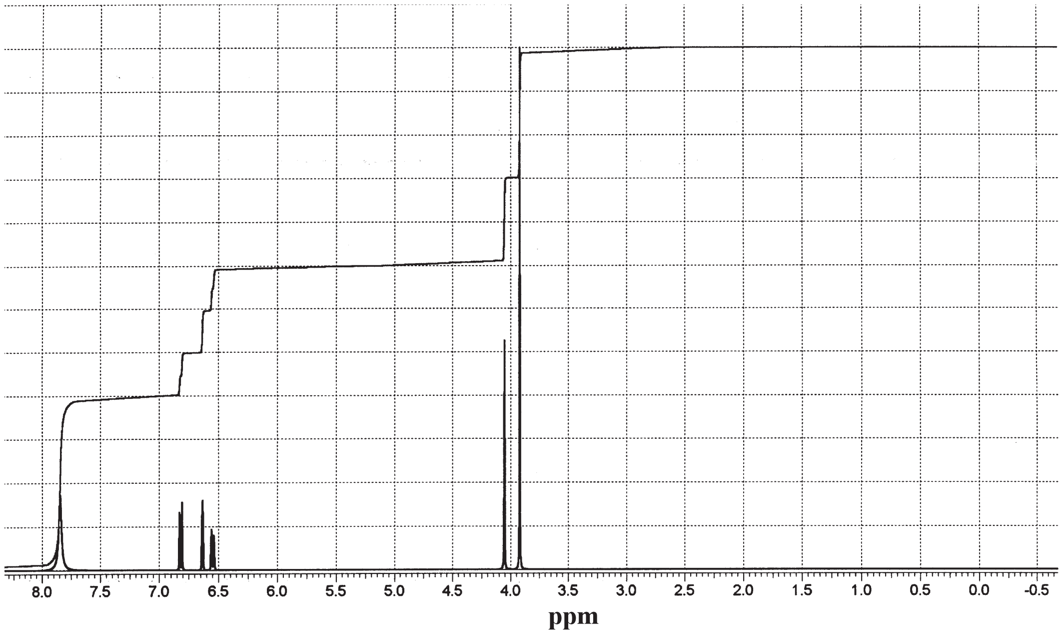
*Either a resonance belonging to the solvent or to an impurity

0.378 g of **B** dissolved in 20 mL of water is titrated with 0.10 M NaOH to give equivalence points at 20.0 mL and 40.0 mL.

c. Draw a structural formula of **B**.

d. Draw a structural formula of **A**.

e. How may stereoisomers of **A** exist?



Figur 2 Calculated ^{1}H NMR spectrum

Problem 16 An Organic Compound

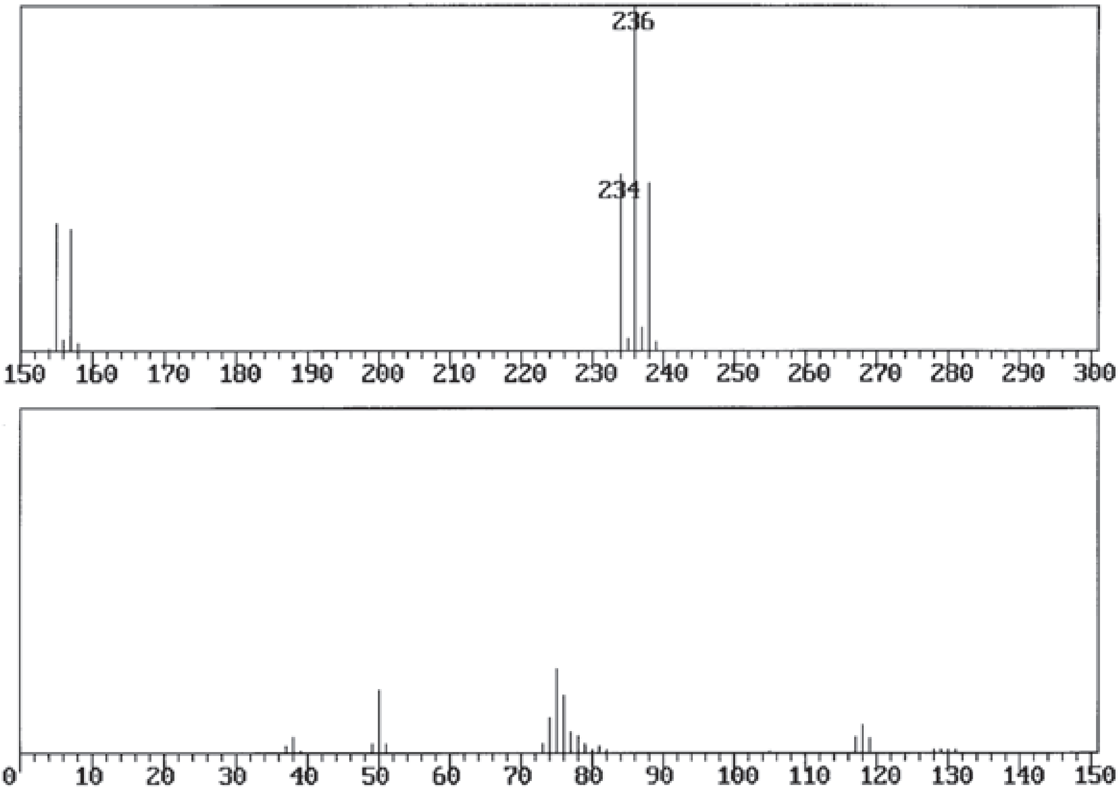


Figure 3 Mass spectrum of an organic compound

The mass spectrum in Figure 3 was recorded of an organic compound which contains three types of atoms: hydrogen, carbon and one unknown.

a. What is the unknown type of atom and how many atoms of that type are present in the molecule?

b. A single structure cannot be determined by mass spectrometry alone. Write down the possible isomers.

c. Explain which ions may correspond to the peaks at $m/Z = 76$, 155 and 157 mass units.

d. The peaks at 117, 118 and 119 should be ascribed to a doubly charged molecular ion rather than to a fragment of the molecule. Why is that?

e. Determine the isomeric form of the compound from its ^{1}H NMR spectrum (Figure 4).

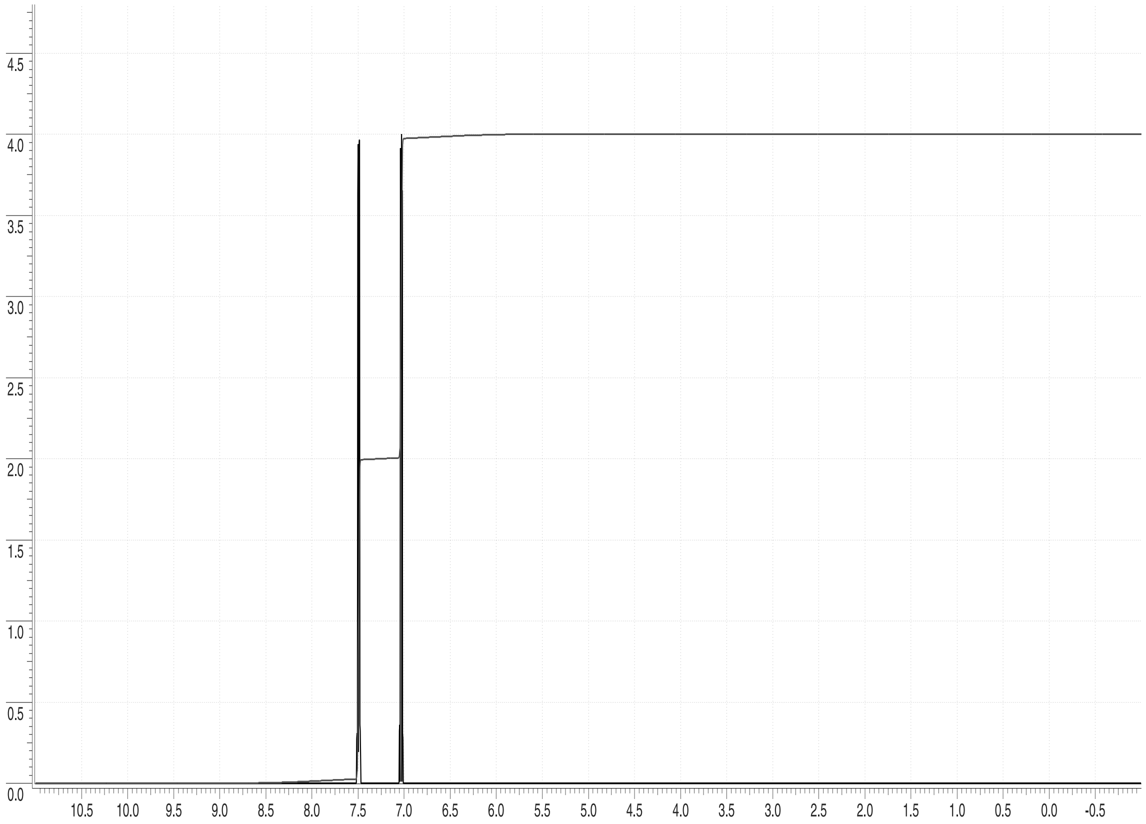
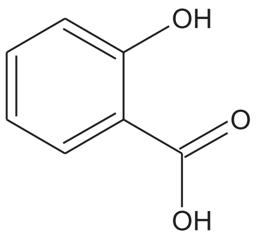


Figure 4 ^{1}H NMR spectrum (Chemical shifts δ in ppm)

f. How many signals will be present in a ^{1}H-decoupled ^{13}C NMR spectrum of the compound?

Problem 17 Heather

Figure 5 shows the infrared spectrum of salicylic acid:



Some of the prominent bands may be assigned as follows:

3239 cm^{-1}:	O-H stretch in phenol
3300-2300 cm^{-1}:	O-H stretch in carboxylic acid
3013 cm^{-1}:	C-H stretch in aromatic compound
1658 cm^{-1}:	C=O stretch
761 and 699 cm^{-1}:	C-H bend in *ortho*-disubstituted aromatic compound

From the plant *Gaultheria procumbens*, which is an American species of heather, an ethereal oil, gaultheria oil, is obtained. The main constituent of this oil is **G**, a derivative of salicylic acid. In the mass spectrum of this derivative, the peak corresponding to the molecular ion is situated at 152 mass units. Another prominent peak in the spectrum is situated at 121 mass units. The infrared spectrum of **G** is shown in Figure 6. The band at 2956 cm^{-1} arises from a C-H stretching vibration occurring in the saturated part of the molecule.

a. Draw the structural formula of **G**.

b. The wavenumber of the 3239 cm^{-1} band is shifted approximately 50 cm^{-1} in the spectrum of the derivative. What could be the reason for this?

c. What is the molar absorptivity of the 238 nm UV band of **G** when a solution of 4.90 mg in 1.000 L in a 1.00 cm cell absorbs 50 % of light with this wavelength?

Another derivative of salicylic acid does not absorb infrared radiation in the region near 3200 cm^{-1}. Instead, two strong bands are observed in the region around 1700 cm^{-1} (see Figure 7). When this derivative is used as a painkiller, it decomposes in the blood to give two compounds, one of which after isolation gives two ^{1}H NMR signals at 2.00 ppm and 12.00 ppm.

d. Draw the structural formula of this derivative.

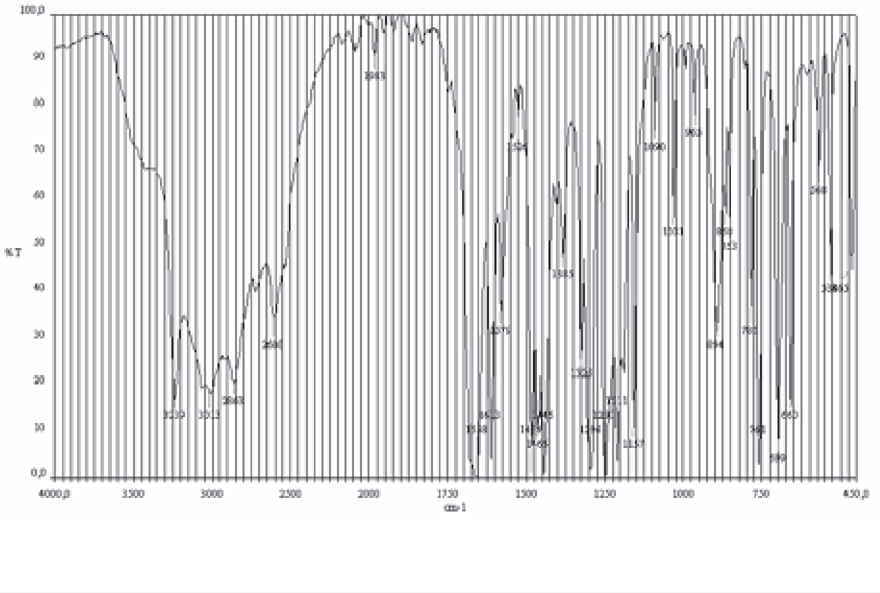


Figure 5

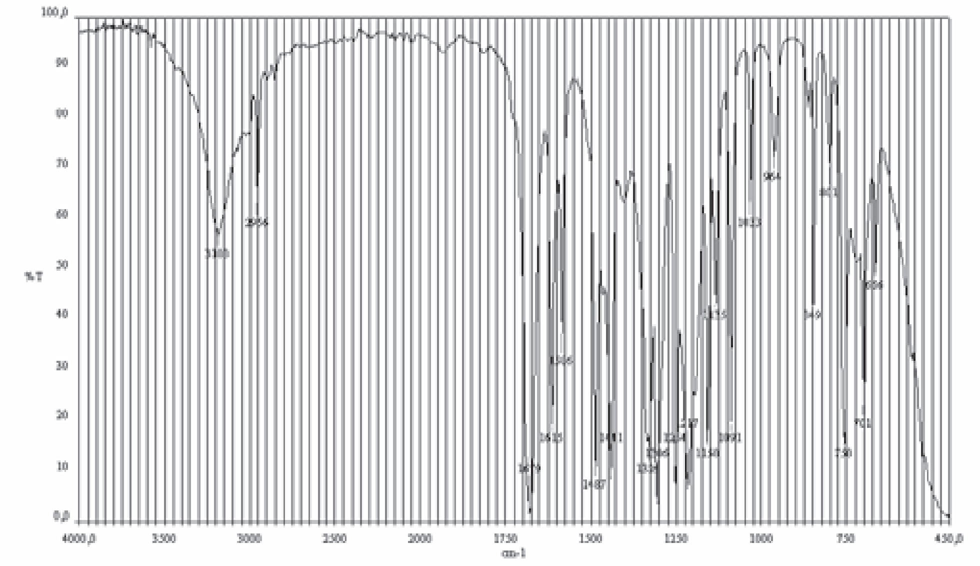


Figure 6

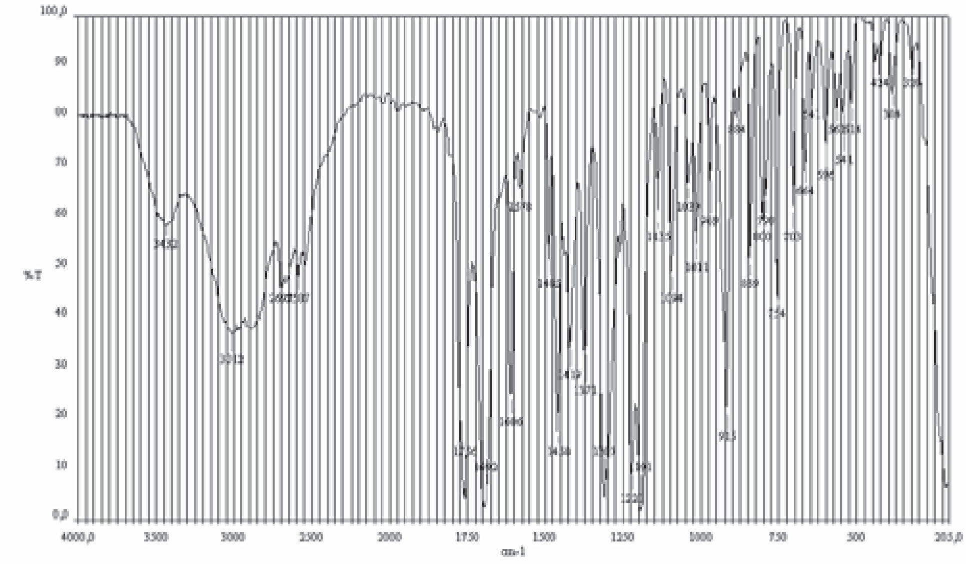
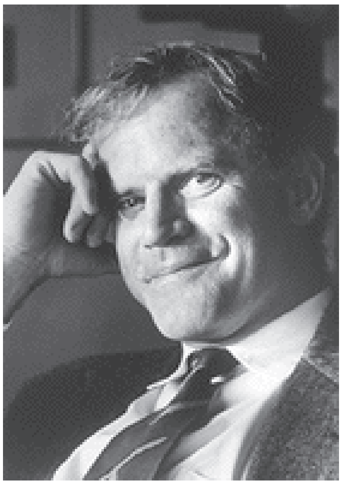


Figure 7

Problem 18 DNA – the PCR Method



Kary B Mullis, 1944 -

In 1993 the Nobel-prize was given to the American molecular biologist Kary B. Mullis for his invention of the polymerase chain reaction (PCR), which by using a heat stable DNA-polymerase enzyme is able to multiply the number of molecules of a given piece of DNA in a cyclic process. Under optimal conditions, the number of double-stranded DNA copies doubles in each cycle.

DNA is composed of 2'-deoxy-nucleotides carrying the bases Adenine (A), Guanine (G), Cytosine (C) and Thymine (T). The molar mass M of the 2'-deoxy-nucleotide-5'-triphosphates (dNTP) is given in the following table

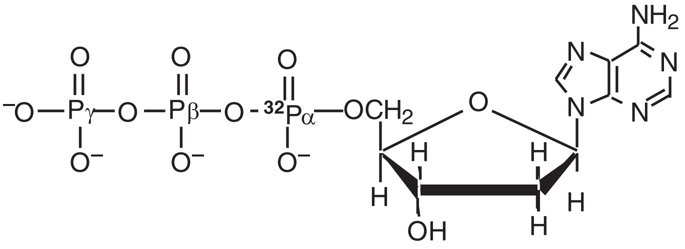
dNTP	**M /g mol^{-1}**
dATP	487
dGTP	503
dCTP	463
dTTP	478

You are given a piece of DNA of 1000 base pairs with a uniform distribution of bases. Using the PCR method you perform 30 cycles.

a. How many copies of your DNA do you obtain?

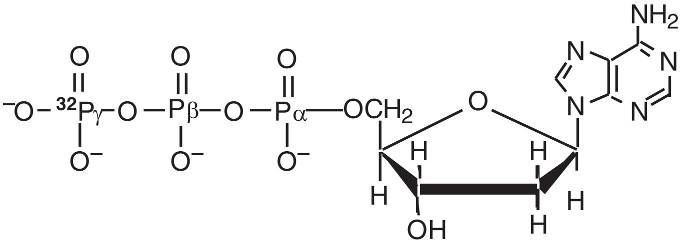
b. Imagine that the process is continued for another 30 cycles. How many copies do you now obtain, and what is the mass of this DNA?

Often, small pieces of single-stranded DNA with a specific sequence are used as so-called probes to find DNA with a complementary sequence to the probe. In order to relocate the probe, it has to be labelled to be become ”visible”. This may be achieved by incorporating a radioactive isotope into the probe. ^{32}P is a commonly used isotope for this purpose. A ^{32}P-labelled DNA probe can be synthesised by including [a-^{32}P]-dATP in the PCR reaction.



[α-^{32}P]-dATP

c. Is the PCR fragment radioactively labelled if [γ-^{32}P]-dATP is included in the PCR-reaction instead?



[γ-^{32}P]-dATP

d. ^{32}P has a half-life of 14.2 days, and during the decay a β-particle is emitted. A probe is synthesised with a specific activity of 1 µCi/pmol probe. Calculate the specific activity after 92 days. How many decays/min does this correspond to per pmol probe?

Problem 19 Proteins, UV Spectra and Light Absorption

The protein lysozyme, found in egg white, is composed of 129 amino acids. It has a molar mass of 14,313 g mol^{-1} and has the following amino acid composition:

Amino acid	**Number**
Ala = Alanine 1	2
Cys = Cysteine	8
Asp = Aspartic acid	7
Glu = Glutamic acid	2
Phe = Phenylalanine	3
Gly = Glycine	1
His = Histidine	1
Ile = Isoleucine	6
Lys = Lysine	6
Leu = Leucine	8
Met = Methionine	2
Asn = Asparagine	14
Pro = Proline	2
Gln = Glutamine	3
Arg = Arginine	11
Ser = Serine	10
Thr = Threonine	7
Val = Valine	6
Trp = Tryptophan	6
Tyr = Tyrosine	3

The aromatic amino acids absorb UV radiation. Thus, it is the amino acids tryptophan, tyrosine and phenylalanine that are responsible for the fact that proteins absorb light with wavelengths between 240 nm and 300 nm.

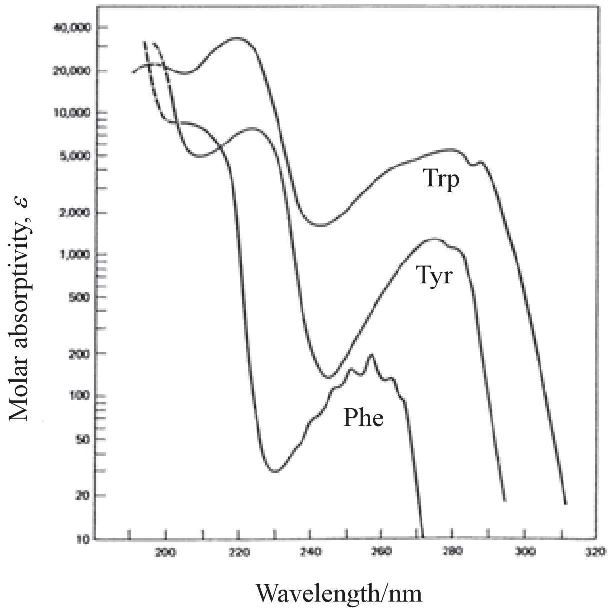


Figure 8 Ultraviolet absorption spectra of the aromatic amino acids at neutral pH

Absorption of light takes place in accordance with the Lambert-Beer Law:

$$A = \varepsilon\ l\ c$$

A is the absorbance (no unit), c is the concentration (M), l is the light path through the sample (cm) and ε is the molar absorptivity or molar absorption coefficient ($\text{M}^{-1}\ \text{cm}^{-1}$). In a protein containing several aromatic amino acids, the sum of the molar absorptivities per amino acid, $\Sigma\varepsilon_{\text{amino acid}}$, is approximately equal to the molar absorptivity, $\varepsilon_{\text{protein}}$, for the protein.

a. Calculate the molar absorptivity $\varepsilon_{\text{lysozym}}$ at 280 nm.

The absorption of a solution of lysozyme is measured using a cuvette with a 1 cm light path. The absorbance is measured as being 1.05.

b. Calculate the the concentration of lysozyme in the sample.

c. Calculate the mass concentration in g/L.

The frequency of the aromatic amino acids in an average protein is calculated from known amino acid sequences from 1021 proteins:

Amino acid	**Frequency**
Phenylalanin	3.9 %
Tryptophan	1.3 %
Tyrosin	3.4 %

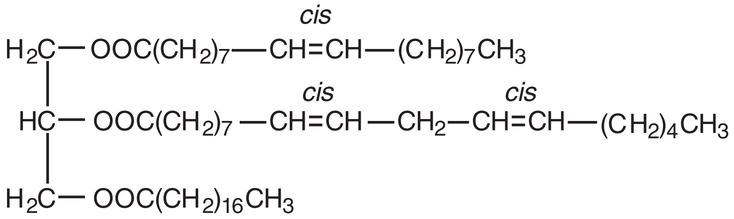
d. Calculate the absorbance of a 1 g/L solution of Lysozyme and calculate the absorbance of a 1 g/L solution of an average protein (the average mass of the amino acids in lysozyme is the same as in an average protein).

A solution of a mixture of lysozyme and an unknown protein is provided. The unknown protein consists of 219 amino acids, of which 14 are phenylalanine, 11 are tyrosine and 2 are tryptophan. Using a lysozyme-specific analysis the mass concentration of lysozyme is calculated to 0.24 g/L.

e. Calculate the concentration of the unknown protein when the the absorbance of the mixture is measured to be 1.85 at 280 nm and a light path of 1 cm is used.

Problem 20 Sunflower Oil

A constituent **S** of oil from sunflower was identified as having the structure



$$\begin{array}{l}
H_2C-OOC(CH_2)_7-\overset{cis}{CH=CH}-(CH_2)_7CH_3 \\
\quad | \\
HC-OOC(CH_2)_7-\overset{cis}{CH=CH}-CH_2-\overset{cis}{CH=CH}-(CH_2)_4CH_3 \\
\quad | \\
H_2C-OOC(CH_2)_{16}CH_3
\end{array}$$

a. How many enantiomers of the constituent **S** exist? Indicate with asterisks (*) the chiral centres of the molecule, if any.

b. The constituent **S** was treated with sodium methoxide to give a mixture of three methyl esters. Suggest the names of the three esters. Use the *Z,E* notation if necessary.

c. The unsaturated methyl esters were treated with ozone then with zinc in order to establish the location of the double bonds in the molecules. Draw the structure of the four compounds that have an aldehyde function. Write their IUPAC names.

The saponification value of an oil is defined as the number of milligrams of potassium hydroxide needed to hydrolyse one gram of the oil. This value is used to compare the relative molecular masses (relative molar masses) of the oils.

d. Calculate the volume of 0.996 M potassium hydroxide that should be used for saponification of 10.0 g of constituent **S**?

e. What is the saponification value of constituent **S**?

The iodine number of an oil is defined as the number of grams of iodine, I_2, that undergo an addition reaction with 100 g of the oil.

f. Calculate the iodine number of constituent **S**.

Practical Problems

Safety

Prior Notices Relating to Examinations, Procedures and Protocols

SAFETY RULES
"A fundamental requirement for all students in the laboratories at the Technical University of Denmark, is to wear laboratory coats and safety glasses. Students are invited to bring their own laboratory coats and safety glasses which are comfortable and familiar to them. However, for those who do not, then glasses and laboratory coats will be provided. It is mandatory that safety glasses be worn during the whole duration of the Practical Examination from entering the laboratory until departure. Glasses must be medium impact and must comply with the safety standards in your own country. If these do not comply with the standards required by the Technical University of Denmark, new glasses will be provided".

SAFETY REGULATIONS
"The following regulations apply to all laboratories used for the Olympiad. Please help your students understand that we are serious about safety. If necessary have this document translated into their own language. Students who break any of these rules will be given one warning only then expelled from the laboratory. Demonstrators have been instructed that there are to be no exceptions to this rule. If students have questions concerning safety issues you should encourage them to ask a demonstrator.
All students will be required to sign a statement agreeing that they have read and understand these rules prior to commencing the practical tasks".

1 Safety glasses conforming to Standards with side shields must be worn at an times. If you wear contact lenses they must be covered with safety goggles which provide a total seal around the eyes. Prescription spectacles with polycarbonate lenses are acceptable provided they include side shields. Eye injuries must be prevented at all costs. The Demonstrator- in-Charge will check all protective equipment to ensure it is satisfactory before admittance to the examination laboratory. We have asked that teams bring their own safety glasses to Denmark but we shall have some in reserve.

2 A long-sleeved knee length laboratory coat and shoes which enclose the feet must be worn. Thongs, sandals and open style shoes are prohibited. Long hair (below the collar) must be contained. Please see that you bring lab coats and flat-heeled non-slip shoes and suitable hair restraints.

3 There is to be no drinking, eating, smoking or chewing of gum in laboratories.

4 Pipetting by mouth is prohibited (see below)

5 All accidents must be reported. In any chemical laboratory there is always danger from accidental spillage of chemicals, broken glass or fire. Part of your training in practical chemistry is to learn the procedures which allow safe working conditions. Specific safety precautions relating to particular experiments are detailed in the practical task notes”.

ACCIDENTS AND FIRST AID

All injuries, illnesses, incidents no matter how minor, must be reported promptly to the Demonstrator-in-Charge who will arrange for immediate corrective actions to be taken.

1 **Chemicals:** All chemicals must be treated with respect, some are corrosive, some are poisonous and many, particularly organic chemicals, are flammable. When using a chemical for the first time you should always read the safety notes included in the practical task paper.

The following general precautions always apply:

a] Chemicals should never be tasted. Chemicals must never be pipetted by mouth. Pipette fillers are provided and must be used at all times.

b] Spillage on the skin: for any spillage of chemicals on the skin, the immediate treatment is the skin must be flushed under running cold water from the tap or the shower hose for a minimum of 15 minutes and then seek first aid/ medical treatment as appropriate. Organic materials can be absorbed through the skin and in these cases follow the cold water washing by a thorough washing with warm water and soap. Contaminated clothing should be removed as soon as possible and thoroughly washed.

c] Chemicals in the eyes: The proper use of safety glasses will greatly reduce the risk of injury to the eyes. If chemicals are splashed into the eye it must be regarded as serious and the immediate treatment is to wash thoroughly by flushing with running cold water for a minimum. of 15 minutes and then seek first aid/medical treatment as appropriate.

2 **Fire:** Many chemicals are flammable and no open flames are permitted when such chemicals are in use. You are required to know the location of the nearest fire extinguisher, fire blanket and safety shower. If a person’s clothing catches fire, put him/her on the floor and roll him/her to smother the flames. Use the fire blanket or a laboratory coat if accessible. Do not allow the victim to stand, even if using a

safety shower on clothing, to prevent rising flames from reaching the head. Do not use any type of chemical fire extinguisher on a person.

3 **Glassware:** Glass is very hard but brittle material and breaks readily under stress or strain; handle all glassware carefully. If breakage occurs it is essential that any particles or splinters of glass in any wound be removed. All cuts must be inspected by the Demonstrator in Charge. Report and clean up any breakages of glassware; replacements may be obtained by the Demonstrator in Charge.

4 **Waste Materials:** Chemicals must not just be washed away. No chemicals are to enter the drainage system. Particular care must be taken in the disposal of some reaction residues. Where this is important details will be given in the notes and labelled designated waste residue bottle receptacles will be provided.

5 **Care of Benches and Apparatus:** Each student is responsible for his/her section of the bench. Any chemicals or water spill must be wiped up immediately. Concentrated acid spills should first be neutralised with sodium bicarbonate and then washed away with plenty of cold water. Your working area must be kept clean at all times. Chemicals spilt on the floor must be washed away immediately and broken glass swept up. Mops, brooms, dust-pans etc. are available from the preparation room.

Helpful Hints for the Practical Examination

Whilst we are not going to tell you the nature of the practical exam we do think it’s fair to give you one or two useful facts. We do not intend to use Bunsen Burners but rather we shall use hot platesmagnetic stirrers work. This year there will be a mixture of plasticware and glassware used in the practical exam. This means that students will have to be in the habit of deciding what can be heated and what cannot be heated on a hot plate. We shall discuss this at the safety talk but in fairness to all students we felt it best to advise you all in advance so this can be explained slowly to them in their own preferred language.

Problem 21 - Experiment

Preparation of Hydrobenzoin

Safety

The rules described in the enclosed ”Safety Rules” and ”Safety Regulations” should be followed strictly.

Accidents and First Aid

See enclosed ”Accidents and First Aid”

Gloves

The chemicals used in the procedure above are not considered harmful. However, if you have problems with hypersensitivity you may consider using gloves (preferentially non-powdered).

Disposal of waste chemicals, spills, and glass ware

The filtrate should be diluted with 5 mL of water, 0.5 mL of acetic acid is added until the solution turns acidic and the mixture is then placed in a waste container for ”aqueous disposal”. Any minor spills should be placed in the same container. Organic solvents (from TLC) are put in a waste container for ”non-halogenic organic compounds”. Pipettes should be flushed with water and placed in buckets for ”glass disposal”. TLC plates, broken glass, used pipettes and gloves should be placed in buckets for ”glass disposal”. Non chemical waste is put into ordinary waste bins.

Cleaning up

The lab bench should be wiped clean with a wet napkin

R and S sentences for chemicals

The regulations (R and S sentences) for the chemicals used in the procedure are as follows

Benzil: R: 36/37/38; S: 26-36.

95 % Ethanol: R: 11; S: 7-16. Flammable.

Ethyl acetate: R: 11; S: 16-23-29-33. Flammable.

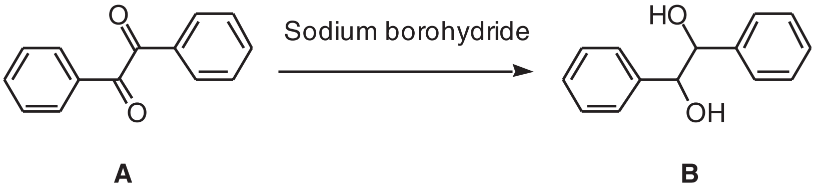
Heptane: R: 11; S: 9-16-23-29-33. Flammable.

Sodium borohydride: R: 15-25-34; S: 2636/37/39-43.12-45; F: 10-21.

20 % acetic acid: R: 10-34; S: 23-26-45.

Preparation of Hydrobenzoin

Hydrobenzoin **B** is an intermediate for the synthesis of new useful products. Hydrobenzoin **B** can be prepared by reduction of Benzil **A** with sodium borohydride (sodium tetrahydridoborate) as follows:



Procedure

Benzil (100 mg, weighed sample in box) is dissolved in 95 % ethanol (1.0 mL) by heating to boiling (use sand bath on hot plate or heat gun). The solution is cooled in an ice bath for ca. 3 min. Then sodium borohydride (ca. 20 mg) is added. After 10 min water (1.0 mL) is added. The mixture is heated to boiling for 10 min. Boiling water (ca.

1 mL) is added until the mixture becomes cloudy. After the mixture has allowed to cool to room temperature it is filtered by suction on a small Buchner funnel. The isolated solid is washed twice with water (1 mL) and pressed dry on the filter. The solid is then collected on a piece of filter paper in order to suck excess of solvent.
When dry the residue is placed in a tara weighed sample tube with lid (For example an Eppendorf tube). The sample tube is closed and weighed. ca. 5 mg of the sample is placed in a another sample tube and dissolved in five drops of ethanol. A capillary tube is dipped into the solution and tapped until ca. 3 mm of solution remains in the tube. The content of the capillary tube is then applied on a TLC plate. A similarly prepared sample of the starting material is applied besides the product as a reference and the TLC plate is eluted with ethyl acetate-heptane 1:6. After elution the plate is visualised under UV-light (254 nm) and the appearance of the plate is drawn, see question **e**. The sample tube with the remaining product is labelled with name and given to the supervisor.

List of Chemicals

Benzil
95 % Ethanol
Sodium borohydride
20 % Acetic acid

List of equipment for each student

2	Test tubes (diameter 2 cm, length ca. 17 cm)
1	250 mL Beaker
1	25 mL Conical flask
1	10 mL Measuring cylinder
1	Wooden clamp
5	Pasteur pipettes.
2	Buchner funnels diameter ca. 10 mm
5	Filter paper discs for Buchner funnels
1	Metal spatula
10	Capillary tubes
5	TLC plates
1	Glasses for development of TLC plates
3	Small sample tubes with lid (for example Eppendorf tubes)

Common equipment

Ice
Sand bath on heating plates or heat guns
UV-lamp (254 nm)
Ink marker

pH indicator paper
Eluent (Ethyl acetate-heptane 1:6) for development of TLC plates
Balance (necessary if yields have to be determined)

Problems

a. Draw a formula of hydrobenzoin which shows its three-dimensional structure.

b. Draw the structural formula of sodium borohydride.

c. Which of the names below is the systematic name (IUPAC name) of hydrobenzoin? Check-mark your choice in the appropriate box.

Dibenzylalkohol ☐

Dibenzoyl ☐

Hydroxy-1,2-diphenylethanol ☐

1,2-Hydroxyphenylethane ☐

1,2-Dihydroxy-1,2-diphenylethane ☐

1-Hydroxyphenyl-2-hydroxyphenylethane ☐

d. Record the following data:

I. The weight of your product:

II. The calculated theoretical yield:

III. The obtained yield in percentage of the theoretical:

IV. Describe crystal appearance and colour of the product:

(Usually a melting point of a product is required. However, in the present case the melting point is of limited value.)

e. Give a sketch of the thin layer chromatographic plate.

f. How many stereoisomers of hydrobenzoin are formed in the reaction ? Checkmark your opinion among the following choices:

1	2	3	4	More than 4

g. How many spots on the TLC-plate do you expect for your product ? ☐

h. Indicate with one check mark which is the best way to discard 10 g of sodium borohydride:

Put into the sink and flush with plenty of water. ☐

Put it directly into the container for inorganic chemical waste. ☐

Pour it slowly into diluted hydrochloric acid then into the sink ☐

Pour it slowly into diluted hydrochloric acid then into the container for inorganic chemical waste. ☐

Pour diluted hydrochloric over it, then put the mixture into the container for inorganic chemical waste. ☐

Procedure for administering liquid reagents using a graded syringe

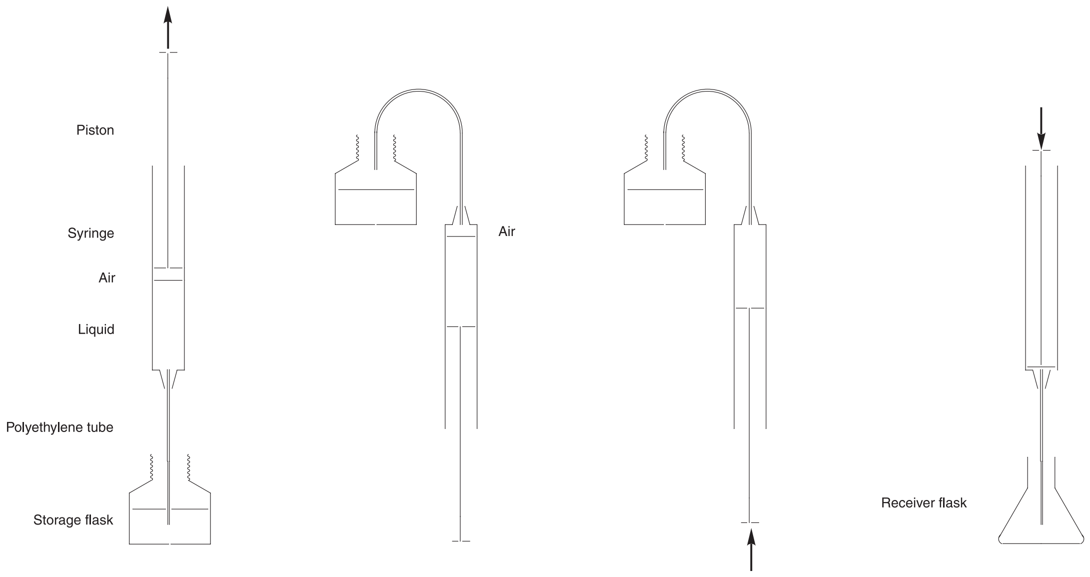
In the present procedure the syringe used is fitted with a polyethylene tube on its tip in order to avoid needles which can cause dangerous injections

Suck a slight excess of the liquid reagent up in the syringe by withdrawing its piston. Turn the syringe upside down, keeping the tip of the polyethylene tube in the storage flask with the liquid. Never draw in the tube.

Let air in the syringe collect in its upper part. Slight tapping may be necessary. Press the piston forward to remove the air, then press the piston further to the desired volume of the liquid. During all these operations the tip of the polyethylene tube is kept in the storage flask with the liquid so that excess of the liquid goes back to the flask. Transfer the syringe to the reaction flask and add the desired volume as described in the recipe.

Excess of liquid in the syringe is washed out before disposal of the syringe.

Measuring volumes of liquids using a syringe



1. Suck up a slight excess of liquid in syringe

2. Turn syringe upside down; the tip of the tube is kept in the storage bottle. Air in the syringe is accumulated at its top

3. Air in the syringe is removed by pressing the piston. Press further until desired volume of liquid is left in the syringe. The tip of the tube is kept in the storage bottle.

4. Turn syringe, place tip of the tube in the receiver flask and press piston until desired volume of liquid has left the syringe.

Mounting of syringe with polyethylene tubing

A graded syringe is equipped with a 10 cm of polyethylene tubing. For a 1 mL syringe a tubing for medical use with an outer diameter 2.42 mm served well.

The tubing is cut in an angle of 45 ° in order to facilitate its pushing into the opening at the tip of the syringe. The tubing should fit snugly so that it is fixed firmly to the syringe.

Problem 22 - Experiment

An Oxalate Complex of Tin(II)

Preparation of potassium bis(oxalato)stannate(II), trihydrate

$$Sn^{2+}(aq) + 2\ C_2O_4^{2-}(aq) \rightarrow [Sn(C_2O_4)_2]^{2-}(aq)$$

In a 25 mL beaker, 2.25 g of $SnCl_2 \bullet 2\ H_2O$ are dissolved in 2.6 mL of 4 M HCl. In a 50 mL beaker, 7.37 g of $K_2C_2O_4 \bullet H_2O$ are dissolved in 25 mL of water. The two solutions are mixed by pouring the tin(II) solution into the oxalate solution, and shortly after crystals start to precipitate. The mixture is allowed to stand for 2 h for crystallization. The crystals are collected by filtration with suction, washed with 2 × 5 mL of water followed by 2 × 5 mL of ethanol, and dried in air overnight.

A. Record the yield in gram.

B. Calculate the theoretical yield in gram and the actual yield in percent.

Analysis of $K_2[Sn(C_2O_4)_2] \bullet 3\ H_2O$ for tin(II) and oxalate

Preparation of 0.02 M $KMnO_4$ solution: In a 400 mL beaker, 3.2 g of $KMnO_4$ are dissolved in 200 mL of demineralized water by heating until complete dissolution. The solution is transferred to a 1 liter flask and diluted with 800 mL of demineralized water. The solution should be stored in the dark when not in use.

Standardisation of the 0.02 M $KMnO_4$ solution:

$$5\ C_2O_4H_2(aq) + 2\ MnO_4^-(aq) + 6\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(g) + 8\ H_2O(l)$$

Approximately 130 mg of "potassium tetraoxalate" [$KH_3(C_2O_4)_2 \bullet 2\ H_2O$, $M = 254.20$ g mol^{-1}] are accurately weighed and transferred quantitatively to a 250 mL conical flask with approx. 50 mL of demineralized water followed by the addition of 25 mL of 2 M sulfuric acid. The solution is heated to 75 – 80 °C before it is titrated with the permanganate solution. The titration has to be performed slowly at the beginning. This means that a new drop should not be added before the previous one has reacted and the solution has turned colourless. When the first drops of titrant have reacted, the reaction will be catalyzed by the manganese(II) ions formed, so at this stage the addition can be speeded up. By the end of the titration permanganate is again added slowly, until one drop gives the solution a rose colour, which does not fade be standing for 30 s.

C. Calculate the concentration of the $KMnO_4$ standard solution.

Analysis of the complex: Tin(II) and the oxalate ligands are oxidized by titration with permanganate:

$$5\ C_2O_4H_2(aq) + 2\ MnO_4^-(aq) + 6\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(g) + 8\ H_2O(l)$$

$$5\ Sn^{II}(aq) + 2\ MnO_4^-(aq) + 16\ H^+(aq) \rightarrow Sn^{IV}(aq) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$$

Approximately 150 mg of the complex are accurately weighed and transferred quantitatively to a 250 mL conical flask with approx. 50 mL of demineralized water followed by the addition of 25 mL of 2 M H_2SO_4. The solution is heated to 75 – 80 °C before it is titrated with the standardised $KMnO_4$ solution as previously described.

D. Calculate the molar mass of the complex from the titration data.

E. Calculate the number of waters of crystallization in the complex.

Problem 23 - Experiment

An Ammonia Complex of Copper(II)

Preparation of tetraamminecopper(II) sulfate, monohydrate

$$[Cu(H_2O)_4]^{2+}(aq) + 4\ NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + 4\ H_2O(l)$$

In a 100 mL conical flask, a solution of copper(II) sulfate in 20 mL of 6 M NH_3 is prepared in the following way: To 5.0 g of pulverized $[Cu(H_2O)_4]SO_4 \cdot H_2O$ is first added approx. 15 mL of the cold ammonia solution, and the mixture is stirred for a while. After decantation the solid residue is dissolved in the remaining approx. 5 mL of ammonia. The solutions are combined and filtered through a pleated filter.

To the blue filtrate is dropwise added 20 mL of ethanol with magnetic stirring, and the reaction mixture is cooled in ice water for 15 min. The blue violet crystals are collected by filteration with suction, washed with 2 × 10 mL of ethanol, and dried at 50 °C for 2 h.

A. Record the yield in gram.

B. Calculate the theoretical yield in gram and the actual yield in percent.

Analysis of $[Cu(NH_3)_4]SO_4 \cdot H_2O$ for copper(II) and ammonia

Preparation af 0.1 M $Na_2S_2O_3$ solution: 12.5 g of $Na_2S_2O_3 \cdot 5H_2O$ and 0.05 g of Na_2CO_3 are dissolved in 500 mL of “boiled out” demineralized water.

Standardization of the 0.1 M $Na_2S_2O_3$ solution

$$2\ Cu^{2+}(aq) + 5\ I^-(aq) \rightarrow 2\ CuI(s) + I_3^-(aq)$$

$$I_3^-(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 3\ I^-(aq) + S_4O_6^{2-}(aq)$$

Approximately 340 mg of $CuCl_2 \cdot 2H_2O$ (M = 170.48 g mol^{-1}) are accurately weighed and transferred quantitatively to a 250 mL conical flask with approx. 50 mL of demineralized water, and 2 M NaOH is added dropwise until the solution becomes cloudy. Then 10 mL of 4 M acetic acid followed by 1 g of KI are added giving a white precipitate of CuI in a brown solution of I_3^-. This is titrated with the $Na_2S_2O_3$ solution. When the brown colour has faded to light yellow, 2 mL of starch indicator are added, and the titration is continued until the colour changes from blue to colourless.

C. Calculate the concentration of the $Na_2S_2O_3$ solution.

Analysis of the complex for copper: Approximately 450 mg of the complex are accurately weighed, transferred quantitatively to a 250 mL conical flask with approx. 50 mL of demineralized water, and titrated with the standardized $Na_2S_2O_3$ solution as described above.

D. Calculate the molar mass of the complex from the titration data.

Preparation of 0.1 M HCl solution: 9 mL of concentrated hydrochloric acid are added to 1000 mL of demineralized water.

Standardisation of the 0.1 M HCl solution:

$$[B_4(OH)_4O_5]^{2-}(aq) + 5\ H_2O(l) \rightarrow 2\ B(OH)_3(aq) + 2\ B(OH)_4^-(aq)$$

$$B(OH)_4^-(aq) + H^+(aq) \rightarrow B(OH)_3(aq) + H_2O(l)$$

Approximately 380 mg of borax ($Na_2[B_4(OH)_4O_5] \cdot 8H_2O$, M = 381.36 g mol^{-1}) are accurately weighed and transferred quantitatively to a 250 mL conical flask with approx. 100 mL of demineralized water. Two drops of methyl red indicator solution are added and the solution is titrated with the HCl solution until one drop changes the colour from lemon yellow to faint orange red.

E. Calculate the concentration of the HCl solution.

Preparation of 0.1 M NaOH solution: Prepare a saturated solution of NaOH and let the solution stand overnight. Such a solution will be nearly carbonate free, due to the precipitation of sodium carbonate. 5 mL of the concentrated base are added to 1000 mL of “boiled out” demineralized water in a plastic bottle.

Standardization of the 0.1 M NaOH solution: 20 mL of the standardized 0.1 M HCl solution are pipetted and transferred to a 250 mL conical flask. 30 mL of water and 2 drops of methyl red indicator are added and the solution is titrated with the 0.1 M NaOH solution.

F. Calculate the concentration of the NaOH solution.

Analysis of the complex for ammonia

$$[Cu(NH_3)_4]^{2+}(aq) + 4\ H^+(aq) \rightarrow Cu^{2+}(aq) + 4\ NH_4^+(aq)$$

20 mL of the standardized 0.1 M HCl solution are pipetted and transferred to a 250 mL conical flask. Approximately 85 mg of the complex are accurately weighed and transferred quantitatively to the flask with 50 mL of demineralized water. 4 drops of alizarine sulphonate (0.1 %) and 4 drops of bromcresol green (0.1 %) indicators are added and the solution is titrated with the 0.1 M NaOH solution. Colour change from a yellow to blue.

G. Calculate the molar mass of the compound from the titration data.

Problem 24 - Experiment

A Thiourea Complex of Copper(I)

Preparation of tris(thiourea)copper(I) sulphate, dihydrate

$$16\ Cu^{2+}(aq) + 8\ (H_2N)_2CS(aq) + 16\ H_2O(l) \rightarrow 16\ Cu^+(aq) + S_8(s) + 16\ NH_4^+(aq) + 8\ CO_2(g)$$

$$Cu^+(aq) + 3(H_2N)_2CS(aq) \rightarrow [Cu\{(H_2N)_2CS\}_3]^+(aq)$$

Dissolve, in a 150 mL beaker, 4.0 g of $(H_2N)_2CS$ in 25 mL of hot water and cool the solution to approx. 30 °C. Add a solution of 4.0 g of $CuSO_4 \cdot 5H_2O$ in 20 mL of H_2O dropwise with magnetic stirring. Finally, under continued stirring, the mixture is cooled in ice water until the separated yellowish oil adheres to the beaker. The mother liquor is decanted and rejected. The oil is then cooled in ice water and stirred vigorously with a solution of 2 g of thiourea in 20 mL of water until the oil has crystallised completely. The crystals are collected by filtration with suction and washed with 2 × 2 mL of ice-cold water.

Recrystallization: The crude product is recrystallized from approx. 70 mL of a 5 % aqueous solution of thiourea which is 0.02 M in H_2SO_4. During the recrystallization the temperature should not exceed 80 °C. The crude product is dissolved by heating and the solution is filtered through a pleated filter. The filtrate is heated until any precipitated crystals have dissolved (a little colloidal sulphur passes the filter, so the solution will not become completely clear) and the solution is cooled to room temperature by standing for 2 - 3 h. The crystals are collected by filtration with suction, washed with 2 × 3 mL of water, and dried in air overnight.

A. Record the yield of the title compound in gram.

B. Calculate the theoretical yield in gram and the actual yield in percent.

Analysis of the complex

Standard 0.02 M Na_2H_2(edta) solution. Approximately 3.8 g of Na_2H_2(edta) •$2H_2O$ [M = 372.25 g mol^{-1}, H_4(edta) ≡ $(HOOC)_2CH_2CH_2(COOH)_2$] - dried for 2 h at 80 °C and cooled in a desiccator - are accurately weighed and transferred quantitatively to a 500 mL volumetric flask, dissolved in demineralized water and diluted to 500 mL.

C. Calculate the concentration of the Na_2H_2(edta) solution.

Analysis of the complex for copper:

$$Cu^{2+}(aq) + H_2(edta)^{2-}(aq) \rightarrow Cu(edta)^{2-}(aq) + 2\ H^+(aq)$$

Approximately 125 mg of the complex are accurately weighed and transferred quantitatively to a 250 mL conical flask with as little water as possible. 5 mL of 4 M HNO_3 are added, and the mixture is heated until the evolution of nitrogen oxides has ceased. Buffer (pH = 10) solution (1.3 M NH_4Cl, 6.8 M NH_3) is added until the solution has turned cloudy and the cloudiness has just disappeared again. Additional three drops are added and the volume is then adjusted to approx. 50 mL with water. A little murexide indicator is added and the solution is titrated with the Na_2H_2(edta) solution until the indicator changes from brownish yellow green to violet.

D. What mass of the compound contains one mole of copper?

Worked Solutions to Problems

1 Acid Rain

a.

i. $p\,V = n\,R\,T$

$$n = \frac{p\,V}{R\,T} = \frac{1.00\text{ bar} \times 33.9\text{ L}}{0.08314\ \frac{\text{L bar}}{\text{mol K}} \times 298.15\text{ K}}$$

$n = 1.368$ mol

$c(\mathrm{SO_2}) = 1.368\ \text{M}$

ii. $\mathrm{SO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq)}$

$[\mathrm{H^+}] = [\mathrm{HSO_3^-}] = x$

$$\frac{x^2}{1.368\ \text{M} - x} = 10^{-1.99}\ \text{M}$$

$[\mathrm{H^+}] = [\mathrm{HSO_3^-}] = 0.1224\ \text{M}$

$$\frac{0.1224\ \text{M}}{1.386\ \text{M}} \times 100\ \% = 8.95\ \%\quad \text{as } \mathrm{HSO_3^-}$$

iii. pH = 0.91

b. $\mathrm{SO_3^{2-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HSO_3^-(aq)}$

$[\mathrm{OH^-}] = [\mathrm{HSO_3^-}] = x$

$$\frac{x^2}{0.01\ \text{M} - x} = \frac{10^{-14}\ \text{M}^2}{10^{-7.18}\ \text{M}} = 10^{-6.82}\ \text{M}$$

$x = [\mathrm{OH^-}] = 3.89 \times 10^{-5}\ \text{M}$

$[\mathrm{H^+}]\,[\mathrm{OH^-}] = 10^{-14}\ \text{M}^2$ $\qquad [\mathrm{H^+}] = 2.57 \times 10^{-10}\ \text{M}$

c.

i. $$K = \frac{[\mathrm{SO_2}]\,[\mathrm{SO_3^{2-}}]}{[\mathrm{HSO_3^-}]^2} = \frac{[\mathrm{SO_2}]\,[\mathrm{SO_3^{2-}}]}{[\mathrm{HSO_3^-}]^2} \times \frac{[\mathrm{H^+}]}{[\mathrm{H^+}]} = \frac{K_{a2}}{K_{a1}} = 10^{-5.26}$$

ii. $[\mathrm{SO_2}] + [\mathrm{HSO_3^-}] + [\mathrm{SO_3^{2-}}] = 0.01\ \text{M}$ and $[\mathrm{SO_2}] = [\mathrm{SO_3^{2-}}]$

$$\frac{[\mathrm{SO_2}]^2}{(0.01\ \text{M} - 2\,[\mathrm{SO_2}])^2} = 10^{-5.26}$$

$[\mathrm{SO_2}] = 2.33 \times 10^{-5}\ \text{M}$

d. $M(\mathrm{BaSO_3}) = 217.39\ \text{g mol}^{-1}$

i. $[\mathrm{Ba^{2+}}] = 7.36 \times 10^{-4}\ \text{M}$

ii. $\mathrm{SO_3^{2-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HSO_3^-(aq)}$

$[\mathrm{OH^-}] = [\mathrm{HSO_3^-}] = x$

$[HSO_3^-] + [SO_3^{2-}] = [Ba^{2+}]$

$$\frac{x^2}{7.36 \times 10^{-4}\ \text{M} - x} = 10^{-6.82}\ \text{M}$$

$x = 1.0479 \times 10^{-5}\ \text{M}$

$[SO_3^{2-}] = 7.26 \times 10^{-4}\ \text{M}$

iii. $K_{sp} = [Ba^{2+}]\,[SO_3^{2-}] = 7.36 \times 10^{-4}\ \text{M} \times 7.26 \times 10^{-4}\ \text{M} = 5.34 \times 10^{-7}\ \text{M}^2$

e. $[Ag^+]^2\,[SO_3^{2-}] = 10^{-13.82}\ \text{M}^3$

$[Ag^+] = 2\,[SO_3^{2-}]$

$[Ag^+] = 3.927 \times 10^{-5}\ \text{M}$

f. $$K = \frac{[Ag^+]^2}{[Ca^{2+}]} = \frac{[Ag^+]^2}{[Ca^{2+}]} \times \frac{[SO_3^{2-}]^2}{[SO_3^{2-}]} = \frac{K_{sp}(Ag_2SO^3)}{K_{sp}(CaSO^3)} = \frac{10^{-13.82}\ \text{M}^3}{10^{-7.17}\ \text{M}^2}$$

$K = 10^{-6.65}\ \text{M}$

g. Reaction: $2\,H_2O(l) + SO_2(aq) + Br_2(aq) \rightarrow SO_4^{2-}(aq) + 2\,Br^-(aq) + 4\,H^+(aq)$

Equilibrium: $HSO_4^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H^+(aq)$ $\quad K_a = 10^{-1.99}\ \text{M}$

$[SO_4^{2-}] + [HSO_4^-] = 0.01\ \text{M}$ and $[H^+] + [HSO_4^-] = 0.04\ \text{M}$

$[HSO_4^-] = 0.04\ \text{M} - [H^+]$ and $[SO_4^{2-}] = [H^+] - 0.03\ \text{M}$

$[H^+] = 0.0324\ \text{M}$

h. $[H^+] = 10^{-3.2}\ \text{M}$

$K_a = 10^{-1.99}\ \text{M}$ $\quad [HSO_4^-] = 10^{-1.28}\,[SO_4^{2-}]$

$[H^+] = 10^{-3.2}\ \text{M} = [HSO_4^-] + 2\,[SO_4^{2-}] + [OH^-]$

$10^{-3.2}\ \text{M} = 10^{-1.28}\,[SO_4^{2-}] + 2\,[SO_4^{2-}] + 10^{-10.8}\ \text{M}$

$[SO_4^{2-}] = 3.074 \times 10^{-4}\ \text{M}$ and $[HSO_4^-] = 1.613 \times 10^{-5}\ \text{M}$

$c(H_2SO_4) = [HSO_4^-] + [SO_4^{2-}]$

$c(H_2SO_4) = 3.24 \times 10^{-4}\ \text{M}$

2 Potassium Chlorate

a. Cathode: $2\,H_2O(l) + 2\,e^- \rightarrow 2\,OH^-(aq) + H_2(g)$

Anode: $2\,Cl^-(aq) \rightarrow Cl_2(g) + 2\,e^-$

b. Reaction: $3\,Cl_2(g) + 6\,OH^-(aq) \rightarrow ClO_3^-(aq) + 5\,Cl^- + 3\,H_2O(l)$

c. Formation of 1 mol $KClO_3$ requires 1 mol KCl and 6 mol electrons.

$m(KClO_3) = 100$ g, $n(KClO_3) = 0.816$ mol formation of 0.816 mol KCl gives: $m(\mathrm{KClO_3}) = 60.83$ g

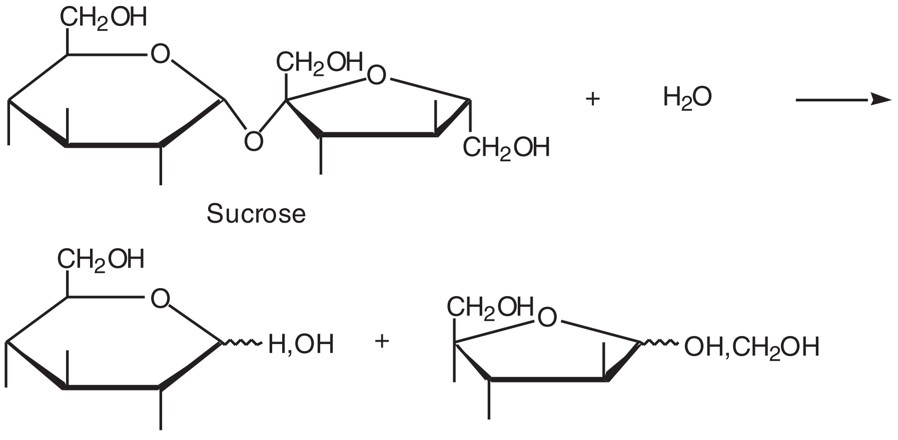
and requires 6 × 0.816 mol electrons

$Q = I\,t$ and Q/F = amount of e^- in moles

$Q = 6 \times 0.816\ \mathrm{mol} \times 96485\ \mathrm{C\ mol^{-1}} = 472390.56\ \mathrm{C} = 472390.56\ \mathrm{A\ s} = 131\ \mathrm{A\ h}$

3 Sugar Inversion

a.



Sucrose

α– + β-D-Glucose

α– + β-D-Fructose

b. $\ln(\alpha_t - \alpha_\infty)$ as a function of time is a straight line, i.e. first order reaction

The slope is $-0.0053\ \mathrm{min^{-1}}$

$k = 0.0053\ \mathrm{min^{-1}} = 8.83 \times 10^{-5}\ \mathrm{s^{-1}}$

c. $k = A \exp(-E_a/(R \times 298\ \mathrm{K}))$ and $2\,k = A \exp(-E_a/(R\ 303\ \mathrm{K}))$

$\ln 2 = (1/298\ \mathrm{K^{-1}} - 1/303\ \mathrm{K^{-1}})E_a/R$

$E_a = 104\ \mathrm{kJ\ mol^{-1}}$.

4 Humus

a. $2\ \mathrm{Mn^{2+}(aq)} + \mathrm{O_2(g)} + 2\ \mathrm{H_2O(l)} \rightarrow 2\ \mathrm{MnO_2(s)} + 4\ \mathrm{H^+(aq)}$

b. $\Delta G_2^\ominus = -2\,F\,E_2^\ominus = -233.5\ \mathrm{kJ\ mol^{-1}}$

$\Delta G_3^\ominus = -2\,F\,E_3^\ominus = -474.7\ \mathrm{kJ\ mol^{-1}}$

$\Delta G_1^\ominus = -2\,\Delta G_2^\ominus + \Delta G_3^\ominus = -7.7\ \mathrm{kJ\ mol^{-1}}$

c. $\Delta G_1^\ominus = -RT \ln K_1$

$K_1 = 22.4\ \mathrm{M^2\ bar^{-1}}$

d. $\mathrm{Mn^{2+}(aq) + hum(aq) \rightleftharpoons Mn(hum)^{2+}(aq)} \qquad \beta = 10^{5}\ \text{M}^{-1}$

$$\mathrm{2\ Mn(hum)^{2+}(aq) + O_2(g) + 2\ H_2O(l) \rightleftharpoons 2\ MnO_2(s) + 4\ H^+(aq) + 2\ hum(aq)}$$

$$K = \frac{[\mathrm{hum}]^2\ [\mathrm{H^+}]^4}{[\mathrm{Mn(hum)^{2+}}]^2\ p(\mathrm{O_2})} = \frac{K_1}{\beta^2} = 2.24 \times 10^{-9}\ \text{M}^4\ \text{bar}^{-1}$$

e. pH = 5:

$$2.24 \times 10^{-9}\ \text{M}^4\ \text{bar}^{-1} = \frac{(10^{-4}\text{M})^2 \times (10^{-5}\text{M})^4}{[\mathrm{Mn(hum)^{2+}}]^2 \times 0.2\ \text{bar}}$$

$[\mathrm{Mn(hum)^{2+}}] = 4.7 \times 10^{-10}\ \text{M}$

pH = 8:

$$2.24 \times 10^{-9}\ \text{M}^4\ \text{bar}^{-1} = \frac{(10^{-4}\text{M})^2 \times (10^{-8}\text{M})^4}{[\mathrm{Mn(hum)^{2+}}]^2 \times 0.2\ \text{bar}}$$

$[\mathrm{Mn(hum)^{2+}}] = 4.7 \times 10^{-16}\ \text{M}$

f. Alkaline soil.

5 Brønsted Acids and Bases

a. $\mathrm{NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)}$

18.7 mmol $\mathrm{NH_4Cl}$ and 3.17 mmol $\mathrm{Ba(OH)_2{\cdot}8H_2O}$ (6.34 mmol $\mathrm{OH^-}$) produce 6.34 mmol $\mathrm{NH_3}$, and 12.4 mmol $\mathrm{NH_4^+}$ is left unchanged.

$$[\mathrm{H^+}] = K_\mathrm{a}\frac{[\mathrm{NH_4^+}]}{[\mathrm{NH_3}]} = 10^{-9.24}\ \text{M} \times \frac{12.4}{6.34} = 1.13 \times 10^{-9}\ \text{M}$$

$\mathrm{pH} = -\log(1.13 \times 10^{-9}) = 8.95$

b. $[\mathrm{NH_4^+}] = 0.124\ \text{M}$

$[\mathrm{Ba^{2+}}] = 0.0317\ \text{M}$

$[\mathrm{H^+}] = 1.13 \times 10^{-9}\ \text{M}$

$[\mathrm{Cl^-}] = 0.187\ \text{M}$

$[\mathrm{OH^-}] = 8.85 \times 10^{-6}\ \text{M}$

c. 10.0 mmol HCl is added. Of this amount 6.34 mmol is neutralised by $\mathrm{NH_3}$. Assuming that the volume is 110 mL, and ignoring the weak acid $\mathrm{NH_4^+}$ we get:

$$[\mathrm{H^+}] = \frac{3.66\ \text{mmol}}{110\ \text{mL}} = 0.0333\ \text{M}$$

$\mathrm{pH} = -\log(0.0333) = 1.48$

d. In the strong acidic solution, $[\mathrm{NH_3}]$ will be very low.

$$[\mathrm{NH_4^+}] = \frac{18.7\ \text{mmol}}{110\ \text{mL}} = 0.170\ \text{M}$$

$$[\mathrm{NH_3}] = \frac{K_\mathrm{a}[\mathrm{NH_4^+}]}{[\mathrm{H^+}]} = \frac{10^{-9.24}\ \text{M} \times 0.170\ \text{M}}{0.0333\ \text{M}} = 2.9 \times 10^{-9}\ \text{M}$$

6 Magnesium Hydroxide

a. pOH = 14.0 – 10.5 = 3.5

$[OH^-] = 10^{-3.5}\ \text{M} = 3.2 \times 10^{-4}\ \text{M}$

This corresponds to a solubility of $Mg(OH)_2$ of 1.6×10^{-4} mol L^{-1} or

9.2×10^{-4} g/100 mL.

b. $K_{sp} = [Mg^{2+}]\,[OH^-]^2 = 1.6 \times 10^{-11}\ \text{M}^3$

c. $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)$

$[Mg^{2+}] = x;\quad [OH^-] = 0.010\ \text{M} + 2x \cong 0.010\ \text{M}$

$$x = \frac{K_{sp}}{[OH^-]^2} = \frac{1.6 \times 10^{-11}\ \text{M}^3}{(0.010\ \text{M})^2} = 1.6 \times 10^{-7}\ \text{M}$$

The solubility is 1.6×10^{-7} mol L^{-1} or 9×10^{-7} g/100 mL.

d. $Mg(OH)_2$ is in large excess, and the hydrochloric acid will be completely neutralised due to the reaction:

$Mg(OH)_2(s) + 2\ H^+(aq) \rightarrow Mg^{2+}(aq) + 2\ H_2O(l)$

Assuming constant volume of 100 mL, this reaction produces a Mg^{2+} concentration of 0.050 M. Then $Mg(OH)_2$ dissolves in the solution:

$[Mg^{2+}] = 0.050\ \text{M} + x \cong 0.050\ \text{M}$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{1.6 \times 10^{-11}\ \text{M}^3}{0.050\ \text{M}}} = 1.8 \times 10^{-5}\ \text{M}$$

pOH = $-\log(1.8 \times 10^{-5}) = 4.7$

pH = 14.0 – 4.7 = 9.3

7 An Unstable Solid

a.

	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$
$H^\ominus/(\text{kJ mol}^{-1})$	–156.9		– 45.9		–20.4
$S^\ominus/(\text{ J K}^{-1}\text{ mol}^{-1})$	113.4		192.6		205.6

$\Delta H^\ominus = -45.9\ \text{kJ mol}^{-1} - 20.4\ \text{kJ mol}^{-1} - (-156.9)\ \text{kJ mol}^{-1} = 90.6\ \text{kJ mol}^{-1}$

$\Delta S^\ominus = 192.6\ \text{J K}^{-1}\text{ mol}^{-1} + 205.6\ \text{J K}^{-1}\text{ mol}^{-1} - 113.4\ \text{J K}^{-1}\text{ mol}^{-1} = 284.8\ \text{J K}^{-1}\text{ mol}^{-1}$

$\Delta G^\ominus = \Delta H^\ominus - T\,\Delta S^\ominus = (90600 - 298.15 \times 284.8)\ \text{J mol}^{-1} = 5687\ \text{J mol}^{-1}$
$= 5.7\ \text{kJ mol}^{-1}$

b.

$\Delta G^\ominus = -RT \ln K_a$

at 25 °C: $-5687 \text{ J mol}^{-1} = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \ \ln K_a$

$K_a = 0.1008$

$K_a = (p(\text{NH}_3)/\text{bar})\ (p(\text{H}_2\text{S})/\text{bar})$

$K_p = p(\text{NH}_3)\ p(\text{H}_2\text{S}) = 0.1008 \text{ bar}^2$

c.

at 35 °C: $\Delta G^\ominus = \Delta H^\ominus - T\,\Delta S^\ominus = (90600 - 308.15 \times 284.8) \text{ J mol}^{-1}$

$= 2839 \text{ J mol}^{-1}$

$K_a = 0.3302$

$K_p = p(\text{NH}_3)\, p(\text{H}_2\text{S}) = 0.3302 \text{ bar}^2$

d.

$p(\text{total}) = p(\text{NH}_3) + p(\text{H}_2\text{S})$

$p(\text{NH}_3) = p(\text{H}_2\text{S}) = 0.5\, p(\text{total})$ (equal amounts)

$K_p = p(\text{NH}_3)\, p(\text{H}_2\text{S}) = 0.5\, p(\text{total}) \times 0.5\, p(\text{total}) = (0.5\, p(\text{total}))^2 = 0.1008 \text{ bar}^2$

$p(\text{total}) = 0.635 \text{ bar}$

$n(\text{gas}) = p\, V / (R\, T) = 0.635 \text{ bar} \times 25.00 \text{ L} / (0.083145 \text{ L bar mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K})$

$= 0.64 \text{ mol}$

$n(\text{NH}_4\text{HS}) = 1.00 \text{ mol} - 0.5 \times 0.64 \text{ mol} = 0.68 \text{ mol}$ *i.e.* there is still solid present

e.

$n(\text{gas}) = p\, V / (R\, T) = 0.635 \text{ bar} \times 100.00 \text{ L} / (0.083145 \text{ L bar mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K})$

$= 2.56 \text{ mol}$

$n(\text{NH}_4\text{HS}) = 1.00 \text{ mol} - 0.5 \times 2.56 \text{ mol} = -0.28 \text{ mol}$! *i.e.* there is no solid left

1.00 mole of solid converted to 2.00 moles of gas

$p(\text{total}) = n(\text{total})\, R\, T / V = 2.00 \times 0.083145 \text{ L bar mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} / 100.00 \text{ L}$

$= 0.50 \text{ bar}$

8 Electrochemistry

a. Cell diagram: $Zn(s)\,|\,Zn^{2+}(aq)\;\|\;Ag^{+}(aq)\,|\,Ag(s)$

This cell diagram implies a cell reaction with oxidation (electron production) on the left-hand side (IUPAC convention):

left, oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

right, reduction: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ (to be multiplied by 2)

Cell reaction: $Zn(s) + 2\,Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2\,Ag(s)$

b. $E^{\ominus}(\text{cell}) = E^{\ominus}(\text{right}) - E^{\ominus}(\text{left}) = 0.80\text{ V} - (-0.76\text{ V}) = 1.56\text{ V}$

The Nernst equation corresponding to cell reaction above:

(Some may prefer to focus on half-cells and half-reactions)

The activity a of a solute is approximated by its concentration (divided by the standard concentration).

The activity of a solid substance is equal to 1.

$$E(\text{cell}) = E^{\ominus}(\text{cell}) - \frac{0.05916\text{ V}}{n}\log\frac{a(Zn^{2+})\,a(Ag)^2}{a(Zn)\,a(Ag^{+})^2}$$

$$= 1.56\text{ V} - \frac{0.05916\text{ V}}{2}\log\frac{0.200}{0.100^2} = 1.52\text{ V}$$

The positive sign of E(cell) implies that the cell reaction as written above is the spontaneous reaction which takes place during discharge of the cell.

Spontaneous reaction: $Zn(s) + 2\,Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2\,Ag(s)$

c. At complete discharge $E(\text{cell}) = 0$ and the cell reaction has reached chemical equilibrium.

$$0 = 1.56\text{ V} - \frac{0.05916\text{ V}}{2}\log K$$

$K = 5.5 \times 10^{52}$, *i.e.* the cell reaction has an equilibrium position to the far right with practically no Ag^{+} ions left in solution. The amount of transported Ag^{+} and electrons:

$n(Ag^{+}) = [Ag^{+}]\,V(\text{solution}) = 0.100\text{ M} \times 1.00\text{ L} = 0.100\text{ mol}$

$n(e^{-}) = n(Ag^{+}) = 0.100\text{ mol}$

The Faraday constant F is the (numeric) electric charge of 1 mole of electrons.

$Q = n(e^{-})\,F = 0.100\text{ mol} \times 96485\text{ C mol}^{-1} = 9649\text{ C}$

d. x designates the resultant $[Ag^{+}]$

the left-hand electrode is unchanged, *i.e.* $[Zn^{2+}]$ remains 0.200 M

$$1.04\text{ V} = 1.56\text{ V} - \frac{0.05916\text{ V}}{2}\log\frac{0.200}{x^2}$$

$x = 7.3 \times 10^{-10}$ M

e. $[\mathrm{Cl^-}]$ = amount added per volume – amount in AgCl precipitate per volume

$= 0.300\ \mathrm{M} - (0.100\ \mathrm{M} - 7.3 \times 10^{-10}\ \mathrm{M}) = 0.200\ \mathrm{M}$

$K_{sp}(\mathrm{AgCl}) = [\mathrm{Ag^+}][\mathrm{Cl^-}] = 7.3 \times 10^{-10}\ \mathrm{M} \times 0.200\ \mathrm{M} = 1.5 \times 10^{-10}\ \mathrm{M}^2$

9 Cyanide in Waste

a. $\mathrm{Cd(OH)_2(s) \rightleftharpoons Cd^{2+}(aq) + 2\ OH^-(aq)}$

$K_{sp} = [\mathrm{Cd^{2+}}][\mathrm{OH^-}]^2 = s\,(2s)^2 = 4\,s^3 = 5.9 \times 10^{-15}\ \mathrm{M}^3$

$s = 1.14 \times 10^{-5}\ \mathrm{M}$

b. $K_{sp} = s(s + 0.010)^2$; $s < 1.14 \times 10^{-5}$ M ; $s << 0.010$ M

$s(0.010)^2 = 5.9 \times 10^{-15}\ \mathrm{M}^3$; $s = 5.9 \times 10^{-11}\ \mathrm{M}$

c. $s = 0.5\,[\mathrm{OH^-}] = c(\mathrm{Cd})$

$c(\mathrm{Cd}) = [\mathrm{Cd^{2+}}] + [\mathrm{Cd(CN)^+}] + [\mathrm{Cd(CN)_2}] + [\mathrm{Cd(CN)_3^-}] + [\mathrm{Cd(CN)_4^{2-}}]$

$0.5\,[\mathrm{OH^-}] = [\mathrm{Cd^{2+}}](1 + K_1[\mathrm{CN^-}] + \beta_2[\mathrm{CN^-}]^2 + \beta_3[\mathrm{CN^-}]^3 + \beta_4[\mathrm{CN^-}]^4)$

$$0.5\,[\mathrm{OH^-}] = \frac{\mathrm{K_{sp}}}{[\mathrm{OH^-}]^2}(1 + K_1[\mathrm{CN^-}] + \beta_2[\mathrm{CN^-}]^2 + \beta_3[\mathrm{CN^-}]^3 + \beta_4[\mathrm{CN^-}]^4)$$

$$[\mathrm{OH^-}] = \sqrt[3]{2 \times K_{sp}(1 + K_1[\mathrm{CN^-}] + \beta_2[\mathrm{CN^-}]^2 + \beta_3[\mathrm{CN^-}]^3 + \beta_4[\mathrm{CN^-}]^4)}$$

$$[\mathrm{OH^-}] = \sqrt[3]{2 \times K_{sp}(1 + K_1[\mathrm{CN^-}] + K_1K_2[\mathrm{CN^-}]^2 + K_1K_2K_3[\mathrm{CN^-}]^3 + K_1K_2K_3K_4[\mathrm{CN^-}]^4)}$$

$$[\mathrm{OH^-}] = \sqrt[3]{2 \times 5.9 \times 10^{-15}(1 + 3.02 \times 10^2 + 3.99 \times 10^4 + 1.70 \times 10^6 + 7.59 \times 10^6)}\ \mathrm{M}$$

$$[\mathrm{OH^-}] = \sqrt[3]{2 \times 5.9 \times 10^{-15} \times 9.32 \times 10^6}\ \mathrm{M} = 4.79 \times 10^{-3}\ \mathrm{M}$$

$s = 2.4 \times 10^{-3}\ \mathrm{M}$

d. $$[\mathrm{OH^-}] = \sqrt[3]{2 \times 5.9 \times 10^{-15}(1 + K_1K_2K_3K_4[\mathrm{CN^-}]^4)}$$

$[\mathrm{OH^-}] = 4.47 \times 10^{-3}\ \mathrm{M}$

$s = 2.24 \times 10^{-3}\ \mathrm{M}$

Percentage deviation: $\dfrac{(2.40 - 2.24) \times 10^{-3}}{2.40 \times 10^{-3}} \times 100\% = 6.7\ \%$

10 Age of Greenland Rock

a. The gain in ^{206}Pb must equal the loss in ^{238}U, thus

$n_t(^{206}\mathrm{Pb}) - n_0(^{206}\mathrm{Pb}) = n_0(^{238}\mathrm{U}) - n_t(^{238}\mathrm{U})$

Since $n_t(^{238}\mathrm{U}) = n_0(^{238}\mathrm{U})\mathrm{e}^{-kt}$ and substituting for $n_0(^{238}\mathrm{U})$ we obtain

$n_t(^{206}\mathrm{Pb}) = n_t(^{238}\mathrm{U})(\mathrm{e}^{kt} - 1) + n_0(^{206}\mathrm{Pb})$

b. From the above equation,

$\{n_t(^{206}\text{Pb})/n(^{204}\text{Pb})\} = \{n_t(^{238}\text{U})/n(^{204}\text{Pb})\}(e^{kt} - 1) + \{n_0(^{206}\text{Pb})/n(^{204}\text{Pb})\}$

relating $n_t(^{206}\text{Pb})/n(^{204}\text{Pb})$ as a linear function of $n_t(^{238}\text{U})/n(^{204}\text{Pb})$. From the data, least-squares fitting yields a slope of $0.769 = e^{kt} - 1$, which with

$k = \ln 2/(4.468\ \text{Ga}) = 1.551\ \text{Ga}^{-1}$ result in $t = 3.7$ Ga.

c. The y-axis intercept represents the $n_0(^{206}\text{Pb})/n(^{204}\text{Pb})$ ratio at the time of crystallization of the analysed minerals.

11 Lead Poisoning

a. $83\ \mu\text{g} / (207.2\ \text{g mol}^{-1} \times 0.10\ \text{L}) = 4.00\ \mu\text{M}$ ($M(\text{Pb}) = 207.2\ \text{g mol}^{-1}$).

b. It is relevant to consider the reaction

$$[\text{Ca(edta)}]^{2-}(\text{aq}) + \text{Pb}^{2+}(\text{aq}) \rightleftharpoons [\text{Pb(edta)}]^{2-}(\text{aq}) + \text{Ca}^{2+}(\text{aq})$$

with equilibrium constant $K = K(\text{Pb}) / K(\text{Ca}) = 10^{7.3}$. Due to the strong complexation and excess of Ca^{2+} ion over total edta^{4-} ligand, essentially all ligand will be tied as the lead or calcium complexes. Since $[[\text{Pb(edta)}]^{2-}] << [[\text{Ca(edta)}]^{2-}]$, the real concentrations of Ca^{2+} and $[\text{Ca(edta)}]^{2-}$ ions would be very close to the formal concentrations, and the expression for K then gives

$[\text{Pb(edta)}^{2-}]/[\text{Pb}^{2+}] = K \times [\text{Ca(edta)}^{2-}]/[\text{Ca}^{2+}]$

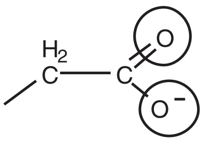
$= 10^{7.3} \times (1.0\ \text{mM} / 2.5\ \text{mM}) = 8.0 \times 10^6$.

c. The $[\text{Pb(edta)}]^{2-}$ complex concentration is 40 % of the original after 2 h. Thus, $0.4 = e^{-k \times 2\,\text{h}}$, yielding $k = 0.458\ \text{h}^{-1}$ and, consequently, $t_{½} = \ln 2 / 0.458\ \text{h}^{-1} = 1.5$ h.

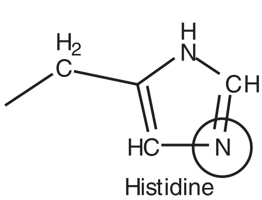
12 Nickel Enzyme

a. $$\text{H}_2\text{NCOO}^-(\text{aq}) + \text{H}_2\text{O(l)} \rightarrow \text{NH}_3(\text{aq}) + \text{HCO}_3^-(\text{aq})$$

b.

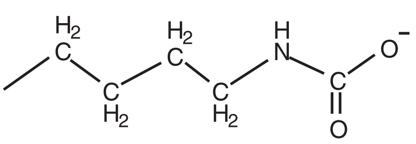


Aspartate



Histidine

c.

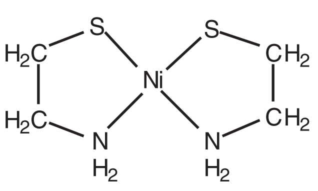


d. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$.

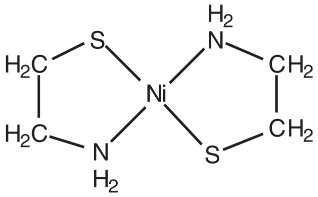
e. Upper energy level: d_{z^2} and $d_{x^2-y^2}$. Lower energy level: d_{xy}, d_{xz} and d_{yz}.

In an octahedral ligand field the mutually orthogonal y, x and z axes (origin at the metal centre) are oriented such that the six ligating atoms each fall on these axes. Thus, the electrons of the ligating atoms generate an arrangement of negative charge around the metal atom. This arrangement affects the different d orbitals differently. The d_{xy}, d_{xz} and d_{yz} orbitals all have their electron density concentrated mainly in areas between the charges of the ligands whereas, by comparison, the d_{z^2} and $d_{x^2-y^2}$ orbitals have their electron density concentrated in areas closer to the ligand charges. Qualitatively, this repulsive interaction raises the energy of the d_{z^2} and $d_{x^2-y^2}$ orbitals compared with that of the d_{xy}, d_{xz} and d_{yz} orbitals.

f.

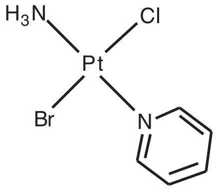


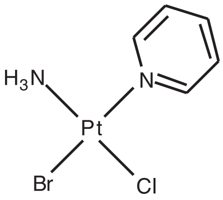
cis

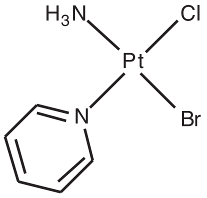


trans

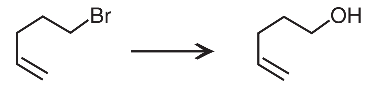
g.



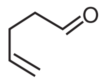




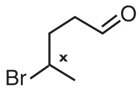
13 Killer Thistle for use in Medical Treatment ?



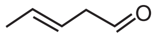
A B



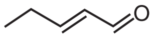
C



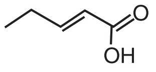
D
Two enantiomers



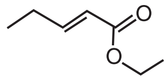
E



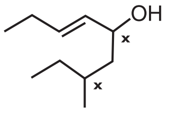
F
Two possible geometric isomers



G



H
Ethyl (*E*) -2- pentenoate

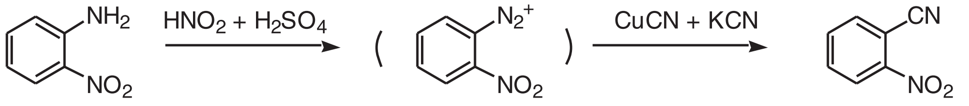


I

I Four isolated stereoisomers
II The diastereomeric pair is formed in unequal amounts
The enantiomeric pairs are formed in equal amounts
i.e. Box No. 2
III The diastereomeric pair have different melting points
The enantiomeric pairs have identical melting points
i.e. Box No. 3

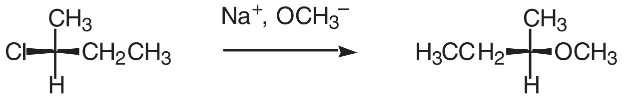
14 Application of Organic Synthesis

a.



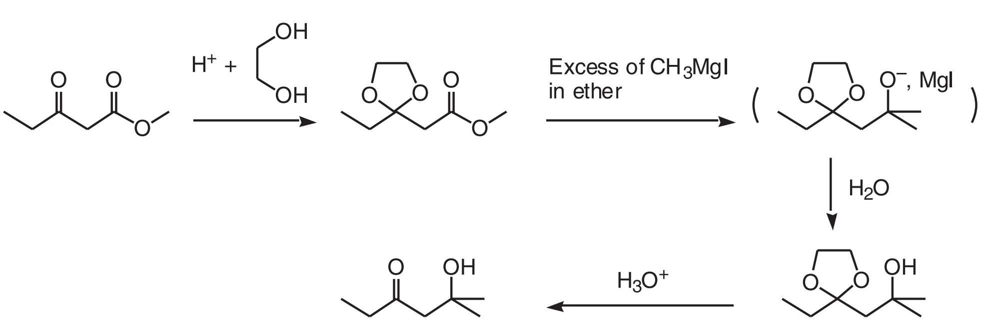
2-Nitrobenzonitrile

b.



(2*R*)-2-Methoxybutane

c.

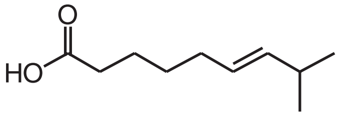


One stereoisomer

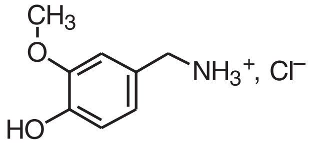
15 Cayenne

a. $C_{18}H_{27}NO_3$

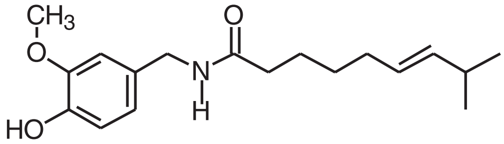
b.



c.



d.

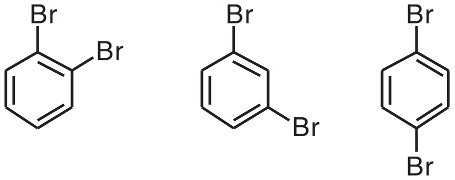


e. Two isomers of A exist.

16 An Organic Compound

a. The isotopic pattern at $m/Z = 234$, 236 and 238 mass units with relative intensities 25:50:25% corresponds to 2 bromine atoms (in bromine ^{79}Br and ^{81}Br have almost the same occurrence).

b. Since only carbon and hydrogen are present besides bromine, the molecular formula must be $C_6H_4Br_2$. The possible isomers are *ortho*-, *meta*- and *para*-dibromobenzene.



c. 155 and 157 correspond to the monobromobenzene cation: $C_6H_4Br^+$, and 76 is the $C_6H_4^+$ ion.

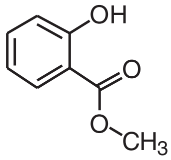
d. Because the intensity ratios are 1:2:1 and the masses only differ by one unit. A fragment with a single charge corresponding to half of the molecule would have given two peaks of equal intensity at 117 and 119 mass units.

e. The ^1H NMR spectrum consists of two signals. The compound must be the *ortho*-isomer, since this has two kinds of hydrogen atoms. The *meta*- and *para*-isomers would have given 3 signals and 1 signal, respectively.

f. Since the *ortho* compound contains 3 kinds of carbon atoms, 3 signals are expected.

17 Heather

a. The derivative is the methyl ester:



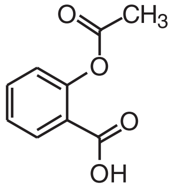
b. Because of a change in the strength of the intramolecular bond.

c. The molar absorptivity is calculated from:

$$\log \frac{100}{50} = \frac{\varepsilon \times 1 \times 4.9 \times 10^{-3}}{152}$$

The result is 9338 M^{-1} cm^{-1}

d. The compound is:



Acetylsalicylic acid

18 DNA – the PCR-method

a. $2^{30} - 1$ copies = 1073741823 copies

b. $2^{60} - 1$ copies = 1.15×10^{18} copies

dNTP average molar mass = 483 g mol^{-1}; $M(\mathrm{HP_2O_7}^{3-})$ = 175 g mol^{-1};

M (1000 bp double-stranded DNA) = ((483 – 175) × 2 × 1000 + 2 × 175)g mol^{-1}

= 616350 g mol^{-1}

Total mass of DNA:

$m(\mathrm{DNA}) = 1.15 \times 10^{18}/N_A \times 616350$ g = 1.18 g

c. No, since the [γ-^{32}P] will be lost with the pyrophosphate in the polymerase reaction.

d. $k = \frac{\ln 2}{t_{½}}$; $k = \frac{0.693}{14.2\ \mathrm{d}} = 0.0488\ \mathrm{d}^{-1}$

$A = A_0 \mathrm{e}^{-kt}$

$A = 1\ \mu\mathrm{Ci/pmol} \times \mathrm{e}^{-0.0488 \cdot 92} = 0.011\ \mu\mathrm{Ci/pmol}$

$1\ \mu\mathrm{Ci} = 3.7 \times 10^4\ \mathrm{Bq} = 2.22 \times 10^6$ dpm (decays per min)

$0.011\ \mu\mathrm{Ci/pmol}$ = 24420 dpm/pmol

19 Proteins, UV spectra and light absorption

a. $\varepsilon_{\text{Tryptophan}} \approx 5600\ \text{M}^{-1}\text{cm}^{-1}$; $\varepsilon_{\text{Tyrosine}} \approx 1400\ \text{M}^{-1}\ \text{cm}^{-1}$

$\varepsilon_{\text{Lysozyme}} \approx (6 \times 5600 + 3 \times 1400)\ \text{M}^{-1}\text{cm}^{-1} \approx 37800\ \text{M}^{-1}\ \text{cm}^{-1}$

b. $$c = \frac{A}{\varepsilon \times l} = \frac{1.05}{37800\ \text{M}^{-1}\ \text{cm}^{-1} \times 1\text{cm}} = 27.8\ \mu\text{M}$$

c. $c_{\text{mass}} = 14313\text{g/mol} \times 27.8\ \mu\text{M} = 0.398\ \text{g/L}$

d. $$1\ \text{g/L} = \frac{1}{14313}\ \text{M} = 69.8\ \mu\text{M}$$

$A = 37800\ \text{M}^{-1}\ \text{cm}^{-1} \times 69.8\ \mu\text{M} \times 1\ \text{cm} = 2.64$

Amino acid frequency in lysozyme: tryptophan: 4.65%; tyrosine: 2.33%

$\varepsilon_{\text{100 amino acids in lysozyme}} = (4.65 \times 5600 + 2.33 \times 1400)\ \text{M}^{-1}\ \text{cm}^{-1} = 29302\ \text{M}^{-1}\ \text{cm}^{-1}$

$\varepsilon_{\text{100 amino acids in average protein}} = (1.3 \times 5600 + 3.4 \times 1400)\ \text{M}^{-1}\ \text{cm}^{-1} = 12040\ \text{M}^{-1}\ \text{cm}^{-1}$

$$A_{\text{1 g/L average protein}} = 2.64\ \frac{12040\ \text{M}^{-1}\ \text{cm}^{-1}}{29302\ \text{M}^{-1}\ \text{cm}^{-1}} = 1.08$$

e. $\varepsilon_{\text{unknown protein}} = (2 \times 5600 + 11 \times 1400)\ \text{M}^{-1}\ \text{cm}^{-1} = 26600\ \text{M}^{-1}\ \text{cm}^{-1}$

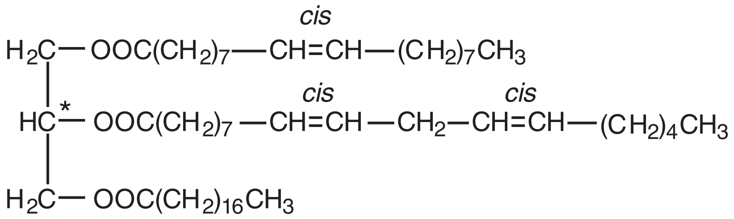
$A_{\text{0,24 g/L lysozyme}} = 0.24 \times 2.64 = 0.63$

$A_{\text{unknown protein}} = 1.85 - 0.63 = 1.22$

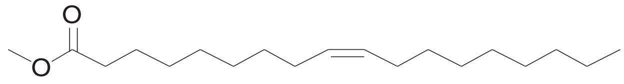
$$c_{\text{unknown protein}} = \frac{1.22}{26600\ \text{M}^{-1}\ \text{cm}^{-1} \times 1\text{cm}} = 45.9\ \mu\text{M}$$

20 Sunflower Oil

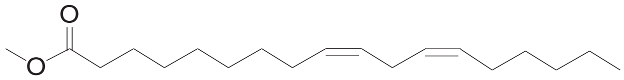
a. The molecules of constituent **S** exist as two enantiomers.



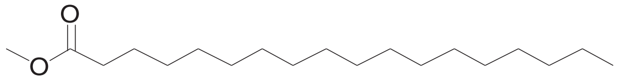
b. The structures and names of the methyl esters are



(*Z*)-methyl octadec-9-enoate or
(*Z*)-octadec-9-enoic acid methyl ester

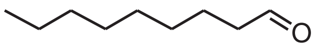


(9*Z*, 12*Z*)-methyl octadec-9,12-dienoate or
(9*Z*, 12*Z*)-octadec-9,12-dienoic acid methyl ester

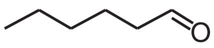


methyl octadecanoate or
octadecanoic acid methyl ester

c. Ozonolysis of **S** followed by treatment of zinc gives the following aldehydes

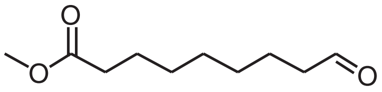


nonal



hexanal

methane dicarbaldehyde



methyl nonalate or
nonanaloic acid methyl ester

d. The amount of used potassium hydroxide is 3 times the amount of the triacylglycerol **S** (a triglyceride).

$n(\mathbf{S}) = 10.0\ \text{g}/885.402\ \text{g mol}^{-1} = 11.29\ \text{mmol}$

$V(\text{KOH}) = 3 \times n/c = 3 \times 11.29\ \text{mmol}/0.996\ \text{M} = 34.0\ \text{mL}$

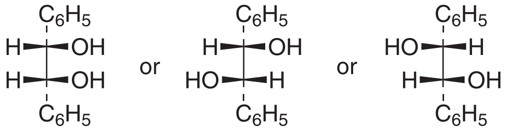
e. SapVal = $3.40\ \text{mmol/g} \times 56.11\ \text{g mol}^{-1} = 191$

f. 112.9 mmol **S** contains 3 × 112.9 mmol C = C double bonds.

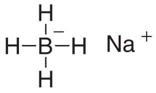
$m(\text{I}_2) = 0.3388\ \text{mol} \times 253.8\ \text{g mol}^{-1} = 85.98\ \text{g}$; Iodine no. = 86

21 Experimental Preparation of Hydrobenzoin

a. For example:



b.



$H-\overset{H}{\underset{H}{B^{-}}}-H \quad Na^{+}$

c. 1,2-Dihydroxy-1,2-diphenylethane

d II. Theoretical yield from 100 mg of benzil is 102 mg.

f. 3

g. 2

h. Pour it slowly into diluted hydrochloric acid then into the container for inorganic chemical waste.

DTU's Fond For Teknisk Kemi
Thomas B. Thriges Fond
Laurits Andersens Fond
Otto Mønsteds Fond
Hofmansgavefonden
Drost Fonden

Novo Nordisk

DTU

CHEMINOVA

UNDERVISNINGS MINISTERIET

TL • Offset A/S

LUNDBECKFONDEN

LEO

STATOIL

Carlsbergs Mindelegat for Brygger J.C.Jacobsen

RADIOMETER COPENHAGEN

KVL

HALDOR TOPSØE A/S

Lyngby-Taarbæk Kommune

Texas Instruments

The Association of Upper Secondary Chemistry Teachers

Kemi Forlaget

ISBN 87-89782-14-3

32nd IChO • Markskellet 43 • DK-6950 Ringkøbing • Denmark
Phone: +45 97 32 35 33 • Fax: +45 97 32 56 33 • E-mail: icho32@post4.tele.dk • www.icho2000.gymfag.dk