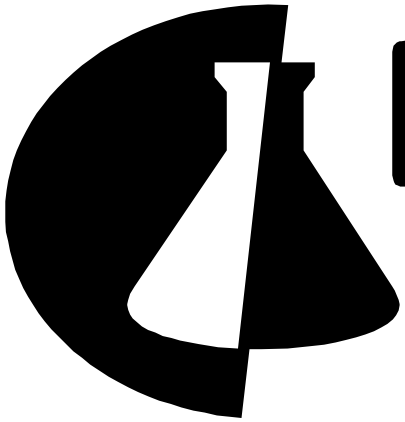

42. International Chemistry Olympiad Japan 2010

National German Competition

Volume 16

Preface

To become a member of the German IChO-team you have to be successful in four rounds of a national competition which is lead by PD Dr. Sabine Nick.

The problems to be solved in the 1st round are sent to all highschools. To solve the problems the students may use all resources available. e.g. textbooks etc.

All those students who solve about 70% of the tasks correctly will receive the problems of the 2nd round, which are to be solved in the same way as mentioned above. These problems are the most difficult ones in the whole competition.

The top 60 of the participants of the 2nd round are invited to the 3rd round, a one-week chemistry camp. Besides lectures and excursions to chemical plants or universities there are two written theoretical tests of 5 hours each.

The top 15 of the 3rd round are the participants of the 4th round, a one-week practical training. There are two written five-hour tests - one theoretical and one practical - under the same conditions as at the IChO. Here the team is selected.

In this booklet all problems of the selection procedure and their solutions are collected. Future participants should use this booklet to become acquainted with the problems of the competition. Therefore the solutions to the problems given in this booklet are more detailed than the answers we expect from the students in the competition.

In the appendix you find tables of historical interest.

Wolfgang Hampe

Contents

Part 1: The problems of the four rounds

Part 2: The solutions to the problems of the four rounds

Part 3: The problems of the IChO

Part 4: Appendix

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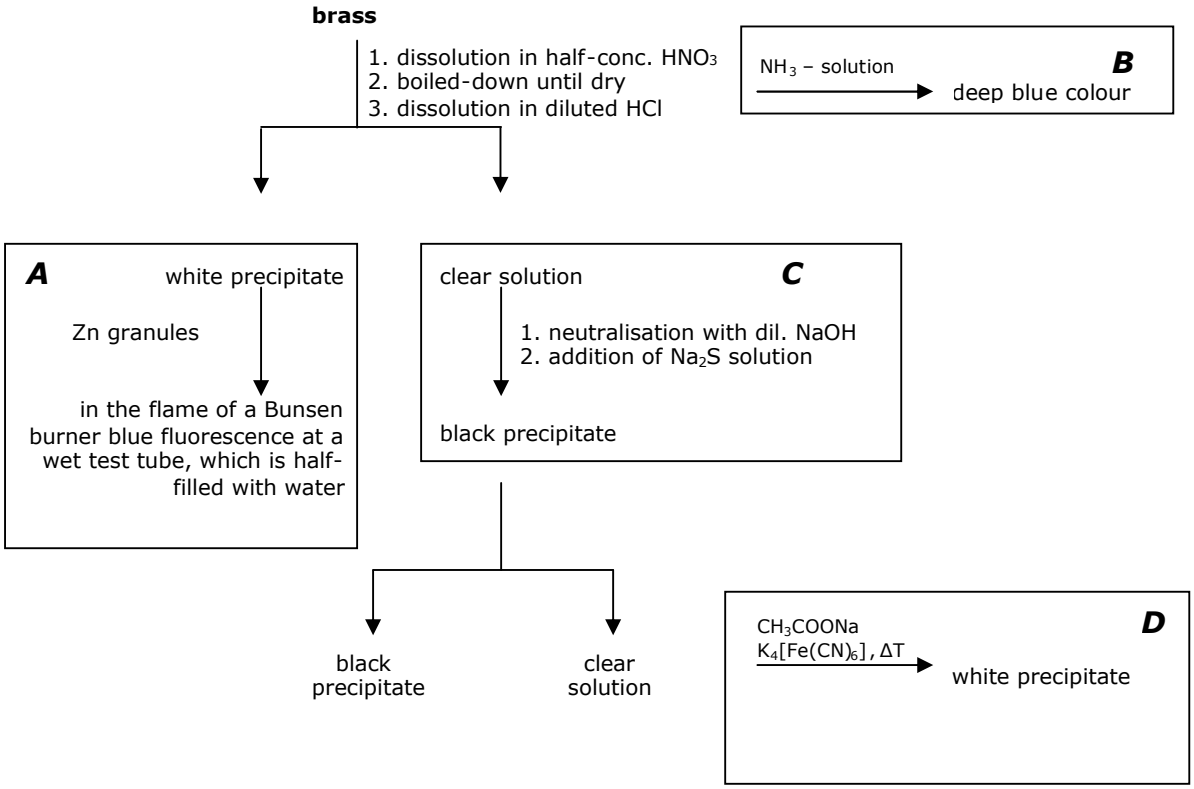
Part 1

The problem set of the four rounds

First Round

Problem 1-1 All that Glitters is not Gold!

The qualitative analysis of a piece of brass following the scheme below provides zinc, tin and copper as components.



There are different theories explaining the fluorescence described in ***A***. Further experiments were performed:

reactants	Sn(II) chloride, diluted HCl	Sn(II) sulfate, diluted H_2SO_4	Sn(IV) chloride, diluted HCl	Sn(II) sulfate, verd. H_2SO_4, Zn	Sn(II) chloride, dil. HCl, Zn
fluorescence observable	yes	no	yes	no	yes

a) *Box **A**: Of which substance does the white precipitate consist?*
Which substance/s is/are responsible for the blue fluorescence?
Why are zinc granules added?

b) *Box **B**: Which compound generates the deep blue colour?*
Write down a reaction equation.

c) *Box **C**: Of which substance does the black precipitate consist?*

d) *Box**D**: Of which substance does the white precipitate consist?*
Write down a reaction equation.

In a qualitative analysis a brass sample of 3,954 g was dissolved, transferred to a 500 mL volumetric flask and filled up with water. Samples of 50 mL were analysed. Copper was electrodeposited. On addition of $(NH_4)_2HPO_4$ zinc was precipitated as zinc ammonium phosphate.
Results:

Cu /mg	294.3	295.8
$Zn(NH_4)PO_4$ /mg	263.9	265.6

e) *Determine the composition of brass in percentage of masses.*

f) *Write down the equation of the reaction which leads to the formation of zinc ammonium phosphate.*
What happens if zinc ammonium phosphate is annealed? Write down a reaction equation.

Precipitating zinc ammonium phosphate attention should be paid to the pH value very accurately. The optimal pH value for this precipitation can be adjusted with methyl red (transition to yellow).

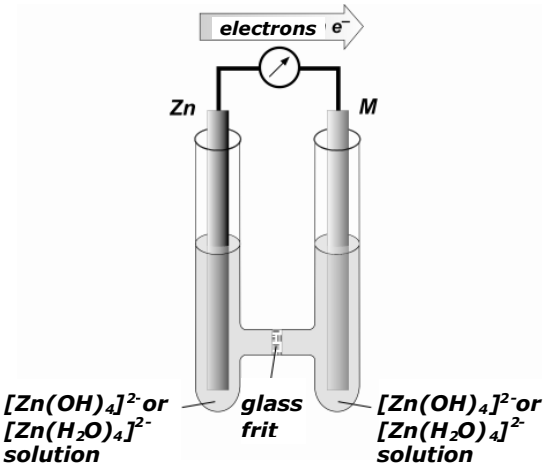
g) *Write down the pH area of transition of methyl red.*
Which are disturbing side reactions which could occur if the pH value is below or above the optimal pH value and which could falsify the result of analysis?

Zinc powder is added to a solution of potassium hydroxide (w = 10 %) and a 1 cent coin is dipped into the solution. After short heating upto the boiling point the coin is covered with a silvery shining metal. Then it is taken out, rinsed with water and put into the flame of a Bunsen burner. After a short time the coin is „gold-plated".
The same experiment can be performed with a solution of zinc(II) chloride (w = 10 %) in the presence of zinc granules. It is also works with a copper sheet and even when the copper is not in direct contact with the metallic zinc.

If you want to explain this particular reaction with the help of the Nernst equation you have to take into account a very low copper(II) concentration in both experiments.

h) Calculate the limit of concentration of copper(II) ions below which the reaction should proceed theoretically
- for the reaction in a potassium hydroxide solution (pH = 14)
- for the reaction in zinc chloride solution (pH ≤ 7).
How many Cu^{2+} ions would then be in 1 L of the solutions?
Can you imagine that copper is the reducing agent with respect to your results? Account for your answer.

The combination of half-cells as shown in the image below leads to an electrochemical cell with the following potentials:



electrode	electrode M	electrolyte 1* potential E /V	electrolyte 2* potential E /V
Zn	Zn	0	0
Zn	Cu	1,1	0,7
Zn	Ag	1,6	1,0
Zn	Fe	0,75	0,8
Zn	Cd	0,3	0,2

* electrolyte 1: solution of $Na_2[Zn(OH)_4]$ (1 mol/L),
electrolyte 2: solution of $ZnCl_2$ (1 mol/L, slightly acidic)

$E^0(Zn/Zn^{2+})$ = –0,763 V; $E^0(Zn/[Zn(OH)_4]^{2-})$ = –1,285 V (pH = 14);
$E^0(Cu/Cu^{2+})$ = +0,340 V.

(Hint: The dependence of the standard potentials E^0 on temperature should not be considered. At pH = 7 the given potential of Zn/Zn^{2+} has to be used, the density of the $ZnCl_2$ solution is approximately d = 1 kg/L.

i) Write down the two half-cell reactions of the electrochemical system Zn/Ag in an alkaline solution. What is reduced, what is oxidized?

j) What could be the driving force of this redox reaction?

k) Why does nearly no voltage occur for the combination Zn/Cd?

Apart from metallic alloys with arbitrary composition caused by- unlimited miscibility of many metals there are intermetallic systems with definite compositions. Well-known examples for these systems are the „Hume-Rothery-phases". These concern binary systems of a metal of the groups 12 (IIb), 13 (IIIa) or 14 (IVa) and a metal of the groups 3 - 11 (Ib, IIIb - VIIIb).
Some systems (phases) of certain compositions are more likely to be formed in which the ratio $\frac{\text{sum of valence electrons}}{\text{sum of the number of atoms}}$ adopts certain values.

Systems with the same ratio of composition form the same structure in solids, e.g. in the bronze system there exists a *β*-phase in body-centred cubic structure with the composition Cu_5Sn. The ratio $\frac{\text{sum of valence electrons}}{\text{sum of the number of atoms}}$ mentioned above in this case is $(5 \cdot 1 + 1 \cdot 4) : (5 + 1) = 3 : 2$.

l) There are three majort Hume-Rothery-phases. Describe the criteria by which they are arranged in these so called β-, γ- and ε-phases.
Give an example of each phase from the copper-zinc system and determine the ratio $\frac{\text{sum of valence electrons}}{\text{sum of the number of atoms}}$ *. State the respective type of structure.*

A metallurgical laboratory has to compare the properties of a sample of brass (Cu / Zn) with the percentage of weight of copper = 24.45% with a sample of bronze (Cu / Sn) of the same type of structure.

m) To which Hume-Rothery-phase and to which type of structure does the brass samples mentioned above belong? Write down the ratio $\frac{\text{sum of valence electrons}}{\text{sum of the number of atoms}}$ *.*

n) Which mass percentage of copper must a bronze sample of the same phase and structure to exhibit? Write down the ratio $\frac{\text{sum of valence electrons}}{\text{sum of the number of atoms}}$ *.*

(If you cdid not solve problem m), take the γ-phase of Cu_5Zn_8 of the brass sample).

Similar to magnesium in Grignard reactions the metals copper and zinc as the main components of brass are often used in specific organic reactions. Each metal has its own specific reaction possibility e.g. copper organic compounds are efficient at forming new C-C bonds.

A compound often used in such reactions is lithium dimethylcuprate, $Li[Cu(CH_3)_2]$. It is formed in ether taking methyl lithium and copper(I) iodate as reactants. At first methyl copper is formed as insoluble polymer which reacts with more methyl lithium to form lithium dimethylcuprate.

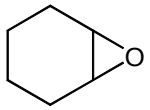
o) Write down the equations of these reactions to form lithium dimethylcuprate.

Lithium dimethylcuprate reacts in a substitution reaction with alkyl- and aryl halides to form products with good yield, e.g. the reaction of bromobutane and lithium dimethylcuprate leads to pentane.

p) Write down the equation of the reaction of iodobenzene and lithium dimethylcuprate. Show the structural formulae of the compounds and the name of the product.

Besides these generally utilisable reactions there are further interesting reactions with lithium dimethylcuprate.
The cuprate reacts with compound 1 in a stereoselective reaction by adding water to form two stereoisomeric alcohols.

compound 1

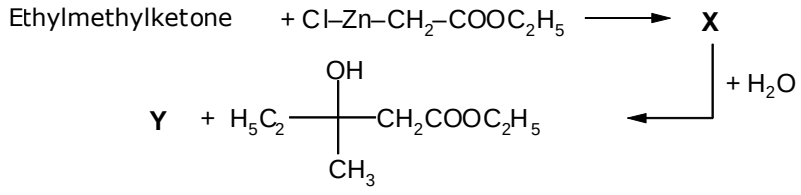


an oxirane

q) Write down the equation of the reaction of compound 1 with lithium dimethylcuprate and water. Give the complete names of the alcohols.

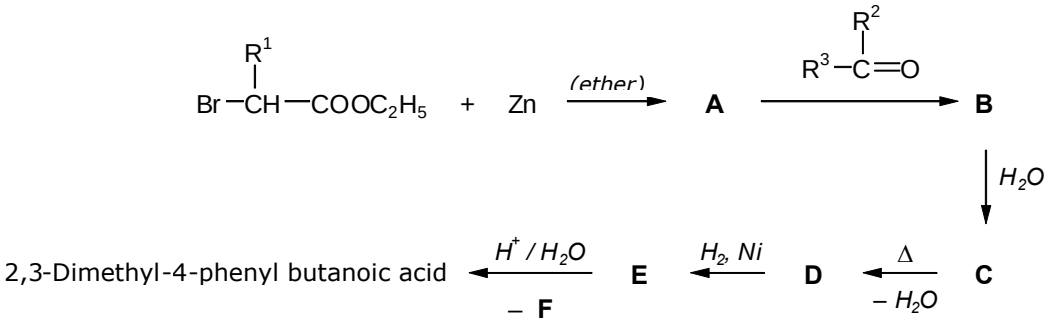
Zinc organic compounds are longer known and more often used. These compounds are applied to synthesize alcohols, more exactly in the synthesis of β-hydroxy esters. Following this path you can get β-hydroxy acids and then in follo-up reactions new unsaturated and saturated carboxylic acids.
Adding zinc to chloroacetic acid methyl ester you get an organic zinc chloride ($Cl–Zn–CH_2–COOC_2H_5$), which in most cases is not isolaled but used for further synthesis.

If this zinc organic compound reacts at first with ethylmethylketone and then with water the following sequence of reactions occurs:



*r) Draw the structural formulae of the compounds **X** and **Y**.*

A sequence of reactions of the synthesis of 2,3-dimethyl-4-phenyl butanoic acid is introduced in the following image. It starts with the reaction of a zinc organic compound with a ketone.



*s) Draw the structural formulae of **A** to **F**. Determine the groups R^1 to R^3, too. Do not consider stereoisomers.*

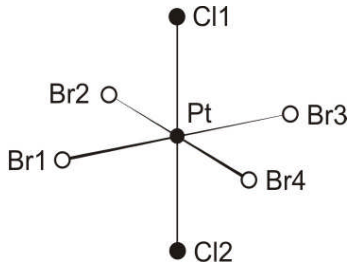
Second Round (homework)

Problem 2-1 Haloplatinates

The uniformly substituted halocompounds of almost all transition metals are well-known. In recent years there have been some successes in the synthesis of mixed halo-complexes which contain several different haloligands.

a) *Write down all complex anions of the system of chloro-bromo-platinates(IV), $[PtCl_nBr_{6-n}]^{2-}$ (n = 0 to 6).*
To denote the stereoisomers use the terms cis, trans, fac and mer (e.g. trans-$[PtCl_xBr_y]^{2-}$).

For a more detailed spectroscopic inspection it is necessary to describe the symmetry of a molecule or ion.



b) *Give the chrystallographic point group of the chloro-bromo-platinate(IV) shown above. Use the Schoenflies symbol.*

c) *Which symmetry elements denote the different signs the Schoenflies symbol is composed of? Mark the atoms in the relevant symmetry elements (e.g. n-fold axis along the X-Y-Z-bond or mirror plane through the points X, Y, Z). Draw additionally an image which shows the spatial positions of all symmetry elements.*

The synthesis of mixed chloro-bromo-platinates(IV) is carried out among others by substitutive replacing of ligands.
Reactants are the hexahalo-complexes $[PtCl_6]^{2-}$ and $[PtBr_6]^{2-}$ which react with Br^- and Cl^-, respectively. Do not consider the kind of counterions and solvents, temperature and possible side reactions. Assume only a complete reaction of the Br^- and Cl^- ions, respectively.
The following reaction leads selectively to one main product:

$$[PtBr_6]^{2-} + 3\ Cl^- \longrightarrow \mathbf{X} + 3\ Br^-$$

d) *Write down the formula of **X** and give its kind of isomer (cis, trans, fac or mer). Account for your answer.*

On the other hand the reaction of $[PtCl_6]^{2-}$ with Br^- leads to mixtures of compounds $[PtCl_nBr_{6-n}]^{2-}$ (n = 0 to 6) of different composition depending on the amount of Br^-.

e) Which stereoisomers (cis, trans, fac or mer) do you mainly expect in the product mixture besides $[PtCl_6]^2$ and $[PtBr_6]^{2-}$? Account for your answer.

The ratio of concentrations of the complex salts $(TBA)_2[PtCl_5Br]$ and $(TBA)_2[PtCl_3Br_3]$ in a mixture is to be examined. As stereoisomers have the same composition there is no labeling. The abbreviation TBA stands for tetra-n-butylammonium cation ($n\text{-}Bu_4N^+$).
The elementary analysis provides an amount of 11.2 % of mass of bromine.

f) Calculate the ratio of concentrations of the two complex salts in the mixture.

$(TBA)_2[PtCl_6]$ reacts with BrF_3 at low temperatures to form a mixture very selectively which contains among opther things a very small amount of the reagent $(TBA)_2[PtCl_6]$ the complex compounds $(TBA)_2[PtFCl_5]$, cis-$(TBA)_2[PtF_2Cl_4]$ und fac-$(TBA)_2[PtF_3Cl_3]$.

g) Why are these compounds formed preferably and why are compounds with symmetrically substituted F-Pt-F axes formed only in traces?
Account for your answer.

The ^{195}Pt-NMR spectrum of the reaction mixture provides the following (multiplet) signals together with the chemical shifts and partially with relative intensities (hint: There are no couplings to the chloroligands):

Multiplet	Chemical shift/ppm	Relative intensities
$(TBA)_2[PtCl_6]$	4749.93	0.242
$(TBA)_2[PtFCl_5]$	5831.01	0.242
	5845.89	
cis-$(TBA)_2[PtF_2Cl_4]$	6887.18	
	6902.11	0.606
	6917.04	
fac-$(TBA)_2[PtF_3Cl_3]$	7899.64	
	7914.68	1
	7929.72	
	7944.75	

h) Explain qualitatively the differences in the chemical shifts of the four signals.

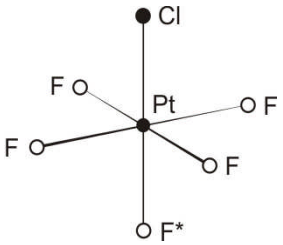
i) Explain the multiplicity of the signals and give the relative intensities in each multiplet as integers.

Instead of an elementary analysis NMR spectra can be used to analyse the ratio of products in reaction mixtures if the spectrometer is calibrated accordingly.

j) Determine the relative intensities of all multiplet signals. Identify afterwards the ratio of concentrations of the compounds using the data of the ^{195}Pt-NMR spectrum.

The essential function of NMR spectroscopy is the clarification of the configuration of compounds. The ^{195}Pt-NMR spectra are a little bit more complicated if there are some fluoro-ligands which are magnetically not eqivalent in the compound.

A chemist needs the complex compound $[PtF_5Cl]^{2-}$ for further inspections.
He separates the product mixture chromatographically and analyses the fractions by ^{195}Pt-NMR spectroscopy.
The expected coupling constants are known as approximation from analogue compounds:
$^1J(PtF)=1915$ Hz and $^1J(PtF^*)=1360$ Hz.



A chemical shift of 1 ppm corresponds to 85,63 Hz at the used frequency of the spectrometer. The counterion of the complex anion does not play any role in this problem.

k) Sketch the expected ^{195}Pt-NMR spectrum.
Explain the multiplet signal and give the relative intensities.

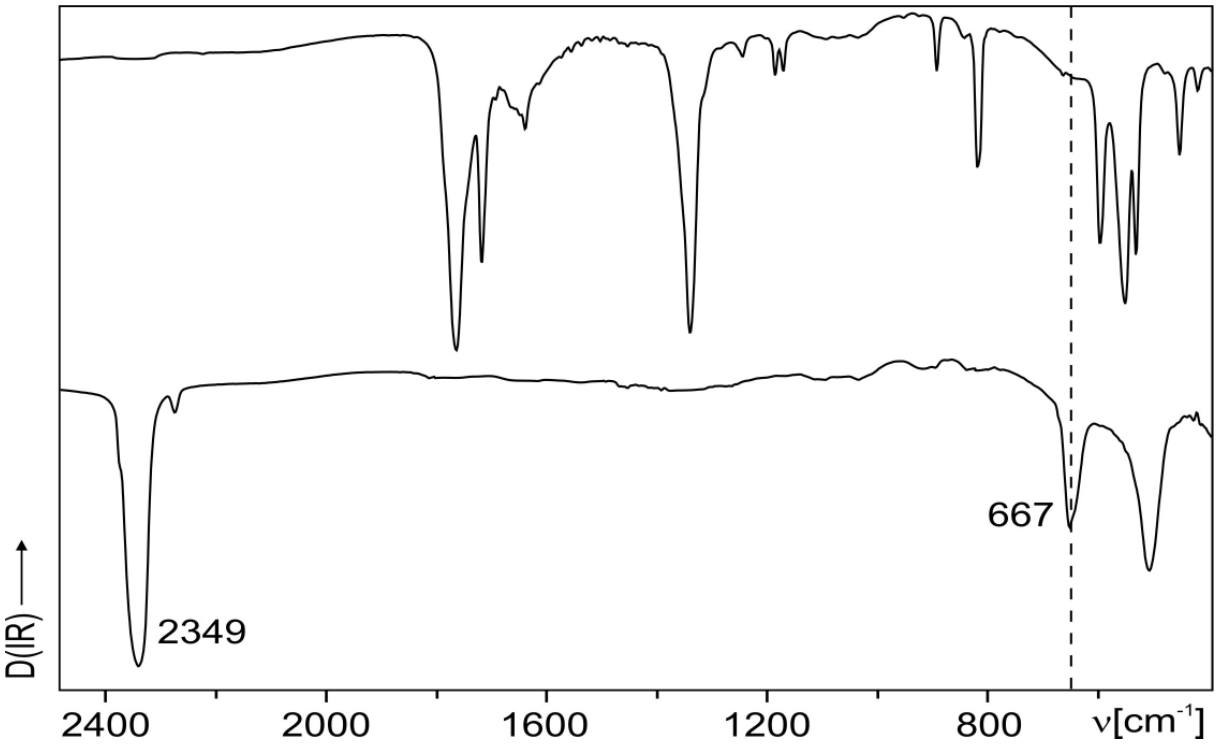
l) Write down the chemical shift (in ppm) of any single signal using the given coupling constants. Appoint 10580 ppm as chemical shift for the center of the signals.

A platinum complex which was not available by normal substitution reactions can be prepared by a "photochemical trick". The radiation of a complex compound **1** with UV light at very low temperatures leads to a new complex compound **2** and another product **3**. **1** and **2** are caesium salts of mononuclear platinum-complex anions which contain fluorine and are twofold negatively charged.

The following five statements were detected:

1. Compound **1** gives a ^{195}Pt NMR spectrum with a triplet of triplets.
2. The elementary analysis of **1** gives 3.84 % of mass of carbon.
3. Product **2** can react stereospecifically with an equimolar amount of chlorine to compound **4**. The ^{195}Pt NMR spectrum of **4** shows a quintuplet.
4. The radiation of **1** is executed in a closed vessel. After the reaction there is an overpressure within the vessel, a gas was generated.
5. The reaction was followed by infrared spectroscopy. A sample of compound **1** gave a certain spectrum (upper part of the image). Then the sample was radiated with UV light for sufficient time and a new spectrum was taken (lower part of the image). Turbidity of the sample after radiation indicates gas occlusions.

   (Hint: The absolute wave numbers are influenced by the temperature of measurement, concentration, kind of the embedding material and more. Thus the information in text books differs a little bit when compared.)



Infrared spectra before (upper part) and after (lower part) radiation

*m) Write down the formulae of **1**, **2** and **3**.*

n) Account for your result and address all the five statements.

Problem 2-2 Reactors

In a chemical plant compound **1** (M_1 = 100 g/mol) and compound **2** (M_2 = 75 g/mol) are initiated to react in a molar ratio of 1:1 to form compound **3** (M_3 = 175 g/mol). To simplify the problem assume that there is no change in volume and that all substances have the density of 1 kg/L.

The firm has a cylindrical boiler with a volume of 9 m^3 which can be filled upto ⅔ of its volume for the process.

Filled upto this height the ratio of filling height to reactor diameter is 1.

The vessel has a jacket to heat or to cool the reaction mixture. Assume that there is no heat exchange through the bottom and through the top so the heat exchange takes place only through the side walls with which the liquid is in contact.

a) 1. *Calculate the masses of the compounds **1** and **2** which are filled into the vessel for the reaction.*

   2. *Calculate the molar amounts of **1** and **2**.*

   3. *Calculate the concentrations c_0 (mol/L) of the compounds **1** and **2** (round up your result to the first decimal place).*

The molar ratio of the reactants being 1:1 at any time the reaction is of second order. The concentrations of the reactants, $c_1(t)$ and $c_2(t)$, depending on time can be calculated by

$$c_1(t) = c_2(t) = \frac{c_0}{1 + k \cdot t \cdot c_0} \qquad \text{with } k = 2.9 \cdot 10^{-4} \text{ L/(mol·s)}$$

b) *Calculate the time until 96% have reacted (round up to full hours).*

c) 1. *Give the rate law $\frac{dc_3}{dt}$ of the formation of compound **3** and the rate $\frac{dc_3}{dt}$ (in mol/(h·L)) at the time when the conversion has reached 96%. Round up to the fifth decimal).*

   2. *Give the production rate $\frac{dm_3}{dt}$ of **3** (in kg/h) of the reactor at the time when conversion has reached 96%. Round up to the second decimal).*

There are two possibilities for the company to run the reactor. They can fill it upto ⅔, heat it up to the operating temperature, run the reaction until 96% have reacted, cool down and, finally, let the reaction mixture run off.

You have to assume that the set-up time in this so called "batch mode" takes two hours before the process (filling) and another two hours after the process (letting off).
Alternativly they could run the reactor continuously and fill in reactants and let out the reaction mixture according to a 96% rate of conversion.

d) *Calculate the rate of production of compound **3** (*in *kg/h) referring to the batch mode.*

   (If you could not solve b) and c) take 5.5 h as reaction time in the batch mode and a production rate of 30.6 kg/h at 96% conversion.)

Alternatively the company takes into consideration whether they can use a plug flow reactor. It consists of a cylindrical pipe with a diameter of 10 cm. At one end the reactants are fed in, at the other end the product mixture is removed.
You may assume that the liquid that is filled in passes at constant velocity.
The process shall guarantee a conversion of 96% and the productivity has to be the same as that of the reactor in batch mode.

e) *Calculate the length of the plug flow reactor to reach these conditions.*

   (If you could not solve d) and b) take as productivity of the batch mode reactor 1000 kg/h with a reaction time of 5.5 hours.)

It is necessary to guarantee the transport of heat inwards or outwards of the reaction mixture. The heat is transferred through the wall of the reactor.

f) 1. *Calculate the area O_B through which the heat of the reaction mixture in a batch reactor is transferred.*

   2. *Calculate the area O_R through which the heat in a plug flow reactor is transferred.*

   3. *Write down the ratio of the two heat transferring areas. Which type of reactor is more suitable for a reaction with strong generation of heat?*

      (If you could not solve e) take 1000 m for the length of the pipe.)

The cooling system of the reaction boiler is designed in a way that the water flowing through it keeps the content of the boiler constantly at 90°C. The cooling water enters the cooling jacket with a temperature of 25°C and leaves it at 60°C.

The reactor shall run continuously at a conversion of 96% with a constant product rate as calculated in c). According to this product rate the reaction mixture which is removed contains 96% of compound **3** and those parts of compounds **1** and **2** which have not reacted.
The leaving mixture has a temperature of 90°C.
In the supply process feeding the compounds **1** and **2** into the reactor the amounts of **1** and **2** which did not react but were removed with the reaction mixture are replaced, too. Because of the great volume of the reactor you may assume that the concentrations of all compounds and the production rate do not change.
The reactants **1** and **2** enter the reactor with a temperature of 20°C.
The reaction of **1** and **2** to **3** is exothermic with a molar reaction enthalpy ΔH_R = - 150 kJ/mol at 90°C.
At 20°C compound **1** is a solid, compound **2** a liquid.
The specific heat capacities of the compounds **1** and **2** and of water are

c_p(**1**, solid)	= 1.6 kJ/(kg·K)	c_p(**1**, liquid)	= 2.4 kJ/(kg·K)
c_p(**2**, liquid)	= 2.5 kJ/(kg·K)	c_p(water)	= 4.18 kJ/(kg·K).

Melting temperature of compound **1**: 32.5°C
with a molar melting enthalpy of ΔH_s(**1**) = 12.8 kJ/mol.
Assume that

- the densities of water and of the compounds **1**, **2** and **3** (1 kg/L each) are not depending on temperature,
- there are no mixing effects,
- the thermodynamic properties of the compounds **1**, **2** and **3** are independent of each other,
- the pressure in the reactor is equal to the constant pressure in the surrounding at any time.

g) 1. Calculate the amount of heat Q_R which is generated per hour by the exothermic reaction.

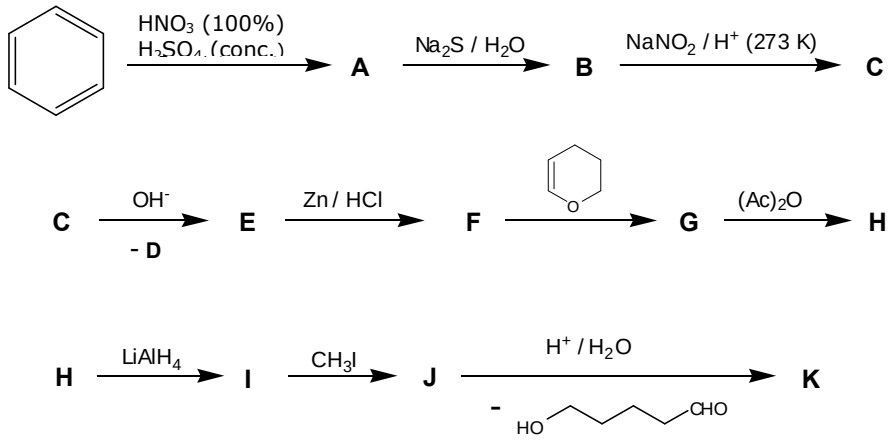
*2. Calculate the amount of heat Q_V which is needed per hour within the reactor after the addition of the compounds **1** and **2.***

3. Calculate the amount of cooling water (in L/h) which flows through the cooling jacket.

(If you could not solve c) take 30.6 kg/h as rate of formation of the product.)

Problem 2-3 A Multiple-Step Synthesis

A tertiary amine **K** has to be produced in a ten-step synthesis starting with benzene.



Hints:

1. The reactions are carried out in a way that **A** is the only existent compound in this series with C_{2V} symmetry.
2. **D** is a gas at standard conditions.
3. **G** reacts in a Hinsberg reaction to a sulfonamide soluble in sodium hydroxide solution.

*a) Complete the above reaction scheme and draw the structural formulae of the compounds **A** to **K.***

*b) Account for the addition of conc. sulfuric acid in the reaction of benzene to form compound **A.***

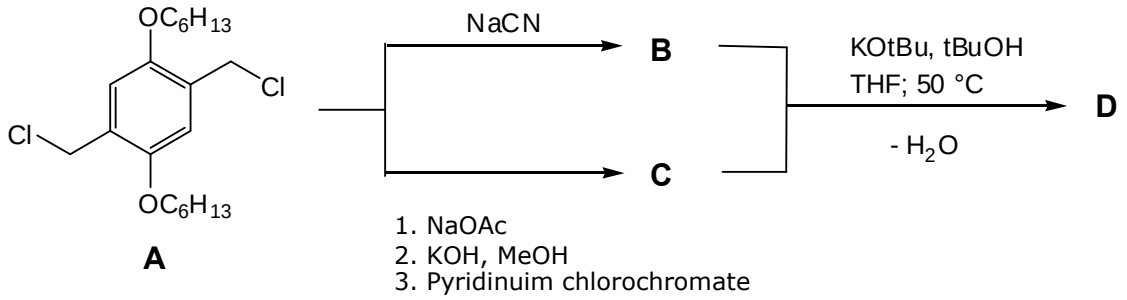
c) Draw resonance structures of the intermediates (carbocation, σ complex) of a reaction of an electrophile at the ortho, meta, and para positions of nitrobenzene.

*d) Account for the favoured formation of **A** on substitution of the ring which already has a substituent. Use the resonance structures of the intermediate and the mesomeric effect of the substituent already present on the benzene ring.*

*e) Why is the reaction of **F** with 3,4-dihydro-2H-pyran (C_5H_8O) to form **G** necessary in the course of reaction?*

Problem 2-4 Shining Polymers

For some years there has been research on developing organic light-emitting diodes (LED) as an alternative to the established LC displays. Conjugated polymers are a class of relevant substances which can be regarded as organic semiconductors according to their properties. They emit light if a potential is applied. They can be used in thin, light and flexible displays.
The following way of synthesis is an example to produce the red polymer **D**. In a first step **A** reacts in equal parts to **B** and **C**, respectively.



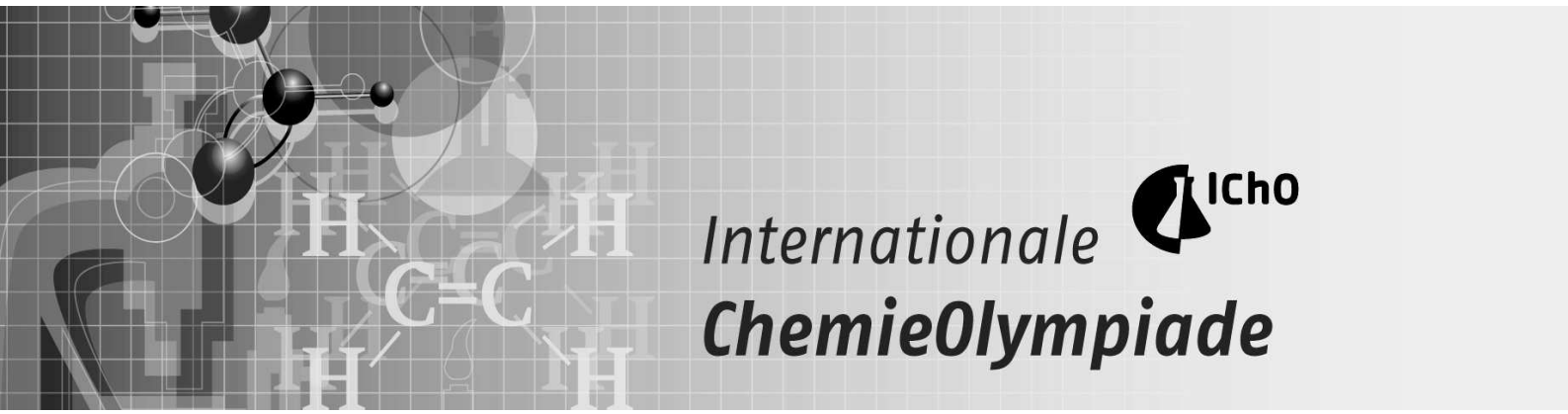
a) *Complete the reaction scheme and draw the structural formulae of the compounds **A** to **D.** Show in case of the polymer at least one of the recurring structural units.*

b) *Give the well-known name of the reaction of **B** and **C** to **D**.*

c) 1. *Of what type of polymerisation is the reaction shown above?*

   2. *How does the mean molar mass M_n of the polymer molecules change as a function of the progress of the reaction? This progress is defined as the ratio of already formed bonds to the maximal number of bonds after complete polymerisation.*

d) *Why is it important to purify **B** and **C** very well before they are used to react to **D**? Give at least two reasons.*



Problems Round 3

Test 1 Göttingen 2010: Problems 3-01 to 3-10

Test 2 Göttingen 2010: Problems 3-11 to 3-20

time	5 hours.
your name	write it on every answer sheet.
relevant calculations	write them down into the appropriate boxes. otherwise you will get no points
atomic masses	use only the periodic table given.
constants	use only the values given in the table.
answers	only in the appropriate boxes of the answer sheets, nothing else will be marked.
draft paper	use the back of the pages of the problem booklet**,** but everything written there will not be marked.
problem booklet	you may keep it.

Good Luck

Useful formulas and data

$\Delta G = \Delta H - T \cdot \Delta S$ $\Delta G = - \Delta E \cdot z \cdot F$ $\Delta G = - R \cdot T \cdot \ln K_{th}$

$\Delta U_{reaction} = \Delta H_{reaction} + W$

$\ln (Kp_1/Kp_2) = \frac{-H^0}{R} \cdot (T_1^{-1} - T_2^{-1})$

$p \cdot V = n \cdot R \cdot T$ for ideal gases and osmotic pressure

Nernst equation : $E = E_0 + \frac{R \cdot T}{z \cdot F} \cdot \ln (c_{Ox}/c_{Red})$

for metals $E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln (c(Me^{z+}/c_0)$

for non-metals $E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln (c_0/c(NiMe^{z-})$

for hydrogen $E = E^0 + \frac{R \cdot T}{F} \cdot \ln \frac{c(H^+)/c_0}{(p(H_2)/p_0)^{1/2}}$

with $c_0 = 1$ mol/L $p_0 = 1.000 \cdot 10^5$ Pa

rate laws	0. order	$c = c_o - k \cdot t$
	1. order	$c = c_o \cdot e^{-k_1 \cdot t}$
	2. order	$c^{-1} = k_2 \cdot t + c_o^{-1}$

Arrhenius equation: $k = A \cdot e^{-Ea/(R \cdot T)}$

A pre-exponential factor.
E_a activation energy

Law of Lambert and Beer: $E = \varepsilon \cdot c \cdot d$

ε molar absorption coefficient
d length of the cuvette
c concentration

Henry's law for dissolving gases in water ($A(g) \rightleftharpoons A(aq)$)

$K_H = \frac{c(A(aq))}{p(A(g))}$ K_H Henry constant

energy of a photon $E = h \cdot c/\lambda$

h Planck's constant
c speed of light
λ wavelength

Speed of light	$c = 3.000 \cdot 10^8$ ms^{-1}
Gas constant	$R = 8.314$ JK^{-1}mol^{-1}
Faraday constant	$F = 96485$ Cmol^{-1}
Avogadro constant	$N_A = 6.022 \cdot 10^{23}$ mol^{-1}
Planck constant	$h = 6{,}6261 \cdot 10^{-34}$ Js

$p_o = 1.000 \cdot 10^5$ Pa 1 atm $= 1.013 \cdot 10^5$ Pa 1 bar $= 1 \cdot 10^5$ Pa

1 Å $= 10^{-10}$ m

A periodic table was provided

Third Round Test 1

Problem 3-01 Multiple Choice

(With one or more correct answers even if the question is written in singular)

a) Which of the following oxidation numbers are correct?

A) +4 for Co in K_3CoF_6	**B)** +7 for Mn in $KMnO_4$	**C)** +6 for V in VO^{2+}	**D)** +3 for Sb in SbO(OH)	**E)** +6 for Cr in $Cr_2O_7^{2-}$

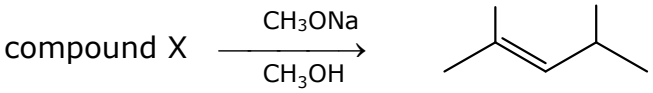
b) Which reactions occur at the cathode or the anode when a diluted aqueous solution of lithium sulfate is electrolysed?

A) $Li^+ + e^- \longrightarrow Li$	**B)** $2\ H_3O^+ + 2e^- \longrightarrow 2\ H_2O + H_2$
C) $SO_2^{2-} \longrightarrow SO_4 + 2e^-$	**D)** $SO_4^{2-} \longrightarrow SO_3 + ½\ O_2 + 2e^-$
E) $2\ OH^- \longrightarrow H_2O + ½\ O_2 + 2e^-$	

c) Which of the following mixtures is the best one to be used as a buffer solution?

A) Equal volumes of acetic acid (c = 1 mol/L) and sodium acetate solution (c = 0.5 mol/L)
B) Equal volumes of acetic acid (c = 0.5 mol/L) and sodium hydroxide solution (c = 0.5 mol/L)
C) Equal volumes of acetic acid (c = 1 mol/L) and sodium hydroxide solution(c = 0.5 mol/L)
D) Equal volumes of acetic acid (c = 0.5 mol/L) and sodium hydroxide solution (c = 1 mol/L)
E) Equal volumes of acetic acid (c = 0.5 mol/L) and sodium acetate solution (c = 1 mol/L)

d) Identify compound X which gives only the single E2 product indicated.

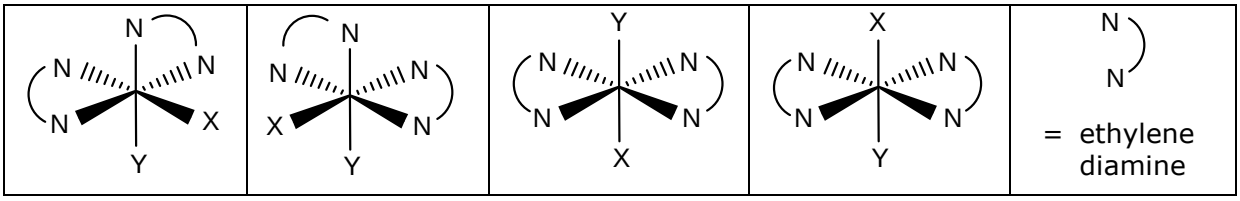


A) 2-bromo-2,4-dimethylpentane
B) 3-bromo-2,4-dimethylpentane
C) 2,3-dibromo-2,4-dimethylpentane
D) 1-bromo-2,4-dimethylpentane

e) The average kinetic energies (E) and the average molecular speeds (v) of H_2 and N_2 are compared at 300 K. Which statement is correct?

A) $E(H_2) = E(N_2)$ and $v(H_2) = v(N_2)$
B) $E(H_2) = E(N_2)$ and $v(H_2) > v(N_2)$
C) $E(H_2) = E(N_2)$ and $v(H_2) < v(N_2)$
D) $E(H_2) = E(N_2)$ and $v(H_2) = v(N_2)$
E) $E(H_2) = E(N_2)$ and $v(H_2) = v(N_2)$

f) 1,2-Ethylene diamine is bidentate, X and Y are monodentate each. Which complexes are enantiomers?



1 2 3 4

A) 1 and 2	**B)** 1 and 3	**C)** 1 and 4	**D)** 2 and 3	**E)** none of them

g) Which of the following species is <u>not</u> electrophilic?

A) H^+	**B)** BF	**C)** $^+NO_2$	**D)** Fe^{3+}	**E)** $CH_2=CH_2$

h) When a reaction reaches equilibrium then

A) the reaction rate of the forward reaction is equal to the reaction rate of the inverse reaction.
B) the concentration of the products is equal to the concentration of the reactants.
C) the concentration of the products and the reactants do not change.
D) no forward reaction takes place anymore.
E) the reaction ends.

i) The electron configuration of a metal in MX_4^{2+} is d^8. Which structure of the complex would you expect (e.g. X = NH_3)?

A) octahedral	**B)** quadratic pyramidal	**C)** tetrahedral	**D)** quadratic planar	**E)** trigonal pyramidal

Problem 3-02 Magnesium Hydroxide

A student prepares a saturated solution of magnesium hydroxide in water at 25°C. This solutions shows a pH value of 10.5.

a) Calculate the solubility S of magnesium hydroxide in water. The result should be given in mol/L and in mg/L.

b) Determine the solubility product constant K_{sp} of magnesium hydroxide.

c) Calculate the solubility S of magnesium hydroxide in a solution of sodium hydroxide (c = 0.010 mol/L) at 25°C.*

A mixture of 100 mL of hydrochloric acid (c = 0.100 mol/L) and 10.0 g of magnesium hydroxide is stirred until equilibrium is reached. Assume that the volume of the mixture is 100 mL, too.

d) Calculate the pH of the solution when the system has reached equilibrium.

Problem 3-03 Concrete and Iron

Many buildings are erected with concrete with an embedded iron grid (so called reinforcement).
Concrete is produced from a mixture of cement, water, sand and little stones.
Cement consists primarily of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In a later step of production a small amount of gypsum, $CaSO_4 \cdot 2H_2O$, is added to improve the hardening of the cement. Due to high temperatures in the final step of production the unwanted semihydrate, $CaSO_4 \cdot ½H_2O$, may form:

$$CaSO_4 \cdot 2H_2O(s) \longrightarrow CaSO_4 \cdot ½H_2O(s) + 1½H_2O(g)$$

Thermodynamic data at p(standard) = 1.00 bar and 25 °C:

Compound	$\Delta H°_f$/(kJ mol^{-1})	S°/(J K^{-1} mol^{-1})
$CaSO_4 \cdot 2H_2O(s)$	–2021.0	194.0
$CaSO_4 \cdot ½H_2O(s)$	–1575.0	130.5
$H_2O(g)$	–241.8	188.6

a) Calculate ΔH° of the conversion of 1.00 kg of $CaSO_4 \cdot 2H_2O(s)$ to $CaSO_4 \cdot ½H_2O(s)$.

b) Calculate the equilibrium pressure of water vapour in a closed vessel containing only $CaSO_4 \cdot 2H_2O(s)$, $CaSO_4 \cdot ½H_2O(s)$ and $H_2O(g)$ at 25° C.

c) Calculate the temperature in °C at which the vapor pressure of water in the system of b) has the value 0.500 bar. Assume that ΔH° and ΔS° are independent of temperature.

In case of damage especially on bridges the iron in the concrete may corrode. The following reactions occur in the beginning:

(1) $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

(2) $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

An electrochemical cell is set up in which these reactions take place (temperature 25°C). The cell is represented by the following diagram:

$$Fe(s) \,|\, Fe^{2+}(aq) \,||\, OH^-(aq), O_2(g) \,|\, Pt(s)$$

Standard potentials (at 25 ºC):

$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$ $\quad E° = -0.44$ V

$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$ $\quad E° = 0.40$ V

d) Calculate the cell potential, ΔE°(cell), at 25 ºC.

e) Write down the equation of the overall reaction during the discharge of the cell at standard conditions.

f) Calculate the equilibrium constant of the overall reaction at 25°C.

g) The discharging is allowed to proceed for 24 h at standard conditions with a constant current of 0,12 A. Calculate the mass of iron which was converted to Fe^{2+} after 24 h. You may assume that there is an excess of water and oxygen.

h) Calculete ΔE of the cell at 25 °C under the following conditions:
$[Fe^{2+}] = 0.015$ M, $pH_{rechte\ Halbzelle} = 9.00$, $p(O_2) = 0.700$ bar.

Problem 3-04 Qualitative Analysis

Five flasks labelled A to E contained aqueous solutions of colourless metal nitrates (c ~ 0,1 mol/L each). These were solutions of
aluminium(III) nitrate, calcium(II) nitrate, lead(II) nitrate,
silver(I) nitrate and zinc(II) nitrate, respectively.
Moreover, there were three reagents, solutions of hydrochloric acid, ammonia and sodium hydroxide (c ~ 1 mol/L each) available.
Reactions were carried out between each reagent and each solution. The results can be found in the table below.

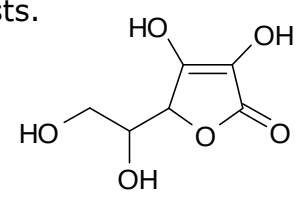
	A	B	C	D	E
$HCl_{(aq)}$	no reaction	↓	no reaction	no reaction	↓
$NH_{3(aq)}$	↓↑	↓↑	↓	no reaction	↓
$NaOH_{(aq)}$	↓↑	↓	↓↑	↓	↓↑

↓: precipitate ↑: the precipitate dissolves in an excess of the reagent

Attach the cations to the letters. For each cation identified write the equation of each reaction observed.

Problem 3-05 Ascorbic Acid I

Linus Pauling (1901-1994) was the first person to be awarded the unshared Nobel Prize twice. He got the prize in chemistry in 1954 for his research concerning the chemical bond and the application of his results to the clarification of the structure of complex substances. In 1962 the Nobel Prize for Peace was given to him because of his commitment against nuclear weapons tests. Later in his life he devoted himself to studies of e.g. vitamin C, ascorbic acid.



Ascorbic acid is a diprotic acid with $pK_a = 4.17$ and $pK_{S2} = 11.6$. Pauling studied the effect of large doses of vitamin C (10 to 18 g) on a daily basis as a preventive agent for common cold and cancer, but this claim has not been backed by medical evidence.

The requirement of vitamin C of an adult is 60 mg/day. The remainder is excreted by urine within the same day. The mean volume of urine amounts to 1.5 L/day.

a) Calculate the (mean) pH of urine of a person who has taken one tablet/day with the content of 1.00 g of ascorbic acid. Assume that the urine does not contain any buffer protolytes and any other acids. Account for the fact that in this calculation only pK_{S1} has to be taken into consideration.

A more realistic assumption is that urine contains a phosphate buffer with a total concentration of all phosphate species of 0.160 mol/L. Assume that the pH of urine has a mean value of 6.60.

$pK_a(H_3PO_4) = 2.15$ $pK_a(H_2PO_4^-) = 7.21$ $pK_a(HPO_4^{2-}) = 12.36$

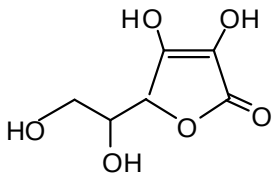
b) Calculate the concentration of all phosphate species before the intake of ascorbic acid.

c) Calculate the (mean) pH after the intake of 1.00 g of ascorbic acid. You may assume that the excreted ascorbic acid in the urine reacts completely with the base of the buffer.
(If you could not solve b) take $c(H_2PO_4^-) = 0.123$ mol/L and $c(HPO_4^{2-}) = 0.0321$ mol/L)

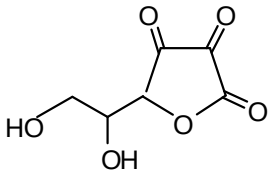
Problem 3-06 Ascorbic Acid II

Ascorbic acid ($C_6H_8O_6$) is readily oxidized according to the half reaction

$$C_6H_8O_6 + 2\ H_2O \rightleftharpoons C_6H_6O_6 + 2\ H_3O^+ + 2\ e^- .$$



Ascorbic acid



Dehydroascorbic acid

Potassium iodate dissolved in hydrochloric acid is a typical oxidizing agent in performing a redox titration of ascorbic acid.

a) Write down the reaction equation.

As soon as ascorbic acid is totally oxidized iodine forms which colours starch indicator blue and thus the end point of the titration can be detected.

b) Write down the reaction equation of this formation of iodine.

To prepare the oxidizing agent approximately 0.14 g of KIO_3 and 3 g of KI are dissolved in 200 mL of water followed by the addition of 20 mL of hydrochloric acid (c = 2 mol/L). Then 10.0 mL of this solution are titrated with a solution of thiosulfate (c = 0.0100 mol/L). Mean value of consumption: 18.6 mL.

c) Calculate the concentration of the potassium iodate solution. Write down the equations of all reactions during the titration.

There are 250 mL of a solution of ascorbic acid of unknown concentration. 25.0 mL of it are transferred to a conical flask. 25 mL of hydrochloric acid (c = 2 mol/L) and 10 drops of starch solution are added.
Mean value of the final value of the titrant: V = 15.4 mL of potassium iodate solution (take in this case $c(IO_3^-) = 3.50 \cdot 10^{-3}$ mol/L).

d) Calculate the mass of ascorbic acid in the total initial solution.

If the titration of ascorbic acid is carried out in 5 M HCl medium, then the reaction proceeds as follows:

$$C_6H_8O_6 + IO_3^- + H^+ + Cl^- \longrightarrow C_6H_6O_6 + H_2O + ICl$$

e) Balance the above reaction.

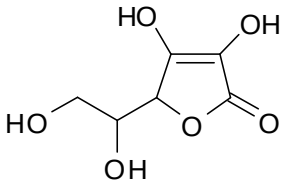
V_1 and V_5 are the volumes of KIO_3 solution required for the titration of 25.00 mL of the ascorbic acid solution in 1 and 5 M HCl, respectively.

f) Give the mathematical relation between V_1 and V_5.

Problem 3-07 Structures I

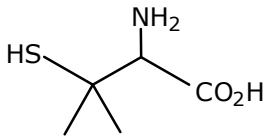
The configuration of molecular compounds is given by the three-dimensional plot of the molecule.

The formula of ascorbic acid given in problem 3-02 does not show the configuration unambiguously.



a) Give the reason for the appearance of stereoisomers in this case. Determine the number of stereoisomers and give the isomeric relation (enantiomers/diastereomers) of each pair. (Don't plot the isomers.)

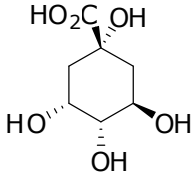
The active pharmaceutical ingredient (*R*)-penicillamine is a long-range drug against rheumatism while the (*S*)-enantiomer is toxic.



Penicillamine

b) Draw the structural formula of (S)- penicillamine.

The image shows the structural formula of quinic acid (**A**).



A

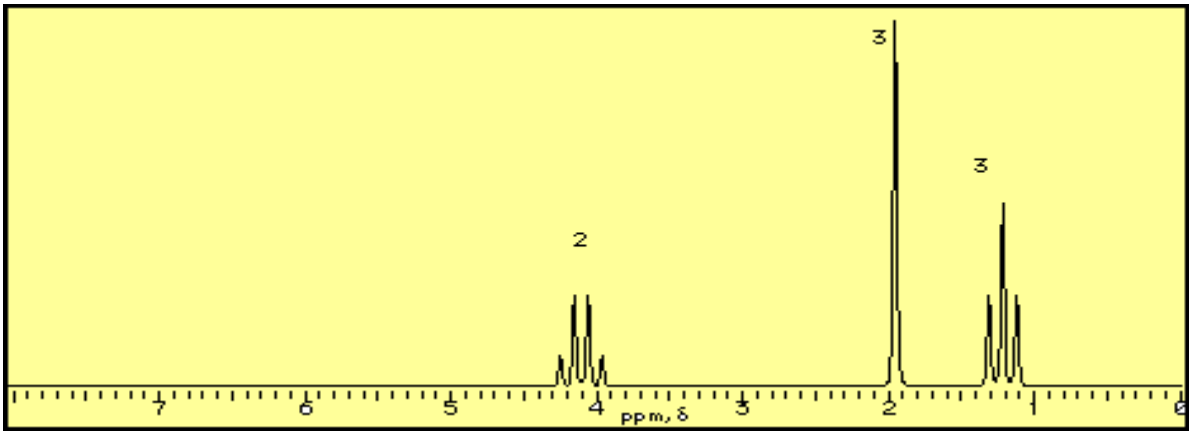
*c) Mark all stereogenic centres of **A**.*

d) Assign R- or S-configuration to all stereogenic centres with the help of the CIP convention. State curiosities.

An essential function of the NMR spectroscopy is the clarification of the configuration of compounds.
A compound has the empirical formula $C_4H_8O_2$.

e) Draw the structures of 3 isomers of $C_4H_8O_2$.

f) Suggest a structure of the compound $C_4H_8O_2$ with the help of the ^{1}H-NMR spectrum shown below and account for your suggestion.



Problem 3-08 Alcohols

The Grignard reagent ethylmagnesium bromide, C_2H_5MgBr, and acetaldehyde (CH_3CHO) react in diethyl ether. In the following hydrolysis butan-2-ol, $C_2H_5CH(OH)CH_3$), and a magnesium salt form.

a) *Propose a reaction mechanism for the formation of the alcohol. Attach the partial charges to the reacting atoms and indicate the electron flow using curved arrows.*

b) *Which effect has diethyl ether as solvent in Grignard reactions?*

c) *Suggest the mechanism of the reaction of acetaldehyde with sec-butylmagnesium bromide to form the respective alcohol. Write the IUPAC name of the alcohol.*

2,3-Dimethyl-2-pentanol was formed from sec-butylmagnesium bromide and a compound X.

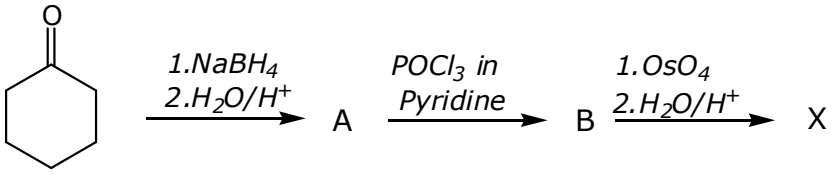
d) *Draw the structure and the name of compound X.*

Breathalysers are used for field sobriety tests. These are test tubes filled with potassium dichromate and sulfuric acid on silica gel. If there is ethanol in the breath the tube shows green colour due to the formation of chromium(III) salts.

e) *Write a balance equation of the reaction of potassium dichromate ($K_2Cr_2O_7$), sulfuric acid and ethanol. In this reaction acetic acid forms.*

Problem 3-09 Synthesis

Compound X can be prepared in the following sequence of reactions:



Notice the following hints:

i) Neither are all side products mentioned in the scheme nor is stoichiometric information given.

ii) Compound B decolours a solution of potassium permanganate.

iii) Compound X has the empirical formula $C_6H_{12}O_2$.

a) *Draw the structures of A, B and X. Write the complete name of X.*

The scheme above contains an elimination, a reduction and an oxidation as reaction steps.

b) Assign these three types of reactions to the different reaction steps.

The first step in the conversion of cyclohexanone to compound A is a nucleophilic addition.

c) Give this first step as reaction mechanism including polarisations and flow of electrons between the nucleophilic and the electrophilic reagent.

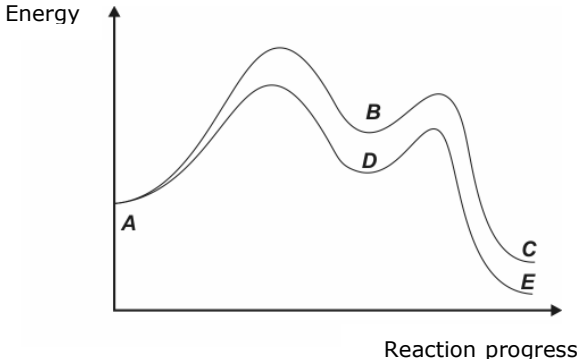
Problem 3-10 Alkenes: Addition Reaction

Alkenes are very reactive and add among others HCl molecules in a good yield, e.g.

$CH_3CH{=}CH_2 + HCl \longrightarrow CH_3CHCl{-}CH_3 + CH_3CH_2{-}CH_2Cl$

(Main product) (Side product)

The following energy diagram of the reaction mechanism shows the course of the main and side reaction.



a) Assign the different reaction steps of the example above to the energy diagram. Therefore give the structure of A to E.

b) Complete the following reaction scheme:
$CH_2{=}CH{-}C_2H_5 + HCl \longrightarrow$ X or Y or Z (side product)

The compounds X and Y form with high yield.

c) Account for the high yield formation in equal amounts of X and Y by drawing the reaction mechanism.

d) Which main product(s) do you expect from the reaction of 1-methylcyclobutene with HCl. Name the product(s).

Third Round Test 2

Problem 3-11 Multiple Choice

(With one or more correct answers even if the question is written in singular)

a) Which of the following compounds is accountable for acid rain?

A) SO_2	B) O_3	C) N_2	D) NO_2	E) none of these compounds

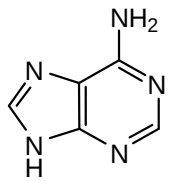
b) Decide, which of the following molecules is nonpolar.

A) NF_3	B) ClF_3	C) SO_3	D) XeF_6	E) none of these compounds

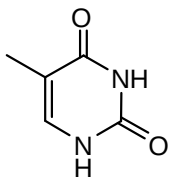
c) pH and pK_a values are used to characterise solutions and acids, respectively. Which of the following statements is correct?

A) Both are logarithmic values.
B) pH < 7 indicates an acidic solution.
C) If pH = pK_{a2} in a diprotic acid the average charge of the species is 0.5.
D) When pH = pK_a in a monoprotic acid 50% of the compound is protolyzed.
E) When pH = pK_a +1 then 10% of a weak acid is protolyzed.

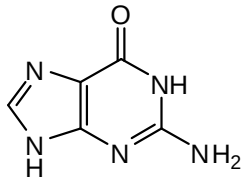
d) DNA replication is an enzyme-catalysed process in which the two strands of the DNA are separated. In a test tube a temperature increase is sufficient to separate the DNA stands by breaking the hydrogen bonds that hold them together. The temperature depends on the number of hydrogen bonds.
Among the 50 base pairs of a DNA segment adenine occurs 28 times. How many hydrogen bonds hold this segment together?



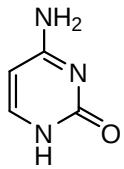
Adenine (A)



Thymine (T)



Guanine (G)



Cytosine (C)

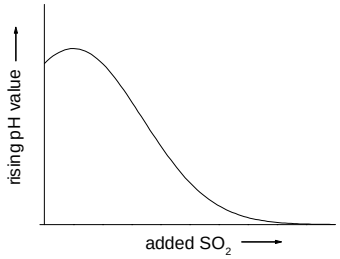
Base pairing in the DNA: A with T and G with C.

A) 50	B) 72	C) 122	D) 128	E) 144

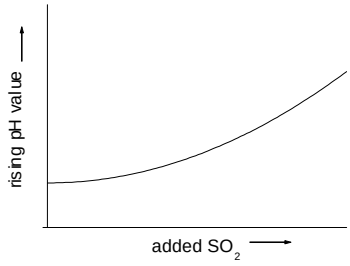
e) Which of the substances below would you expect to be gaseous at 30°C and standard pressure?

A) C_8H_{18}	B) BF_3	C) CH_3COOH	D) Li_2O	E) CH_3CHO

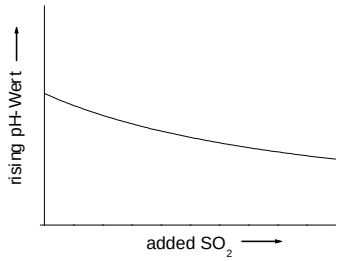
f) If you add SO_2 to a solution of H_2S at room temperature the pH value changes. Which of the following plots indicates the relationship between pH value and added volume of SO_2 soonest?



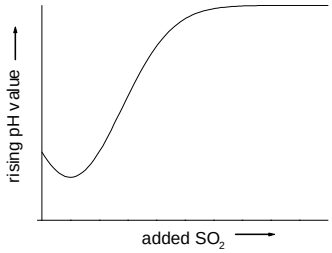
A



B



C



D

E None of the plots.

k) A $\longrightarrow$ B is a reaction of first order. Which of the following plots should show a straight-line graph?

A) c(A) = f(1/t)	B) 1/c(A) = f(t)	C) ln c(A) = f(t)	D) ln c(A) = f(1/t)	E) none of these plots

q) Which of the following species is <u>not</u> linear?

A) CO_2	B) N_2O	C) N_3^-	D) XeF_2	E) O_3

Problem 3-12 Iron and Steel

In 1783 the brothers Montgolfier let rise hot-air balloons. They thought that smoke was the driving force to cause buoyancy and so they burned smoldering bales of straw. In the same year Jacques Charles, professor of physics, ran ex-

periments with balloons filled with hydrogen. The filling lasted four days because the hydrogen was produced by sousing 500 kg of scrap iron with 225 kg of sulfuric acid.
(Weather conditions: 20°C, 1027 hPa, air: 21% oxygen, 79 % nitrogen)

a) Calculate the maximal volume of hydrogen which could be produced in this way and the value of buoyancy caused by this amount of hydrogen.

Scrap iron does not only contain pure iron but also iron oxides. A sample of 0.2145 g contains a mixture of iron and iron(III)-oxide. This sample is completely dissoluted in concentrated hydrochloric acid and then treated with a saturated solution of SO_2 in water. The excess of SO_2 is removed by adding sulfuric acid and boiling.
In a following titration with a solution of potassium permanganate (c = 0.0198 mol/L) 36.45 mL are used.

b) Write the equations of all reactions involved and calculate the mass ratio (%) of iron and iron(III)-oxide in the sample.

Problem 3-13 Tensides

Surfactants consist of molecules with a hydrophilic and a hydrophobic part. In water they can form micelles. $C_{12}H_{25}$-(O-CH_2-CH_2)$_5$-OH (=A) is an example of such a surfactant.
A surfactant molecule can generally be modelled as shown below where a circle represents the polar head (K) and a rectangle the non-polar tail (S) of the molecule.

a) Fill in the formula of A in the circle and the rectangular correctly.
b) Choose the type of surfactant A among the following:
- non ionic, - anionic, - cationic, - others.

Surfactant molecules can group together as micelles if the concentration reaches the critical micelle concentration (c_K). At smaller concentrations than c_K there exist only monomers. As soon as c_K is reached all further added surfactant molecules form micelles. Then the concentration of the monomers is c_K independent of how much surfactant is added.

A stock solution of A with c = 0.500 mol/L was available. This concentration is far above c_K.
$8.00 \cdot 10^{-3}$ cm^3 of this stock solution were added to 100 cm^3 of water in a very sensitive calorimeter. The raise of temperature was $1.25 \cdot 10^{-4}$ K.
The heat capacity of the calorimeter including 100 cm^3 of water amounted to 452 JK^{-1}, the temperature in the vessel was 298 K.

c) Calculate the quantity of heat released in the calorimeter.

A further portion of $8.00 \cdot 10^{-3}$ cm^3 of the stock solution of A was given into the calorimeter. Now the raise of temperature was $0.74 \cdot 10^{-4}$ K.

A third addition of such a portion did not lead to any raise in temperature.

d) Explain this phenomenon.

e) Calculate c_K of the surfactant A.

$\Delta G° = -RT \cdot \ln (c_K/c_0)^{-1}$ of the transition $A_{monomer} \rightleftharpoons A_{micelle}$ can be computed (c_0 = 1 mol/L).

f) Calculate $\Delta G°$ and $\Delta S°$ of the transition of $A_{monomer}$ into $A_{micelle}$.

Aufgabe 3-14 Kinetics

3-Methylcyclobutene (3-MCB) undergoes an intramolecular rearrangement.

a) Write down the reaction equation together with the structural formulae of the reactant and the product. Which two factors are the driving force of this reaction?

In the following table the reaction rate is given, measured at 123.5 °C against the initial partial pressure of 3-methylcyclobutene.

Partial pressure of 3-MCB in kPa	0.931	2.38	2.86	3.64	5.99
reaction rate in 10^{-7} mol L^{-1} s^{-1}	0.389	1.00	1.21	1.55	2.52

b) Show that the reaction is of 1st order by using the data above to draw a plot.

Determine the reaction rate constant k of the rate law $v = - dc/dt = k \cdot f(c)$.

From measurements at other temperatures it is known that the rate constant of this reaction follows the Arrhenius equation.

The activation energy is 132.09 kJ/mol.

c) *Calculate the pre-exponential factor A for this reaction. (Take here $k = 1.50 \cdot 10^{-4}\ s^{-1}$.)*

Reactions of the type A $\longrightarrow$ B often show a distinct pressure dependency of the reaction order, contrary to an intuitive assumption of a rate law of 1st order.
To explain this phenomenon Frederik Lindemann proposed in 1921 a mechanism consisting of three elementary reactions.
In a first collision reaction two molecules of A collide with one absorbing the energy of the other one (i.e. it gets activated). In this model this activated molecule possesses the necessary activation energy and rearranges to B. The third reaction is the reversion of the activation.

d) *Write down the equations of these three elementary reactions. Label the activated species with an asterisk (*). It is not necessary to label the other partner of the collision specifically. Use the notations k_1, k_2 and k_3 for the rate constants.*

To find the rate laws of complicated reaction systems often the steady-state approximation is used.

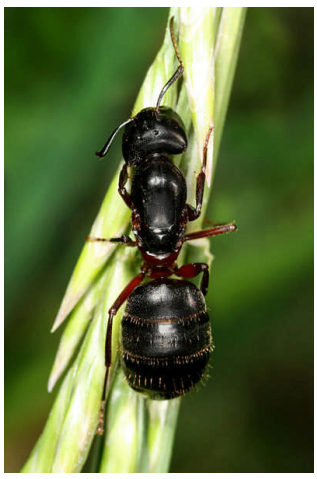
e) *Give the steady-state approximation of the mechanism of d).*

f) *Derive a formula of the rate of formation of B containing only [A] = c(A) and the constants k_1, k_2 and k_3, using the result of e).*

g) *Which reaction order can be assumed in the case of a very high pressure of A? Derive the resulting rate law and give the order of the reaction.*

h) *Which reaction order can be assumed in the case of a very low pressure of A? Derive the resulting rate law and give the order of the reaction.*

Problem 3-15 Ants



The "simplest" carboxylic acid, methanoic acid, is also called formic acid after the Latin word formica for ant. It naturally occurs in ants[1] and used to be prepared by distilling ants.

[1] Photo: Richard Bartz, Munich

When an ant bites, it injects a solution containing 50% of volume of methanoic acid. A typical ant may inject $6 \cdot 10^{-3}$ cm^3 of this solution.
When you are bitten by an ant it does not inject you with all of its methanoic acid but keeps a little reserve of 20%.

a) *Which is the total volume of pure methanoic acid contained in a typical ant (before it bites)?*

b) *How many ants would have to be used to produce 1 L of pure methanoic acid?*

Bicarbonate (sodium hydrogen carbonate) is often used to treat ant stings.

c) *Write the equation for the reaction between sodium hydrogen carbonate and methanoic acid.*
What mass of sodium hydrogen carbonate would be needed to neutralise the sting of the ant completely? (ρ(methanoic acid) = 1.2 g·cm^{-3})

As soon as the methanoic acid is injected it dissolves in water. $1 \cdot 10^{-2}$ cm^3 of pure methanoic acid is dissolved in water to form 2.00 cm^3 of a solution. The pH of this methanoic acid solution is 2.34.

d) *Calculate the acid dissociation constant K_a for methanoic acid and α, the degree of protolysis.*

e) *What volume of acetic acid has to be filled up with water to 2.00 cm^3 to form a solution having the same pH value?*
Compare with the respective volume of methanoic acid.
(pK_a(acetic acid) = 4.76 , ρ(acetic acid) = 1.05 g·cm^{-3})

Problem 3-16

180 cm^3 of hydrochloric acid with the unknown concentration x were given into a beaker and 120 cm^3 of silver nitrate solution (c = 0.05 mol/L) were added (T = 298 K).
Afterwards two electrodes were held into the beaker, a silver plate and a hydrogen electrode.
The potential of this electrochemical cell was measured: 0.807 V. In doing so the hydrogen electrode was the negative pole.

a) Calculate x.

The experiment was repeated in the same way, only the (unknown) concentration x of the hydrochloric acid was changed. 0.378 V were measured.

b) Calculate x again.

Solubility product: $K_{sp}(AgCl) = 1.78 \cdot 10^{-10}$ at 298 K
Standard potential: $E°(Ag/Ag^+) = + 0.800$ V

Problem 3-17 Structures II

The structures of ionic compounds are described by their unit cells.

The unit cell of $NiSO_4$ is orthorhombic (i.e. the three axes form an angle of 90° to each other) with the values a = 633.8 pm, b = 784.2 pm, c = 515.5 pm. An approximate measurement of the density gives 3.9 g/cm^3.

a) Find the number of formula units per unit cell and calculate the exact density.

The structure of nickel(II) oxide is identical to the structure of sodium chloride.
The O^{2-} ions are arranged in a face-centered cubic lattice, all of the octahedral interstice sites are occupied by Ni^{2+} ions.
The density of nickel(II) oxide is 6.67 g/cm^3.
If you treat nickel(II) oxide with lithium oxide and oxygen white crystals with the composition $Li_xNi_{1-x}O$ form which are good semiconductors:

$$½ \cdot x\ Li_2O + (1-x)\ NiO + ¼ \cdot x\ O_2 \longrightarrow Li_xNi_{1-x}O$$

The structure of $Li_xNi_{1-x}O$ is the same as of NiO, however, some nickel atoms are replaced by lithium atoms and some of the Ni^{2+} ions are oxidized to establish charge neutrality.
A semiconductor with the density of 6.21 g/cm^3 was produced.

b) Draw an image of the unit cell of nickel(II) oxide.

c) Calculate x. (Assumption: The volume of the unit cell did not change.)

d) Calculate the percentage of Ni^{3+} ions, related to all nickel ions in the semiconductor crystal.
Write down the simplest empirical formula of this semiconductor using Ni(II), Ni(III) and integers as indices.
(If you could not solve c) take x= 0.15).

Problem 3-18 Oxidation Reactions

Malonic acid (*cis*-$C_2H_2(COOH)_2$) reacts with potassium permanganate in cold alkaline aqueous solution to form meso-tartaric acid ($C_4H_6O_6$).

a) Draw the 3D-structure of meso-tartaric acid (e. g. in Fischer projection). Mark all stereogenic centres and assign R or S configuration to each of them.

To explain the stereochemistry of the reaction an ester with manganese(V) acid (H_3MnO_4) is supposed to be an intermediate.

b) Draw the structural formula of this intermediate.

c) Which other products do you expect besides meso-tartaric acid when acidifying the solution? Give one example and explain why more products form.

A cold alkaline aqueous solution of potassium permanganate is added to cyclooctene.

d) Write the reaction scheme. Pay attention to the correct stereochemistry.

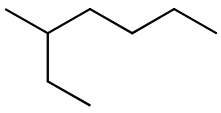
Under these conditions the reaction leads to a yield of only 7 %. On addition of a catalytic amount of a quaternary ammonium salt (e. g. $C_6H_5CH_2N(CH_3)_3Cl$) the yield rises to 50 %.

e) Account for this rise of yield.

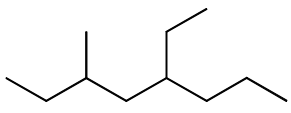
Aufgabe 3-19 Names and Structures of Organic Compounds

Organic compounds are named by rules set by IUPAC.

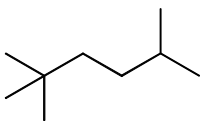
a) Write the correct IUPAC names for the following organic compounds:



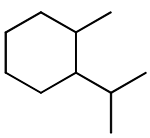
(A)



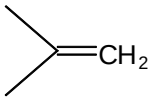
(B)



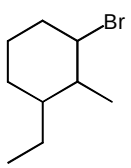
(C)



(D)

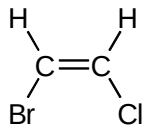


(E)

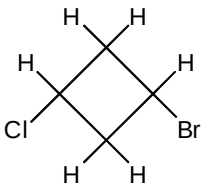


(F)

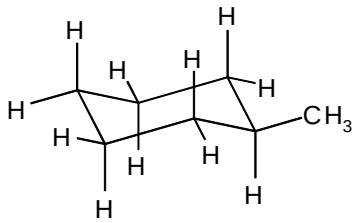
b) Decide whether there are stereoisomers to the following compounds. If your answer is positive give the kind of isomerism.



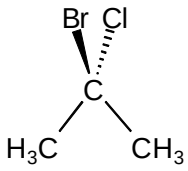
(A)



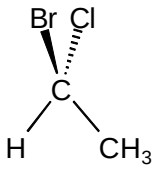
(B)



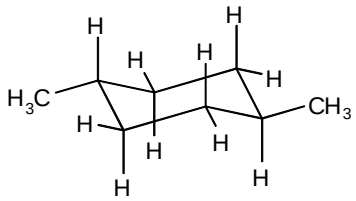
(C)



(D)



(E)



(F)

In the case of stereogenic carbon atoms with four substituents a verbal method for indicating the three-dimensional arrangement of the substituents is the R/S nomenclature.

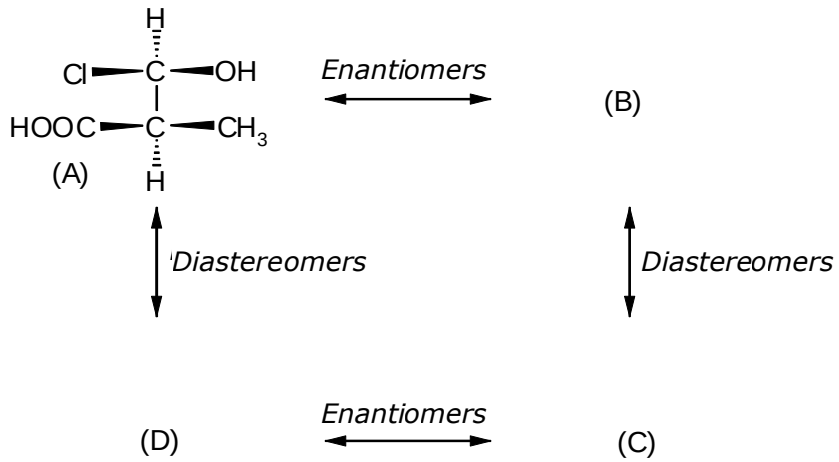
c) Assign priorities to the following sets of substituents according to the R/S sequence rules. Start with the substituent with the highest priority.

i) –CH_2CH_3; –H; –CH_3; –$CH(CH_3)_2$

ii) –OH; –CH_3; –Br; –CH_2OH

iii) –OH; –COOH; –$COOCH_3$; –C≡N

d) Complete the following scheme:



e) Assign R or S to all stereogenic centres of the compounds A to D.

f) What is the name of the isomerism between the compounds A and C as well as between B and D?

Problem 3-20 Pyridine

The cyclic pyridine molecule (C_5H_5N) is flat. All carbon-carbon bonds have the same length of 139 nm, intermediate between typical single and double bonds.

a) Draw a three-dimensional image of pyridine which shows the positions of the π electrons and of the free electron pair. In which hybrid orbital is the lone electron pair located?
Account for the most important property of pyridine using your image.

Pyridine reacts with bromine, fuming sulfuric acid or a mixture of nitric acid and sulfuric acid at 3-position of the ring.

b) Write the three reaction equations. What is the name of the reaction mechanism in all three cases?

c) Account for the preference of the 3-position in the ring by drawing an image of the intermediate in 3-position (carbocation structure).

d) Give the reason for the fact that all above reactions take place only under drastic conditions and with very low yield.

The reaction of 2-bromopyridine with sodium amide ($NaNH_2$) leads to an aminopyridine with good yield.

e) Write down the reaction equation..

f) Show the most important steps of the mechanism of this reaction. What is the name of this reaction?
Compare the reactivity of this reaction to the respective reactivity of bromobenzene. What is similar, what is different?

Fourth Round (theoretical problems)

(A periodic table and the same list of formulae and data as in the third round were provided)

Problem 4-1 Structures[2]

The atoms in silica and silica glass are held together by single covalent Si-O bonds. The structure forming units in silica are SiO_4 tetrahedrons connected at the corners. To simplify the problem assume this ideal connection is always existent.

a) Give the coordination number of the silicon and oxygen atoms.

The density of silica glass amounts to ρ = 2.203 g/cm^3.

b) Determine the average volume of a tetrahedral unit. How many bonds are there on average in this volume?

A frequent defect in the structure of silica glass is an oxygen vacancy. Oxygen atoms in the lattice are missing and the neighbouring Si atoms of the missing oxygen atom stabilize by forming an Si-Si bond.
An amorphous silica sample is characterized by the formula $SiO_{1.9}$.

c) Determine the percentage of the number of Si-Si bonds referring to the total number of bonds in $SiO_{1.9}$.

d) Derive an expression for the $n_{Si\text{-}Si}/n_{Si\text{-}O}$ ratio in a sample of SiO_x as a function of x ($n_{Si\text{-}Sit}$ = number of Si-Si bonds, $n_{Si\text{-}O}$= number of Si-O bonds).
Give the number of x when, on average, each Si atom forms one Si-Si bond.

If SiO_2 is heated in a high vacuum to high temperatures (>1000 °C) it will decompose into gaseous silicon monoxide (SiO) and oxygen according to the following reaction equation:

$$2\ SiO_2\ (s) \rightleftharpoons 2\ SiO\ (g) + O_2\ (g)$$

At a temperature of 1300 °C the equilibrium constant K_p for this reaction is $K_p = 3.9 \cdot 10^{-24}$.

e) Calculate the partial pressure of SiO that will result from the equilibrium if solid SiO_2 is heated to 1300 °C in a high vacuum.

f) How can gaseous SiO be produced without oxygen being formed as well? Write down the reaction equation supporting your proposal!

[2] a) to d): following PP Hungary 2008

Problem 4-2 Two Redox Analyses

A

In order to determine the content of copper in a solution of Cu^{2+} ions potassium iodide is added. The colour of the solution changes to yellow brown and a greyish white precipitate is formed.

a) What is the reason for the yellow brown colour of the solution? Define the greyish white precipitate.

b) Give a balanced equation for the reaction.

Copper sulfate ($CuSO_4$) is white, copper sulfate pentahydrate ($CuSO_4 \cdot 5\ H_2O$) is blue. If exposed to air copper sulfate slowly takes up water and the colour changes slowly to blue.
4.79 g of a sample of copper sulfate, which was exposed to air for a long time is dissolved in a volumetric flask, and 20 cm^3 of concentrated sulfuric acid are added. Then the volumetric flask is filled up with water to 100 cm^3.
2 g potassium iodide are added to 10 cm^3 of this solution which is then diluted to approximately 100 cm^3 and titrated with sodium thiosulfate (c = 0.100 mol/L), using starch solution as an indicator. The average volume of sodium thiosulfate needed: V = 25.40 mL.

c) Give a balanced equation for the titration reaction.

d) Calculate the amount of water (in g) in the sample. What is the ratio (amount of substances) of copper sulfate and water in the sample?

B

If 1.7334 g of zinc react with an excess of conc. sulfuric acid 601 cm^3 of a gas mixture (1.022 bar, 20°C) form. Besides hydrogen it contains two more gases, each of them contain sulfur in a lower oxidation state than in sulphuric acid. This mixture is shaken out with a solution of potassium permanganate in diluted sulfuric acid. In doing so 30.00 cm^3 of he $KMnO_4$ solution (c = 0.2 mol/L) are consumed.

e) Give the names of the gases in the mixture.

f) Write the equations of the reactions in which these gases are formed.

Reactants are always zinc and sulfuric acid. Neglect all reactions in which zinc is not involved either directly or indirectly.

g) Calculate the composition of the mixture in percent by volume. Write the necessary reaction equations.

Problem 4-3 Redox Reactions

a) Given the standard potentials below calculate the solubility L (in g/L) of lead sulfate in water at 298 K.

Standard potentials:

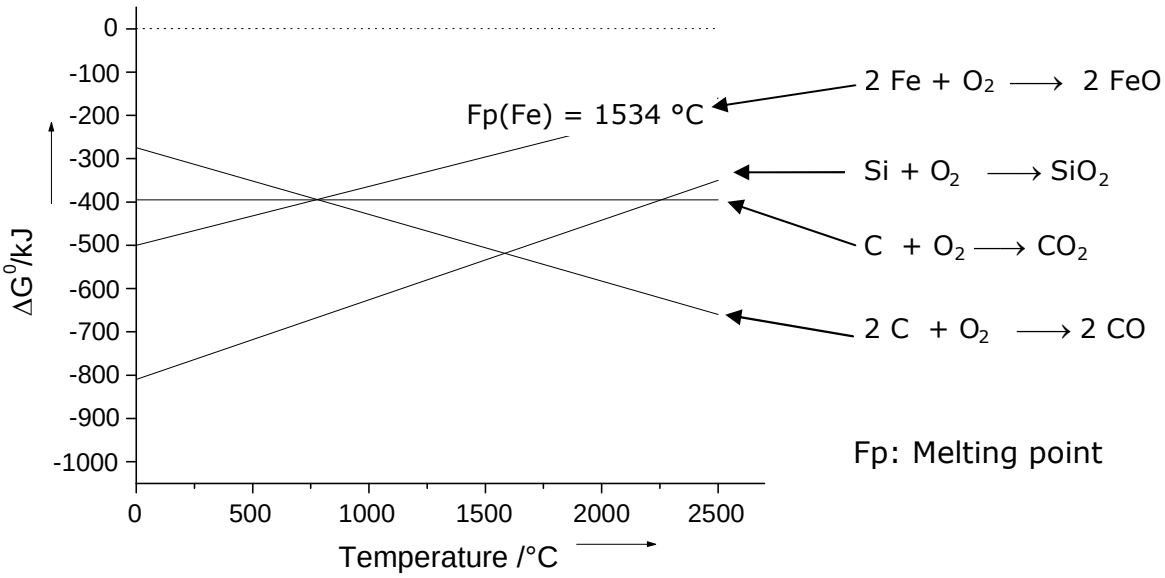
$PbSO_4(s) + 2\ e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$ $\quad E^\ominus_1 = -0.356$ V

$Pb^{2+}(aq) + 2\ e^- \rightleftharpoons Pb(s)$ $\quad E^\ominus_2 = -0.126$ V

$Pb(s)|PbSO_4(s)|NaHSO_4$ (aq) (0,600 mol/L) || $Pb^{2+}(aq)$ ($2{,}5\cdot10^{-5}$ mol/L)|Pb(s) represents an electrochemical cell the potential of which amounts to $\Delta E = 0.061$V.

b) Calculate the dissociation constant (K_{a2}) of HSO_4^-.

The following graph shows the change in ΔG^0 with temperature of a few reactions.



c) Give an equation for ΔG of the reactions in the diagram as a function of $p(O_2)$.

A mixture containing FeO and SiO_2 is heated with coke.

d) State which of the oxides will be reduced first. Account for your answer shortly.

e) State the minimum temperature at which the reduction of FeO and SiO_2 will start.

f) Give the balanced chemical equations for the reactions in d) and e).

Problem 4-4

a) Take the given data to calculate the proton affinity X of NH_3:

$$NH_{3(g)} + H^+ \longrightarrow NH_4^+ \quad \Delta H° = X$$

Standard enthalpies of formation	$\Delta H°_f(NH_4Cl_{(s)})$	= - 313.5 kJ/mol
	$\Delta H°_f(NH_{3(g)})$	= - 46 kJ/mol
$\Delta H°_{diss}(Cl_{2(g)})$ = 242 kJ/mol	$\Delta H°_{diss}(H_{2(g)})$	= 430.5 kJ/mol
Ionization energy (H)	I(H)	= 1312.5 kJ/mol
Electron affinity (Cl)	EA(Cl)	= - 348 kJ/mol
Lattice energy	$U(NH_4Cl)$	= - 651.1 kJ/mol

$PbCO_3$ and ZnO are used for white pigments. H_2S reacts with these compounds to form the respective sulfides.

b) Write the equations for these reactions.

c) Find out whether the presence of $7.0 \cdot 10^{-9}$ g/L H_2S in the air hinders the use of these pigments.

d) State which of these pigments is less suitable. Account for your statement.

In case of PbS, H_2O_2 can be used to reestablish the white colour. Thereby $PbSO_4$ is formed.

e) Write the equation for this reaction.
Is it possible to reach the same effect by air ventilation only (from the thermodynamical point of view)?

For c) to e):

T = 298 K and air pressure p = 1.000 bar

Composition of air in percentage of volume:

N_2: 77.90 O_2: 20.70 CO_2: 0.026 H_2O: 0.40 other gases: 1.03

	$PbCO_3(s)$	$H_2S(g)$	PbS(s)	ZnO(s)	ZnS(s)	$CO_2(g)$	$H_2O(g)$	$PbSO_4(s)$
$\Delta G°_f$ in kJ/mol	- 626.0	- 33.0	- 92.6	- 318.0	- 184.8	- 394.2	- 228.5	- 811.5

$p_{standard}$: p° = 1.000 bar

Problem 4-5 Rotational Spectroscopy

The free rotation of gas molecules can be described in simple cases by the model of a rigid rotor. The model implies that the shape of the molecule does not change by rotation. The energy levels of this model system can be calculated using the Schrödinger equation.

The energy levels turn out to be:

$$E(J) = h \cdot c \cdot B \cdot J(J+1)$$

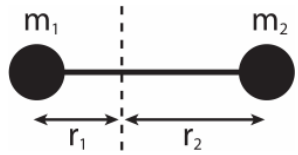
where J = 0,1,2,… (quantum number), c = speed of light,
h = Planck's constant, $B = h/(8\pi^2 \cdot c \cdot I)$.

B is called rotational constant and its value is related to the moment of inertia in the way stated. B is directly proportional to the energy, E, and normally given in cm^{-1}, a common unit in infrared and microwave spectroscopy.

I, the moment of inertia, is a key quantity needed to describe the rotational motion of an object, e.g. when a molecule rotates around its centre of gravity and all distances refer to this centre:

$$I = \Sigma m_i r_i^2$$

For diatomic molecules this formula can be simplified:



$I = m_1 r_1^2 + m_2 r_2^2 = \mu \cdot R^2$

where R = bond length ($= r_1 + r_2$),

μ = reduced mass ($= \frac{m_1 \cdot m_2}{m_1 + m_2}$).

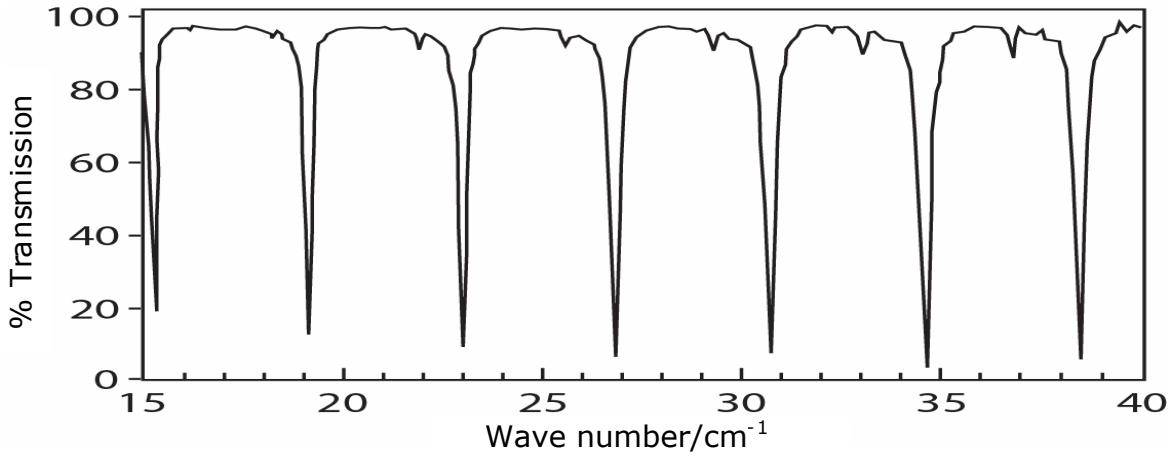
Transitions between different rotational energy levels can be brought about by microwave radiation. J changes by +1 in case of absorption, by -1 in case of emission of a photon.

a) Determine the difference in energy between two adjacent rotational energy levels J and J+1.

Even at room temperature you can detect rotational spectra with a series of bands caused by the small difference in energy between different rotational energy levels. That is why the thermal energy is sufficient to initiate rotational energy levels of J = 1,2,3,… besides the ground state of J = 0.

b) How large is the spacing between two of these adjacent lines in a rotational spectrum (given as transmission as a function of wave number)?

On the next page you find the rotational spectrum of CO.

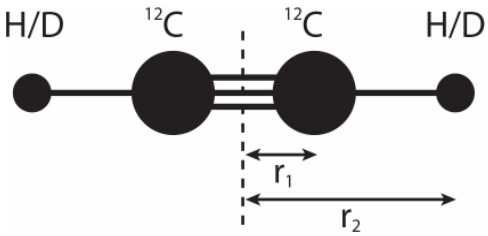


c) *Determine B for CO from the diagram and calculate the bond length.*

d) *Which transitions J → J+1 correspond to the shown peaks?*

e) *In the spectrum you find side bands (e.g. at 36.9 cm^{-1}) with much lower intensities. Account for the reasons of the occurence of these additional lines. Justify your assumption by calculation.*

The two bond lengths in the linear molecule of acetylene, C_2H_2, cannot be determined by only one rotational spectrum.
Nevertheless, to find these bond lengths a spectrum of acetylene with the two hydrogen atoms replaced by deuterium (C_2D_2) was used additionally.



The following rotational constants B were detected:
$B(^{12}C_2H_2) = 1.1766 \ cm^{-1}$ $B(^{12}C_2D_2) = 0.84767 \ cm^{-1}$

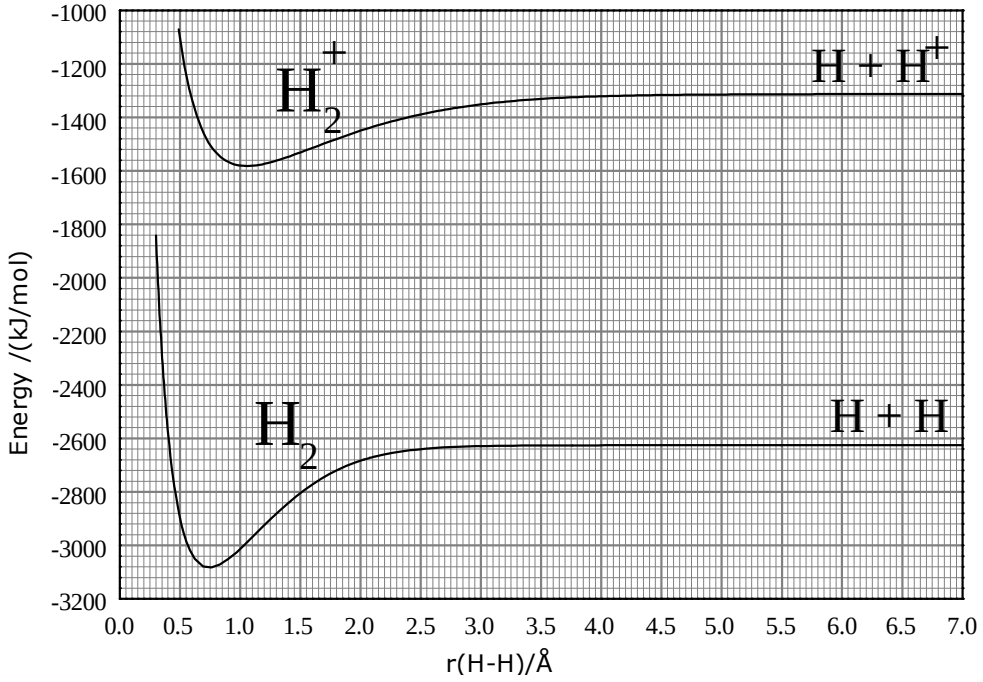
f) *Find the bond lengths in acetylene. Assume that these bond lengths in C_2H_2 and $^{12}C_2D_2$ are identically.*

Masses of isotopes

Isotope	H	D=^{2}H	^{12}C	^{13}C	^{14}C	^{16}O	^{18}O
Molar mass/(g/mol)	1.0078	2.0141	12.000	13.003	14.003	15.995	17.999

Problem 4-6

The following graph shows the potential energy curves of the H_2 molecule and its cation H_2^+. Use the information given in the graph to answer the following questions.



Use the diagram to determine the following values as accurately as possible:

a) *Equilibrium bond length of H_2 and H_2^+, respectively.*

b) *Bond energies of H_2 and H_2^+, respectively.*

c) *Ionization energy of the H_2 molecule.*

d) *Ionization energy of the H atom.*

You may use electromagnetic radiation with a frequency of $3.9 \cdot 10^{15}$ Hz to ionize H_2.

e) *Calculate the speed of the leaving electron. (Neglect molecular vibrational energy.) m(electron) = $9.1 \cdot 10^{-31}$ kg.*

He_2 is an unknown species while He_2^+ has already been detected.

f) *Use a qualitative MO diagram to find the respective bond orders and explain this phenomenon.*

Problem 4–7 Lead

Lead is generally produced from lead sulfide (PbS) which is found in nature.
Two processes are applied: the so called roast-reaction process and the roast-reduction process. In both cases at first lead sulfide is "roasted" whereas the oxidation state remains unchanged. Depending on the oxygen supply two different lead containing products form together with a gaseous compound.

a) Write down balanced equations for the reactions with plenty and with a lesser quantity of oxygen in the roast process.

Following the roast process the products are treated furthermore.
The gaseous compound is formed in many other technical processes. The reaction of it with another sulfur containing gas is used to produce elementary sulfur. In this case a comproportionation takes place.

b) Write down the equation for the yield of sulfur. Attach oxidation numbers to all elements. What is the name of this sulfur producing process?

In order to produce lead (crude lead, pig lead) the lead containing products of the roast process are either treated with unroasted lead sulfide (roast-reaction process) or reduced with carbon (roast-reduction process).

c) Write down the reaction equations.

In most cases crude lead contains a small amount of silver which is embedded in lead ore. To get the silver the crude lead is transformed into so called argentiferous lead (silver content 2.5 to 12 %). The argentiferous lead is molten and air is blown into the melt. In doing so lead is oxidized to product **T**, silver not (at first).

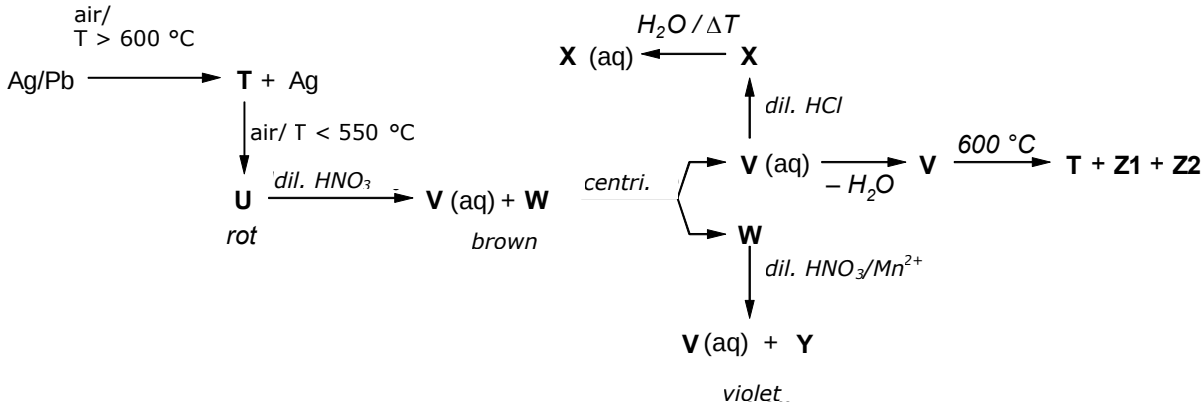
If dispersed **T** is heated in air at temperatures below 550°C a red product **U** forms.

If **U** is heated in diluted nitric acid the colour of the mixture changes to brown. Centrifugation of this mixture provides a solution of **V** and a solid **W**.

If the solution of **V** is treated with a diluted solution of HCl a white precipitate **X** forms which is soluble in hot water.

If **W** is boiled in an acidified solution of manganese(II) ions the colour of the solution turns dark violet because of the formation of compound **Y**.

If V is heated up to 600°C it decomposes to **T**, **Z1** and **Z2**.



*d) Identify the compounds **T** to **Z2**? Write down the equations of the respective reactions.*

Lead crystallises in a cubic close-packed structure. The Pb-Pb distance in the solid is 3,49 Å.

e) Determine the density of lead.

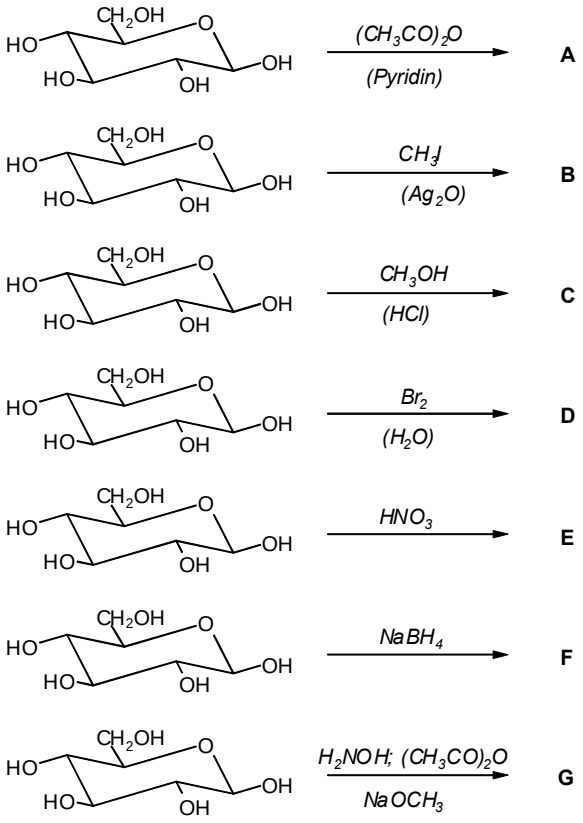
Lead can be detected unambiguously very easily in the wet chemical separation process. Often precipitates form which then in excess dissolve as complex compounds.
In a strong alkaline solution (e.g. pH >12) lead forms $[Pb(OH)_3]^-$ complexes.

f) Suggest a structure of this complex anion following the Valence Shell Electron Pair Repulsion-Theory (VSEPR). Draw the 3-D structure.

g) Write down the equations of the reactions of a Pb(II) solution with
- *i) diluted sulfuric acid,*
- *ii) concentrated sulfuric acid,*
- *iii) aqueous solution of iodide,*
- *iv) solution of ammonia.*

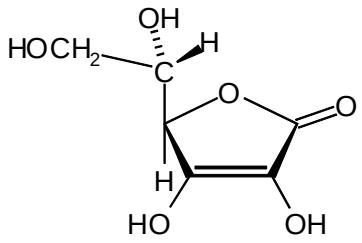
Problem 4-8 Sugar

Sugars react in many ways.
In the following reaction schemes different reactions of β-D-glucopyranose are outlined.
Thereby mono- and dicarboxylic acids of the sugar, a deoxidized sugar, a D-pentose, a glycoside, an ester and an ether are formed.



a) Draw the structural formulae of the compounds A to C in chair-form, and of D to G in Fischer projection.

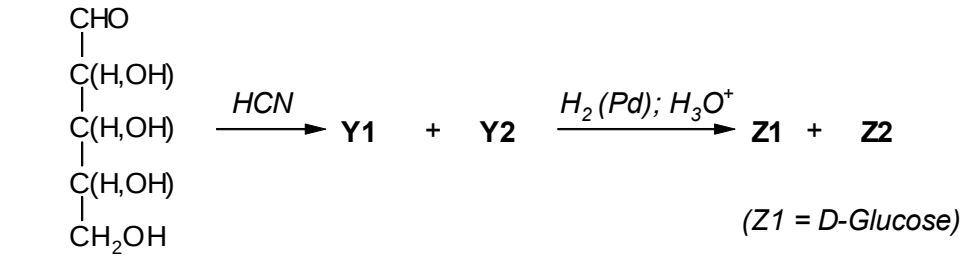
Vitamin C (ascorbic acid) has the following structure:



b) Indicate all sterogenic centers of Vitamin C and assign R/S labels to them.

c) Does the formula above show the image of a D- or an L-sugar? Rationalize your decision by drawing a respective image of the structural formula.

The configuration of sugar X has to be determined. Therefore the following reactions are executed:



Compound X

d) Draw the Fischer projections of the compounds X, Y1, Y2, Z1 and Z2.

e) In water compound Z2 forms two kinds of pyranose, Z21 and Z22. Draw their structures in Haworth projection.

Problem 4-9 Determination of Structures with IR and NMR

Under two different conditions 2-methylpropene reacts in different ways to form two different compounds.

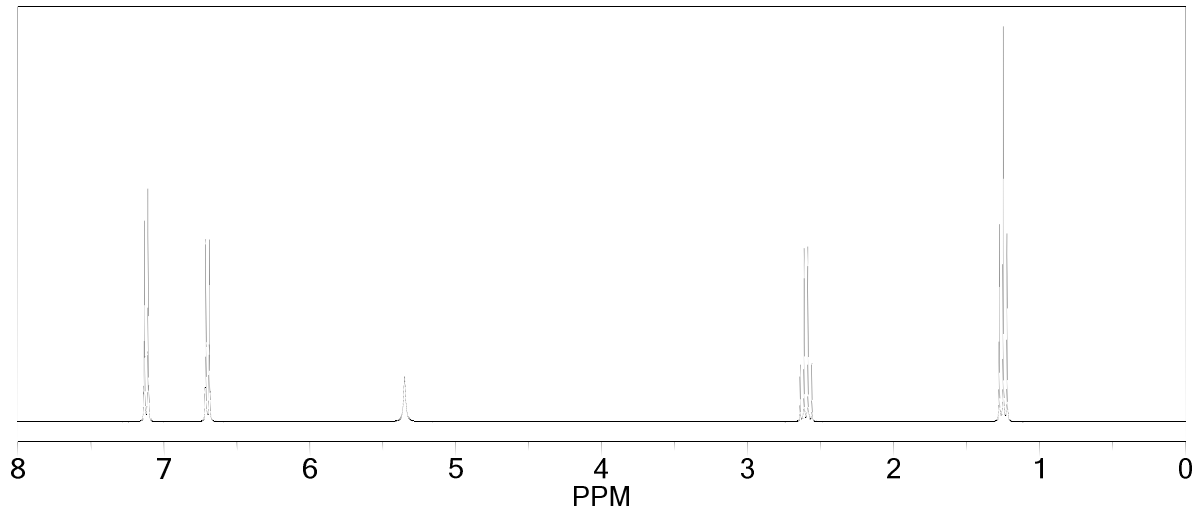
a) Write down the two reaction schemes and the structural formulae of the products. What is the name of the reaction mechanisms of both reactions?

With the help of ^{13}C NMR spectra it has to be decided which product formed.
The^{13}C NMR spectrum of product 1 shows the following signals: δ (ppm, $CDCl_3$, 300 K), 21.6 (quartet), 30.7 (doublet), 43.7 (triplet). The ratio of intensities is quartet : doublet : triplet = 2 : 1 : 1.
(The ^{13}C NMR spectrum is recorded in a way that any coupling to protons is NOT removed, NO "broadband proton decoupling")

b) Assign this ^{13}C NMR spectrum to one of the products . Rationalize your decision with the help of the spectrum.

c) Which ^{13}C NMR signals do you expect for the other product of a)? Give the number of signals and the splitting patterns. Which ratio of intensities of the signals do you expect?

For another compound with the empirical formula $C_8H_{10}O$ a ^{1}H NMR spectrum and an IR spectrum were made.
^{1}H NMR spectrum:



Multiplicity	Chemical shift	Intensity
triplet	1.25 δ	3
quartet	2.60 δ	2
singlet	5.35 δ	1
multiplet	6.7-7.12 δ	4

IR spectroscopy

Type of peaks	Wave number
broad band	3500 cm^{-1}
band	1500 cm^{-1}
band	1600 cm^{-1}
band	830 cm^{-1}

d) Suggest a structure that matches to the given data.
Assign as many signals and bands of both spectra to different atoms or groups of the compound.
(A table with characteristic IR bands is provided.)

The compound N,N-dimethylformamide shows at room temperature three signals in the ^1H NMR spectrum: 2.9 δ (singlet), 3.0 δ (singlet), 8.0 δ (singlet).
If the compound is heated up to appr. 180 °C the ^1H NMR spectrum shows only two signals: 2.95 δ (singlet), 8.0 δ (singlet).

e) Explain this phenomenon.

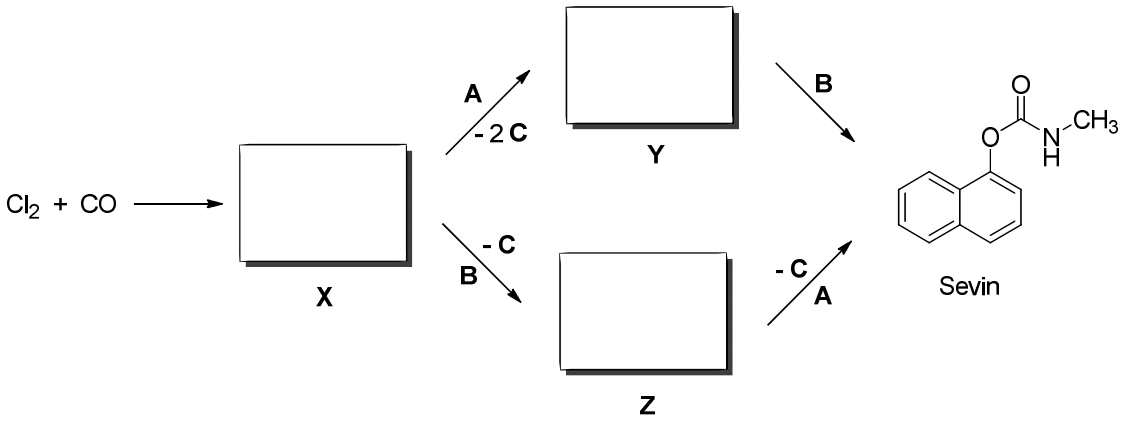
Problem 4–10 Two Disasters in Chemical Plants

Bhopal (India), 1984

The catastrophe of Bhopal is among the worst chemical accidents in history. It is estimated that the outflow of the fugitive compound **Y** caused at least 10,000 deaths and 200,000 people injured.

In the plant concerned the insecticide sevin had been produced. A German company developed a different method of synthesis starting with the same reactants but leading to sevin on a pathway with the less dangerous intermediate **Z**.

On both ways the volatile low-molecular gas **C** forms.

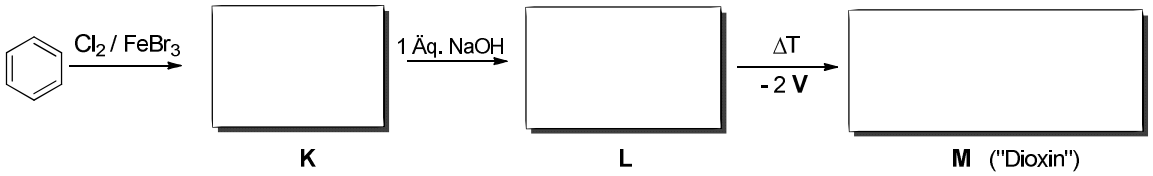


*a) Draw the structural formulae of **X**, **Y** and **Z** and of **A** and **B**. Identify **C**.*

*b) What is the trivial name of **X**? To which family does Y belong? Identify **B**.*

Seveso (Italy), 1976

During the production of compound **L** a momentous accident happened in Seveso in 1976. **L** was synthesized by the reaction of **K** (*M* = 215.89 g/mol) with one equivalent of NaOH. A tank overheated and thus **L** then reacted in a condensation reaction to form **M** (dioxin).



*a) Draw the structural formulae of **K**, **L** and **M**? Identify **V**.*

*b) Write the name of the reaction of **K** to **L**? Suggest a reaction mechanism. How is the intermediate stabilized?*

c) What is the driving force of the reaction of L to M? Why does high temperature favour this reaction?

Fourth Round (practical problems)

Problem 4-11 Synthesis of Glucose Pentaacetate

In this experiment the pentaacetate derivative of glucose is prepared by esterification using acetic anhydride.

Equipment:
Stand with clamps (2x), 100 mL round bottomed flask, 100/250 mL round bottomed flask, 2 cork rings, reflux condenser, tubing, oil bath, magnetic stirrer with magnetic stir bar, 400 mL beaker, spatula, glass rod, glass rod with wiper, suction pump, suction flask with rubber ring, Büchner funnel, filter paper (4x) for Büchner funnel, plastic bowl, labelled 100 mL beaker for the product.

Substances*:*

D-Glucose	(4 g in the round bottomed flask)
Sodium acetate (trihydrate)	(2 g in the plastic box)
Acetic anhydride (caustic, C)	(20 g in the test tube)
Ethanol (harmful to health, Xn)	Silicon oil for oil bath
Demineralised water	Ice

Safety precautions:
Wear eye protection and protective clothing.

Procedure:
A suspension of 4 g of D-glucose (0.02 mol), 2 g of sodium acetate (0.01 mol) and 20 g of acetic anhydride (0.2 mol) are heated in a 100 mL round bottomed flask under reflux. Allow the mixture to boil softly for 10 minutes.
Then the hot reaction mixture is added to 250 mL of ice water.
An oil is formed. It is stirred until it solidifies. Allow the mixture to stand for 10 minutes, stir from time to time.
Isolate the crude product using filtration through a **Büchner funnel**. Wash with 100 mL of demineralised water.
The solid is recrystallized twice in the round bottom flask with ethanol and then oven-dried at 80°C

Disposal:
Give all liquids into the provided containers the filter paper into the waste bin.

a) Calculate the maximum theoretical yield and your own yield in % relating to D-glucose.
b) Draw the structural formula of the product.
c) The melting point may possibly vary significantly. What could be the reason?

Hand in your product labellede with its number to the supervisor after measuring the yield in the provided beaker. Write the number of your beaker onto the answer sheet.

Problem 4-12 Complexometric Determination of Iron(II) and Iron(III)

In this experiment iron in two different oxidation states is determined.
At first you have to quantify the mass concentration β_3 of iron(III) by direct titration with standardized Na_2EDTA solution using 5-sulfosali-cylic acid as indicator. Then nitric acid is added to another sample and the total concentration β_{total} of iron is determined.

Equipment:
Volumetric flask (100 cm^3) with stopper, pipette (20 cm^3), pipette (10 cm^3), graduated pipette (2 cm^3), pipette control, 300 mL Erlenmeyer flask (wide mouth, 2x), spatula, burette (25 cm^3) with funnel and clamp, stand with clamps, Bunsen burner, tetrapod with plate.

Substances:

Solution of $Na_2EDTA \cdot 2\ H_2O$	c(Na_2EDTA) = 0,1 mol/L,
Solution of 5-sulfosalicylic acid	in ethanol, w = 5 % in ethanol
Hydrochloric acid,	c(HCl) = 2 mol/L (burning, C)
Nitric acid conc.,	w(HNO_3) = 65 % (burning, C)
Demineralised water	

Sample solution in a labelled 100-mL volumetric flask

Safety precautions::
Wear eye protection and protective clothing.

Procedure:

The provided solution in the 100 mL volumetric flask has to be filled up to 100 mL and mixed well to form your test solution.

To determinate iron(III) exactly 20 mL of the test solution are transferred to an Erlenmeyer flask, 0.5 mL of diluted hydrochloric acid are added and then the solution is filled up with demineralized water to appr. 100 mL.

After addition of 1 mL of 5-sulfosalicylic acid you titrate with standardized Na_2EDTA solution (c = 0.1 mol/L), end-point is the colour change from violet to slightly yellow. Shortly before the end of the titration the addition of Na_2EDTA solution should be done very slowly.

To quantify the total concentration of iron exactly 10 mL of the test solution are transferred to an Erlenmeyer flask and diluted with appr. 20 mL of demineralized water. 1 mL of conc. nitric acid is added (under the hood).

The reaction mixture is heated to boiling for at least one minute. After cooling down the solution is filled up to appr. 100 mL with demineralised water and 1 mL of 5-sulfosalicylic acid is added. Then the titration with Na_2EDTA solution is executed as described above.

Disposal:

All solutions can be poured into the sink.

a) *Calculate the mass concentration β_3 (mg/L) of iron(III) in your test solution.*

b) *Calculate the mass concentration β_{tota} (mg/L) of iron(II) and iron(III) in your test solution.*

c) *Calculate the mass concentration β_2 (mg/L) of iron(II) in your test solution.*

d) *Why was concentrated nitric acid added to the sample? Write down the reaction equation.*

Part 2

The answers to the problems of the four rounds

The solutions are more detailed than expected from the pupils. That may facilitate their comprehension in case of mistakes.

Answers Round 1

Solution to problem 1-1

a) White precipitate: tin stone (cassiterite), SnO_2, which forms on oxidative dissolution. Tin chlorides are responsible for the blue fluorescence.
Zinc reduces Sn(IV) to Sn(II) and thus makes it possible to dissolute the sparingly soluble tin stone.

b) Cuprammonium complex

$$[Cu(H_2O)_6]^{2+} + 4\ NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4\ H_2O$$

c) Precipitate: black copper sulphide and white zinc sulphate.

d) Precipitate: sparingly zinc salt $K_2Zn_3[Fe(CN)_6]_2$

$$3\ Zn^{2+} + 2\ K^+ + 2\ [Fe(CN)_6]^{4-} \rightleftharpoons K_2Zn_3[Fe(CN)_6]_2$$

e) Each sample contains 395.4 mg of alloy.

Copper:	mean value: 295.05 mg Cu.	this is 74.6 % Cu
zinc:	mean value: 264.75 mg	
	$\frac{264.75\,mg \cdot 65.39\,mg}{178.39\,mg}$ = 97.05 mg	this is 24.5 % Zn.
tin:	(100 – 74.6 – 24.5) % = 0.9 % Sn	

f) $Zn^{2+} + 2\ (NH_4)_2HPO_4 \rightleftharpoons Zn(NH_4)PO_4 + 2\ NH_4^+ + (NH_4)H_2PO_4$

(There are other possibilities of equations for this reaction)

$$2\ Zn(NH_4)PO_4 \rightleftharpoons Zn_2P_2O_7 + 2\ NH_3 + H_2O$$

g) Transition interval of methyl red: 4.4 – 6.2

$Zn(NH_4)PO_4$ is soluble in acidic and in ammoniac solutions.

Possible side reactions

<u>pH too high:</u>

$$Zn^{2+} + 2\ OH^- \rightleftharpoons Zn(OH)_2$$
$$Zn^{2+} + 4\ OH^- \rightleftharpoons [Zn(OH)_4]^{2-}(aq)$$
$$Zn^{2+} + 2\ PO_4^{3-} \rightleftharpoons Zn_3(PO_4)_2$$
$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

<u>pH too low:</u>

$$HPO_4^{2-} + H_3O^+ \rightleftharpoons H_2PO_4^- + H_2O$$
$$Zn^{2+} + 2\ H_2PO_4^- + 2\ H_2O \rightleftharpoons Zn(H_2PO_4)_2 \cdot 2\ H_2O$$
$$Zn^{2+} + H_3PO_4 \rightleftharpoons \text{no precipitation}$$

h) <u>Alkaline solution:</u>

The potential of $Zn/[Zn(OH)_4]^{2-}$ at pH = 14 is E = –1,285 V. To make a reduction of Zn(II) with copper possible the potential of Cu/Cu^{2+} has to drop at leastto the potential of Zn/Zn^{2+}. Thus the Cu(II) concentration results in

$$E = E° + \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{c(Cu^{2+})}{1\,mol/L}$$

$$-1{,}285\ V = 0{,}34\ V + \frac{8.314\ Jmol^{-1}K^{-1} \cdot 373.15\ K}{2 \cdot 96485\ Cmol^{-1}} \cdot \ln \frac{c(Cu^{2+})}{1\,mol/L}$$

$\Rightarrow$ $c(Cu^{2+}) = 1.268 \cdot 10^{-44}$ mol/L

Amount of Cu(II) ions in 1 L solution:

$Z = 6.022 \cdot 10^{23} \cdot 1.268 \cdot 10^{-44}\ L^{-1} = 7.636 \cdot 10^{-21}\ L^{-1}$

Zink(II) chloride solution:

Concentration of Zn^{2+} in the zinc (II) chloride solution(d = 1 kg/m^3) = 0.73 mol/L.

Potential of Zn/Zn^{2+}:

$$E = E° + \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{c(Zn^{2+})}{1\,mol/L}$$

$$E = E° + \frac{8.314\ Jmol^{-1}K^{-1} \cdot 373.15\ K}{2 \cdot 96485\ Cmol^{-1}} \cdot \ln \frac{0{,}73}{1} = 0.768\ V$$

Concentration of copper(II) ions (s. o.):

$$-0.768\ V = 0.34\ V + \frac{8.314\ Jmol^{-1}K^{-1} \cdot 373.15\ K}{2 \cdot 96485\ Cmol^{-1}} \cdot \ln \frac{c(Cu^{2+})}{1\,mol/L}$$

$\Rightarrow c(Cu^{2+}) = 1.172 \cdot 10^{-30}$ mol/L

Amount of Cu(II) ions in 1 L solution:

$Z = 6.022 \cdot 10^{23} \cdot 1.172 \cdot 10^{-30}\ L^{-1} = 7.058 \cdot 10^{-7}\ L^{-1}$

In both cases the copper concentration is so small that copper does not come into consideration to be a reducing agent.

i) Anode: $Zn(Zn) + 4\ OH^- \rightleftharpoons [Zn(OH)_4]^{2-} + 2\ e^- + Zn$

Cathode: $[Zn(OH)_4]^{2-} + Ag + 2\ e^- \rightleftharpoons Zn(Ag) + 4\ OH^-$

Zinc(II) is reduced, zinc(0) is oxidized.

j) Forming the alloy is favoured to depositing pure zinc metal.

k) Cadmium and zinc form an eutectic mixture but no intermetallic compound. Thus this process is not preferred.

l) The three most important Hume-Rothery-phases are the β-. γ- and ε-phases

Phase	Type of structure	Examples	$\frac{\text{sum of valence electrons}}{\text{sum of the number of atoms}}$
β-phase	body-centred cubic	CuZn	(1+2) : (1+1) = 3 : 2
γ-phase	complicated cubic structure	Cu_5Zn_8	(5+16) : (5+8) = 21 : 13
ε-phase	hexagonal close-packed	$CuZn_3$	(1+6) : (1+3) = 7 : 4

m) The general composition of the brass sample is Cu_xZn_y. The phase contains 24.45 % of copper and 75.55 % (100 % - 24.45 %) of zinc.

$$0.2445 = \frac{x \cdot M(Cu)}{x \cdot M(Cu) + y \cdot M(Zn)} \quad (1) \qquad \text{and} \qquad 0.7555 = \frac{y \cdot M(Zn)}{x \cdot M(Cu) + y \cdot M(Zn)} \quad (2)$$

(1)/(2): $\frac{0.2445}{0.7555} = \frac{x \cdot M(Cu)}{y \cdot M(Zn)}$

$M(Cu) = 63.546\ g\ mol^{-1}$ $M(Zn) = 65.39\ g\ mol^{-1} \Rightarrow$

$0.3236 = 0.9718 \cdot \frac{x}{y}$ $y = 3.003\ x$ $\Rightarrow$ $y \approx 3\ x$

stoichiometric composition of the brass sample: $CuZn_3$.

$\frac{\text{sum of valence electrons}}{\text{sum of the number of atoms}} = (1 + 6) : (1 + 3) = 7 : 4.$

An ε-phase is existent with hexagonal close-packed structure.

n) The stoichiometric composition of bronze of ε-Phase is Cu_3Sn with the same $\frac{\text{sum of valence electrons}}{\text{sum of the number of atoms}} = (3 + 4) : (3 + 1) = 7 : 4$ corresponding to the brass sample.

Mass percentage of copper:

$$\frac{3 \cdot M(Cu)}{3 \cdot M(Cu) + M(Sn)} \cdot 100\ \% = \frac{3 \cdot 63.546\ g\,mol^{-1}}{3 \cdot 63.546\ g\,mol^{-1} + 118.71\ g\,mol^{-1}} \cdot 100\% = 61.63\ \%$$

(If you took γ-Phase Cu_5Zn_8 (γ-phase) you get for bronze of the same phase $Cu_{31}Sn_8$

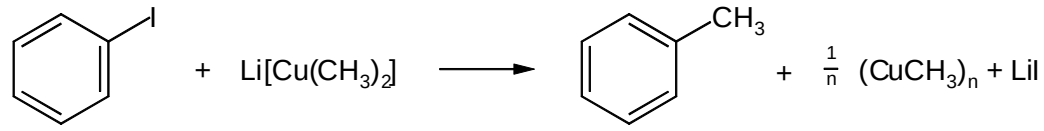
Mass percentage of copper:

$$\frac{31 \cdot M(Cu)}{31 \cdot M(Cu) + 8 \cdot M(Sn)} \cdot 100\% = \frac{31 \cdot 63.546\ g\,mol^{-1}}{31 \cdot 63.546\ g\,mol^{-1} + 8 \cdot 118.71\ g\,mol^{-1}} \cdot 100\% = 67.47\ \%)$$

o) $CH_3Li + CuI \longrightarrow \frac{1}{n}\ (CuCH_3)_n + LiI$

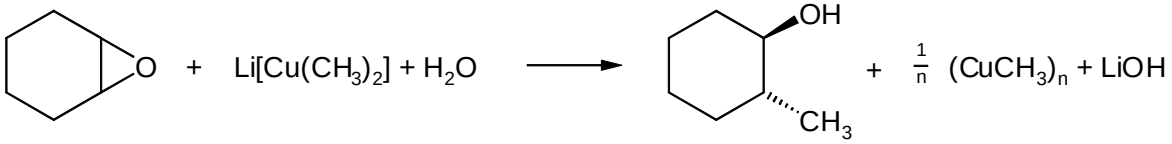
$\frac{1}{n}\ (CuCH_3)_n + CH_3Li \longrightarrow Li[Cu(CH_3)_2]$

p)



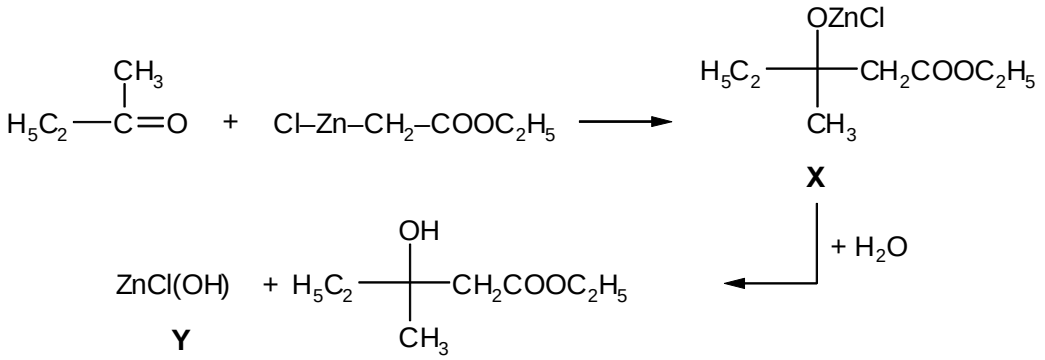
toluene
methylbenzene

q)

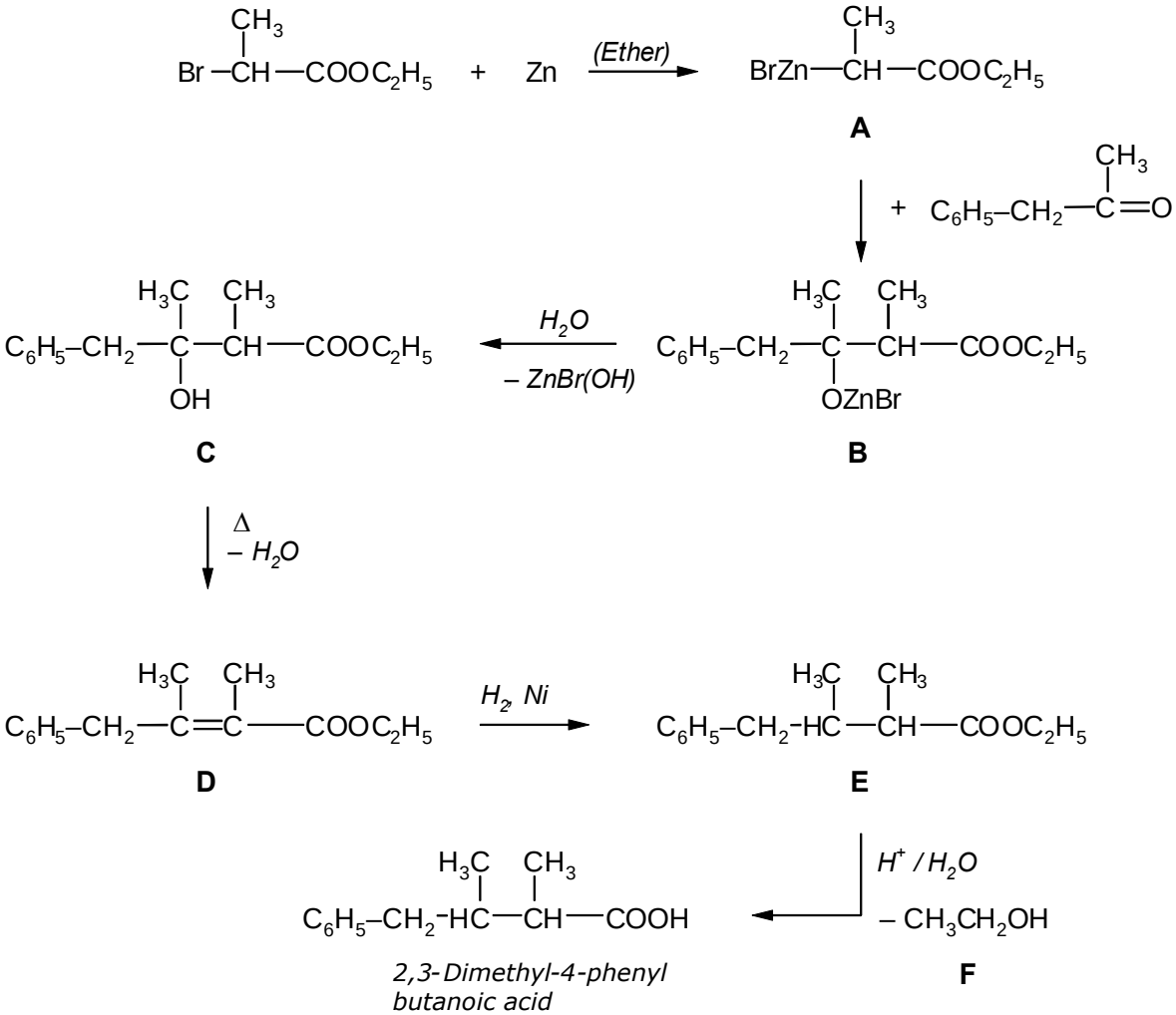


trans-2-methylcyclohexanol
or 1R,2R-2-methylcyclohexanol
or 1R,2R-2-methylcyclohexanol, resp.

r)



s)



2,3-Dimethyl-4-phenyl butanoic acid

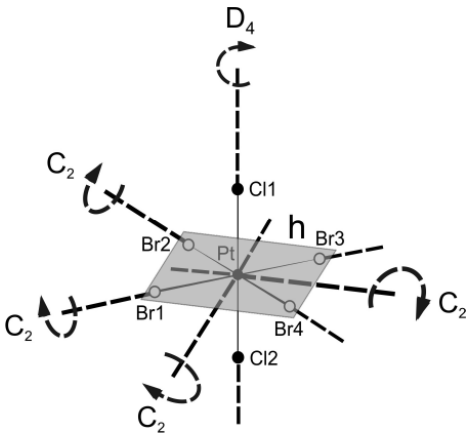
Answers Round 2

Solution to problem 2-1:

a) $[PtBr_6]^{2-}$ $[PtClBr_5]^{2-}$ *cis*-$[PtCl_2Br_4]^{2-}$ *trans*-$[PtCl_2Br_4]^{2-}$
fac-$[PtCl_3Br_3]^{2-}$ *mer*-$[PtCl_3Br_3]^{2-}$ *cis*-$[PtCl_4Br_2]^{2-}$ *trans*-$[PtCl_4Br_2]^{2-}$
$[PtCl_5Br]^{2-}$ $[PtCl_6]^{2-}$

b) D_{4h}

c) 4-fold axis (D_4) along theCl1-Pt-Cl2-bond (the axis of the highest fold number has priority).
Additionally the letter D together with the index 4 denotes that there are four 2-fold axes perpendicular to the 4-fold D_4 axis:
Two 2-fold axes along Br1-Pt-Br3 and Br2-Pt-Br4 bonds, two more in an angle of 45° to the Br-Pt-Br bonds. Perpendicular to the 4-fold axis there is a mirror plane (index h) which contains the atoms Pt, Br1, Br2, Br3 und Br4. The four 2-fold a



d) **X** = *fac*-$[PtCl_3Br_3]^{2-}$.
In the reaction of $[PtBr_6]^{2-}$ with Cl^-, $[PtClBr_5]^{2-}$ is generated in a first quick step. The chloroligand in the generated Cl-Pt-Br axis is loosened, the bromoligand is tightened according to the trans effect. Thus in a mixed substituted axes the substitution of bromine by chlorine is hindered. So in the following steps one bromoligand in each of the remaining two Br-Pt-Br axes is substituted by chlorine.

e) It is most likely that trans-$[PtCl_4Br_2]^{2-}$ and trans-$[PtCl_2Br_4]^{2-}$ form.
In the reaction of $[PtCl_6]^{2-}$ with Br^-, $[PtCl_5Br]^{2-}$ forms in a first slow step. The chloroligand in the Cl-Pt-Br axis now is loosend (trans effect) and in a following quick step replaced to generate trans-$[PtCl_4Br_2]^{2-}$. Then trans-$[PtCl_4Br_2]^{2-}$ reacts slowly to mer-$[PtCl_3Br_3]^{2-}$ which again reacts quickly to trans-$[PtCl_2Br_4]^{2-}$ according to the loosening of the chloroligand (trans effect). In the same way the product $[PtBr_6]^{2-}$ forms.

f) Molar masses of the salts:
$(TBA)_2[PtCl_5Br]$: M = 936.61 g/mol $(TBA)_2[PtCl_3Br_3]$: M = 1025.42 g/mol
x = n$(TBA)_2[PtCl_5Br]$) y = n($(TBA)_2[PtCl_3Br_3]$)

$$\frac{(x+3y)\cdot 79.9\,g/mol}{x\cdot 936.61\,g/mol + y\cdot 1025.42\,g/mol} = 0.112 \qquad x+3y = 0.112\cdot\frac{(936.61x+1025.42y)}{79.9}$$

$x + 3y = 1.313x + 1.437y$ $x = 4.994y$ $x \approx 5y$
c($(TBA)_2[PtCl_5Br]$) : c($(TBA)_2[PtCl_3Br_3]$) = 5 : 1.

g) After the substitution of the first chlorine atom the second one in the now existing F-Pt-Cl axis is tightened according to the trans effect and a further substitution of it is difficult to access. In the further course of reaction one chlorine atom in each of the residual Cl-Pt-Cl axes is substituted by fluorine.

h) Fluorine is more electronegative than chlorine and thus takes away electron density from the platinum atom. The higher the ratio of fluorine to chlorine the more electron density is taken away from the central atom. A smaller electron density results in a smaller magnetic shielding, so the chemical shift of the complex with a higher content of fluorine appears at a lower field (higher ppm values).

i) By the coupling of two adjacent nuclei signal splitting occurs. The number of multiplets, the multiplicity M, is given by $M = 2n \cdot I + 1$.
n is the number of equivalent neighbour atoms, I is their nuclear spin.
The spin of the relevant NMR active isotopes ^{195}Pt and ^{19}F amounts to I = ½. These are the only NMR active isotopes of the natural abundance of both elements. Furthermore ^{19}F is the only isotope of fluorine so always all fluorine atoms are „visible".
Platinum-fluorine-system: $M = n + 1$

Complex compounds	Number of adjacent coupling nuclei with I = ½	Multiplicity M	Relative intensities
$(TBA)_2[PtCl_6]$	0	1 (singulet)	1
$(TBA)_2[PtFCl_5]$	1	2 (doublet)	1 : 1
cis-$(TBA)_2[PtF_2Cl_4]$	2	3 (triplet)	1 : 2 : 1
fac-$(TBA)_2[PtF_3Cl_3]$	3	4 (quartet)	1 : 3 : 3 : 1

j) Relative intensities of all multiplet signals:

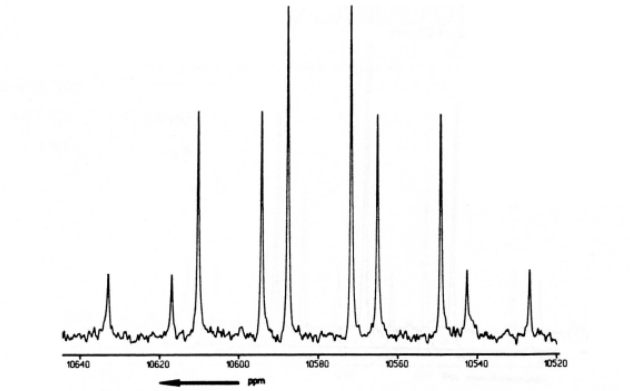
Complex compounds	Chemical shift / ppm	Relative Intensities of the single signals	Relative intensities of the muliplet signals
$(TBA)_2[PtCl_6]$	4749.93	0.242	0.242
$(TBA)_2[PtFCl_5]$	5831.01	0.242	0.484
	5845.89	0.242	
cis-$(TBA)_2[PtF_2Cl_4]$	6887.18	0.303	1.212
	6902.11	0.606	
	6917.04	0.303	
fac-$(TBA)_2[PtF_3Cl_3]$	7899.64	0.333	2.666
	7914.68	1	
	7929.72	1	
	7944.75	0.333	

$c((TBA)_2[PtCl_6])$: $c((TBA)_2[PtFCl_5])$: $c(cis\text{-}(TBA)_2[PtF_2Cl_4])$: $c(fac\text{-}(TBA)_2[PtF_3Cl_3])$

1 : 0.484 / 0.242 : 1.212 / 0.242 : 2.666 / 0.242

1 : 2 : 5 : 11

k) A quintuplet of signals with he relative intensities 1:4:6:4:1 is to be expected of the coupling of the ^{195}Pt nucleus with four magnetically equivalent ^{19}F nuclei of the symmetrically substituted F-Pt-F axes.
The signals of the quintuplet split to a doublet with relative intensities 1:1 due to the coupling of the ^{195}Pt nucleus with the ^{19}F nucleus of the asymmetrically substituted F*-Pt-Cl axis. A doublet of quintuplets results. As the coupling constant ^{1}J(PtF*) is smaller than ^{1}J(PtF) a multiplet with the relative intensities 1:1:4:4:6:6:4:4:1:1 arises.



(In the solution of the students a sketch without scale is satisfactory)

l) If the coupling constants are converted from Hz to ppm the signal centers of both quintuplets are shifted by –7.94 ppm and 7.94 ppm (half of ^{1}J(PtF*)) from the common signal center at 10580 ppm. The single signals of each quintuplet show a distance of 22.36 ppm (^{1}J(PtF)).

The chemical shifts are:

10580 ppm - 7.94 ppm – 2*22.36 ppm =	10527.34 ppm
10580 ppm + 7.94 ppm – 2*22.36 ppm =	10543.22 ppm
10580 ppm - 7.94 ppm – 22.36 ppm =	10549.7 ppm
10580 ppm + 7.94 ppm – 22.36 ppm =	10565.58 ppm
10580 ppm - 7.94 ppm =	10572.06 ppm
10580 ppm + 7.94 ppm =	10587.94 ppm
10580 ppm - 7.94 ppm + 22.36 ppm =	10594.42 ppm
10580 ppm + 7.94 ppm + 22.36 ppm =	10610.3 ppm
10580 ppm - 7.94 ppm + 2*22.36 ppm =	10616.78 ppm
10580 ppm + 7.94 ppm + 2*22.36 ppm =	10632.66 ppm

m) **1**: $Cs_2[PtF_4(C_2O_4)]$ (or $Cs_2[PtF_4(ox)]$) **2**: $Cs_2[PtF_4]$ **3**: CO_2

n) 1. The ^{195}Pt-NMR spectrum of **1** with a triplet of triplets points to two groups of fluorine atoms at the central platinum atom, which are among each group magnetically equivalent. It has to be a complex compound of the configuration cis-

$Cs_2[PtF_4L_2]$ with two equivalent ligands in cis-position or a bidentate symmetrical chelate ligand.

2. Mass percentage of carbon of $Cs_2[PtF_4(C_2O_4)]$ ($Cs_2[PtF_4(ox)]$): 3.84 %.

3. The reaction of $Cs_2[PtF_4]$ with chlorine is an oxidation and leads to a hexa- coordinated platinum(IV) compound (*trans*-$Cs_2[PtF_4Cl_2]$) maintaining the configu-ration of the Pt-F_4 plane. The ^{195}Pt NMR spectrum documents the preservation of the configuration, the observed quintuplet indicates four magnetically equivalent fluoro-ligands.

4. Carbon dioxide generated in the process is a gas und produces overpressure in the closed vessel.

5. In the infrared spectra the disappearing of the carbonyl band of the oxalato ligand of **1** is observed in the range of 1200 to 1800 cm^{-1}. The two new absorptions at 667 and 2349 cm^{-1} arise from the generated carbon dioxide (**3**).

Solution to problem 2-2

a) 1. Used volume of the reactor: $V = \frac{2}{3} \cdot 9000\ L = 6000\ L$

compound **1**: $V_1 = 100/(100+75)\cdot 6000\ L = 3428.6\ L$
compound **2**: $V_2 = 75/(100+75)\cdot 6000\ L = 2571.4\ L.$
$\rho = 1\ kg/L \Rightarrow$ $m_1 = 3428.6\ kg$ $m_2 = 2571.4\ kg$

2. $n_1 = m_1/M_1 = 3428.6\ kg/(0.1\ kg/mol) = 34285.7\ mol$
$n_2 = m_2/M_2 = 2571.4\ kg/(0.075\ kg/mol) = 34285.7\ mol$

3. $c_0 = 34285.7\ mol/6000\ L = 5.71\ mol/L$

b) Concentrations of the reactants after conversion of 96%:

$c_1(t) = c_2(t) = 0.04 \cdot c_0 = 0.04 \cdot 5.71\ mol/L = 0.2284\ mol/L$

$$c_1(t) = \frac{c_0}{1 + k \cdot t \cdot c_0} \quad \Rightarrow \quad t = \frac{1}{k} \cdot \left(\frac{1}{c_1(t)} - \frac{1}{c_0} \right)$$

$c_1(t) = 0.2284\ mol/L$ $c_0 = 5.71\ mol/L$ $k = 2.9 \cdot 10^{-4}\ L/(mol\cdot s)$
$\Rightarrow t = 14493.6\ s \approx 4\ h.$

c) 1. $$\frac{dc_3}{dt} = -\frac{dc_1}{dt} = k \cdot c_1^2.$$

$c_1 = 0.2284\ mol/L$ $k = 2.9 \cdot 10^{-4}\ L/(mol\cdot s)$ $\Rightarrow$

$$\frac{dc_3}{dt} = 2.9 \cdot 10^{-4} \frac{L}{mol \cdot s} \cdot 0.2284^2 \frac{mol^2}{L^2} = 1.5128 \cdot 10^{-5} \frac{mol}{L \cdot s}$$

$$\frac{dc_3}{dt} = 0.05446\ mol/(L\cdot h)$$

2. V = 6000 L molar mass of **3**: M_3 = 0.175 kg/mol ⇒

$$\frac{dm_3}{dt} = \frac{dc_3}{dt} \cdot V \cdot M_3 \qquad \frac{dm_3}{dt} = 0.05446 \frac{mol}{L \cdot h} \cdot 6000 L \cdot 0.175 \frac{kg}{mol} = 57.18 \text{ kg/h}$$

d) In the batch mode 6000 L · 0.96 kg/L are produced. The time requirement is 4 hours for the total set-up time and 4 hours for the reaction. Then the product rate comes to 6000 · 0.96 kg / 8 h = 720 kg/h.
In a continuously run reactor the productivity comes to 57.18 kg/h (see result c)).
The ratio is 12.6/1 in favour of the batch mode.
(Alternative data: Product rate = 606 kg/h, ratio = 19.8/1)

e) To reach a conversion of 96% takes 4 hours. The productivity has to be 720 kg/h (720 L/h). This means that the stream of reactants has to be 720 kgh^{-1}/0.96 = 750 kg/h (750 L/h). To guarantee the filling in volume a residence time of 4 h the volume V of the plug flow reactor has to be V = 750 L/h · 4 h = 3000 L.
$V = \pi \cdot r^2 \cdot l$ r = 0.05 m ⇒ $l = 3\ m^3/(\pi \cdot 0.0025\ m^2)$ l = 382 m
(Alternative data: stream of reactants = 1041.7 L/h, volume of the reactor = 5729.2 L, length of the pipe = 729.5 m)

f) 1. Used volume of the batch reactor: V = ⅔ · 9000 L = 6000 L = 6 m^3

Filling height h = diameter d = 2·r

$$V = \pi \cdot r^2 \cdot h = \pi \cdot r^2 \cdot d = 2\pi \cdot r^3 \quad \Rightarrow \quad r = \sqrt[3]{\frac{V}{2\pi}}, \qquad r = \sqrt[3]{\frac{6m^3}{2\pi}} = 0.985\,m$$

$O_B = 2\pi \cdot r \cdot h$ with h = 2r and r = 0.985 m
$O_B = 4\pi \cdot r^2$ O_B = 12.2 m^2

2. $O_R = d \cdot \pi \cdot l$ with d = 0.1 m and l = 382 m
O_R = 0.1 m · π · 382 m O_R = 120 m^2
(Alternative data: O_R = 314 m^2)

3. O_R / O_B = 120/12.2 = 9.8 in favour of the plug flow reactor.
Performing reactions with high heat development the plug flow reactor is favoured because it shows a tenfold larger exchange area.
(Alternative data: O_R /O_B = 25.7)

g) 1. Production per hour of compound 3: 57.18 kg. Generated heat Q_R:
$Q_R = \Delta H_R \cdot 57.18$ kg/M_3 with ΔH_R = -150 kJ/mol and M_3 = 0.175 kg/mol
Q_R = -150 kJ/mol · 57.18 kg/0.175 kg/mol Q_R = -49011.43 kJ
(Alternative data: Q_R = -26228.57 kJ)

2. According to a production rate of 57.18 kg/h the reactor is loaded per hour with the following masses m_{11} and m_{21} of the compounds **1** und **2:**

m_{11} = 57.18 kg · 100 g/mol / (175 g/mol) = 32.67 kg
m_{21} = 57.18 kg · 75 g/mol / (175 g/mol) = 24.51 kg

The removed mixture contains 4% of the reactants **1** and **2** with a total mass of

2.3825 kg (57.18 kg/0.96 – 57.18 kg). Additionally loaded masses m_{12} and m_{22}:

m_{12} = 2.3825 kg · 100 g/mol / (175 g/mol) = 1.36 kg

m_{22} = 2.3825 kg · 75 g/mol / (175 g/mol) = 1.02 kg

Totally added masses per hour m_1 and m_2 of the compounds **1** und **2**t:

$m_1 = m_{11} + m_{12}$ = 34.03 kg

$m_2 = m_{21} + m_{22}$ = 25.53 kg

Heat per hour (Q_1) needed for compound **1**:

- heating of the solid compound **1** from 293.15 K to the melting point 305.65 K,
- melting enthalpy ΔH_s(**1**) = 12.8 kJ/mol),
- heating the liquid compound 1 from 305.65 K to 363.15 K.

Q_1 = 1.6 kJ/(kg·K) · 34.03 kg · (305.65 K - 293.15 K)
+ 12.8 kJ/mol · 34.03 kg / 0.1 kg/mol
+ 2.4 kJ/(kg·K) · 34.03 kg · (363.15 K – 305.65 K)

Q_1 = 680.6 kJ + 4355.84 kJ + 4696.14 kJ Q_1 = 9732.58 kJ

Heat per hour (Q_2) needed for compound **2**:

Q_2 = 2.5 kJ/(kg·K)·25.53 kg·(363.15 K – 293.15 K) Q_2 = 4467.75 kJ

Total amount of heat per hour (Q_V) = $Q_1 + Q_2$

Q_V = 9732.58 kJ + 4467.75 kJ Q_V = 14200.33 kJ

(Alternative data: Q_1 = 364.27 kJ + 2331.33 kJ + 2513.47 kJ
Q_1 = 5209.07 kJ Q_2 = 2390.53 kJ Q_V = 7599.6 kJ)

3. Total amount of heat per hour (Q_{tot}) released in the reactor:

$Q_{tot} = Q_R + Q_V$ Q_{tot} = -49011.43 kJ + 14200.33 kJ Q_{tot}= -34811.1 kJ

Per hour 34811.1 kJ have to be taken away by the cooling water.

With a difference of temperature of 35 K between inlet and outlet you need

$m_{water} = |Q_{tot}| / c_p(water) / \Delta T$

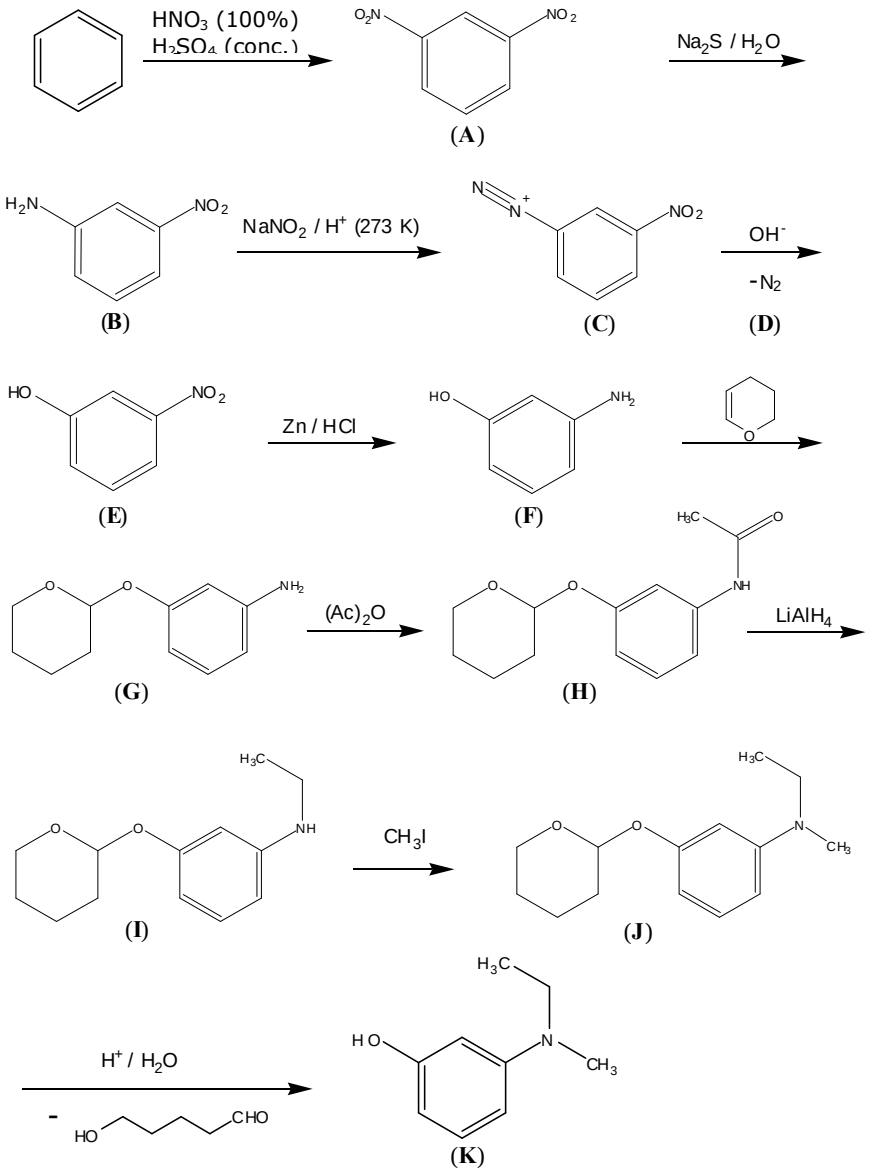
m_{water} = 34811.1 kJ / 4.18 kJ/(kg · K) / 35 K m_{Wasser} = 237.94 kg

stream of cooling water: 237.94 L/h ≈ 238 L/h

(Alternative data: Q_{tot} = -18628.97 kJ, m_{water} = 127.3 kg ⇒ 127.3 L/h)

Solution to problem 2-3

a)



b) Aromatic nitration is an electrophilic aromatic substitution with the nitronium ion, NO_2^+, as electrophile. It is generated from HNO_3 in strongly acidic solutions:

$$HNO_3 + H_3O^+ \rightleftharpoons H_2NO_3^+ + H_2O \qquad H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O$$

However, the autoprotolysis equilibrium of nitric acid lies on the side of the reactants and hence the nitrating effect of nitric acid alone is very weak:

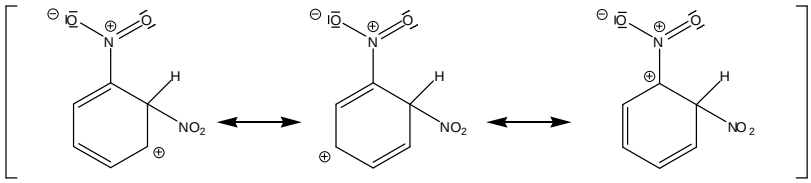
$$HNO_3 + HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$

By adding concentrated sulfuric acid the concentration of the nitronium ions is considerably raised:

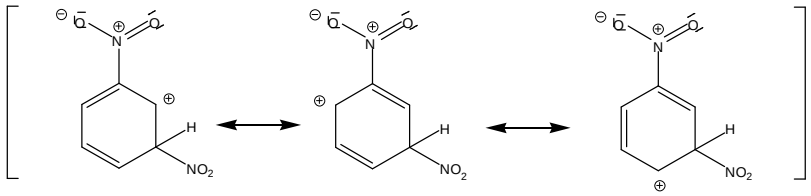
$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

c)

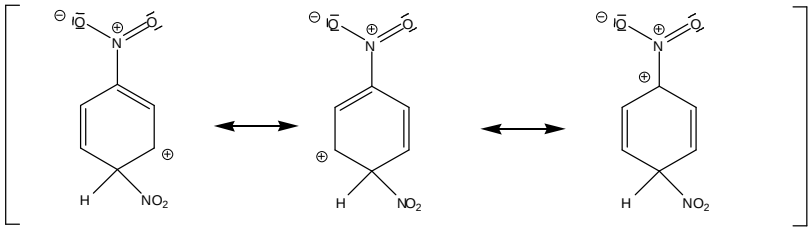
ortho



meta



para

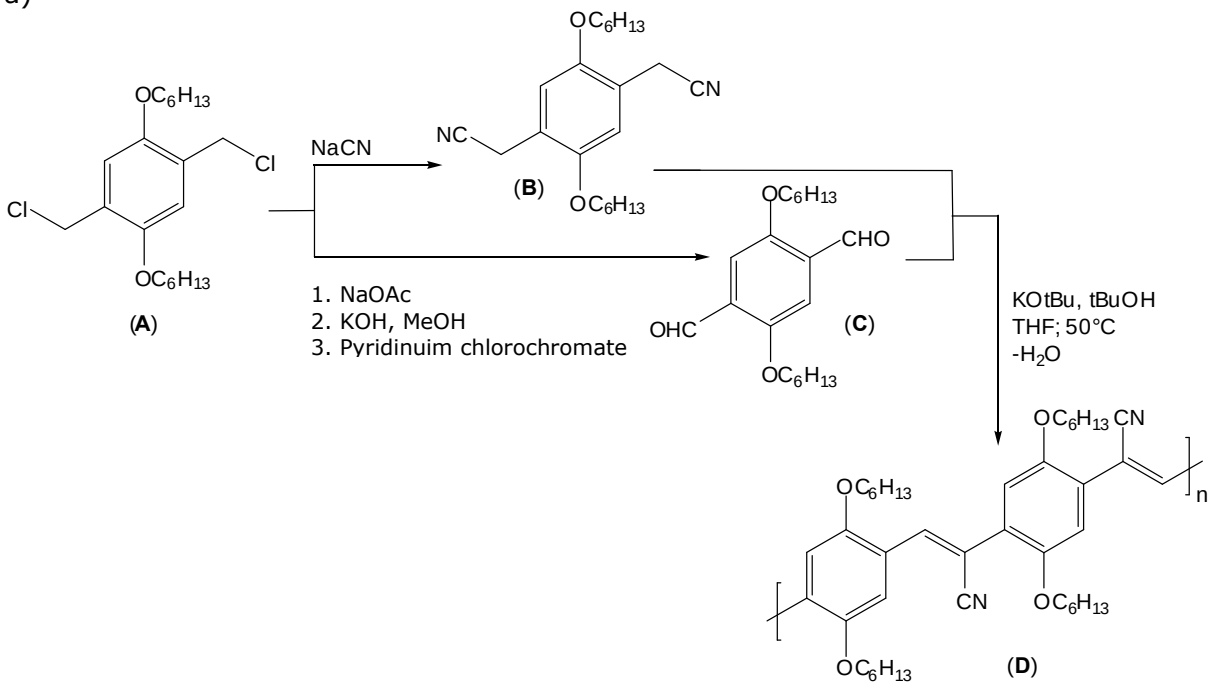


d) The NO_2 group is a substituent with an electron-withdrawing resonance effect (-M). This effect deactivates a further substitution at all positions of the ring. This deactivation is most strongly felt at the ortho and para position with a least stable mesomeric structure with a positive charge on two adjacent atoms. As a result the ortho and para intermediates are less stable so reaction with NO_2^+ occurs still more easily at the meta position.

e) The reaction with 3,4-dihydro-2H-pyran (C_5H_8O) protects the hydroxyl group of **F**. Otherwise this hydroxyl group would react in the next step of synthesis with acetic anhydride to form an acetic ester.

Solution to problem 2-4

a)



b) Knoevenagel condensation

c) 1. Polycondensation

2. In each step of coupling a small molecule, in this case water, is split off. In doing so the mean molar mass of the polymer is doubled. After the first coupling step which corresponds to a conversion of 50% referring to the maximal number of possible bonds, there exist (statistically) dimers. In the next coupling step (conversion 75%) tetramers form and so on.
The mean molar mass increases in the beginning very slowly and only at high conversions very steeply because the chain length doubles in each step (so called step-growth polymerisation)

d) (1) As it is a polycondensation very high conversions have to be reached in order to achieve high molar masses. Therefore it is important to start with both monomers (and thus with their functional groups, too) exactly with a 1:1 ratio.

(2) Impurities (foreign matter) may react with the functional groups and so stop the reaction. Then in a polycondensation process there are only low-molecular polymers generated (e.g. at a conversion of 98% only an average of 64 monomers per polymer are coupled).

Answers Round 3 Test 1

Solution to problem 3-01

a) B, D, E b) B, E c) C d) B e) B f) A g) E h) A, C i) D

Solution to problem 3-02

a) $p(OH) = 3.5 \quad \Rightarrow \quad c(OH) = 10^{-3.5}$ mol/L $\quad \Rightarrow c(Mg^{2+}) = ½ \cdot 10^{-3.5}$ mol/L

$S = 1.6 \cdot 10^{-4}$ mol/L $S' = S \cdot M(Mg(OH)_2)$ $S' = 9.3$ mg/L

b) $K_L = c(Mg^{2+}) \cdot c(OH^-)^2 / (mol/L)^3 = ½ \cdot (10^{-3.5})^3$ $K_L = 1.6 \cdot 10^{-11}$

c) $c(Mg^{2+}) = x = S^*$ $c(OH^-) = 0.01$ mol/L $+ 2x \approx 0.01$ mol/L

$$S^* = \frac{K_L \cdot (mol/L)^3}{c^2(OH^-)} = \frac{1.6 \cdot 10^{-11}\,(mol/L)}{0.01^2}$$ $S^* = 1.6 \cdot 10^{-7}$ mol/L

d) $n(HCl) = 0.1\ L \cdot 0{,}1\ mol/L = 0.01$ mol

$n(Mg(OH)_2 = 10\ g / 58.32\ g \cdot mol^{-1} = 0.17$ mol

$Mg(OH)_2$ is in large excess and the hydrochloric acid will be completely neutralised:

$$Mg(OH)_2 + 2\ H_3O^+ \longrightarrow Mg^{2+} + 4\ H_2O$$

The reaction produces $c(Mg^{2+}) = 0.05$ mol/L. Then $Mg(OH)_2$ dissolves in the solution

$c(Mg^{2+})_{total} = 0.05$ mol/L $+ x \approx 0.05$ mol/L

$$c(OH^-) = \sqrt{\frac{K_L \cdot (mol/L)^3}{c(Mg^{2+})}} = \sqrt{\frac{1.6 \cdot 10^{-11} \cdot (mol/L)^3}{0.05\,mol/L}}$$ $c(OH^-) = 1.79 \cdot 10^{-5}$ mol/L

$\Rightarrow pOH = 4.75$ $pH = 14i - 4.75$ $pH = 9.25$

Solution to problem 3-03

a) $\Delta H° = (-1575.0 + 1.5 \cdot (-241.8) - (-2021.0))\ kJ \cdot mol^{-1}$ $\Delta H° = 83.3\ kJ \cdot mol^{-1}$

$n = m/M$ $n(CaSO_4 \cdot 2H_2O) = 1000g/172.18\ gmol^{-1} = 5.808$ mol

$\Delta H°(1\ kg) = 83.3\ kJ \cdot mol^{-1} \cdot 5.808$ mol $\Delta H°(1\ kg) = 484$ kJ

b) $\Delta H° = 83.3\ kJ \cdot mol^{-1}$

$\Delta S° = (130.5 + 1.5 \cdot 188.6 - 194.0)\ JK^{-1}mol^{-1} = 219.4\ JK^{-1}mol^{-1}$

$\Delta G° = \Delta H° - T \cdot \Delta S°$ $\Delta G° = (83300 - 298.15 \cdot 219.4)\ J \cdot mol^{-1} = 17886\ J \cdot mol^{-1}$

$\Delta G° = -R \cdot T \cdot \ln K$ $\ln K = -17886\ J \cdot mol^{-1} / (8.314\ JK^{-1}mol^{-1} \cdot 298.15\ K)$

$\ln K = -7.216$ $K = 7.35 \cdot 10^{-4}$ $K = p(H_2O)^{3/2} / p(Standard)^{3/2}$

$p(H_2O) = (7.35 \cdot 10^{-4})^{2/3}$ bar $p(H_2O) = 8.14 \cdot 10^{-3}$ bar

c) $p(H_2O) = 0.500$ bar $K = 0.500^{3/2}$ $K = 0.354$

$\Delta G° = -R \cdot T \cdot \ln K$ and $\Delta G° = \Delta H° - T \cdot \Delta S° \Rightarrow -R \cdot T \cdot \ln K = \Delta H° - T \cdot \Delta S°$

$$T = \frac{\Delta H°}{\Delta S° - R \cdot \ln K}$$ $$T = \frac{83300}{219.4 - 8.314 \cdot \ln 0.354}\,K$$ $T = 365$ K. $\vartheta = 92°C$

d) $\Delta E = E°(right) - E°(left) = 0.40\ V - (-0.44V)$ $\Delta E = 0.84$ V

e) $2\ Fe + O_2 + 2\ H_2O \longrightarrow 2\ Fe^{2+} + 4\ OH^-$

f) $\Delta G° = - n \cdot F \cdot \Delta E$ $\quad \Delta G° = - 4 \cdot 96485 \cdot 0.84\ Jmol^{-1}$ $\quad \Delta G° = - 3.24 \cdot 10^5\ Jmol^{-1}$

$\Delta G° = - R \cdot T \cdot \ln K$ $\quad \ln K = 130.7$ $\quad K = 5.78 \cdot 10^{56}$

g) $Q = I \cdot t$ $\quad Q = 0.12\ A \cdot 24 \cdot 60 \cdot 60\ s$ $\quad Q = 10368\ C$

$n(e^-) = Q/F$ $\quad n(e^-) = 10368\ C/(96485\ C \cdot mol^{-1})$ $\quad n(e^-) = 0.1075\ mol$

$m(Fe) = n(Fe) \cdot M(Fe) = 1/2 \cdot 0.1075\ mol \cdot 55.85\ gmol^{-1})$ $\quad m(Fe) = 3.00\ g$

h) $K = c(Fe^{2+})^2 \cdot c(OH^-)^4 / p(O_2)$

$$\Delta E(cell) = \Delta E°(cell) - \frac{R \cdot T}{4 \cdot F} \cdot \ln \frac{c(Fe^{2+})^2 \cdot c(OH^-)^4}{p(O_2)}$$

$pH = 9.00 \Rightarrow c(OH^-) = 1.00 \cdot 10^{-5}\ mol/L.$

$$\Delta E(cell) = 0.84\ V - \frac{8.314 \cdot 298.15}{4 \cdot 96485} V \cdot \ln \frac{0.015^2 \cdot (1.00 \cdot 10^{-5})^4}{0.700}$$

$\Delta E(cell) = 1.19\ V$

Solution to problem 3-04

A: Zn^{2+}	-	$Zn^{2+} + Cl^-$	$\longrightarrow$	no reaction
	-	$Zn^{2+} + 2\ NH_3 + 2\ H_2O$	$\longrightarrow$	$Zn(OH)_2\,(s) + 2\ NH_4^+$
		$Zn(OH)_2\,(s) + 4\ NH_3$	$\longrightarrow$	$[Zn(NH_3)_4]^{2+} + 2\ OH^-$
	-	$Zn^{2+} + 2\ OH^-$	$\longrightarrow$	$Zn(OH)_2\,(s)$
		$Zn(OH)_2\,(s) + 2\ OH^-$	$\longrightarrow$	$[Zn(OH)_4]^{2-}$
B: Ag^+	-	$Ag^+ + Cl^-$	$\longrightarrow$	$AgCl\,(s)$
	-	$Ag^+ + NH_3 + H_2O$	$\longrightarrow$	$AgOH\,(s) + NH_4^+$ (oder $Ag_2O\ (s)$)
		$AgOH\ (s) + 2\ NH_3$	$\longrightarrow$	$[Ag(NH_3)_2]^+ + OH^-$
	-	$Ag^+ + OH^-$	$\longrightarrow$	$AgOH\,(s)$
		$2\ AgOH\ (s)$	$\longrightarrow$	$Ag_2O + H_2O$
C: Al^{3+}	-	$Al^{3+} + Cl^-$	$\longrightarrow$	no reaction
	-	$Al^{3+} + 3\ NH_3 + 3\ H_2O$	$\longrightarrow$	$Al(OH)_3(s) + 3\ NH_4^+$
		$Al(OH)_3$ does not dissolve in an excess of NH_3		
	-	$Al^{3+} + 3\ OH^-$	$\longrightarrow$	$Al(OH)_3\,(s)$
		$Al(OH)_3\,(s) + OH^-$	$\longrightarrow$	$[Al(OH)_4]^-$
D: Ca^{2+}	-	$Ca^{2+} + Cl^-$	$\longrightarrow$	no reaction
	-	$Ca^{2+} + NH_3$	$\longrightarrow$	no reaction
	-	$Ca^{2+} + 2\ OH^-$	$\longrightarrow$	$Ca(OH)_2\,(s)$
E: Pb^{2+}	-	$Pb^{2+} + 2\ Cl^-$	$\longrightarrow$	$PbCl_2\,(s)$
	-	$Pb^{2+} + 2\ NH_3 + 2\ H_2O$	$\longrightarrow$	$Pb(OH)_2\,(s) + 2\ NH_4^+$
		(insoluble in an excess of NH_3)		
	-	$Pb^{2+} + 2\ OH^-$	$\longrightarrow$	$Pb(OH)_2\,(s)$
		$Pb(OH)_2\,(s) + OH^-$	$\longrightarrow$	$[Pb(OH)_3]^-$

Solution to problem 3-05

a) $M(C_6H_8O_6) = 176.12$ g/mol

excreted remainder = 0.94 g/1.5 L . $\frac{0.94\,g}{176.12\,g/mol \cdot 1.5L} = 3.56 \cdot 10^{-3}$ mol/L

	$C_6H_8O_6 + H_2O \longrightarrow$	$C_6H_7O_6^-$ +	H_3O^+
initial in mol/L	$3.56 \cdot 10^{-3}$	0	0
equilibrium n mol/L	$3.56 \cdot 10^{-3} - x$	x	x

$10^{-4.17} = \frac{x^2}{3{,}56 \cdot 10^{-3} - x}$ x mol/L = $c(H_3O^+)$ = $4.58 \cdot 10^{-4}$ mol/L pH = 3.34

Compared to pK_{a1}, pK_{a2} is so small that the second step of protolysis does not contribute to the H_3O^+ concentration using 3 significant figures.

b) pH = 6.60 $c(H_3O^+)/c_0 = 10^{-6.60}$

$[c(H_3PO_4) + c(H_2PO_4^-) + c(HPO_4^{2-}) + c(PO_4^{3-})]/c_0 = 0.160$

$a + b + c + d = 0.160$ (1)

$10^{-2.15} = \frac{b \cdot 10^{-6.60}}{a}$ $a = b \cdot 10^{-4.45}$ (2)

$10^{-7.21} = \frac{c \cdot 10^{-6.60}}{b}$ $b = c \cdot 10^{+0.61}$ (3)

$10^{-12.36} = \frac{d \cdot 10^{-6.60}}{c}$ $c = d \cdot 10^{+5.76}$ (4)

(2) in (1): $b \cdot (1+10^{-4.45}) + c + d = 0.160$ (5)

(3) in (5) $c \cdot (1+10^{0.61} \cdot (1+10^{-4.45})) + d = 0.160$ (6)

(4) in (6) $c \cdot (1+10^{0.61} \cdot (1+10^{-4.45})) + c \cdot 10^{-5.76} = 0.160$

$c = 0.160/[(1+10^{0.61} \cdot (1+10^{-4.45}) + 10^{-5.76}]$

$c = 3.15 \cdot 10^{-2}$	$c(HPO_4^{2-}) = 3.15 \cdot 10^{-2}$ mol/L
$b = 1.28 \cdot 10^{-1}$	$c(H_2PO_4^-) = 1.28 \cdot 10^{-1}$ mol/L
$a = 4.54 \cdot 10^{-6}$	$c(H_3PO_4) = 4.54 \cdot 10^{-6}$ mol/L
$d = 5.47 \cdot 10^{-8}$	$c(PO_4^{3-}) = 5.47 \cdot 10^{-8}$ mol/L

The calculation is much simpler if you assume in an initial calculation that at pH = 6.60 only $H_2PO_4^-$ and HPO_4^{2-} are present. The results are the same.

c) The buffer consists of $H_2PO_4^-$ and HPO_4^{2-}, $pH = pK_a + \lg \frac{c(HPO_4^{2-})}{c(H_2PO_4^-)}$.

$3.56 \cdot 10^{-3}$ mol/L of ascorbic acid react with HPO_4^{2-} to form $(3.15 \cdot 10^{-2} - 3.56 \cdot 10^{-3})$ mol/L of HPO_4^{2-} and $(1.28 \cdot 10^{-1} + 3.56 \cdot 10^{-3})$ mol/L of $H_2PO_4^-$.

$pH = 7.21 + \lg \frac{0.0279}{0.132}$ pH = 6.54

(alternatively pH = 6.56)

Solution to problem 3-06

a) $3\ C_6H_8O_6 + IO_3^- \longrightarrow 3\ C_6H_6O_6 + 3\ H_2O + I^-$

b) $IO_3^- + 5\ I^- + 6\ H_3O^+ \longrightarrow 3\ I_2 + 9\ H_2O$

c) $I_2 + 2\ S_2O_3^{2-} \longrightarrow 2\ I^- + S_4O_6^{2-}$

18.6 mL of $S_2O_3^{2-}$ solution contain $n(S_2O_3^{2-}) = 1.86 \cdot 10^{-4}$ mol

this corresponds to $n(I_2) = ½ \cdot 1.86 \cdot 10^{-4}$ mol in 10 mL of the iodate solution. To form this amount of iodine you need $n(IO_3^-) = \frac{1}{3} \cdot n(I_2) = \frac{1}{6} \cdot 1.86 \cdot 10^{-4}$ mol of IO_3^-

$\Rightarrow$ $c(IO_3^-) = \frac{1}{6} \cdot 1.86 \cdot 10^{-4}$ mol / 0.010 L $\quad c(IO_3^-) = 3.10 \cdot 10^{-3}$ mol/L

d) $n(IO_3^-) = 15.4 \cdot 10^{-3}$ L $\cdot\ 3.5 \cdot 10^{-3}$ mol/L $= 5.39 \cdot 10^{-5}$ mol

$3 \cdot n(IO_3^-) = 1.617 \cdot 10^{-4}$ mol

in 250 mL of ascorbic acid: $n_{250}(C_6H_8O_6) = 1.617 \cdot 10^{-3}$ mol

$M(C_6H_8O_6) = 176.12$ g/mol

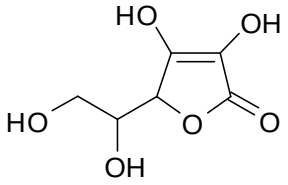
$m(C_6H_8O_6) = 176.12$ g/mol $\cdot\ 1.617 \cdot 10^{-3}$ mol $\quad m(C_6H_8O_6) = 0.285$ g

e) $2\ C_6H_8O_6 + IO_3^- + 2\ H^+ + Cl^- \longrightarrow 2\ C_6H_6O_6 + 3\ H_2O + ICl$

f) $V_5 = \frac{3}{2} \cdot V_1$ or $V_1 = \frac{2}{3} \cdot V_5$

Solution to problem 3-07

d) There are two stereogenic centres (*), which account for 4 different stereoisomers:



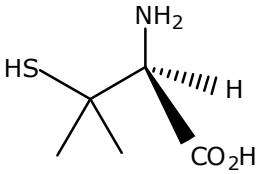
I) *R,R*-form II) *S,S*-form

III) *R,S*-form IV) *S,R*-form

I) and II) , III) and IV) are pairs of enantiomers,

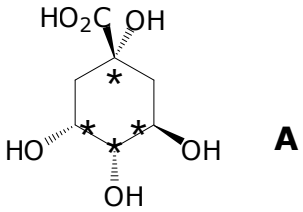
I) and III) , I) and IV), II) and III) , II) and IV) are pairs of diastereomers.

b)



(*S*)-Penicillamine

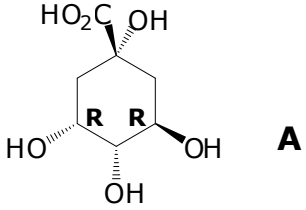
c)



A

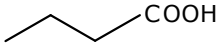
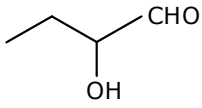
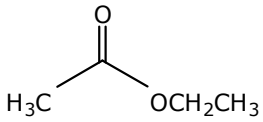
A contains 4 stereogenic centres (*)

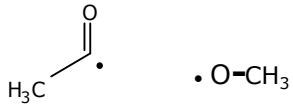
d) You can assign the R-configuration to two stereogenic centres unambiguously.



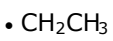
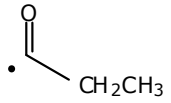
A

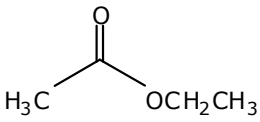
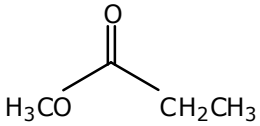
At the remaining two stereogenic centres the CIP convention fails to find a decision about the priority of two groups. They are equivalent following this convention. Thus quinic acid has a chiral molecule at which you cannot distinguish between all different enantiomers/diastereomers if you use the CIP convention. There are other rules of labeling.

e) e.g.   

f) The singlet with 3 protons is characteristic for an isolated and CH_3 group with no protons on the adjacent atom e.g. 

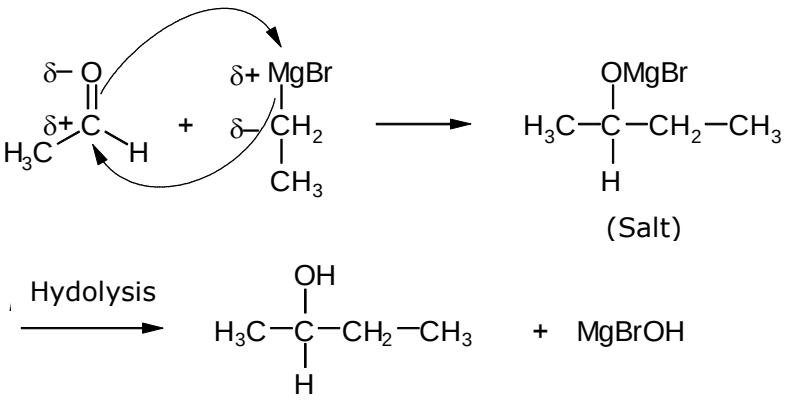
The triplet shows coupling interaction of 3 equivalent protons with 2 equivalent protons at the adjacent C atom, and the quartet shows coupling interaction of 2 equivalent protons with 3 equivalent protons e.g.

 and 

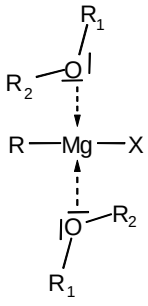
⇒ two suggestions: **A**:  and **B**: 

The chemical shift of the CH_2 group is approximately 4.1 ppm. This is a hint that it is bonded directly to an oxygen atom.
The chemical shift of the methyl group is approximately 2 ppm, a hint to the adjacent carbonyl group ⇒ proposal **A**.

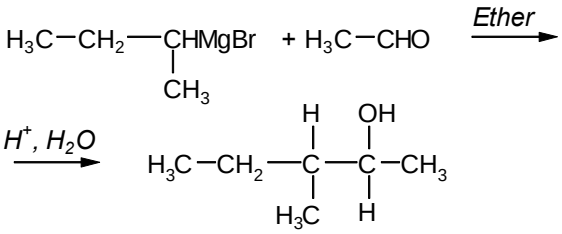
Solution to problem 3-08

a) 

b) Two molecules of ether coordinate to the Grignard compound R-Mg-X:
This leads to an electron octet at the metal centre. The magnesium complex becomes soluble, aggregation is prevented and the reactivity is enhanced.



c)

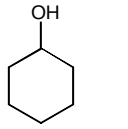


d) X: $H_3C–CO–CH_3$ (acetone)

e) $2\ K_2Cr_2O_7 + 8\ H_2SO_4 + 3\ C_2H_5OH \longrightarrow 2\ Cr_2(SO_4)_3 + 2\ K_2SO_4 + 3\ CH_3COOH + 11\ H_2O$

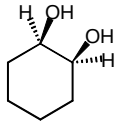
Solution to problem 3-09

a)



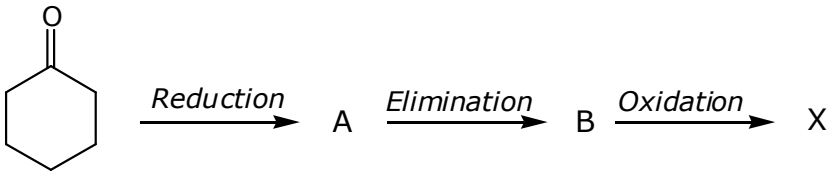
Compound A

Compound B

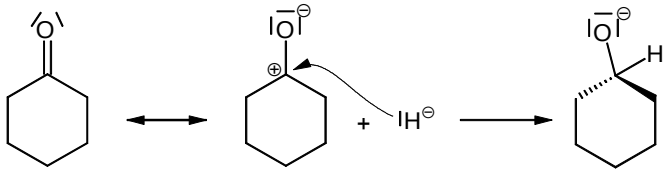


Compound X:
1,2-cis-Cyclohexanediol

b)



c) Nucleophilic addition:



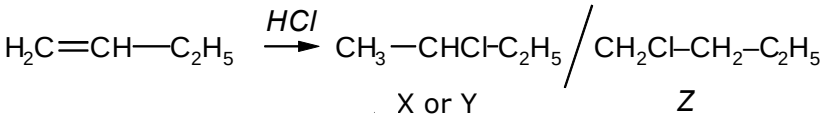
H^- reacts as nucleophile. Actually more complex „hydride structures" are existent, H^- has to be regarded as a representative of them.

Solution to problem 3-10

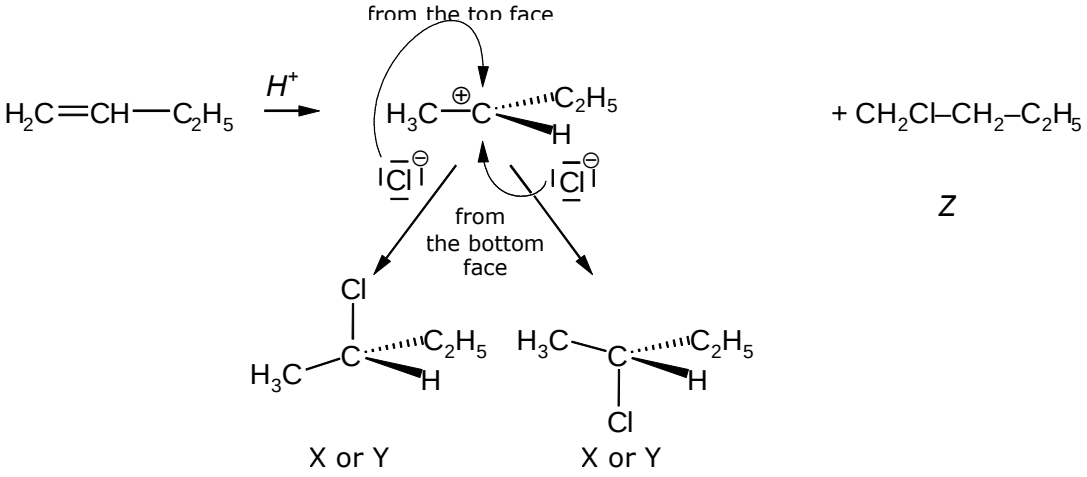
a)

A: Initial compound	$CH_3CH{=}CH_2$
B: Intermediate of the side reaction: Primary carbocation (higher energy)	$CH_3CH_2-\overset{\oplus}{C}H_2$
C: Intermediate of the main reaction: Secondary carbocation (lower energy)	$CH_3\overset{\oplus}{C}H-CH_3$
D: Product of the side reaction	$CH_3CH_2CH_2Cl$
E: Product of the main reaction	$CH_3CHClCH_3$

b)



c)



A racemate forms: There is no preference of the Cl attack on the secondary carbocation from the top or the bottom face.

d) Only one main product forms as C(1) is not a stereogenic centre: 1-chloro-1-methylcyclobutane.
(There are more side products : (1R,2S)-1-chloro-2-methylcyclobutane,
(1R,2R)-1-chloro-2-methylcyclobutane,
(1S,2R)-1-chlor-2-methylcyclobutane,
(1S,2S)-1-chloro-2-methylcyclobutane.)

Answers of Round 3 Test 2

Solution to problem 3-11

a) A, D b) C, D c) A, B, D d) C e) B, E

f) A (Initial reaction $SO_2 + 2\ H_2S \longrightarrow \frac{3}{8}\ S_8 + 2\ H_2O$ that is $c(H_3O^+)$ decreases, pH increases. Not until all H_2S has reacted SO_2 reacts with water to form sulfurous acid.)

g) C h) E

Solution to problem 3-12

a) $Fe + H_2SO_4 \longrightarrow Fe^{2+} + SO_4^{2-} + H_2$

$n_{max}(Fe) = \frac{0.5 \cdot 10^6\ g}{55.85\ g/mol} = 8953\ mol$ $n(H_2SO_4) = \frac{225 \cdot 10^3\ g}{98.09\ g/mol} = 2294\ mol$

$\Rightarrow$ $n(H_2) = 2294\ mol$ $V = n \cdot R \cdot T/p$ $V = 54.41\ m^3$

buoyancy = (mass of the replaced air) · g

$m(1\ m^3\ of\ air) = m(0.210\ m^3\ of\ O_2) + m(0.79\ m^3\ of\ N_2)$

$n = p \cdot V/(R \cdot T)$ $n(O_2) = 8.853\ mol$ $n(N_2) = 33.31\ mol$

$m = n \cdot M$ $m(O_2) = 283.3\ g$ $m(N_2) = 932.7\ g$

buoyancy $= 54.41 \cdot m \cdot (1\ m^3\ Luft) \cdot 9.81\ m \cdot s^{-2} = 54.41\ m^3 \cdot 1.216\ kgm^{-3} \cdot 9.81\ ms^{-2}$

buoyancy = 649 N

b) $Fe + 2\ H_3O^+ \longrightarrow Fe^{2+} + H_2 + 2\ H_2O$

$Fe_2O_3 + 6\ H_3O^+ \longrightarrow 2\ Fe^{3+} + 9\ H_2O$

$2\ Fe^{3+} + SO_3^{2-} + 3\ H_2O \longrightarrow 2\ Fe^{2+} + SO_4^{2-} + 2\ H_3O^+$

$SO_3^{2-} + 2\ H_3O^+ \longrightarrow SO_2 + 3\ H_2O$

$MnO_4^- + 5\ Fe^{2+} + 8\ H_3O^+ \longrightarrow Mn^{2+} + 5\ Fe^{3+} + 12\ H_2O$

$n(Fe_{total}) = 5 \cdot n(MnO_4^-) = 5 \cdot 0.0198\ mol/L \cdot 36.45 \cdot 10^{-3}\ L = 3.609 \cdot 10^{-3}\ mol$

$n(Fe_{total}) = n(Fe) + 2 \cdot n(Fe_2O_3)$ $n(Fe) = 3.609 \cdot 10^{-3}\ mol - 2 \cdot n(Fe_2O_3)$

$m_{total} = n(Fe) \cdot M(Fe) + n(Fe_2O_3) \cdot M(Fe_2O_3)$

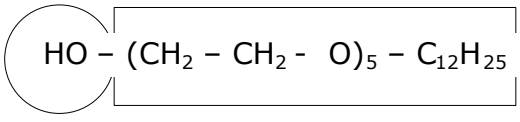
$0.2145\ g = [3.609 \cdot 10^{-3}\ mol - 2 \cdot n(Fe_2O_3)] \cdot 55.85\ g/mol + n(Fe_2O_3) \cdot 159.7\ g/mol$

$n(Fe_2O_3) = 2.695 \cdot 10^{-4}\ mol$ $m(Fe_2O_3) = 0.04304\ g \Rightarrow$ 20.07 % Fe_2O_3

79.93 % Fe

Solution to problem 3-13

a)



b) non ionic

c) $Q = C_p \cdot \Delta T = 452\ J \cdot K^{-1} \cdot 1.25 \cdot 10^{-4}\ K$ $Q = 0.0565\ J$

d) 1. addition: all micelles converted to monomers.

2. addition: 0.74/1.25 of the micelles converted to monomers, the rest remained as micelles.

3. addition: No more monomers were formed.

e) After addtion of $8 \cdot 10^{-6}$ L·(1+ 0.74/1.25)·0.5 mol/L the critical surfactant concentration was reached in 100 cm^3 of the solution.

$c_K = 8 \cdot 10^{-6} \cdot (1 + 0.74/1.25) \cdot 0.5$ mol / 0.1 L $c_K = 6.368 \cdot 10^{-5}$ mol·L^{-1}

f) $\Delta G° = -RT \cdot \ln c_K^{-1} = -8.314$ $JK^{-1}mol^{-1} \cdot 298$ K· ln $(6.368 \cdot 10^{-5})^{-1}$

$\Delta G° = -23.937$ kJ·mol^{-1} (1)

You may assume that approximately the total amount of A was existent in the form of micelles. Thus the total amount of the added surfactant A is converted from $A_{micelle}$ into $A_{monomer}$.

$n = 8 \cdot 10^{-6}$ L · (1 + 0.74/1.25) · 0.5 mol/L = $6.368 \cdot 10^{-6}$ mol

$$\Delta H° = -\frac{Q}{n} = -\frac{452\ J K^{-1} \cdot (1.25 + 0.74) \cdot 10^{-4} K}{6.368 \cdot 10^{-6}\ mol} = -14.125\ kJ \cdot mol^{-1}$$

This heat is released if micelles convert to monomers.

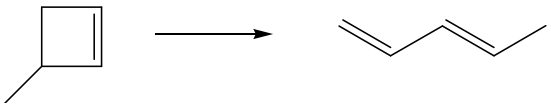
For the reverse process is $\Delta H° = +14.125$ kJ·mol^{-1} (2)

$\Delta G° = \Delta H° - T\Delta S° \Leftrightarrow \Delta S° = (\Delta H° - \Delta G°)/T$

insert (1) and (2): $\Delta S° = 127.7$ J·K^{-1}·mol^{-1}

Solution to problem 3-14

a) Driving force:
- release of the high ring strain,
- formation of a conjugated system



1,3-Pentadiene

b) The plot of v = - dc/dt as a function of p gives a straight line through (0/0):

v = m · p with m = $4.22 \cdot 10^{-11}$ mol·L^{-1}·s^{-1}·Pa^{-1}

or m = $4.22 \cdot 10^{-7}$ mol·m^{-3}·s^{-1}·Pa^{-1}

p is proportional to c.

⇒ reaction order = 1 : v = k · c

m · p = k · c

p·V = n·R·T and c = n/V

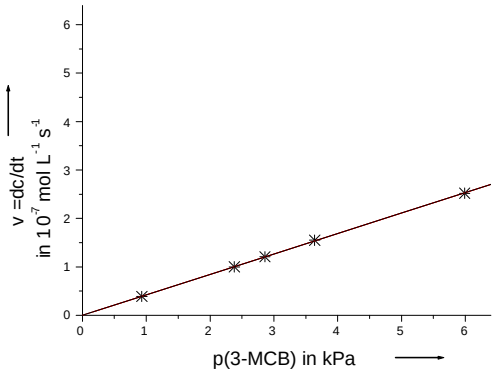
⇒ k = m · (p/c) (1)

p/c = R · T = 8.314 J·mol^{-1}·K^{-1} · 396.65 K

p/c = 3297.7 J·mol^{-1} = 3297.7 Pa·mol^{-1}·m^3

inserted in (1):

k = $4.22 \cdot 10^{-11}$ mol·L^{-1}·s^{-1}·Pa^{-1}·3297.7 Pa·mol^{-1}·m^3 $k = 1.39 \cdot 10^{-4}$ s^{-1}



c) Arrhenius equation $k = A \cdot e^{-Ea/(R \cdot T)}$ ⇒ $A = k/(e^{-Ea/(R \cdot T)})$

$$A = \frac{1.50 \cdot 10^{-4}\ s^{-1}}{e^{132090\ J/mol/(8.314\ Jmol^{-1}K^{-1} \cdot 396.65\,K)}}$$

k_1

$A = 6.03 \cdot 10^{-22}$ s^{-1}

d) $A + A \longrightarrow A^* + A$

$A^* \xrightarrow{k_2} B$

$A^* + A \xrightarrow{k_3} A + A$

e) $\frac{d[A^*]}{dt} = 0 = k_1 \cdot [A]^2 - k_2[A^*] - k_3 \cdot [A^*] \cdot [A]$

f) from e) $[A^*] = \frac{k_1 \cdot [A]^2}{k_3 \cdot [A] + k_2} \quad \Rightarrow \quad \frac{d[B]}{dt} = k_2 \cdot [A^*] = \frac{k_2 \cdot k_1 \cdot [A]^2}{k_3 \cdot [A] + k_2}$

g) high pressure of A $\Rightarrow$ $k_3 \cdot [A] >> k_2$

$\frac{d[B]}{dt} = \frac{k_2 \cdot k_1 \cdot [A]^2}{k_3 \cdot [A] + k_2} \approx \frac{k_2 \cdot k_1 \cdot [A]^2}{k_3 \cdot [A]} = \frac{k_2 \cdot k_1}{k_3} \cdot [A]$ reaction order = 1

h) low pressure of A $\Rightarrow$ $k_3 \cdot [A] << k_2$

$\frac{d[B]}{dt} = \frac{k_2 \cdot k_1 \cdot [A]^2}{k_3 \cdot [A] + k_2} \approx \frac{k_2 \cdot k_1 \cdot [A]^2}{k_2} = k_1 \cdot [A]^2$ reaction order = 2

Solution to problem 3-15

a) $V = 0.5 \cdot 6 \cdot 10^{-3}\ cm^{-3} / 0.8$ $V = 3.75 \cdot 10^{-3}\ cm^3$

b) $n = 1\ L / V$ $n = 1000 / 3.75 \cdot 10^{-3}$ $n = 2.7 \cdot 10^5$ ants

c) $NaHCO_3 + HCOOH \longrightarrow HCOONa + H_2O + CO_2$

$n(\text{methanoic acid}) = V(\text{methanoic acid}) \cdot \rho(\text{methanoic acid}) / M(\text{methanoic acid})$

$n(\text{methanoic acid}) = 0.5 \cdot 6 \cdot 10^{-3}\ cm^{-3} \cdot 1.2\ gcm^{-3} / 46.03\ gmol^{-1} = 7.82 \cdot 10^{-5}\ mol$

$m(Na(HCO_3) = 7.82 \cdot 10^{-5}\ mol \cdot 84.02\ gmol^{-1}$ $m(NaHCO_3) = 6.57 \cdot 10^{-3}\ g$

d) $c_0\,(HCOOH) = \frac{1 \cdot 10^{-2}\ cm^3 \cdot 1.2\ g/cm^3}{46.03\ g/mol} / 2\ cm^3 = 0.130\ mol/L$

$c(H_3O^+) = c(HCOO^-) = 10^{-2.34}\ mol/L$

$\Rightarrow$ $c(HCOOH) = 0.130\ mol/L - 10^{-2.34}\ mol/L$

$K_a = \frac{(10^{-2.34})^2}{0.130 - 10^{-2.34}}$ $K_a = 1.67 \cdot 10^{-4}$

$\alpha = c(HCOO^-) / c_0(HCOOH)$ $\alpha = 10^{-2.34} / 0.13$ $\alpha = 0.035 = 3.5\%$

e) $K_s = \frac{c(H_3O^+)^2}{c(HOAc)}$ $10^{-4.76} = \frac{(10^{-2.34})^2}{c(HOAc)/(1\ mol/L)}$ $c(HOAc) = 1.202\ mol/L$

$c_0\,(HOAc) = 1.202\ mol/L + 10^{-2.34}\ mol/L = 1.207\ mol/L$

$n_0(HOAc) = 1.207\ mol/L \cdot 0.002\ L = 2.414 \cdot 10^{-3}\ mol$

$m_0(HOAc) = 2.414 \cdot 10^{-3}\ mol \cdot 60.05\ g/mol = 0.1450\ g$

$\rho = m/V$ $V = 0.1450\ g / 1.05\ gcm^{-3}$ $V \approx 0.14\ cm^3$ acetic acid

You need the 14-fold amount of acetic acid.

Solution to problem 3-16

First of all:

180 cm^3 of HCl (c = x) $\Rightarrow$ $n_0(Cl^-) = n_0(H^+) = 0.18\ L \cdot x$

$\Rightarrow$ in the mixture $c(H^+) = x \cdot 0.18/0.30 = 0.6 \cdot x$

120 cm^3 of $AgNO_3$ (c = 0.05 mol/L) $\Rightarrow$ $n_0(Ag) = 6 \cdot 10^{-3}$ mol

$\Delta E = E(Ag^+) - E(H^+)$

$E(H^+) = \frac{R \cdot T}{F} \ln \frac{c(H^+)}{c_0}$ $E(H^+) = \frac{R \cdot T}{F} \ln \frac{0{,}6 \cdot x}{c_0}$ with $c_0 = 1$ mol/L

$E(Ag^+) = E°(Ag^+) + \frac{R \cdot T}{F} \ln \frac{c(Ag^+)}{c_0}$ $E(Ag^+) = 0.800\ V + \frac{R \cdot T}{F} \ln \frac{c(Ag^+)}{c_0}$

$\Rightarrow \Delta E = 0.800\ V + \frac{R \cdot T}{F} \ln \frac{c(Ag^+)}{c(H^+)}$ $\Delta E = 0.800\ V + \frac{R \cdot T}{F} \ln \frac{c(Ag^+)}{0.6 \cdot x}$

a) $\Delta E = 0.807$ V

$\Rightarrow \ln \frac{c(Ag^+)}{c(H^+)} = \frac{(0.807 - 0.800)\,V \cdot F}{R \cdot T} = 0{,}2726$ $\frac{c(Ag^+)}{c(H^+)} = 1.313$

$\Rightarrow$ $n_0(Ag^+) > n_0(H^+)$. virtual all Cl^- precipitates as AgCl,
there is an excess of $n(Ag^+) = n_0(Ag^+) - n_0(Cl^-)$:

$\Rightarrow c(Ag^+) = \frac{0.006\,mol - 0.18\,L \cdot x}{0.3\,L} = 0.02$ mol/L - 0.6·x

$\frac{c(Ag^+)}{c(H^+)} = \frac{0.02\,mol/L - 0.6 \cdot x}{0.6 \cdot x} = 1.313$ $\Rightarrow$ x = 0.0144 mol/L

b) $\Delta E = 0.378$ V $\Rightarrow \frac{c(Ag^+)}{c(H^+)} = e^{\frac{-0.422\ V \cdot F}{R \cdot T}} = 7.29 \cdot 10^{-8}$

$\Rightarrow$ $n_0(Cl^-) = n_0(H^+) > n_0(Ag^+)$. virtual all Ag^+ precipitates as AgCl,
there is an excess of $n(Cl^-) = n_0(Cl^-) - n_0(Ag^+)$:

$c(Cl^-) = \frac{0.18\ L \cdot x\ - 6 \cdot 10^{-3}\ mol}{0.3L} = 0.6 \cdot x - 0.02$ mol/L

$\Rightarrow c(Ag^+)/c_0 = \frac{K_L}{c(Cl^-)/c_0} = \frac{1.78 \cdot 10^{-10}}{0.6 \cdot x/c_0 - 0.02}$

$\Rightarrow \frac{c(Ag^+)}{c(H^+)} = \frac{1.78 \cdot 10^{-10}}{0.6 \cdot x/c_0 - 0.02} : (0{,}6 \cdot x/c_0) = 7.29 \cdot 10^{-8}$

$\Rightarrow (x/x_0)^2 - \frac{1}{30} \cdot x/c_0 - 6.78 \cdot 10^{-3} = 0$ x = 0.101 mol/L

Solution to problem 3-17

a) $V_{cell} = a \cdot b \cdot c$ $V_{cell} = 2.562 \cdot 10^8\ pm^3 = 2.562 \cdot 10^{-22}\ cm^3$

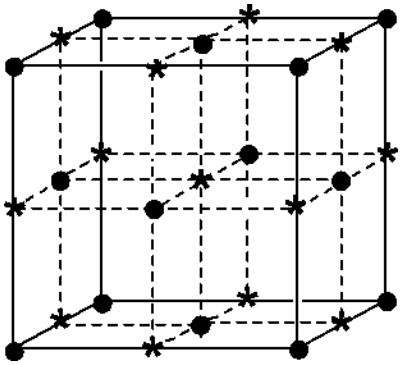
$m_{cell} = \rho_{appr} \cdot V_{Zelle}$ $m_{cell} \approx 3.9\ g/cm^3 \cdot 2.562 \cdot 10^{-22}\ cm^3 = 9.992 \cdot 10^{-22}$ g

$m(NiSO_4) = \frac{154.76\,g/mol}{N_A} = 2.570 \cdot 10^{-22}$ g

$m_{cell}/\ m(NiSO_4) \approx 3.89 \approx 4$ $\Rightarrow$ 4 formula units/cell

$\rho_{exact} = 4 \cdot m(NiSO_4)/\ V_{Zelle}$ $\rho_{exact} = 4.01\ g/cm^3$

b)



● oxygen ions

* nickel ions

(As both kind of ions form a cubic-close packing a labelling the other way round is correct, too.)

c) Using the density of nickel oxide the edge of the unit cell, a, can be calculated.
In a unit cell there are 8·1/8 + 6·½ = 4 oxygen ions and 12·¼ + 1 = 4 nickel ions.

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{4 \cdot (M(Ni) + M(O))}{N_a \cdot a^3}$$

M(Ni) = 58.69 g/mol, M(O) = 16 g/mol $\Rightarrow$ $a = 4.206 \cdot 10^{-8}$ cm

With the same formula, the calclated $a = 4.206 \cdot 10^{-8}$ cm and the given density = 6.21 g/cm^{-3} you can determine x replacing M(Ni) by [(1-x)·M(Ni) + x·M(Li)]:

$$6.21\ \text{g/cm}^{-3} = \frac{4 \cdot [(1-x) \cdot 58.69 + x \cdot 6.941 + 16]\ \text{g} \cdot \text{mol}^{-1}}{6.022 \cdot 10^{23}\ \text{mol}^{-1} \cdot (4.206 \cdot 10^{-8}\ \text{cm})^3} \Rightarrow \quad x = 0.10$$

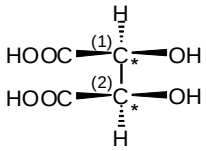
d) For each lithium ion a nickel ion has to be removed and another nickel ion has to be oxidized to Ni^{3+}.
$Li_{0,1}Ni_{0,9}O$ refers ato $LiNi_9O_{10}$. One out of 9 nickel ions is oxidized: 11.1%

$LiNi(III)Ni(II)_8O_{10}$

(x=0.15: $Li_{0.15}Li_{0.85}O$ refers to $Li_3Ni_{17}O_{20}$.
3 out of 17 nickel ions are oxidized: 17,6% $Li_3Ni(II)_{14}Ni(III)_3O_2$

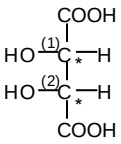
Solution to problem 3-18

a) *meso*-tartaric acid

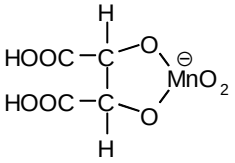


1*S*, 2*R*

Fischer projection:

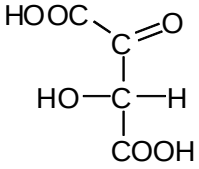


b) Intermediate: cyclic ester



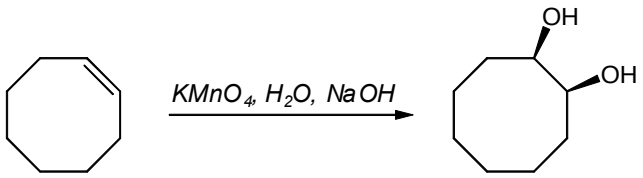
(Mn(V))

c) There are more oxidation products, e.g..



In addition C-C bonds are cleaved.
Reason: The oxidation potential of permanganate is strongly dependent on the ph value because protons are needed for the reduction. The potential is rising with the acidity of the solution and so organic compounds are easier oxidized and sometimes unselectively destroyed.

d)



syn addition

e) Cyclohexene does not dissolve in water while permanganate ions are insoluble in the organic phase. The quaternary ammonium salt facilitates the migration of the permanganate anions from water into the organic phase (phase transfer catalyst) bringing the reactants together.

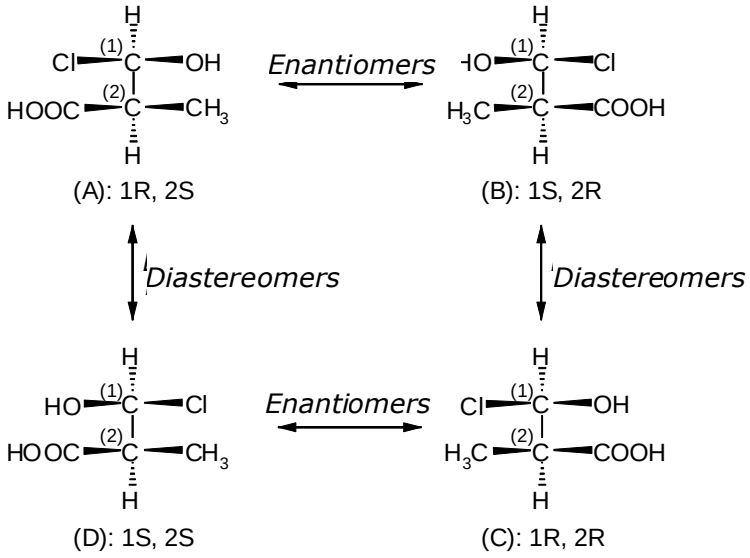
Solution to problem 3-19

a) A: 3-Methylheptane
B: 5-Ethyl-3-methyloctane
C: 2,2,5-Trimethylhexane
D: 1-Isopropyl-2-methylcyclohexane
E: 2-Methylpropene
F: 1-Brom-3-ethyl-2-methylcyclohexane

b) A: *E/Z* isomerism
B: *E/Z* isomerism
C: no isomerism
D: no isomerism
E: Enantiomers
F: E/Z isomerism

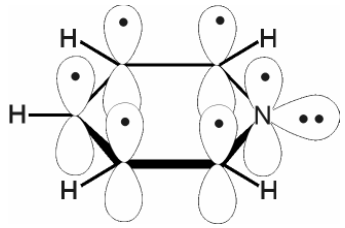
c) i) $-CH(CH_3)_2$; $-CH_2CH_3$; $-CH_3$; $-H$
ii) $-Br$; $-OH$; $-CH_2OH$; $-CH_3$
iii) $-OH$; $-COOCH_3$; $-COOH$; $-C\equiv N$

d) and e)



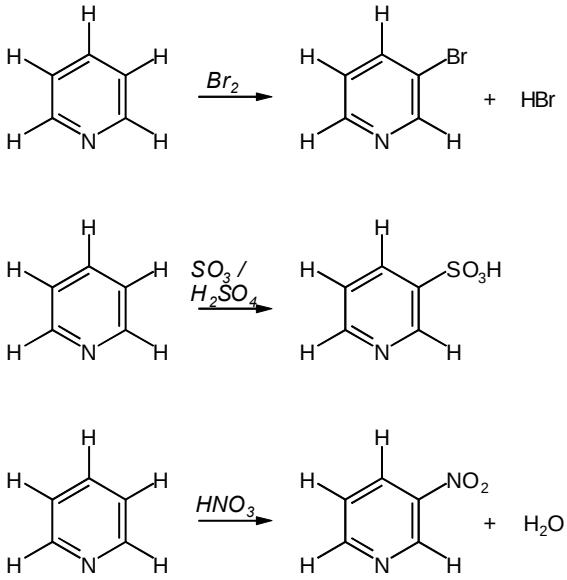
f) The compounds (A) and (C) as well as (B) and (D) are diastereomers.

Solution to problem 3-20

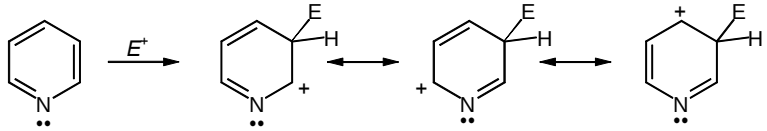


a)
6 π electrons in the ring $\Rightarrow$ pyridine is an aromatic compound.
The lone pair electrons occupy an sp^2 orbital in the plane of the ring.

b) Electrophilic aromatic substitution:



c) Intermediate:
The first step of the electrophilic substitution is the addition of the electrophile (E^+) at C atom number 3:

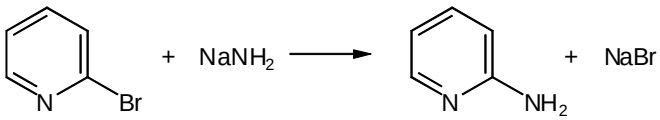


Only on addition at the C atom in 3-position the positive charge can be spread over three C atoms. This leads to a decrease in energy of the intermediate and thus to a preference of the reaction progress.
The addition of E^+ at C2 or C4 leads to a charge spread over two C atoms and the more electronegative N atom. This is energetically unfavourable.

d) The low reactivity of pyridine is caused by a combination of factors.
One is that acid-base complexation between the basic ring nitrogen atom and the incoming electrophile places a positive charge on the ring, thereby deactivating it. Equally important is that the electron density of the ring is decreased by the elec-

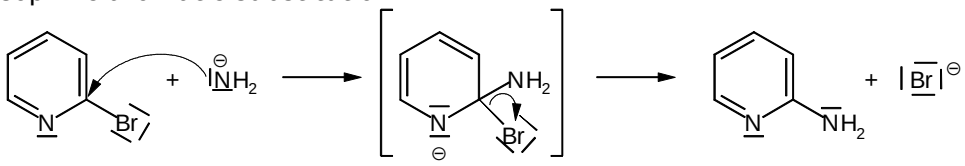
tron- withdrawing inductive effect of the electronegative nitrogen atom. Thus the electrophilic attack of E^+ is handicapped.

e)



(2-Aminopyridine)

f) Nucleophilic aromatic substitution:



The mechanism is analogue to the nucleophilic substitution of bromobenzene. Benzene prefers electrophilic substitutions. Not until electrons are withdrawn e.g. by NO_2 substituents the charge density in the ring is that downsized that a nucleophilic addition becomes possible. In pyridine this effect is caused by the electronegative N atom.

Answers Round 4 (theoretical)

Solution to problem 4-1

a) Si: 4 O: 2

b) 1 cm^3 contains (ρ/M(SiO_2)*) · N_A = $2.208 \cdot 10^{22}$ SiO_2 units
V = 1 cm^3/ $2.208 \cdot 10^{22}$ SiO_2 units = 4.529 $cm^3 \cdot 10^{-23}$/ SiO_2 unit
(or $4{,}529 \cdot 10^{-2}$ nm^3 = 45,29 $Å^3$= $4{,}529 \cdot 10^{7}$ pm^3)/SiO_2 unit).
Each Si atom forms 4 bonds $\Rightarrow$ each SiO_2 unit contains 4 bonds.
*As each oxygen atom belongs to two tetrahedrons its mass in a SiO_4 unit has to be divided by 2.

c) $SiO_{1.9}$ relates to $Si_{10}O_{19}$. In $Si_{10}O_{19}$ one Si-O-Si bond is replaced by one Si-Si bond.
There is a total number of 4·10 – 1 = 39 bonds, one of them is an Si-Si bond
$\Rightarrow$ p = 1/39 · 100% = 2.56 % of the bonds are Si-Si bonds.

d) Denote n = number of Si atoms in a sample of SiO_x.
Number of valence electrons: $n(e^-) = 4 \cdot n + 2 \cdot n \cdot x$
number of bonds formed: $n(e^-)/2 = 2 \cdot n + n \cdot x$
2·n·x of these are Si-O bonds.
The remaining $2 \cdot n + n \cdot x - 2 \cdot n \cdot x = n \cdot (2 - x)$ are Si-Si bonds

$$\Rightarrow \quad \frac{n_{Si-Si}}{n_{Si-O}} = \frac{n \cdot (2-x)}{2 \cdot n \cdot x} = \frac{2-x}{2 \cdot x} = \frac{1}{x} - 0.5$$

If each Si atom forms one Si-Si bond 3 Si-O bonds remain in a unit. As each O atom belongs to two units: x = 1.5

e) According to the reaction equation, $p(SiO) = 2 \cdot p(O_2)$.
$p(O_2) = x$ and $p(SiO) = 2x$

$\Rightarrow$ $K_p = p(SiO)^2 \cdot p(O_2)/{p_0}^3 = (2x)^2 \cdot x/{p_0}^3 = 4\,x^3/{p_0}^3$ p_0 = 1.000 bar

$x = \sqrt[3]{\frac{K_p}{4}}$ bar = $9.92 \cdot 10^{-9}$ bar $p(SiO) = 2\,x = 1.98 \cdot 10^{-8}$ bar

(Note: The pressure is quite low. Thus the reaction has to be carried out under high-vacuum conditions because in doing so it is quite easy to exclude other gases as impurities)

f) Gaseous SiO can be produced in a comproportionation reaction by heating a mixture of solid Si and solid SiO_2:

$$Si(s) + SiO_2(s) \longrightarrow 2\ SiO(g) \qquad \text{(temperature > 1100 °C)}$$

Solution to problem 4-2

a) Yellow brownish solution: I_2 or I_3^-, precipitate: CuI.

b) $2\ Cu^{2+}(aq) + 4\ I^-(q) \longrightarrow 2\ CuI(s) + I_2(aq)$ or
$2\ Cu^{2+}(aq) + 5\ I^-(aq) \longrightarrow 2\ CuI(s) + I_3^-(aq)$

c) $I_2 + 2\ S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I_2$

d) 25,4 mL of $Na_2S_2O_3$ solution contain (c = 0.1 mol/L) $2{,}54\cdot10^{-3}$ mol of $S_2O_3^{2-}$.
1 mol of $S_2O_3^{2-}$ is equivalent to 1 mol of Cu^{2+}.
The original sample contains $10\cdot2{,}54\cdot10^{-3}$ mol of Cu^{2+} thus the mass of copper sulfate is $2{,}54\cdot10^{-2}$ mol·M($CuSO_4$).
m($CuSO_4$ in the sample) = $2.54\cdot10^{-2}\cdot159.62$ g = 4.05 g
m(H_2O in he sample) = 4.79 g – 4.05 g = 0.74 g
n($CuSO_4$) : n(H_2O) = $2.54\cdot10^{-2}$: 0.74/18.02 = 1 : 1.62

B

e) H_2, H_2S, SO_2

f) $Zn + H_2SO_4 \longrightarrow Zn^{2+} + SO_4^{2-} + H_2$
$Zn + H_2SO_4 \longrightarrow ZnO + H_2O + SO_2$
$(ZnO + H_2SO_4 \longrightarrow Zn^{2+} + SO_4^{2-} + H_2O)$
$4\ Zn + H_2SO_4 \longrightarrow 4\ ZnO + H_2S$
$(ZnO + H_2SO_4 \longrightarrow Zn^{2+} + SO_4^{2-} + H_2O)$

g) $n(Zn) = \frac{m(Zn)}{M(Zn)}$ $n(Zn) = \frac{1.7334}{65.41}\text{mol} = 26.5\cdot10^{-3}$ mol

$n(H_2) + n(SO_2) + 4\cdot n(H_2S) = n(Zn)$
$n(H_2) + n(SO_2) + 4\cdot n(H_2S) = 26.5\cdot10^{-3}$ mol (1)
$n(\text{mixture}) = \frac{p\cdot V}{R\cdot T}$ $n(\text{mixture}) = \frac{1.022\cdot10^5\,\text{Pa}\cdot601\cdot10^{-6}\,\text{m}^3}{8.314\,\text{JK}^{-1}\text{mol}^{-1}\cdot293.15\,\text{K}} = 25.2\cdot10^{-3}$ mol
$n(H_2) + n(SO_2) + n(H_2S) = n(\text{mixture})$
$n(H_2) + n(SO_2) + n(H_2S) = 25.2\cdot10^{-3}$ mol (2)
(1) - (2): $3\cdot n(H_2S) = 1.3\cdot10^{-3}$ mol $\Rightarrow$ $n(H_2S) = 0.433\cdot10^{-3}$ mol (3)
SO_2 and H_2S only are oxidized by the solution of potassium permanganate:
$2\ MnO_4^- + 6\ H_2O + 5\ SO_2 \longrightarrow 2\ Mn^{2+} + 5\ SO_4^{2-} + 4\ H_3O^+$
$8\ MnO_4^- + 14\ H_3O^+ + 5\ H_2S \longrightarrow 8\ Mn^{2+} + 5\ SO_4^{2-} + 26\ H_2O$
$5\cdot V(MnO_4^-)\cdot c(MnO_4^-) = 2\cdot n(SO_2) + 8\cdot n(H_2S)$
$\Rightarrow$ $n(SO_2) = ½\cdot(5\cdot30\cdot10^{-3}\cdot0.2 - 8\cdot0.433\cdot10^{-3})$ mol $n(SO_2) = 13.3\cdot10^{-3}$ mol
$n(H_2) = n(\text{mixture}) - n(SO_2) - n(H_2S)$ $n(H_2) = 11.5\cdot10^{-3}$ mol
Composition of the gas mixture (rounding leads to a sum of 100.1%):
Hydrogen: $100\%\cdot11.5\cdot10^{-3}/25.2\cdot10^{-3} = 45.6$ %
Sulfur dioxide: $100\%\cdot13.3\cdot10^{-3}/25.2\cdot10^{-3} = 52.8$ %
Hydrogen sulfide: $100\%\cdot0.433\cdot10^{-3}/25.2\cdot10^{-3} = 1.7$ %

Solution to problem 4-3

a) $\Delta G° = -\ n\cdot F\cdot E°$
(1) $PbSO_4 + 2\ e^- \rightleftarrows Pb + SO_4^{2-}$ $\Delta G_1° = 2\cdot F\cdot0.356$ V
(2) $Pb^{2+} + 2\ e^- \rightleftarrows Pb$ $\Delta G_2° = 2\cdot F\cdot0.126$ V
(1)-(2) $PbSO_4 \rightleftarrows Pb^{2+} + SO_4^{2-}$ $\Delta G_1° - \Delta G_2° = 2\cdot F\cdot0.230$ V
$\Delta G° = -\ RT\cdot\ln K_{sp}$ $\Rightarrow$ $\ln K_{sp} = -\frac{2\cdot F}{R\cdot T} = -17.91_3$ $K_{sp} = 1.66\cdot10^{-8}$
$L = \sqrt{K_{sp}}$ mol/L· M($PbSO_4$), $L = \sqrt{1.66\cdot10^{-8}}$ mol/L·303.3 g/mol L = 0.039 g/L

b) $\Delta E = E_{right} - E_{left}$

$\Delta E = E(Pb^{2+}/Pb) - E(PbSO_4/Pb + SO_4^{2-})$

$\Delta E = -0.126\ V + \frac{R \cdot T}{2 \cdot F} \ln([Pb^{2+}]/(1\ mol/L)) + 0.356\ V - \frac{R \cdot T}{2 \cdot F} \ln((1\ mol/L)/[SO_4^{2-}])$

$0.061\ V = 0.23\ V + \frac{R \cdot T}{2 \cdot F} \ln(2.5 \cdot 10^{-5}) + \frac{R \cdot T}{2 \cdot F} \ln([SO_4^{2-}]/(1\ mol/L))$

$\Rightarrow \quad \ln([SO_4^{2-}]/(1\ mol/L)) = -2.566 \qquad [SO_4^{2-}] = 0.0768\ mol/L$

$$HSO_4^- + H_2O \rightleftarrows SO_4^{2-} + H_3O^+$$

c in mol/L $\quad 0.600 - 0.0768 \qquad 0.0768 \quad 0.0768$

$K_{a2} = \frac{0.0768^2}{0.600 - 0.0768} \qquad K_{a2} = 0.0113 \qquad (pK_{a2} = 1.95)$

c) $\Delta G = \Delta G° + RT \cdot \ln(p°/p(O_2))$ with $p° = 1.000 \cdot 10^5$ Pa

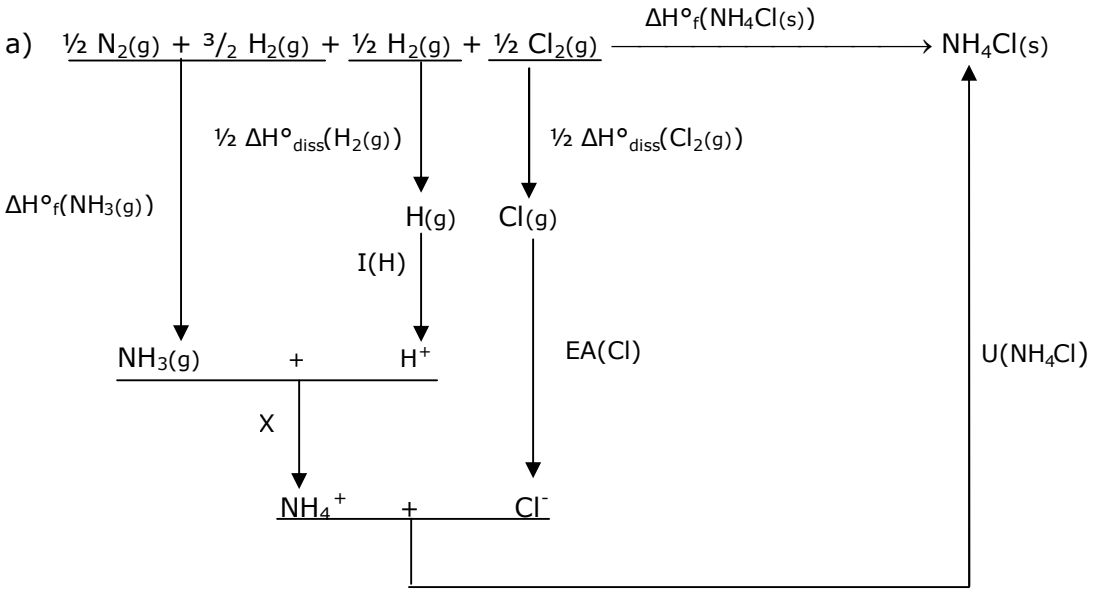
d) If ΔG(oxidation of carbon) + ΔG(reduction of oxide) < 0 kJ the reactions proceed voluntarily. The reactions start if this term = 0 kJ.
This condition is given when the respective lines cross the line of the formation of CO_2 and CO respectively. Thus FeO will be reduced first.

e) Determining the temperature by reading directly or b interpolation
FeO: starting temperature ≈ 780 °C
SiO_2: starting temperature ≈ 1580 °C

f) $2\ FeO + C \longrightarrow CO_2 + 2\ Fe$ (1) and $FeO + C \longrightarrow CO + Fe$ (2)
(at higher temperatures the 2nd reaction is favoured)
$SiO_2 + 2\ C \longrightarrow 2\ CO + Si$

Solution of problem 4-4

a)



$-313.5\ kJ/mol = [-46 + ½ \cdot (242 + 430.5) + 1312.5 - 348 + X - 651.1]\ kJ/mol$

$X = -917\ kJ/mol$

b) $PbCO_3(s) + H_2S(g) \longrightarrow PbS(s) + CO_2(g) + H_2O(g)$ (1)

$ZnO(s) + H_2S(g) \longrightarrow ZnS(s) + H_2O(g)$ (2)

c) $7\cdot10^{-9}$ g/L = $7\cdot10^{-6}$ g/m^3 correspond to $\frac{7\cdot10^{-6}\ g/m^3}{34.08\ g/mol} = 2.054\cdot10^{-7}$ mol/m^3.

$p(H_2S) \cdot 1\ m^3 = 2.054 \cdot 10^{-7}\ mol \cdot R \cdot T$ $p(H_2S) = 5.09\cdot10^{-4}$ Pa = $5.09\cdot10^{-9}$ bar

$p(CO_2) = 2.6 \cdot 10^{-4}$ bar $p(H_2O) = 4 \cdot 10^{-3}$ bar

$\Delta G = \Delta G° + R\cdot T\cdot \ln Q$

(1) $\Delta G = (-92.6 - 394.2 - 228.5 + 626.0 + 33.0) \cdot 1000$ J/mol + $RT\cdot\ln\frac{2.6\cdot10^{-4}\cdot4\cdot10^{-3}}{5.09\cdot10^{-9}}$

ΔG = - 56300 J/mol + 13180 J/mol ≈ -43 kJ/mol

(2) $\Delta G = (-184.8 -228.5 + 318.0 + 33.0) \cdot 1000$ J/mol + $RT\cdot\ln\frac{4\cdot10^{-3}}{5.09\cdot10^{-9}}$

ΔG = - 62300 J/mol + 33632 J/mol ≈ - 29 kJ/mol

Both reactions may run spontaneously, so both pigments are not appropriate.

d) $PbCO_3$ is less suitable because

- reaction (1) runs already at lower concentrations of H_2S, ($\Delta G(1) < \Delta G(2)$, whereby both enthalpies of formation show the same dependency of $p(H_2S)$)
- PbS is black while ZnS is white.

e) Reaction with hydrogen peroxide:

$PbS + 4\ H_2O_2 \longrightarrow PbSO_4 + 4\ H_2O$

Reaction at air ventilation:

$PbS + 2\ O_2 \longrightarrow PbSO_4$ $\Delta G° = -811.5$ kJ/mol + 92.6 kJ/mol = - 718.9 kJ/mol

ΔG = - 718.9 kJ/mol + $RT\cdot\ln\frac{1}{0.207^2}$ $\Delta G \approx$ - 711 kJ/mol

$\Rightarrow$ This reaction runs spontaneously according to thermodynamics.

Solution to problem 4-5

a) $\Delta E_{J\rightarrow J+1} = E(J+1) - E(J) = h\cdot c\cdot B\cdot(2J+2)$

b) The position of the bands in the spectrum is consistent with the energy difference $\Delta E_{J\rightarrow J+1}$:

$\Delta E_{0\rightarrow1} = 2\cdot h\cdot c\cdot B$ $\Delta E_{1\rightarrow2} = 4\cdot h\cdot c\cdot B$ $\Delta E_{2\rightarrow3} = 6\cdot h\cdot c\cdot B$

Thus the distance between two adjacent lines amounts to 2·B.

c) You can read from the diagram: $6\cdot2\cdot B = (38.5 - 15.4)\ cm^{-1}$

$B = 1.93\ cm^{-1}$ (= 193 m^{-1})

$B = h/(8\pi^2\cdot c\cdot I)$ und $I = \mu\cdot R^2$ $\Rightarrow$ $R^2 = h/(8\pi^2 c\mu B)$

with $\mu(^{12}C^{16}O) = \frac{12.000\cdot15.999}{12.000+15.999}\ g\cdot mol^{-1}\cdot(6.022\cdot10^{23}\ mol^{-1})^{-1} = 1.139\cdot10^{-26}$ kg.

$$R^2 = \frac{6.6261\cdot10^{-34}\ \text{J}\cdot\text{s}}{8\,\pi^2\cdot3\cdot10^{8}\ \text{m}\cdot\text{s}^{-1}\cdot1.139\cdot10^{-26}\ \text{kg}\cdot193\,\text{m}^{-1}} = 1.273\cdot10^{-20}\ \text{m}^2$$

$\Rightarrow$ $R \approx 113$ pm

d) The first band shown in the image lies at 15.4 cm^{-1}.
This comes to (15.4 cm^{-1}/1.93 cm^{-1}) · B $\approx$ 8·B. $\Rightarrow$ transition 3→4 .
The following bands belong to the transitions 4→5. 5→6….. 9→10.

e) You find a series of side bands with smaller line distances which means smaller rotational constants:
$4 \cdot 2B' = (36.9 - 22.0)\ cm^{-1}$ $B' = 1.86\ cm^{-1}$
On the one hand a reason could be another compound which contaminates CO. However, more obviously the isotope ^{13}C which is a natural component with a frequency of approx. 1%, causes these additional bands.
Calculation:
$B(^{13}C^{16}O) = [\mu(^{12}C^{16}O) / \mu(^{13}C^{16}O)] \cdot B(^{12}C^{16}O)$ $[\mu(^{13}C^{16}O) = 1.191\cdot10^{-26}\ kg]$
$= 1.85\ cm^{-1} \approx B'$

f) $B = h/(8\pi^2\cdot c\cdot I)$ $\Rightarrow$ $I = h/(8\pi^2\cdot c\cdot B)$
$I(^{12}C_2H_2) = 2.3775 \cdot 10^{-46}\ kg\ m^2$ $I(^{12}C_2D_2) = 3.3000 \cdot 10^{-46}\ kg\ m^2$
Assuming that the bond lengths of both compounds are identical the moments of inertia of them are:
$I(^{12}C_2H_2) = 2\cdot m(^{12}C)r_1^2 + 2\cdot m(H)r_2^2$ (1)
$I(^{12}C_2D_2) = 2\cdot m(^{12}C)r_1^2 + 2\cdot m(D)r_2^2$ (2)
(2) – (1): $I(^{12}C_2D_2) - I(^{12}C_2H_2) = 2\cdot r_2^2 \cdot (m(D) - m(H))$

$$\Rightarrow r_2 = \left[\frac{(3.3000-2.3775)\cdot10^{-46}\ \text{kg}\,\text{m}^2}{(2.0141-1.0078)\cdot10^{-3}\ \text{kg}\,\text{mol}^{-1}/(6.022\cdot10^{23}\ \text{mol}^{-1})}\right]^{1/2}$$ $r_2 \approx 166$ pm

$\Rightarrow$ $r_1 \approx 60$ pm

Then the bond lengths are $R_{CC} = 2\cdot r_1 \approx 120$ pm
$R_{CH} = r_2 - r_1 \approx 106$ pm.

Solution to problem 4-6

a) H_2: 0.75 Å (library reference 74 pm) H_2^+: 1.05 Å (library reference 106 pm)
b) H_2 : ~ [-2630–(-3080)] KJ/mol = 450 KJ/mol (library reference 432 KJ/mol)
H_2^+: ~ [- 1320–(-1590)] KJ/mol = 270 KJ/mol (library reference 256 KJ/mol)
c) $IE(H_2)$ ~ [-1590–(-3080)] KJ/mol = 1490 KJ/mol (library reference 1498 KJ/mol)
d) IE(H) ~ [- 1320–(-2630)] KJ/mol = 1310 kJ/mol (library reference 1312 KJ/mol)

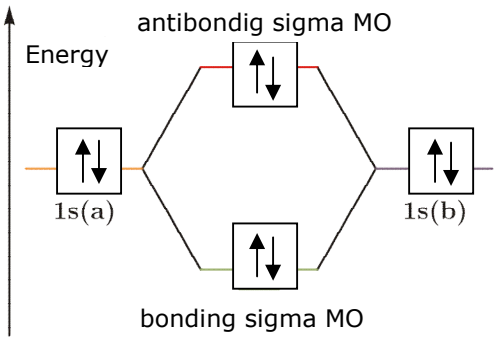
e) $\frac{1}{2}\, m_e v^2 = h\cdot\nu - IE(H_2)$ $v = \sqrt{\frac{2\cdot(h\cdot\nu - IE(H_2))}{m_e}}$

$h \cdot \nu = 2.5818 \cdot 10^{-18} J$

$IE(H_2) = (1490\ kJ/mol) / 6.022 \cdot 10^{23}\ /mol)$ $\quad IE(H_2) = 2.4743 \cdot 10^{-21}\ kJ$

$$v = \sqrt{\frac{2 \cdot (2.5818 \cdot 10^{-18} - 2.4743 \cdot 10^{-18})J}{9.1 \cdot 10^{-31} kg}} \qquad v = 486\ km/s$$

f)



MO diagram of He_2 (simplified)

He_2 has four electrons, two would go into the bonding, two into the antibonding MO. The prediction is that He_2 is not lower in energy than two He atoms so you would not expect He_2 to form.

However, He_2^+ has three electrons, so only one has to go into the anitbonding orbital. We might reasonably expect the effect of two bonding electrons to overweight the antibonding electron thus making He_2^+ to be stable with respect to dissociation.

Experimental work indicates that the bond dissociation energy is 241 kJ/mol).

Bond order of He_2: (2 bonding – 2 antibonding electrons) : 2 = 0

Bond order of He_2^+: (2 bonding – 1 antibonding electron(s)) : 2 = 0.5

Solution to problem 4 - 7

a) Small amount of oxygen: $2\ PbS + 3\ O_2 \longrightarrow 2\ PbO + 2\ SO_2$

plenty of oxygen: $PbS + 2\ O_2 \longrightarrow PbSO_4$

b) $\overset{+IV,-II}{SO_2} + 2\ \overset{+I,-II}{H_2S} \longrightarrow \overset{0}{^3/_8\ S_8} + 2\ H_2O$

In Germany this method is called "Claus-Process".

c) Roast-reaction process: $2\ PbO + PbS \longrightarrow 3\ Pb + SO_2$

$PbSO_4 + PbS \longrightarrow 2Pb + 2\ SO_2$

roast-reduction process: $2\ PbO + C \longrightarrow 2\ Pb + CO_2$

(or $PbO + C \longrightarrow Pb + CO$)

$2\ PbSO_4 + C \longrightarrow 2\ Pb + CO_2 + SO_2$

(or $PbSO_4 + 2\ C \longrightarrow Pb + 2\ CO + SO_2$)

d) T = PbO, $2\ Pb + O_2 \longrightarrow 2\ PbO$

U = Pb_3O_4, $3\ PbO + ½\ O_2 \longrightarrow Pb_3O_4$

V = $Pb(NO_3)_2$,

W = PbO_2, $Pb_3O_4 + 4\ HNO_3 \longrightarrow \mathbf{2}\ Pb(NO_3)_2 + PbO_2 + 2\ H_2O$

X = $PbCl_2$, $Pb^{2+} + 2\ Cl^- \longrightarrow PbCl_2$

Y = MnO_4^-, $2\ Mn^{2+} + 5\ PbO_2 + 4\ H^+ \longrightarrow 2\ MnO_4^- + 5\ Pb^{2+} + 2\ H_2O$

Z1/Z2= NO_2 / O_2,

$Pb(NO_3)_2 \xrightarrow{600\ °C} PbO + 2\ NO_2 + ½\ O_2$

e) Distance of Pb-Pb = 3.49 Å ⇒ radius of a lead atom = (3.49/2) Å

r = $1.745 \cdot 10^{-8}$ cm

The unit cell of a close-packed structure contains Z = 4 atoms.

The face diagonal of a cube is a $\sqrt{2}$.

(a = edge length of the cube). This diagonal is occupied by two hemispheres and one full sphere. Thus its length is 4 r.

$4\ r = a\sqrt{2} \Rightarrow a = 2\ r\ \sqrt{2}$

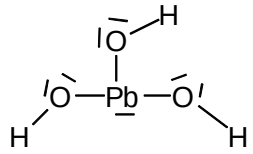
$\Rightarrow a = 4{,}936 \cdot 10^{-8}$ cm $\qquad V_{unit\ cell} = 1.2023 \cdot 10^{-22}\ cm^3$

$$d = \frac{4 \cdot M(Pb)}{V_{unit\ cell} \cdot N_A}$$

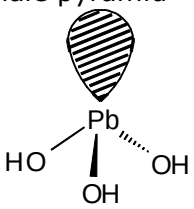
$$d = \frac{4 \cdot 207.2\ g \cdot mol^{-1}}{1.023 \cdot 10^{-22}\ cm^3 \cdot 6.022 \cdot 10^{23}\ mol^{-1}} = 11.45\ g \cdot cm^{-3}$$

f) Valence electrons: 1 · 4 + 3 · 6 + 3 · 1 + 1 = 26 electrons -> 13 electron pairs

Lewis structure:



VSEPR: trigonale pyramid



g) i) $Pb^{2+}\ (aq) + H_2SO_4\ (aq) \longrightarrow PbSO_4\ (s) + 2\ H^+\ (aq)$

ii) $Pb^{2+}\ (aq) + 2\ H_2SO_4 \longrightarrow H_2[Pb((SO_4)_2]\ (aq) + 2\ H^+\ (aq)$

iii) $Pb^{2+}\ (aq) + 2\ I^-\ (aq) \longrightarrow PbI_2\ (s)$

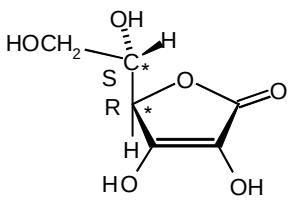
$PbI_2\ (s) + 2\ I^-\ (aq) \longrightarrow [PbI_4]^{2-}$

iv) $Pb^{2+}\ (aq) + 2\ NH_3\ (aq) + 2\ H_2O \longrightarrow Pb(OH)_2\ (s) + 2\ NH_4^+\ (aq)$

Solution to problem 4–8

a) See next page

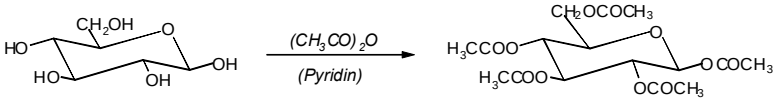
b)



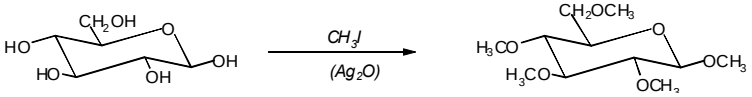
Ascorbic acid

Answers Round 4 (theoretical)

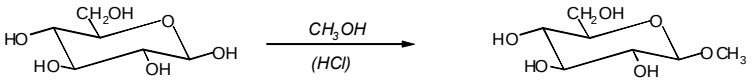
a)



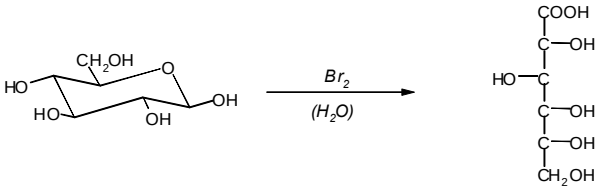
A = ester



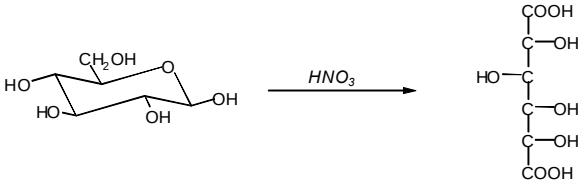
B = ether



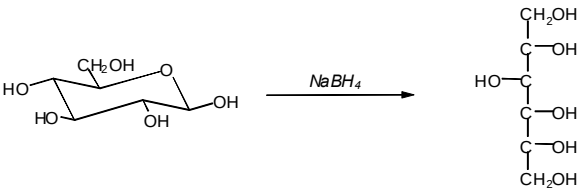
C = glycoside



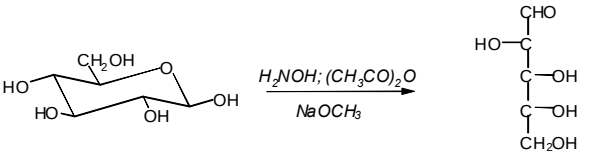
D = monocarboxylic acid



E = dicarboxylic acid



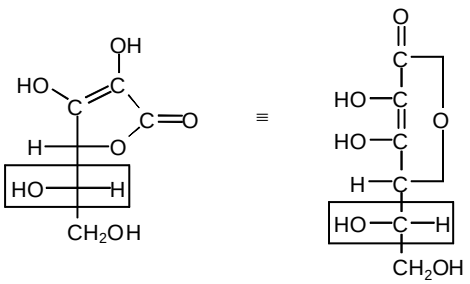
F = reduced sugar



G (D-Pentose)

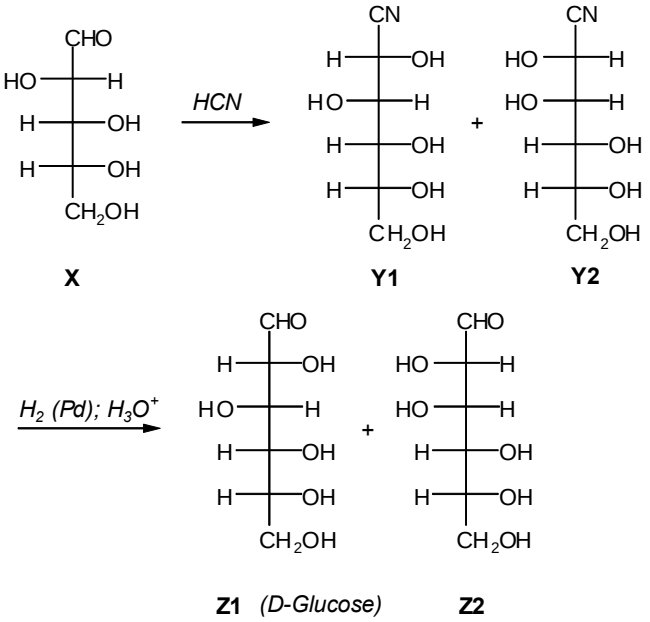
G = D-pentose

c)

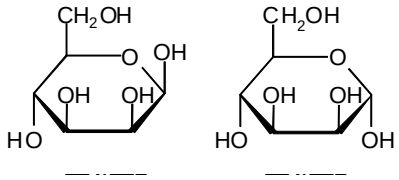


OH group on the left ⇒ L

d)



e)



Solution to problem 4–9

a) $(CH_3)_2C{=}CH_2 + HBr \longrightarrow (CH_3)_3CBr$

Reaction with a tert. carbenium ion as intermediate: Markovnikov product.

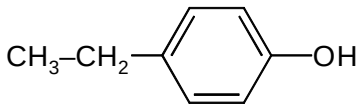
$(CH_3)_2C{=}CH_2 + HBr \longrightarrow (CH_3)_2CH\text{-}CH_2Br$

Reaction of a bromine radical (Br·) and an alkyl radical: anti-Markovnikov product.

b) The spectrum matches with the anti-Markovnikov product: $(CH_3)_2CH\text{-}CH_2Br$.
There are three non equivalent ^{13}C atoms,
quartet: CH_3 group (2x) triplet: CH_2 group (1x) doublet:CH group (1x)

c) Two non equivalent ^{13}C atoms are expected:
quartet: CH_3 group (3x) singlet: tert. C atom (1x)

d)



Justification

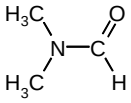
Infrared spectrum:

The band at 3500 cm^{-1} can be assigned to an OH vibration, the bands at 1500, 1600 and 830 cm^{-1} indicate an aromatic ring.

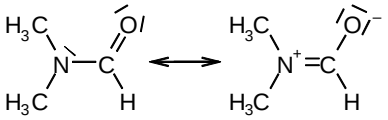
Assumption: The compound may be a phenol.

^{1}H-NMR-Spektrum:
Signal at 1,16 δ (triplet) indicates 3 H, it is coupling with the signal at 2,54 δ (quartet) which indicates 2 H. A CH_3-CH_2 group is existent.
The signal at 6,80 δ (multiplet) indicates an aromatic ring (4 H), the signal at 5,50 δ (singlet) refers to the H atom of the OH group.
Thus the compound could be an o-, m- or p-ethylphenol.
The symmetrical splitting of the muliplet indicates p-ethylphenol.

e) N,N-Dimethylformamide:



The three signals in the ^{1}H-NMR spectrum show that all H atoms in the CHO group and in both methyl groups have a different surrounding. This can be explained only by the fact that the free rotation about the N-C bond is restricted. It has a partial double bond character:

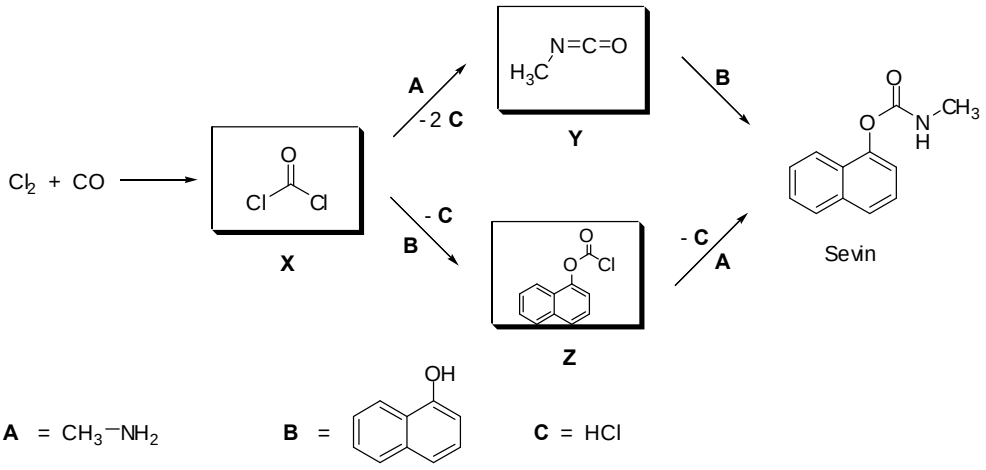


However the barrier of free rotation can be overcome by heating up to 180 °C. Then the CH_3 group can rotate and their H atoms show only one signal.

Solution to problem 4-10

Bhopal (India), 1984

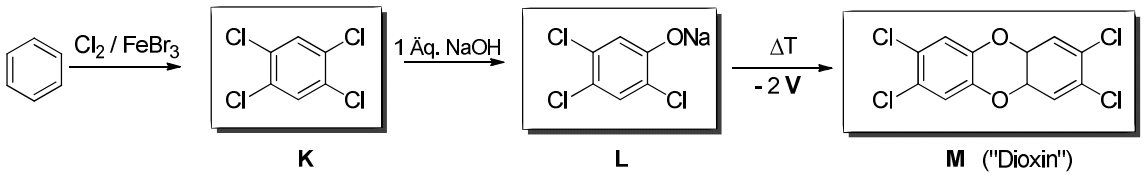
a)



b) **X**: Phosgene, **Y** is an isocyanate,
B = α-naphthol (or 2-hydroxynaphthalene or 1-naphthol).

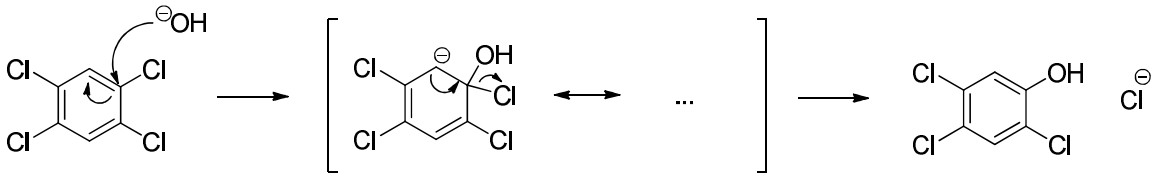
Seveso (Italy), 1976

c)



V: NaCl

d)



Nucleophilic aromatic substitution (S_NAr). The stronger electron-withdrawing inductive effect of the chlorine substituents outweighs their electron-donating resonance effect. Thus the positive charge of the ring can stabilize the negative charge of the attacking OH^- ion.

e) In this reaction two particles generate three and thus the entropy rises, $\Delta_rS > 0$. Due to the Gibbs-Helmholtz equation: the higher the temperature the more negative Δ_rG when $\Delta_rS>0$.

Answers Round 4 (theoretical)

Part 3

42nd International Chemistry Olympiad

Theoretical and Practical Problems

23. + 21. July 2010

Constants and Formulae

Avogadro constant:	$N_A = 6.022 \cdot 10^{23}$ mol^{-1}	Ideal gas equation:	$pV = nRT$
Gas constant:	$R = 8.314$ J K^{-1} mol^{-1}	Gibbs energy:	$G = H - TS$
Faraday constant:	$F = 96485$ C mol^{-1}	$\Delta_r G^\circ = -RT \log_e K = -nFE^\circ_{cell}$	
Planck constant:	$h = 6.626 \cdot 10^{-34}$ J s	Nernst equation:	$E = E^\circ + \frac{RT}{zF} \ln \frac{c_{ox}}{c_{red}}$
Speed of light:	$c = 2.998 \cdot 10^8$ m s^{-1}	Energy of a photon:	$E = \frac{hc}{\lambda} = h\nu$
Zero of the Celsius scale:	273.15 K	Beer-Lambert law:	$A = \log_{10} \frac{I_0}{I} = \varepsilon c l$

In equilibrium constant calculations all concentrations are referenced to a standard concentration of 1 mol L^{-1}. Consider all gases ideal throughout the exam.

Periodic table with relative atomic masses

1																	18
1 H 1.01	2											13	14	15	16	17	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc -	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -							

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Problem 1

In 1894, Lord Rayleigh reported that chemically prepared nitrogen had a different mass from that extracted from the atmosphere, as shown in Tables 1 and 2. Later, this difference was attributed to the presence of argon in *atmospheric nitrogen*. The masses of gases were measured by using a glass vessel with a known volume under atmospheric pressure (1.013×10^5 Pa).

Table 1. Mass of *Chemical Nitrogen in the Vessel*

From nitric oxide	2.3001 g
From nitrous oxide	2.2990 g
From ammonium nitrite purified at a red heat	2.2987 g
From urea	2.2985 g
From ammonium nitrite purified in the cold	2.2987 g
Mean	2.2990 g

Table 2. Mass of *Atmospheric Nitrogen in the Vessel*

O_2 was removed by hot copper (1892)	2.3103 g
O_2 was removed by hot iron (1893)	2.3100 g
O_2 was removed by ferrous hydrate (1894)	2.3102 g
Mean	2.3102 g

a) Calculate the volume V [in m^3] of the vessel used by Rayleigh from the mean mass of *chemical nitrogen*, which must have been pure nitrogen. Assume that the measurements were carried out at a temperature of 15.0 °C.

b) Estimate the mole fraction x of argon in Rayleigh's *atmospheric nitrogen*, by assuming that argon and nitrogen were the only constituents. Use the mean masses of the *atmospheric* and *chemical nitrogen* for the calculation.

Ramsay and Clève discovered helium in cleveite (a mineral consisting of uranium oxide and oxides of lead, thorium, and rare earths; an impure variety of uraninite) independently and virtually simultaneously in 1895. The gas extracted from the rock showed a unique spectroscopic line at around 588 nm (indicated by D_3 in Figure 1), which was first observed in the spectrum of solar prominence during a total eclipse in 1868, near the well-known D_1 and D_2 lines of sodium.

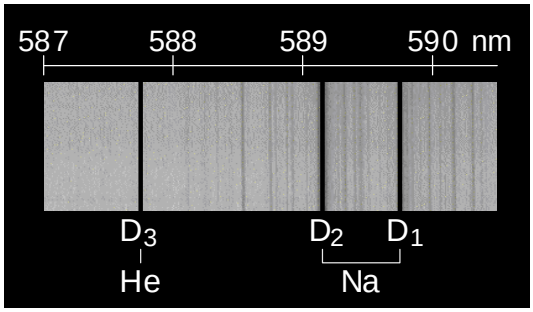


Figure 1. Spectral lines around 588 nm

c) Calculate the energy E [in J] of a photon with the wavelength of the D_3 line of helium shown in Figure 1.

Figure 2 shows an energy diagram of the atomic orbitals of helium. The arrows indicate the "allowed" transitions according to the spectroscopic principle.

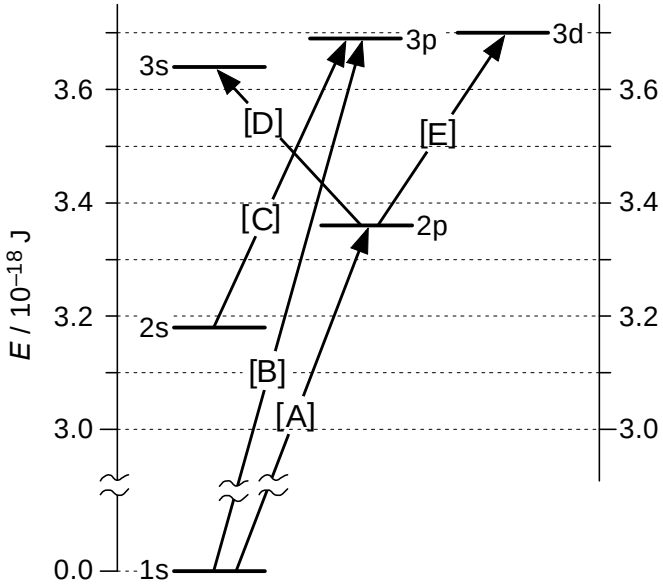


Figure 2. Energy diagram of atomic orbitals of helium
when an electron resides in the 1s orbital.

d) Identify the transition that corresponds to the D_3 line of helium among the transitions [A] to [E] indicated in Figure 2. Mark your choice on the answer sheet.

e) Which equation explains the occurance of helium in cleveite among [A] to [D] below? Mark one on the answer sheet.

[A] $^{238}U \rightarrow {}^{234}Th + \alpha$ [B] $UHe_2 \rightarrow U + 2He$

[C] $^{240}U \rightarrow {}^{240}Np + \beta^-$ [D] $^{235}U + n \rightarrow {}^{95}Y + {}^{139}I + 2n$

Argon is also found in minerals such as *malacon*.

f) Which equation explains the occurance of argon in rocks among [A] to [D] below? Mark one on the answer sheet.

[A] $ArF_2 \rightarrow Ar + F_2$
[B] $ArXe \rightarrow Ar + Xe$
[C] $^{40}K \rightarrow {}^{40}Ar + \varepsilon/\beta^+$ (electron capture / positron emission)
[D] $^{126}I \rightarrow {}^{126}Ar + \beta^-$

One of the strongest pieces of evidence for the monoatomicity of argon and helium is the ratio of the heat capacity under constant pressure to that at constant volume, $\gamma = C_p / C_V$, which is exactly 5/3 (1.67 ± 0.01) for a monoatomic gas. The ratio was derived from the measurement of speed of sound, v_s, by using the following equation, where f and λ are the frequency and wavelength of the sound respectively, and R, T, and M denote the molar gas constant, absolute temperature, and molar mass, respectively.

$$v_s = f\lambda = \sqrt{\frac{\gamma RT}{M}}$$

For an unknown gas sample, the wavelength of the sound was measured to be λ = 0.116 m at a frequency of f = 3520 Hz (Hz = s^{-1}) and temperature of 15.0 °C and under atmospheric pressure ($1.013 \cdot 10^5$ Pa). The density ρ of the gas for these conditions was measured to be 0.850 ± 0.005 kg m^{-3}.

g) Calculate the molar mass M [in kg mol^{-1}] of this gas.

h) Calculate the heat capacity ratio γ for this gas sample.

i) What is the identity of this gas choosing from [A] to [D]? Mark one on the answer sheet.

[A] HCl [B] HF [C] Ne [D] Ar

Problem 2

Crystal structure of alkali metal halide

In crystals of ionic compounds, cations are generally arranged in the interstices of the close-packed lattice of anions. The structure of an ionic crystal such as

sodium chloride becomes stable when the cations are in contact with the nearest anions.

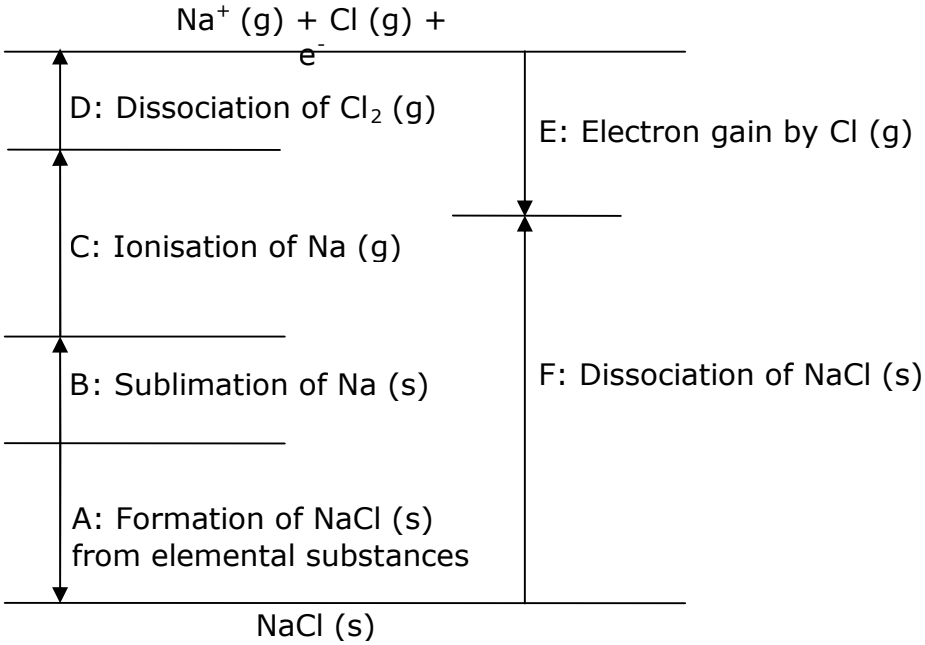
a) In the crystal of sodium chloride, both Na^+ and Cl^- ions form a face-centered cubic lattice. Give the numbers of Na^+ and Cl^- ions in a unit cell and the co-ordination numbers of Na^+ and Cl^- ions in sodium chloride crystal.

b) The ionic radii of Na^+ and Cl^- ions in the crystal of sodium chloride are 0.102 nm and 0.181 nm, respectively. Calculate the density [in kg m^{-3}] of the sodium chloride crystal.

Born-Haber cycle and lattice enthalpy

In ionic inorganic compounds such as sodium chloride, the heat of lattice formation from gaseous ions is very high, and the contribution of the change in entropy is small. Therefore, the lattice formation enthalpy is estimated from enthalpy data by using a Born-Haber cycle.

c) The figure below shows the Born-Haber cycle of NaCl. The labels "g" and "s" represent "gas" and "solid" states respectively. Show chemical equations for steps A and F.



d) Calculate the enthalpy of the lattice formation of NaCl [in kJ mol^{-1}] by using the following enthalpy data for the respective steps in the above Born-Haber cycle.

Formation of NaCl (s)	Sublimation of Na (s)	Ionisation of Na (g)	Dissociation of Cl_2 (g)	Electron gain by Cl (g)
–411 kJ mol^{-1}	109 kJ mol^{-1}	496 kJ mol^{-1}	242 kJ mol^{-1}	–349 kJ mol^{-1}

Synthesis of sodium carbonate by the ammonia-soda process (Solvay process)

Sodium carbonate (anhydrous soda ash) is a raw material in the manufacture of glass, medicaments, alkaline detergents, etc.

e) The total chemical reaction in the ammonia-soda process is represented as follows:

$2NaCl + CaCO_3 \longrightarrow Na_2CO_3 + CaCl_2$

This reaction between sodium chloride and calcium carbonate does not proceed directly. The process comprises the following five reactions:

$CaCO_3 \xrightarrow{\Delta}$ [A] + [B]

$NaCl + NH_3 +$ [B] $+ H_2O \longrightarrow$ [C] + [D]

2 [C] $\xrightarrow{\Delta} Na_2CO_3 + H_2O +$ [B]

[A] $+ H_2O \longrightarrow$ [E]

[E] + 2 [D] $\longrightarrow CaCl_2 + 2H_2O + 2NH_3$

Δ represents applying heat treatment.

Insert the chemical formulas of the appropriate compounds in the blank spaces [A]–[E] in the above reactions.

Problem 3

The chemical oxygen demand (COD) refers to the amount of oxidizable substance, such as organic compounds, in a sample solution, and it is used as an indication of water quality in seas, lakes, and marshes. For example, the COD of drinking water is kept below 1 mg L^{-1}. The COD [in mg L^{-1}] is represented by mass of O_2 [in mg], which accepts the same amount of electrons which would be accepted by a strong oxidizing agent, when 1 L of a sample solution is treated with it. An example of the operation is presented below.

****

Analytical Operation

A 1.00 L sample solution was acidified with a sufficient amount of sulphuric acid, and chloride ions were removed by the addition of silver nitrate solution. 0.100 L

of $5.00 \cdot 10^{-3}$ mol L^{-1} potassium permanganate solution was added to the sample solution, and the mixture was heated for 30 min. Then $1.00 \cdot 10^{-1}$ L of $1.25 \cdot 10^{-2}$ mol L^{-1} disodium oxalate ($Na_2C_2O_4$ or NaOOC-COONa) standard solution was added, and the mixture was stirred well. Oxalate ions that remained unreacted were titrated with $5.00 \cdot 10^{-3}$ mol L^{-1} potassium permanganate solution: $3.00 \cdot 10^{-2}$ L of the solution was used for the titration.

****

a) Give the equation of the redox reaction of potassium permanganate and disodium oxalate.

b) Calculate the amount of O_2 [in mg] that will oxidize the same number of moles of oxidizable substance as $1.00 \cdot 10^{-3}$ L of $5.00 \cdot 10^{-3}$ mol L^{-1} potassium permanganate does.

c) From the following choices, select the correct reason for the removal of chloride ions and write the letter on the answer sheet.

[A] Some of the chloride ions react with potassium permanganate, resulting in an error in the calculation of the COD.

[B] Some of the chloride ions react with disodium oxalate, resulting in an error in the calculation of the COD.

[C] Some of the chloride ions react with organic compounds in the sample solution, resulting in an error in the calculation of the COD.

[D] A colour is developed during titration, resulting in an error in the calculation of the COD.

d) Calculate the COD [in mg L^{-1}] of the sample solution described in the analytical operation above.

Problem 4

A rechargeable lithium ion battery has been developed in Japan.
The standard electromotive force of the battery is 3.70 V. Assume that the half-reaction at the cathode is

$$CoO_2 + Li^+ + e^- \longrightarrow LiCoO_2,$$

and the half-reaction at the anode is

$$LiC_6 \longrightarrow 6C + Li^+ + e^-.$$

a) Write the total reaction equation of the battery and calculate the value of the standard Gibbs energy of the reaction [in kJ mol^{-1}].

b) The battery cell is constructed using $LiCoO_2$ and graphite (C) as the electrode materials. Calculate the mass of the anode in the completely charged state, and in the completely discharged state, if 10.00 g of $LiCoO_2$ and 10.00 g of graphite (C) are present initially.

c) Calculate the maximum energy generated per mass of the lithium ion battery cell [in kJ kg^{-1}]. Assume that the correct ratio for complete reaction between the cathode and anode materials is used and the sum of the mass of electrodes is 50.0% of the total mass of the battery cell. In comparison, the energy density of lead-acid batteries used for vehicles is about 200 kJ kg^{-1}.

d) Because an aqueous solution cannot be used as an electrolyte, an organic solution is used in the lithium ion battery cell. Give the chemical formula of the gas generated if water is present in the electrolyte.

Problem 5

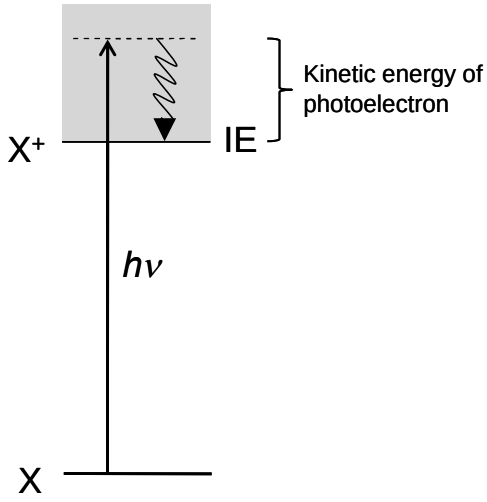


Figure 1. Schematic diagram of photoelectron spectroscopy.

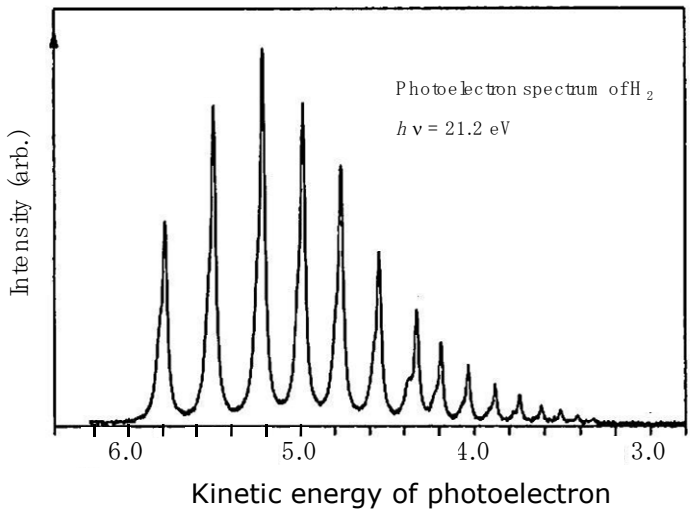


Figure 2. Photoelectron spectrum of H_2. The energy of the incident light is 21.2 eV.

When an atom X absorbs radiation with a photon energy greater than the ionization energy of the atom, the atom is ionized to generate an ion X^+ and an electron (called a photoelectron) is ejected at the same time. In this event, the energy is conserved as shown in Figure 1, that is,

Photon energy ($h\nu$) = ionization energy (IE) of X + kinetic energy of photoelectron.

When a molecule, for example, H_2, absorbs short-wavelength light, the photoelectron is ejected and an H_2^+ ion with a variety of vibrational states is produced. A photoelectron spectrum is a plot of the number of photoelectrons as a function of the kinetic energy of the photoelectrons. Figure 2 shows a typical photoelectron spectrum when H_2 in the lowest vibrational state is irradiated by monochromatic light of 21.2 eV. No photoelectrons are detected above 6.0 eV. eV is a unit of energy and 1.0 eV is equal to $1.6 \cdot 10^{-19}$ J.

a-1) Determine the energy difference ΔE_{A1} [in eV] between H_2 (v = 0) and H_2^+ (v_{ion} = 0) to the first decimal place. v and v_{ion} denote the vibrational quantum numbers of H_2 and H_2^+, respectively.

a-2) Determine the energy difference ΔE_{A2} [in eV] between H_2^+ (v_{ion} = 0) and H_2^+ (v_{ion} = 3) to one decimal place.

b) The electronic energy levels E_n^H of a hydrogen atom are given by the equation

$$E_n^H = -\frac{Ry}{n^2} \quad (n = 1, 2, 3\cdots).$$

Here n is the principal quantum number, and Ry is a constant with dimensions of energy. The energy difference between the n = 1 and the n = 2 states of the hydrogen atom is 10.2 eV.
Calculate the ionization energy E_B [in eV] of the hydrogen atom to one decimal place.

c) The energy threshold for the generation of two electronically excited hydrogen atoms H* (n = 2) from H_2 (v = 0) has been determined as 24.9 eV by an experiment.
Determine the bond energy E_C [in eV] of H_2 to one decimal place.

d) Considering an energy cycle, determine the bond energy E_D [in eV] of H_2^+ to one decimal place. If you have not calculated values for E_B and E_C, then use 15.0 eV and 5.0 eV for E_B and E_C, respectively.

e) Calculate the threshold energy E_E [in eV] of the following dissociative ionization reaction to the first decimal place:

$$H_2 \longrightarrow H^*\ (n=2) + H^+ + e^-$$

If you have not calculated values for E_B and E_C, then use 15.0 eV and 5.0 eV for E_B and E_C, respectively.

f) When H_2 absorbs monochromatic light of 21.2 eV, the following dissociation process occurs at the same time.

$$H_2 \xrightarrow{21.2\ eV} H\ (n=1) + H\ (n=1)$$

Two hydrogen atoms move in opposite directions with the same speed.

Calculate the speed u [in m s^{-1}] of the hydrogen atoms generated in the above reaction. H_2 is assumed to be at rest. If you have not calculated a value for E_C, then use 5.0 eV.

Problem 6

Read the description of four isomeric organic compounds, **A**, **B**, **C**, and **D**. All have molecular formula $C_8H_{10}O$ and contain a benzene ring. Answer the questions that follow. If there are stereoisomers, give all structural formulas. Note that any wrong isomers will be penalised.

- (1) At room temperature, a piece of sodium metal was added separately to **A**, **B**, and **C** in test tubes and the evolution of hydrogen gas was observed only in the case of **C**.
- When an iron(III) chloride aqueous solution was added separately to **C** and **D**, no colouration was observed in **C**, whereas **D** became coloured.
- **A** was oxidized when (2) aqueous potassium permanganate was added to it and the mixture was heated; the acidification of the heated mixture and the isolation of the product afforded benzoic acid.
- If (3) a hydrogen atom in the benzene ring were to be replaced by a chlorine atom, it would be possible to obtain four kinds of monochlorinated structural isomers from **B**, while only two kinds of such isomers would be obtained from **D**.
- Hydrogenation of the benzene ring in **C** and **D** using a catalyst gave saturated alcohol(s). It was found that the saturated alcohol(s) obtained from **C** has(have) no stereogenic carbons, but the one(s) from **D** has(have) stereogenic carbon(s).

a) Among all the isomeric organic compounds of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that do NOT yield hydrogen gas in the underlined procedure [1], in which a piece of sodium is added to the neat samples in the case of the liquid samples and to the concentrated solution of the samples in an aprotic solvent in the case of the solid ones.

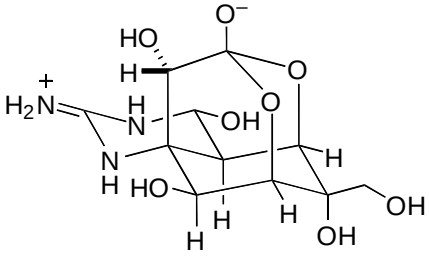
b) Among all the isomeric organic compounds of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that yield benzoic acid in the underlined procedure (2).

c) Among all the isomeric organic compounds of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that could yield four different monochlorinated structural isomers when the underlined transformation in (3) is performed.

d) Give the structural formulae of **A**, **B**, **C**, and **D**. Where there are several possible isomers give the structural formulae of all of them.

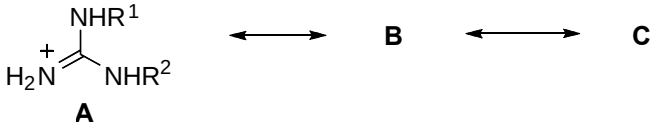
Problem 7

Certain varieties of puffer fish, *Fugu* in Japanese, are highly prized as foods in Japan. Since the viscera (especially ovaries and livers) of the fish contain a potent toxin (tetrodotoxin), food poisoning often results from its ingestion. Studies on tetrodotoxin (**1**) have been performed since the beginning of the 20th century; its chemical structure was elucidated in 1964.



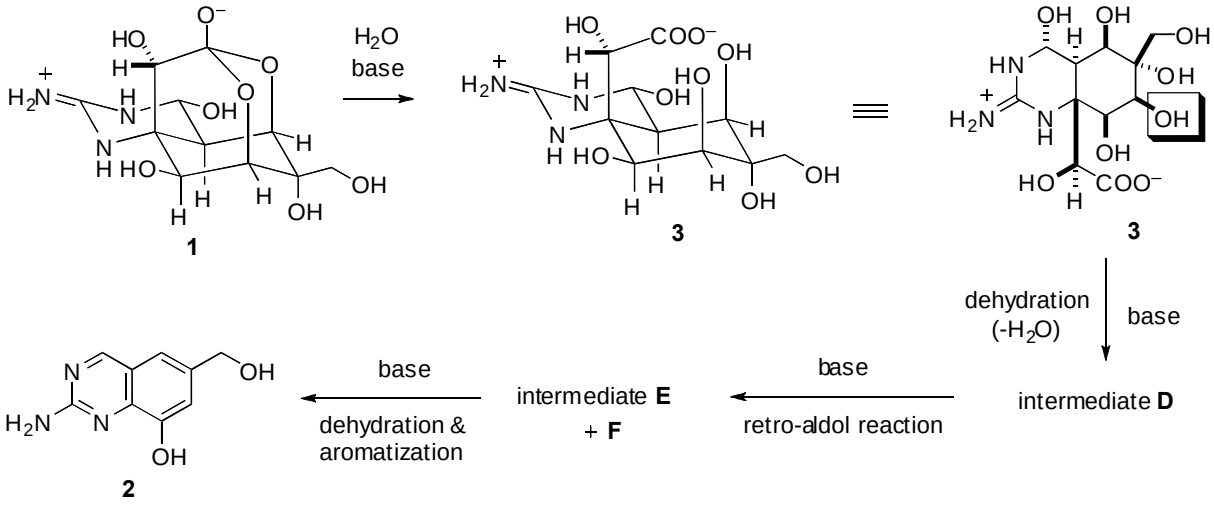
tetrodotoxin (**1**)

a) The guanidine group in tetrodotoxin is strongly basic. The guanidinium ion resulting from protonation on the guanidine group is stabilised by the existence of resonance structures. Draw two resonance structures **B** and **C**.

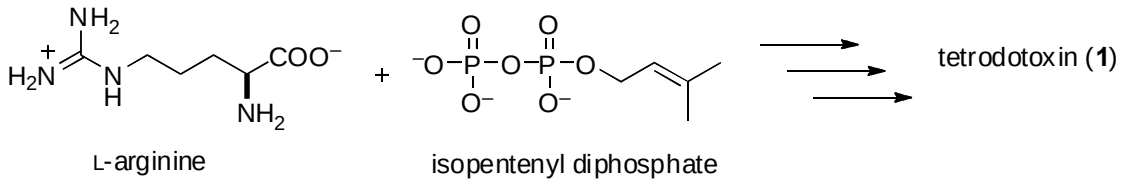


b) Many derivatisation reactions were performed to elucidate the structure of tetrodotoxin. Treatment of tetrodotoxin (**1**) with hot ethanolic potassium

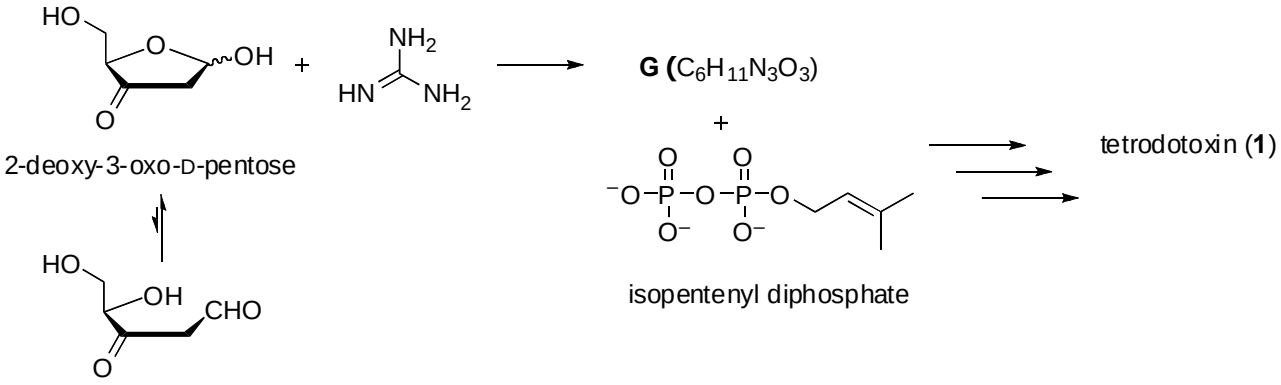
hydroxide gave quinazoline derivative **2**, which provided an insight into the nature of the fundamental skeleton of tetrodotoxin. The reaction mechanism can be described as follows. First, tetrodotoxin is hydrolysed into carboxylate **3**. Then the hydroxyl group highlighted with a frame is eliminated by the base to give intermediate **D**. A retro-aldol reaction of **D** cleaves a carbon-carbon bond to provide intermediates **E** and **F**. Finally, the dehydration and aromatisation of **E** produces the quinazoline derivative **2**. Draw structures of the postulated intermediates **D**, **E**, and **F**.



c) Although the biosynthesis of tetrodotoxin still remains to be clarified, it is proposed that tetrodotoxin may be biologically synthesised from L-arginine and isopentenyl diphosphate. Among all the carbons contained in tetrodotoxin, circle all those that are expected to be of L-arginine origin.



d) In the 1990s, an alternative biosynthetic pathway of tetrodotoxin was proposed. Condensation between 2-deoxy-3-oxo-D-pentose and guanidine provides intermediate **G** of molecular formula $C_6H_{11}N_3O_3$. **G** contains a cyclic guanidine moiety. Tetrodotoxin may be synthesised biologically from intermediate **G** and isopentenyl diphosphate. Draw a structure of the postulated intermediate **G** showing its stereochemistry.



Problem 8

The esterification reaction between bi-functional molecules typically gives a linear chain polymer as shown in eq.(1) by polycondensation (often called "condensation polymerisation"). The control of polymerisation conditions and procedures determines the length of polymer strands, i.e., *the average degree of polymerisation*, ***X*** (note that ***X*** = 2***n*** in the present instance). Because ***X*** and ***n*** are averaged numbes, they are not always integer values.

$$n\ \mathrm{HOOC\text{-}R^1\text{-}COOH} + n\ \mathrm{HO\text{-}R^2\text{-}OH} \longrightarrow \mathrm{HO\text{-}[COR^1CO\text{-}OR^2O]}_n\text{-}\mathrm{H} + (2n-1)\mathrm{H_2O} \quad (1)$$

X can be estimated from the consumption of functional groups (here, -COOH and -OH). Let us define the degree of reaction, **p**, as **p** = (N_0 - N) / N_0.
N_0 and N denote the total numbers of functional groups before and after the polymerisation respectively and **p** $\leq$ 1.
For each functional group of the dicarboxylic acid molecules (**A**) and diol molecules (**B**), we add the suffixes of "$_A$" or "$_B$" such as N_{A0}, N_{B0}, N_A or N_B, respectively, i.e., $N_0 = N_{A0} + N_{B0}$ and $N = N_A + N_B$. When the initial feed is unbalanced such as $N_{A0} \leqq N_{B0}$, **X** is expressed by $\mathbf{p}_A$ and **r** as shown in eq.(2), where $\mathbf{r} = N_{A0} / N_{B0}$ ($\leqq 1$). If **r** = 1, $\mathbf{p}_A$ is identical to **p** and eq.(2) becomes the same to the Carothers equation.

$$\boldsymbol{X} = (1 + \boldsymbol{r}) / (1 + \boldsymbol{r} - 2\boldsymbol{p}_A\boldsymbol{r}) \quad (2)$$

a) A sample of nylon-6,6 was prepared by polycondensation of an e*quimolar* mixture of adipic acid (hexanedioic acid) and hexamethylenediamine (hexane-1,6-diamine).

a-1) Show the chemical structure of this nylon-6,6 sample. [Caution: what are the end groups when polycondensation was started from the *equimolar* mixture?]

a-2) When this nylon-6,6 sample carries an average molecular weight, ***M***, of 5507.25 [in g mol^{-1}], give the value of ***X*** to *two decimal places*.

a-3) Give the ***p*** value necessary to prepare this nylon-6,6 sample of ***M*** = 5507.25 [in g mol^{-1}] to *five decimal places*. If you get no numerical answer in a-2), use 52.50 instead.

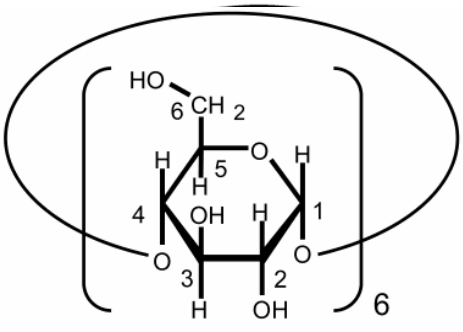
b) The low-molecular-weight polyester (oligoester) is prepared from a mixture of 36.54 g of adipic acid (hexanedioic acid) and an unknown amount ***W*** [in g] of butane-1,4-diol (Bdiol). Under the condition of $\boldsymbol{p}_A \to 1$, the oligoester with ***X*** = 11.00 carrying Bdiol units at both chain ends is obtained.

b-1) Show the *precise* chemical structure of this oligoester of ***X*** = 11.00.

b-2) Calculate the unknown amount, ***W*** [in g], to the first decimal place.

Problem 9

α-Cyclodextrin (αCyD), which is a cyclic oligosaccharide of six α(1→4) linked α-D-glucopyranoside units, can be topologically represented as toroids (Figure 1). α-D-glucopyranoside units in αCyD are usually in the most stable chair conformation.



αCyD

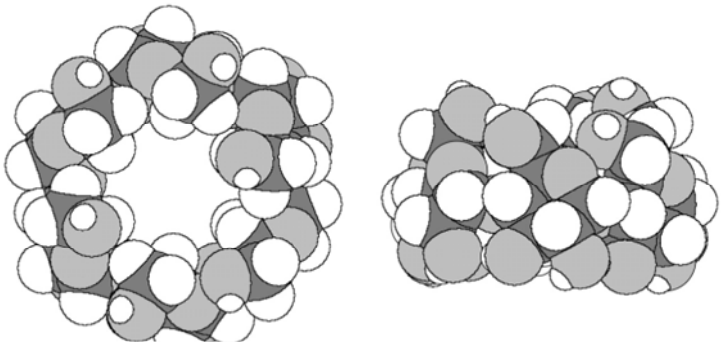
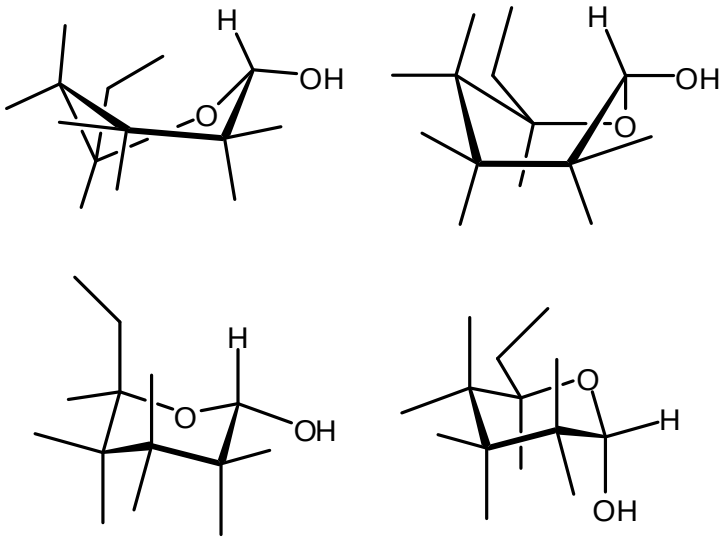


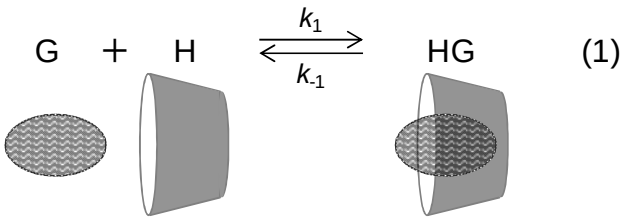
Figure 1. Space filling model of □CyD. Left: view through the hole. Right: side view.

a) Give the absolute configuration (*R* or *S*) at stereogenic carbons C-2 and C-5 of D-glucose. Also, draw a stereostructure of the open chain form of D-glucose.

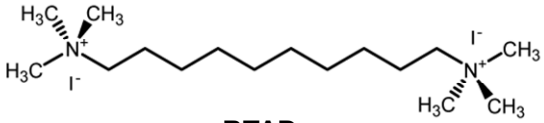
b) Choose the most stable conformation from the four incomplete α-D-glucopyranose formulae given in the answer box and enclose it in a box. Also, add four OH groups and four H atoms to complete the -D-glucopyranose formula.



αCyD in water is able to host hydrophobic molecules. When the host/guest (H/G) stoichiometry is 1/1, the inclusion complexation can be given by the following equilibrium.



where k_1 and k_{-1} are the rate constants for the forward and backward reactions respectively. The complexation of a guest in αCyD causes a chemical shift change in the ^{1}H NMR spectrum. Figure 2 shows a part of the ^{1}H NMR spectrum (the signal shown is that from H-1 of αCyD) showing the chemical shift change in the presence of varying amounts of 1,10-bis(trimethylammonium)decane diiodide (BTAD). The doublet peak at 5.06 ppm is from H-1 of free αCyD, while the doublet at 5.14 ppm is from H-1 of αCyD complexed with BTAD. (Note that the spectra given in Figure 2 were measured in the complexation equilibrium state.)



BTAD

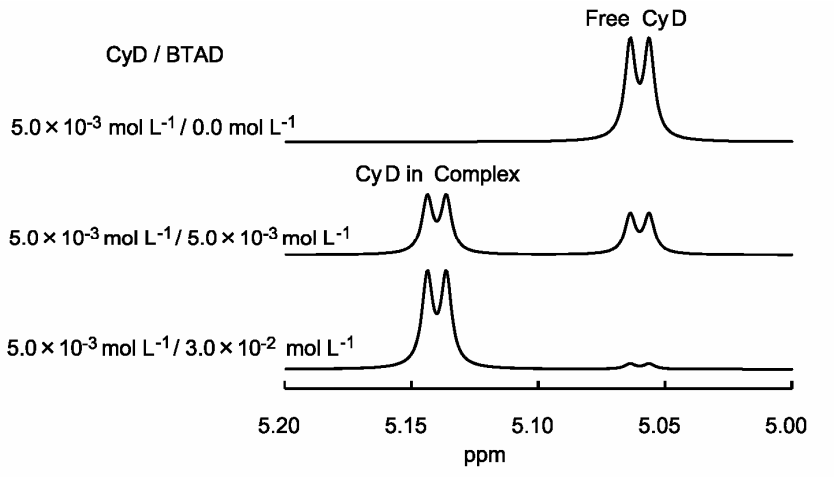
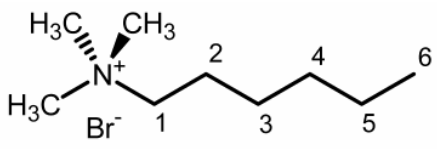


Figure 2. Expanded ^{1}H NMR spectra (signals from H-1 of αCyD) of solutions containing $5.0 \cdot 10^{-3}$ mol L^{-1} αCyD and 0-$3.0 \cdot 10^{-2}$ mol L^{-1} BTAD.

c) In the spectrum of $5.0 \cdot 10^{-3}$ mol L^{-1}/$5.0 \cdot 10^{-3}$ mol L^{-1} αCyD/BTAD, the relative peak areas of the doublets at 5.06 and 5.14 ppm are 0.41 and 0.59, respectively. Calculate, to 2 significant figures, the concentration equilibrium constant, *K,* for the formation of the inclusion complex of αCyD/BTAD.

Complexation of αCyD with hexyltrimethylammonium bromide (HTAB) appears in the ^{1}H NMR spectra in a different way from the αCyD/BTAD complexation. Figure 3 shows a part of the ^{1}H NMR spectra (H-6 signal of HTAB) in αCyD/HTAB solutions. The H-6 signal from free HTAB is a triplet at 0.740 ppm and the H-6 signal from HTAB complexed with αCyD is a triplet at 0.860 ppm. In a mixture the signal appears as one triplet (not two triplets), whose chemical shift depends upon the fraction of the concentrations of free and complexed HTAB.



HTAB

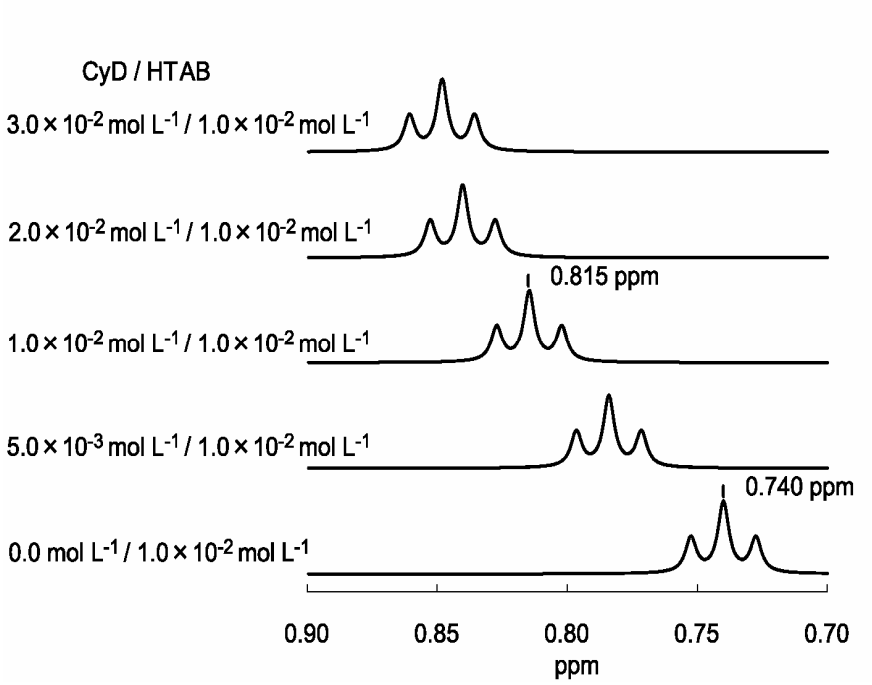


Figure 3. Expanded ^{1}H NMR spectra (H-ω signal of HTAB) of solutions containing $1.0 \cdot 10^{-2}$ mol L^{-1} HTAB and 0-$3.0 \cdot 10^{-2}$ mol L^{-1} αCyD.

d) The signal of HTAB in αCyD/HTAB solutions appears as one triplet, which shifts depending on the concentration of αCyD. Choose the rational interpretation(s) just from these spectra and write the letter on the answer sheet.
hint: When a guest molecule move in and out of αCyD rapidly and repeatedly, only one signal of the guest is observed at the weighted average of the chemical shifts of the free guest and the shift of the guest included in αCyD.

a. k_1 of αCyD/HTAB > k_1 of αCyD/BTAD
b. k_1 of αCyD/HTAB < k_1 of αCyD/BTAD
c. K of αCyD/HTAB > K of αCyD/BTAD
d. K of αCyD/HTAB < K of αCyD/BTAD

e) The signals of HTAB in $1.0 \cdot 10^{-2}$ mol L^{-1}/$1.0 \cdot 10^{-2}$ mol L^{-1} αCyD/HTAB are positioned at 0.815 ppm. Calculate the value of K, to 2 significant figures, for the complexation of αCyD/HTAB.

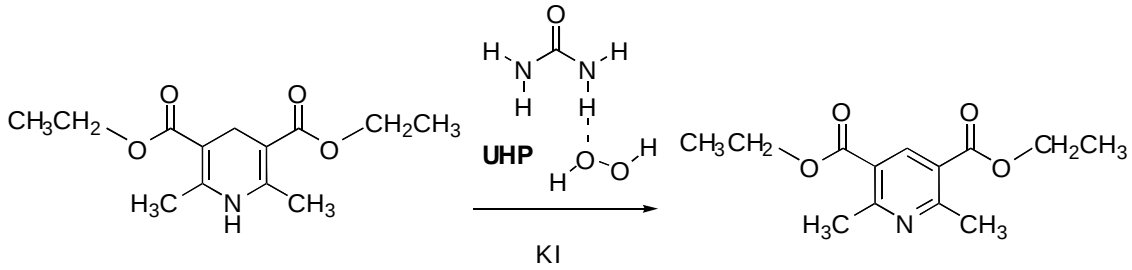
f) At 40.0 ºC and 60.0 ºC, the values of K for the complexation of αCyD/HTAB are $3.12 \cdot 10^2$ and $2.09 \cdot 10^2$ respectively. Calculate, to 2 significant figures, the enthalpy change, ΔH^o [in kJ mol^{-1}], and the entropy change, ΔS^o [in J K^{-1} mol^{-1}]. (Ignore the temperature dependence of ΔH^o and ΔS^o.)

Practical Test

Given was a list of general information, apparatus per student, chemicals on each desk, risks and fafety phrases and a Periodic table with relative atomic masses

Task 1 Reaction of Hantzsch Ester with Urea Hydrogen Peroxide

In this experiment, you are required to synthesise a pyridinedicarboxylate derivative from 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester (1,4-DHP or Hantzsch ester) by oxidation with urea hydrogen peroxide (UHP), an environmentally-friendly oxidant.



1,4-DHP

Procedures

(1) Place a 22-mm magnetic stirring bar in a 100-mL test tube. Clamp the test tube above the magnetic stirrer plate. Add 1,4-DHP (1 g) (labelled as 1,4-DHP_powder), and potassium iodide (150 mg) to the test tube, followed by ethanol (5 mL), with a 5-mL graduated pipette.

(2) Add 1 g UHP in a single portion (wear gloves) and stir the mixture. (**Caution: this reaction is exothermic.**)

(3) For thin layer chromatography (TLC) analysis, prepare a mixture of ethyl acetate:heptane (1:2 in volume) with the cone-shaped measuring cylinder and place an appropriate amount of the mixture in a TLC developing chamber. Add 1 mL of ethyl acetate to the vial (labelled as 1,4-DHP_TLC) to dissolve 1,4-DHP (3 mg).

(4) Check your TLC plates before using. If they are damaged, they can be replaced without penalty. Draw a start line on the lower portion of a TLC plate with a pencil (see Fig. 1.1).

(5) During the reaction, the reaction mixture becomes clear (usually within 20 min). When the reaction mixture becomes clear (a precipitate may form when it cools, but this will not affect the TLC analysis), take a small portion of the mixture using a glass capillary and load it to make two spots in the

centre and right positions on the TLC plate as shown in Fig 1.1. Load an appropriate amount of the 1,4-DHP solution prepared in procedure (3) in the centre and left positions, so that there are three spots in total on the plate, with the centre spot containing both the reaction mixture and 1,4-DHP (see Fig. 1.1). Develop the TLC plate in the TLC chamber (see Figs. 1.1 and 1.2). Mark the solvent front with the pencil. Visualise the spots using a UV lamp (254 nm) and draw a line around the UV-active spots on the TLC clearly with the pencil. Assess the completion of the reaction based on the TLC results. Repeat the TLC analysis after ten minutes, if you find significant amounts of 1,4-DHP in the reaction mixture. [Note that you will perform TLC analysis again in procedure (8).] Place the last TLC plate in the zipped storage bag marked "A", making sure that the bag is labelled with your student code number.

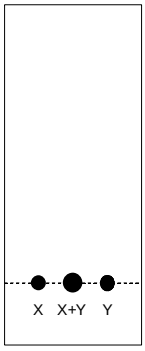


Fig. 1.1 Spots on the TLC plate before development;
X: 1,4-DHP,
Y: Reaction mixture.

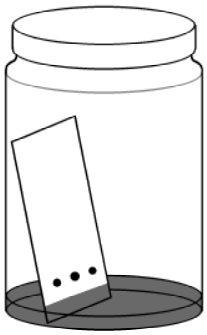


Fig. 1.2 TLC plate placed in the TLC developing chamber.

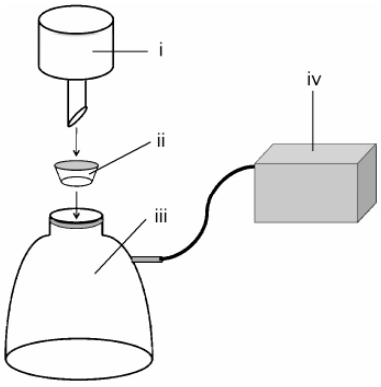


Fig. 1.3 Suction filtration equipment:
i, Büchner funnel;
ii, rubber seal;
iii, suction flask;
iv, diaphragm vacuum pump.

(6) Set up the suction filtration equipment (see Fig. 1.3). Connect the suction flask to the diaphragm vacuum pump. Place a Büchner funnel fitted with a rubber seal onto the suction flask. Place the glass microfibre filter sheet on the funnel.

(7) Add water (5 mL) to the reaction mixture using a 10-mL plastic measuring cylinder. Add sodium metabisulfite (1 g), transfer the contents of the tube (including the stirring bar) into a 200-mL conical beaker and wash the test tube with water (30 mL) into this beaker. Place the 200-mL conical beaker on the magnetic stirrer and stir the solution. Add saturated sodium hydrogencarbonate solution in small portions using a 2-mL graduated pipette until the pH of the aqueous phase becomes just over 7 (check the pH with pH test paper). Filter the precipitate formed through the Büchner funnel, with suction using the diaphragm vacuum pump, and wash the precipitate with a small portion of water. Suck air through the precipitate for one minute to dry the product.

(8) Transfer the filtrate from the suction flask to a 300-mL conical beaker. Transfer a 2 mL portion of the filtrate to a 10-mL test tube using a 2-mL graduated pipette. Place a 10-mm magnetic stirring bar in the test tube and fix it securely with the clamp over the stirrer plate. Add 1 mL of ethyl acetate to the test tube using a 2-mL graduated pipette and stir the solution vigorously for 30 seconds. Stop stirring and wait for the solution to separate into two layers. Analyse the upper layer by TLC to see if there is any product remaining in the filtrate. Spot the filtrate on the plate in the same way as in procedure (5). Mark the solvent front and the spot(s), if any. Place the TLC plate in the zipped storage bag marked "B", making sure that the bag is labelled with your student code. If you detect any product on the TLC plate, add more saturated sodium hydrogencarbonate solution.

(9) At this stage, if you find a precipitate formed, collect it by filtration by passing the suspension through the microfibre already containing your product, thus combining the precipitates, and wash it with a small volume of water. If you find no precipitate, skip this filtration process.

(10) Suck air through the precipitate for 10 minutes to dry the product. Place your product and the glass microfibre filter sheet in the crystallisation dish. Cover the dish with the lid marked with your student code. Avoid placing the stirring bar in the dish. Place the crystallisation dish with the lid in the zipped storage bag marked "C".

a) Copy (sketch) the TLC plate in bag "A" on your answer sheet.

b) Determine and record the R_f values (to 2 decimal places) of the spots on the TLC plate in bag "A".

c) Draw the structural formula of the organic cation present before adding sodium hydrogencarbonate.

d) What is (are) the final product(s) derived from UHP? Give the chemical formula(e) of the product(s).

e) Submit the following:
   i) TLC plate in bag "A"
   ii) TLC plate in bag "B"
   iii) Your product and filter paper in the crystallisation dish placed in bag "C".

Task 2 Determination of Fe(II) and Fe(III) by visual colourimetry

In this experiment, you are required to determine the concentrations of Fe(II) and Fe(III) in a given sample solution, which simulates a dissolved magnetite ore, by visual colourimetric analysis involving a colour reaction between Fe(II) and 2,2'-bipyridine (bpy) to form an intensely red complex, $Fe(bpy)_3^{2+}$.

The amount of $Fe(bpy)_3^{2+}$ complex can be quantified by visual colourimetric measurement using Nessler tubes. This is a quite simple technique that was employed before photoelectric instruments were generally available, but an accuracy of better than ±5% can be achieved. In this technique, a pair of Nessler tubes is used: one is filled with a reference solution, and the other is filled with the solution to be tested. The intensities of the colours of the two solutions, as judged by eye, are balanced by adjusting the height of liquid column of the solution being tested.

When the colours look the same, the concentration can be calculated from that of the reference solution with a known concentration and the height of the column of each solution based on the Beer – Lambert law:

$$A = \varepsilon c l$$

where A is the absorbance, c is the concentration, l is the path length and ε is the molar absorption coefficient. First, you will learn to employ this technique by conducting **measurements A** and **B**, and then you will determine the concentrations of Fe(II) and Fe(III) with **measurements C** and **D**.

Procedures

(1) Add 5 mL of acetate buffer solution, 5 mL of disodium hydrogenphosphate solution (to mask any Fe(III) ions present), 5 mL of 2,2'-bipyridine solution and 10.00 mL of sample solution into a 50-mL volumetric flask using appropriate pipettes for each and dilute the resulting solution with water to the 50-mL mark. Stopper the flask and mix the solution well. Allow it to stand for at least **20 min** to develop colour fully. This solution is named "**sample 1**."

(2) Add 5 mL of acetate buffer solution, 5 mL of 2,2'-bipyridine solution and 5.00 mL of sample solution into a 50-mL volumetric flask. Add 20 mg of sodium thioglycolate powder (an excess) to reduce the Fe(III) to Fe(II). Dilute the solution with water to the 50-mL mark, stopper the flask and mix the solution well. Allow it to stand for at least **20 min**. This solution is named "**sample 2**."

(3) Perform visual colourimetric measurements A – D based on the "Instructions for visual colourimetric measurement" shown below.

Instructions for visual colourimetric measurement

Set a pair of Nessler tubes on a Nessler tube rack placed on an LED light box (do not remove it from the bag at any time) and turn on the light (see Fig. 2.1). Pour the "**standard $Fe(bpy)_3^{2+}$ solution 1**" provided into one tube to an appropriate height (70 – 90 mm is recommended). The etched marks on the tube indicate fixed heights from the bottom in mm. Use this as a reference for **measurements A - D**. Pour the solution to be measured into the other tube, and then compare its colour intensity with that of the reference solution by looking downward through the solutions toward the LED light box. Adjust the height of the liquid column of the test solution by adding or removing the solution with a graduated pipette until the colour intensity of the two soloutions is identical. Record the height of the two solutions, estimating your readings to a precision of at least 1 mm.

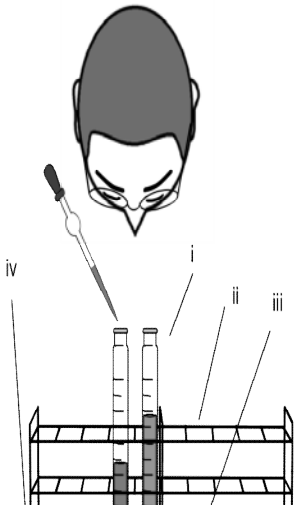


Fig. 2.1 Visual colorimetric measurement:
i, Nessler tube;
ii, Nessler tube rack;
iii, LED light box in a zipped storage bag; iv, power switch.

Note that when two intensities of colour are close, but not identical, they may be indistinguishable to the human eye. The appropriate value for the height of the test solution, *h*, should be determined by taking this into account. When adjusting the height of the test solution, take note of both when the colours first appear identical, and when they stop appearing identical. Then take an average between the values of lower and higher limits.

Measurement A: Perform a measurement using "**standard $Fe(bpy)_3^{2+}$ solution 1**" as both the reference and the test solutions. In this measurement, pour the reference solution into a Nessler tube to achieve an appropriate height, and then pour the test solution into the other Nessler tube until the intensity of the colours of the two solutions first seem to match each other. (When the colour-intensities match, the heights should IDEALLY be the same, but note the earlier comment about the sensitivity of the human eye.) Then add more test solution until you determine that the colour-intensities have become different from each other. Report both the lower and higher limits of the height of the liquid column of test solution with the same intensity of colour as the reference solution.

a) Report your results for **measurement A** using the table provided on the answer sheet.

Measurement B: Perform a measurement of "**standard $Fe(bpy)_3^{2+}$ solution 2**" as a test solution using "**standard $Fe(bpy)_3^{2+}$ solution 1**" as a reference.

b) Report your results for **measurement B** using the table provided on the answer sheet.

Measurement C: Perform measurement of **sample 1.**

c) Report your results for **measurement C** using the table provided on the answer sheet.

Measurement D: Perform measurement of **sample 2.**

d) Report your results for **measurement D** using the table provided on the answer sheet.

e) Express the concentration of the test solution, *c*, using the concentration of the reference solution, *c'*, and the height of each liquid column, *h* and *h'*.

f) Calculate the concentrations of Fe(II) and Fe(III) in the original sample solution in mg L^{-1}.

Task 3 Polymers in Analysis

Polymers can be used in various analyses. In this task, you are first required to analyse a polysaccharide using a polymer-polymer interaction, which will then be utilised to identify polymers in the second part.

3.1 Analysis of Polysaccharide by Colloid Titration

You are provided with a solution of a polysaccharide containing sulphonate ($-SO_3^-$) and carboxylate ($-COO^-$) groups. You are asked to determine the concentrations of these two groups by colloid titration, under basic and acidic conditions, based on the differences in the abilities of these groups to be protonated. A back-titration technique is used.

When these groups are ionised, the polysaccharide becomes a poly-anion. Upon addition of the poly-cation, poly(diallyldimethylammonium) (provided as its chloride salt, PDAC), it forms a poly-ion complex. PDAC solution is standardised using the standard solution of potassium poly(vinyl sulfate) (PVSK) provided. At the endpoint of colloid titrations, the number of anionic groups is equal to that of cationic groups.

Procedures

(1) Take precisely 20 mL of the PDAC solution using a volumetric pipette into a 100-mL conical beaker. Add 2 drops of toluidine blue (TB) into the conical beaker. Titrate the resulting blue solution with the 0.0025 mol L^{-1} PVSK (monomer unit concentration) standard solution. At the endpoint, the colour turns purple. Note that the solution becomes gradually turbid as the endpoint approaches. The endpoint is determined when the colour remains purple for 15-20 seconds. Repeat if necessary.

1a) Record the PVSK solution volume (in mL) consumed in the standardisation of PDAC. Record your reading to 0.05 mL.

(2) Take precisely 5 mL of the polysaccharide solution and 20 mL of the PDAC solution using volumetric pipettes into another conical beaker. Add 0.4 mL of 0.5 mol L^{-1} NaOH and 2 drops of TB to the solution. Titrate the resulting blue solution with the PVSK standard solution in a similar manner. Repeat if necessary. (The appearance of coagulation may be different, depending on the pH of the solution.)

1b) Report the PVSK solution volume (in mL) consumed in the titration under basic conditions. Record your reading to 0.05 mL.

1c) Mark with a cross in the appropriate box(es), the acid group(s) ionised under the basic conditions on the answer sheet.

(3) Repeat procedure 2 above with the addition of 0.5 mL of 0.5 mol L^{-1} HCl instead of 0.5 mol L^{-1} NaOH.

1d) Report the PVSK solution volume (in mL) consumed in the titration under acidic conditions. Record your reading to 0.05 mL.

1e) Mark with a cross in the appropriate box(es), the acid group(s) fully ionised under acidic conditions on the answer sheet.

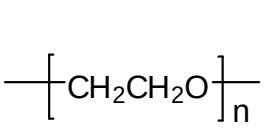
1f) Calculate the concentrations of the $-SO_3^-$ (or $-SO_3H$) groups and the $-COO^-$ (or -COOH) groups (in mol L^{-1}) in the given polysaccharide solution.

3.2 Identification of compounds

You are provided with five solutions **(X-1~5, "X" designates your sample code, which is a letter in the Roman alphabet from A to H)**, and each solution contains one of the compounds below (all of which are used). The concentration is 0.05 mol L^{-1} (for polymers, monomer unit concentration). Your task is to identify all the compounds by carrying out the following procedures.

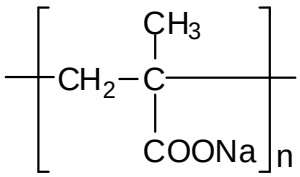
$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$

(TEG)



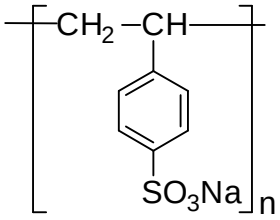
(PEO)

MW = 100,000

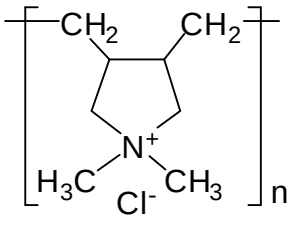


(PMANa)

MW = 9,500



(PSSNa)
MW = 70,000



(PDAC)
MW = 200,000-350,000

[Abbreviations: **TEG**, triethylene glycol;
PEO, poly(ethylene oxide);
PMANa, poly(sodium methacrylate);
SSNa, poly(sodium 4-styrenesulfonate);
PDAC, poly(diallyldimethylammonium chloride)
MW stands for molecular weight]

Helpful comments

1) Aggregates observed in **Task 3.1** could be observed when mixing two polymer solutions in an appropriate combination, in which an interaction takes place between the two polymers. They can be utilized to identify polymer samples.
2) The volume of a solution measuring 5 mm in height from the bottom of the vial is approximately 1 mL. Rememeber that you have only 10 mL of each solution.

Procedures

(1) Mix similar volumes of two solutions together in a vial.
(2) If necessary, you can acidify the resulting mixture. Ten drops of hydrochloric acid (0.5 mol L^{-1} HCl) from a plastic Pasteur pipette are sufficient for this purpose.

Identify the compound in each solution based on the experimental results. For each solution, mark one of the five boxes to indicate your identification. You are also asked to fill in the blanks with one of the letters in the Roman alphabet, from A to H, to indicate your sample code.

The Answers to the Theoretical Problems of the IChO

Solution to problem 1

a) The amount *n* of the pure nitrogen (*chemical nitrogen*), M = 28.02 g mol^{-1}, is

$n = \frac{m}{M} = \frac{2.2290\,g}{28.02\,g/mol} = 8.205\cdot10^{-2}$ mol

Then, from the ideal gas law, $p\cdot V = n\cdot R\cdot T$

$V = \frac{8.205\cdot10^{-2}\cdot8.314\cdot288.15}{1.013\cdot10^{-5}}\ m^3 = 1.940\cdot10^{-3}\ m^3$.

b) The equation for the ratio of the mass of *atmospheric* nitrogen to the mass of *chemical* nitrogen is

$$\frac{28.02\cdot(1-x)+39.95\,x}{28.02} = \frac{2.3102}{2.2990} \Rightarrow$$

$$x = \frac{(2.3102-2.2990)/2.2990}{39.95-28.02}\cdot28.02 \qquad x = 1.14\cdot10^{-2}$$

c) According to Figure 1, the wavelength of the D_3 line is approximately 587.7 nm .

The corresponding photon energy is $E = \frac{h\,c}{\lambda}$

$E = \frac{6.626\cdot10^{-34}\cdot2.998\cdot10^{8}}{587.7\cdot10^{-9}}$ J $\qquad E = 3.380\times10^{-19}$ J.

d) The energy, 3.382×10^{-19} J, matches with the energy of the transition [E] between the 2p and 3d orbitals.

e) [A] $^{238}U \longrightarrow {}^{234}Th + \alpha$

f) [C] $^{40}K \longrightarrow {}^{40}Ar + \varepsilon/\beta^+$ (electron capture / positron emission)

g) The density ρ is given by $\rho = \frac{n\,M}{V}$ Combining with the ideal gas law gives:

$M = \frac{\rho\,R\,T}{p} = \frac{0.850\cdot8.314\cdot288.15}{1.013\cdot10^{5}}$ kg/mol $\qquad M = 0.0201$ kg mol^{-1} (20.1 g mol^{-1})

h) From the equation for the sonic velocity. $f\cdot\lambda = \sqrt{\frac{\gamma\,R\,T}{M}}$.

$\gamma = \frac{M}{R\,T}\cdot(f\,\gamma)^2 = \frac{2{,}01\cdot10^{-2}}{8.314\cdot288.15}\cdot(3520\cdot0.115)^2 \qquad \gamma = 1.40$

i) [B] From M = 20.1 g mol^{-1}. this gas must be HF or Ne.
From γ = 1.4 ($\neq$ 5/3$\approx$1.67). this is NOT a monoatomic gas .
Thus this gas must be [B] HF.
Note: It is not possible to distinguish between HF (M = 20.01) and Ne (M = 20.18) from the molar mass only, which is 20.10±0.12 by taking into account the uncer-

tainty of ρ (±0.005 / 0.850 = ±0.6%). However. the precision of γ = 1.40 is enough to exclude the possibility of monoatomic gas (γ = 5/3≈1.67).

Solution to problem 2

a) Number of ions Na^+: 4 Cl^-: 4
Coordination number Na^+: 6 Cl^-: 6

b) Length of lattice l : l = 2·0.102 nm + 2·0.181 nm = 0. 566 nm
Density ρ:
$\rho = \frac{(22.99+35.45)\cdot 4}{(0.566\cdot 10^{-9})^3 \cdot 6.022\cdot 10^{23}}$ g/m^3 = 2.14·10^6 g/m^3 = 2.14·10^3 kg/m^3

c) A: Na (s) + 1/2Cl_2 (g) ⟶ NaCl (s)
F: NaCl (s) ⟶ Na^+ (g) + Cl^- (g)

d) Enthalpy conservation condition: –A + B + C + D/2 = F – E
[–(–411) + 109 + 496 + (242/2)] kJ/mol = F + 349 kJ/mol
F = 788 kJ/mol
The lattice formation enthalpy of NaCl = –F = –788 kJ mol^{-1}

e) A: CaO B: CO_2 C: $NaHCO_3$ D: NH_4Cl E: $Ca(OH)_2$

Solution to problem 3

a) $2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 \longrightarrow 2MnSO_4 + 5Na_2SO_4 + K_2SO_4 + 10CO_2 + 8H_2O$
or
$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + 10CO_2 + 8H_2O + K_2SO_4$
or
$2\ MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

b) The reactions of potassium permanganate and O_2 are as follows:
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$
hence 1 mol of $KMnO_4$ amounts to 1.25 mol of O_2
5 · 5.00·10^{-3} mol/L · 10^{-3} L = 4 · X/32 mol
where X is the amount of O_2 ⇒ X = 2.00·10^{-4} g = 2.00·10^{-1} mg .

c) [A]

d) The amounts of electrons used for reduction and oxidation are equal, then
5 · 5.00·10^{-3} mol/L · (100 mL+A)/10^3 L = 2 · 1.25·10^{-2} mol/L · 100/10^3 L + X
where A is the amount of potasium permanganate used for the final titration and X is the amount of electrons for the oxidizable substance
⇒ X = 2.50·10^{-5} · A
at A = 30.0 mL X = 7.50·10^{-4} mol

$\Rightarrow$ COD = 32/4 g mol^{-1} · $7.50 \cdot 10^{-4}$ mol·10^3 mg/g · 1/1 L^{-1} = 6.00 mg L^{-1}

Solution to problem 4

a) $CoO_2 + LiC_6 \longrightarrow LiCoO_2 + 6C$
$\Delta G^0 = -nFE^0 = -1 \cdot 96485$ C $mol^{-1} \cdot 3.70$ V = −357 kJ mol^{-1}

b) The amount of $LiCoO_2$ is (10.00/97.87) mol = 0.1022 mol.
the amount of C is (10.00/12.01) mol = 0.8326 mol > 0.1022 mol·6 = 0.6132 mol
$\Rightarrow$ the mass in the completely charged state of the anode is
10.00 g + 0.1022 mol · 6.94 g/mol = 10.71 g.

c) The mass of 1 mol $LiCoO_2$ is 97.87 g
the mass of 6 mol C is 12.01 · 6 g = 72.06 g
the total mass of the electrode is (97.87 + 72.06) g = 169.93 g
the mass of the cell is 169.93 g / 0.500 = 340 g
the maximum energy generated is 357 kJ.
thus the maximum energy per unit mass of the cell is 1050 kJ kg^{-1}

d) H_2 or H_2 and O_2

Solution to problem 5

a-1) The spectral peak at 5.8 eV in Fig. 2 corresponds to the electron with the highest kinetic energy. which is generated by the reaction $H_2(v = 0) \longrightarrow H_2^+(v_{ion} = 0) + e$. accordingly. ΔE_{A1} = 21.2 eV − 5.8 eV ΔE_{A1} = 15.4 eV

a-2) One can estimate from Fig. 2 that the energy difference ΔE_{A2} between H_2^+ ($v_{ion} = 0$) and H_2^+ ($v_{ion} = 3$) is approximately 0.8 eV ΔE_{A2} = 0.8 eV

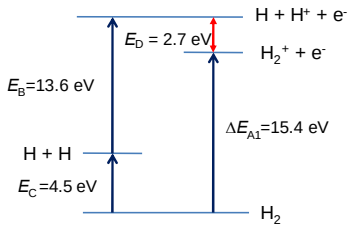
b) The ionization energy corresponds to $n = \infty$. accordingly.

$\Delta E_{n=2 \leftarrow n=1} = \frac{3}{4} Ry = 10{,}2\,eV$ $\Delta E_{n=\infty \leftarrow n=1} = Ry$

$\Rightarrow E_B$ = 10.2 eV $\frac{4}{3}$ E_B = 13.6 eV

c) 24.9 eV = the binding energy of a hydrogen molecule + 10.2 eV + 10.2 eV
$\Rightarrow$ the binding energy of a hydrogen molecule = E_C = 4.5 eV

d) From the figure below
$E_D = E_B + E_C - \Delta E_{A1}$ = (13.6 + 4.5 − 15.4) eV = 2.7 eV
E_D (eV) = 2.7 eV



e) From the figure above, the threshold energy for the dissociative ionization reaction

$$H_2 \longrightarrow H^* (n = 2) + H^+ + e^-$$

is $E_B + E_C + 10{,}2$ eV = (13,6 + 4,5 + 10,2) eV = 28,3 eV.

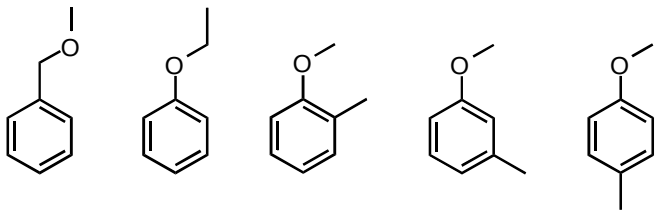
f) The excess energy is 16.7 eV (= 21,2 eV – 4.5 eV). Because two hydrogen atoms are generated upom photodissociation, half of the excess energy is released as translational energy of the hydrogen atoms.

$$\frac{1}{2}mu^2 = 8.35\ \text{eV} = 1.34 \cdot 10^{-18}\ \text{J} \qquad m = \frac{1.008 \cdot 10^{-3}\ \text{kg mol}^{-1}}{6.022 \cdot 10^{23}\ \text{mol}^{-1}} = 1.67 \cdot 10^{-27}\ \text{kg}$$

$$u^2 = 1.6 \cdot 10^9\ \text{m}^2\ \text{s}^{-2} \qquad u \approx 4.0 \cdot 10^4\ \text{m s}^{-1}$$

Solution to problem 6

a)



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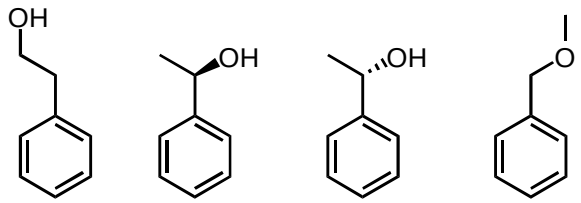

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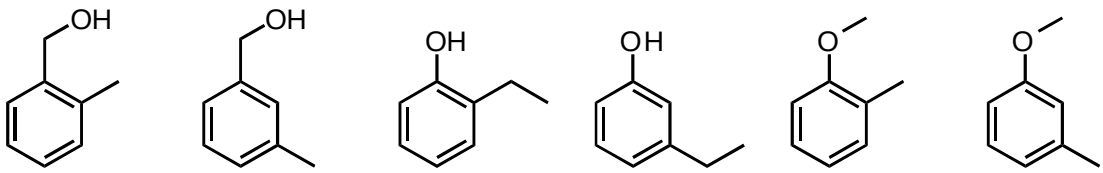
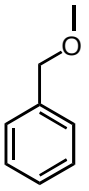
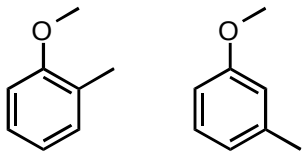


d) **A**



B



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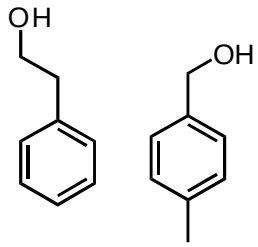
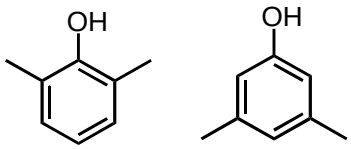
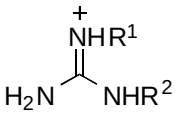


D

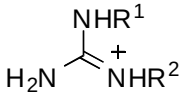


Solution to problem 7

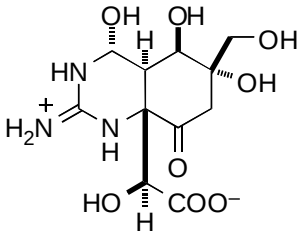
a) **B**



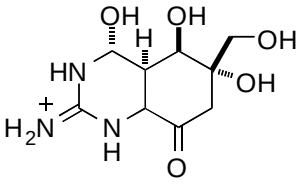
C



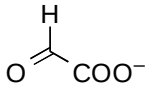
b) **D**



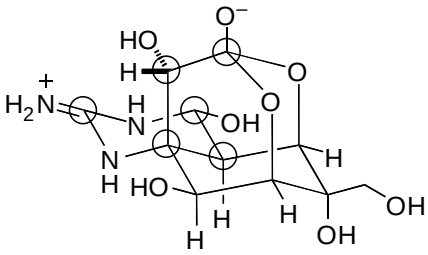
E



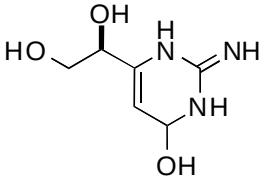
F

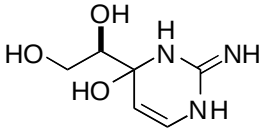


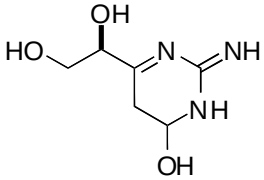
c)

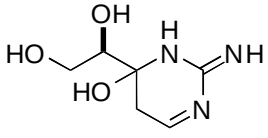


d) **G**



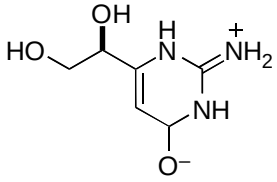






acceptable

Each zwitter ionic structure (and protonated structure) like below is acceptable



Tautomers concerning guanidine moiety are all acceptable.

Solution to problem 8

a-1) HO-[CO$(CH_2)_4$CO-NH$(CH_2)_6$NH]$_n$-H

a-2) The unit molecular weight. M_u. is calculated to be

M_u = ½ · (12.01 · 12 + 1.01 · 22 + 14.01 · 2 + 16.00 · 2) g/mol = 113.18 g/mol

X = (5507.25 - 18.02) / M_u = (5507.25 - 18.02) / 113.18 = 48.50. or

X = 2n = 2 × [(5507.25 - 18.02) / 226.36] X = 48.50

a-3) From eq.(2) at $\boldsymbol{r}$ = 1 (Carothers eq.). X = 48.50 = 1 / (1 - p).
then $\boldsymbol{p}$ = 0.97938_1

b-1) [HO$(CH_2)_4$O]$_{1.000}$-[CO$(CH_2)_4$CO-O$(CH_2)_4$O]$_{5.000}$-H or
HO$(CH_2)_4$O-[CO$(CH_2)_4$CO-O$(CH_2)_4$O]$_{5.000}$-H is accurate, however,
HO$(CH_2)_4$O-[CO$(CH_2)_4$CO-O$(CH_2)_4$O]$_5$-H is acceptable

b-2) Mw(adipic acid) = 146.16 Mw(Bdiol) = 90.14

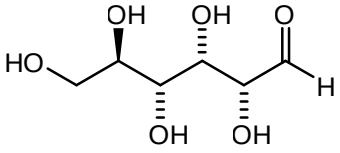
Ans.1 Since X = 11.00. the oligoester contains 5.00 units of adipate and 6.00 units of Bdiol. [cf) 5.00 + 6.00 = 11.00 = X] When $p_A \approx 1$. the initial molar feed ratio of the monomers is equal to the molar composition of the resulting oligoester.
$[\text{adipic acid}]_0 / [\text{Bdiol}]_0$ = 5.00 / 6.00.
W = 90.14·(6.00 / 5.00) ·(36.54 / 146.16) = 27.0 g

Ans.2 From eq.(2). when $p_A \approx 1$. X = (1 + r) / (1 - r). Therefore.
11.00 = [1 + {(36.54 / 146.16) / (W / 90.14)}] / [1 - {(36.54 / 146.16) / (W / 90.14)}]
11.00 = [(W / 90.14) + 0.2500] / [(W / 90.14) - 0.2500]
11.00 · [(W / 90.14) - 0.2500] = [(W / 90.14) + 0.2500]. 10.00 · (W / 90.14) = 3.000
W = 3.000 · 90.14 / 10.00 = 27.04_2 W = 27.0 (g)

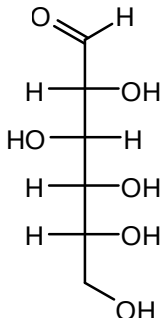
Solution to problem 9

a) Absolute configuration at C-2: R
Absolute configuration at C-5: R

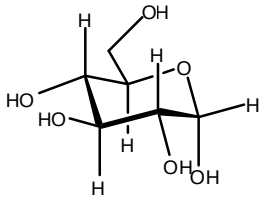
Chain form:

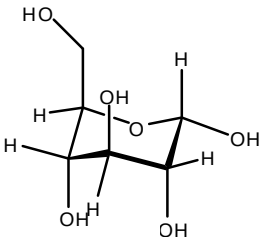


or



b)





c) $K = \frac{c(HG)}{c(H)\cdot c(G)} = \frac{c_0(\alpha CyD)\cdot a_{5.14}}{c_0(\alpha CyD)\cdot a_{5.06}\cdot[c_o(BTAD) - c_0(\alpha CyD)\cdot a_{5.14}]}$

$= \frac{5.0\cdot10^{-3}\cdot0.59}{5.0\cdot10^{-3}\cdot0.41\cdot[5.0\cdot10^{-3} - 5.0\cdot10^{-3}\cdot0.59]} = \frac{5.0\cdot10^{-3}\cdot0.59}{(5.0\cdot10^{-3}\cdot0.41)^2}$

$K = 7.0\cdot10^2$

$a_{5.06}$: relative area of the peak at 5.06 ppm = mole fraction of free αCyD

$a_{5.14}$: relative area of the peak at 5.14 ppm = mole fraction of αCyD complexed with BTAD

d) a. k_1 of αCyD/HTAB > k_1 of αCyD/BTAD

e) In $1.0\cdot10^{-2}$ mol L^{-1}/$1.0\cdot10^{-2}$ mol L^{-1} αCyD/HTAB.

$f_{10/10} = \frac{s_{10/10} - s_{free}}{s_{complex} - s_{free}} = \frac{0.815 - 0.740}{0.860 - 0.740}$ $\qquad f_{10/10} = 0.625$

s_{free}. $s_{complex}$: chemical shift of HTAB in free. and complexed state

$s_{10/10}$: chemical shift of HTAB in 10.0 mM/10.0 mM αCyD/HTAB

$f_{10/10}$: mole fraction of complexed HTAB in 10.0 mM/10.0 mM αCyD/HTAB

$$K = \frac{c(HG)}{c(H)\cdot c(G)} = \frac{[HTAB]_0 \cdot f_{10/10}}{\{[\alpha CyD]_0 - f_{10/10}\cdot[HTAB]_0\}\cdot[HTAB]_0\cdot(1 - f_{10/10})}$$

$$K = \frac{1.0\cdot10^{-2}\ mol/L\cdot 0.625}{1.0\cdot10^{-2} mol/L\cdot(1-0.625)^2} \qquad K = 4.4\cdot10^2$$

f) From $\Delta G^o = -RT \ln K$.

ΔG^o (40.0 °C) = $-8.314 \cdot 313.2 \ln (3.12\cdot10^2) = -14.94\cdot10^3$ J mol^{-1}

ΔG^o (60.0 °C) = $-8.314 \cdot 333.2 \ln (2.09\cdot10^2) = -14.79\cdot10^3$ J mol^{-1}

From $\Delta G^o = \Delta H^o - T\Delta S^o$

$-14.94\cdot10^3 = \Delta H^o - 313.2 \cdot \Delta S^o$

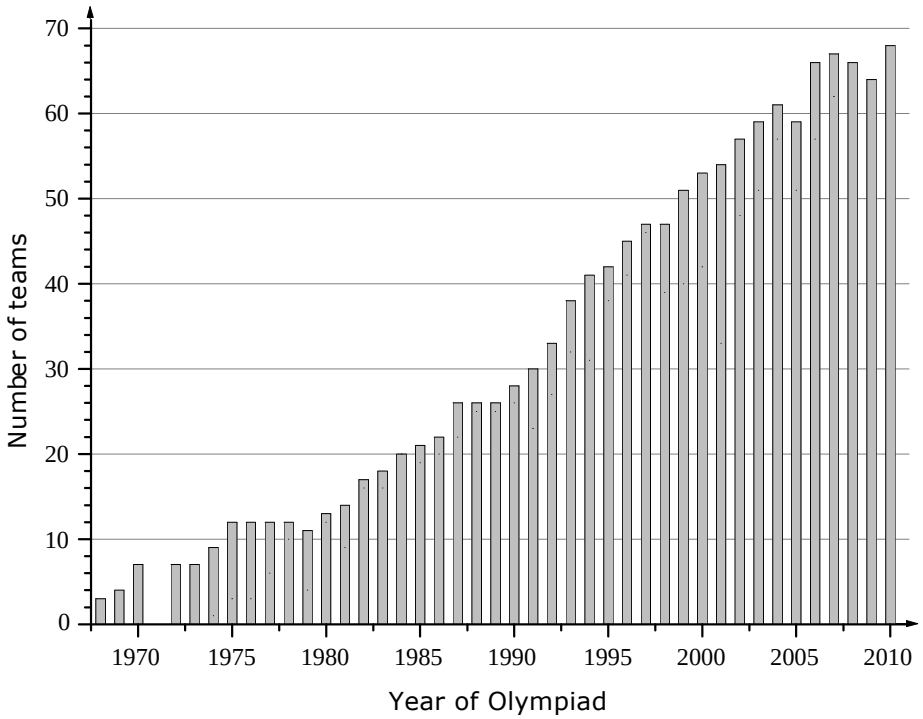
$-14.79\cdot10^3 = \Delta H^o - 333.2 \cdot \Delta S^o$

$\Delta S^o = -7.5$ J K^{-1} mol^{-1} $\Delta H^o = -17$ kJ mol^{-1}

About the history of the International Chemistry-Olympiads

The idea of chemistry olympiads was born 1968 during an Czechoslovakian national olympiad that was attended by observers from Poland and Hungary. These three countries participated in the first IChO 1968 in Prague. The number of teams attending the IChO in the following years are shown in the plot below.

Number of teams attending the IChO



The participating countries are shown in the following table.

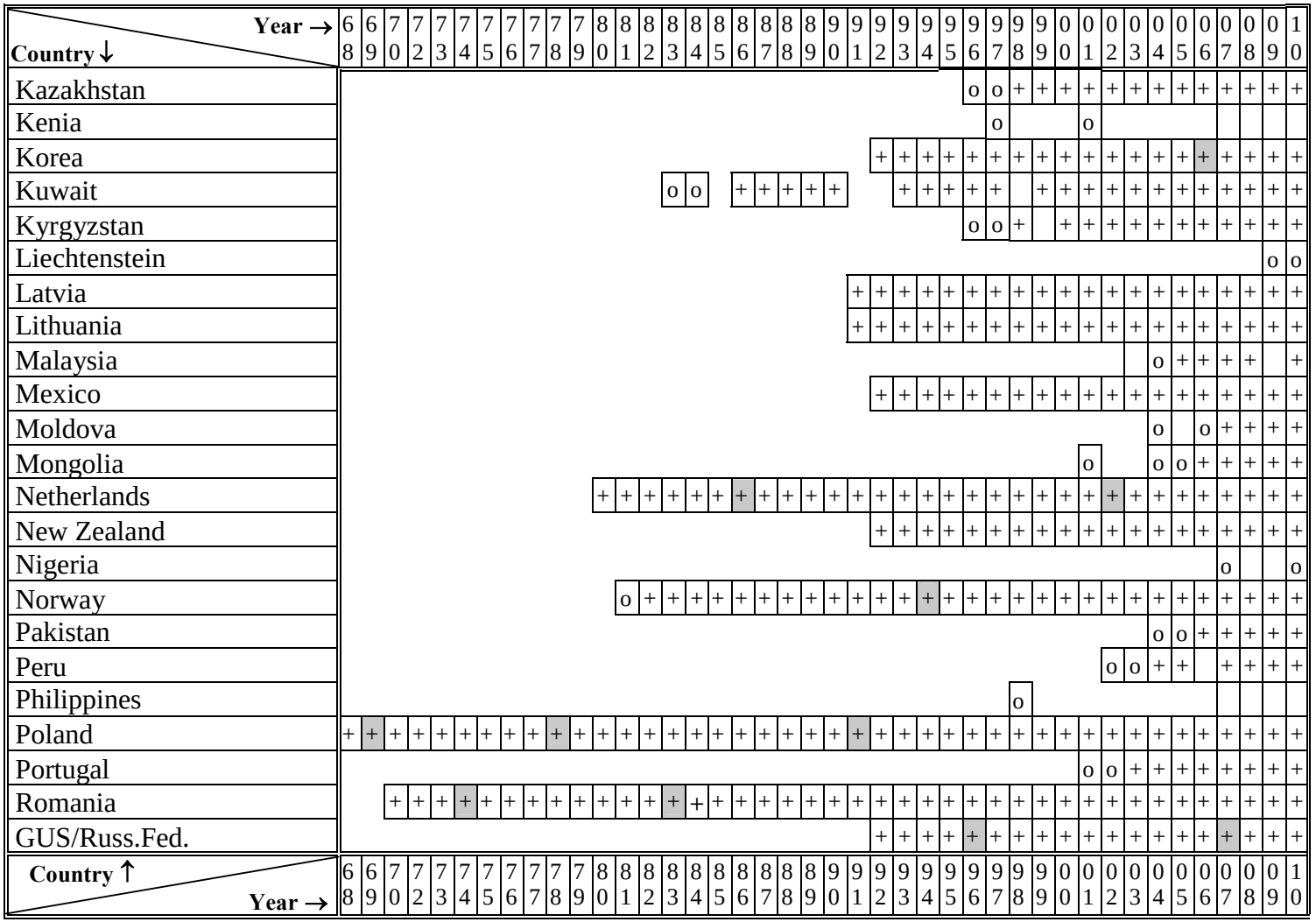
Participating Delegations

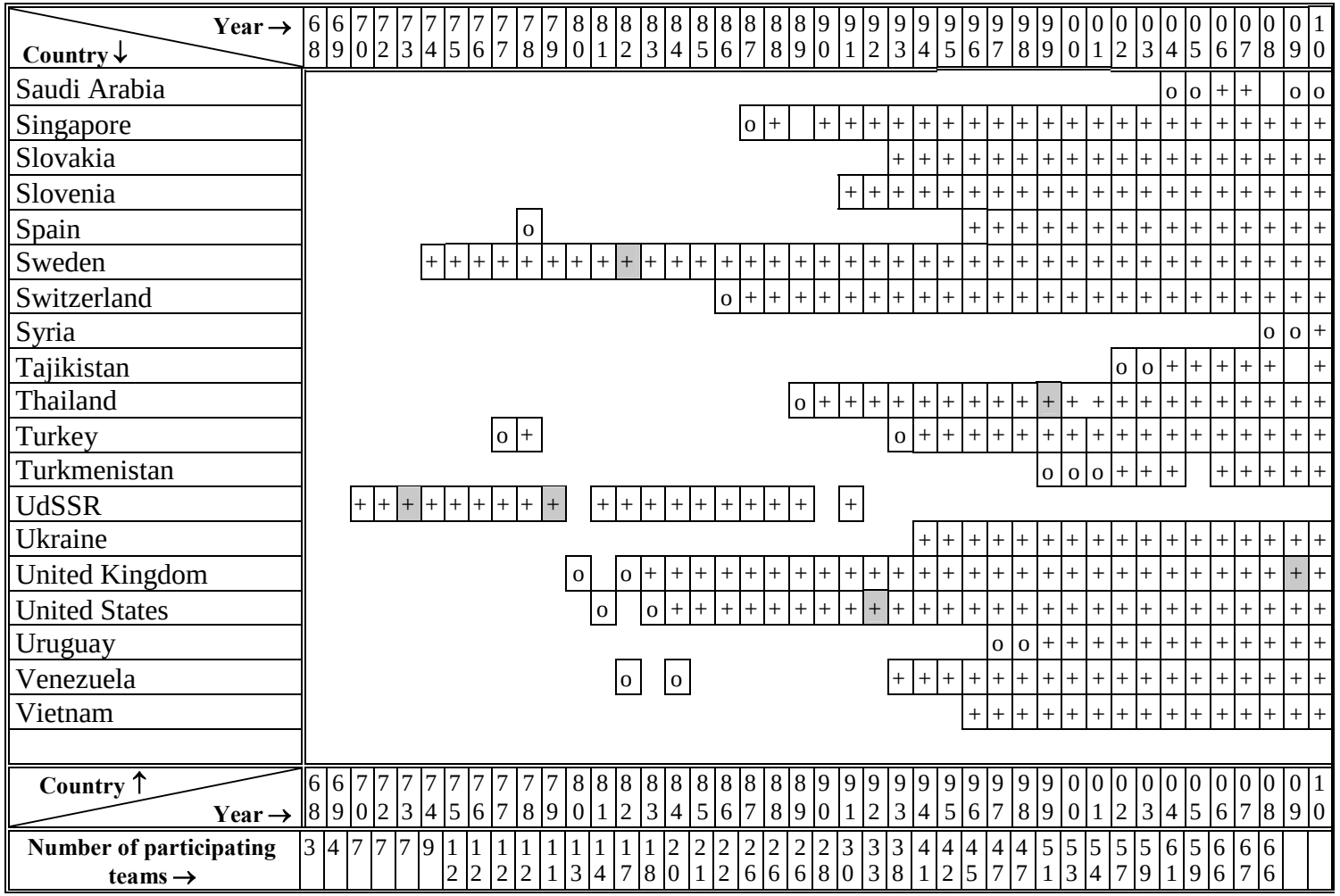
in alphabetical order

+ = host. + = participant. o = observer

Country ↓ \ Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10
Argentina																											+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Armenia																																				o	o	+	+	+	+	+	+
Australien																			o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Austria							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Azerbaijan																												o	o		+	+	+	+	+	+	+	+	+	+	+	+	+	+
Belarus																											+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Brasil																												o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Bulgaria		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Canada																o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
China																			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+	+	+	+	+	+
Chinese Taipei																								+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Costa Rica																																									o	o	+
Croatia																														o	o	+	+	+	+	+	+	+	+	+	+	+	+
↑ Country / Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10

Country ↓ \ Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10
Cuba																	+	o	+	+	+	+	+	+		+	+	+	+	+		+		+	+	+	+	+	+	+	+	+	+	+
Cyprus																					o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Czech Rep.																									+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Czechoslovakia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+																				
Denmark														+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DDR		o	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+	+	+	+	+																						
Egypt																																o	o	+	+	+	+	+					
Estonia																										+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Finland									o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
France												o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Germany						o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Greece																+	+	+	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Hungary	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Iceland																																o	o	+	+	+	+	+	+	+	+	+	+
India																												o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Indonesia																											o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Iran																									+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ireland																												o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Israel																																				o	o	+	+	+	+	+
Italy													+	+	+	+	+	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Japan																																	o	+	+	+	+	+	+	+	+	+	+
Jugoslavia						+	+	+	+					+	+	+	+	+	+													o											
Country ↑ \ Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10


Year →
Country ↓
68 69 70 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 00 01 02 03 04 05 06 07 08 09 10
Kazakhstan
Kenia
Korea
Kuwait
Kyrgyzstan
Liechtenstein
Latvia
Lithuania
Malaysia
Mexico
Moldova
Mongolia
Netherlands
New Zealand
Nigeria
Norway
Pakistan
Peru
Philippines
Poland
Portugal
Romania
GUS/Russ.Fed.
Country ↑
Year →



Year → / Country ↓	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10
Saudi Arabia																																				o	o	+	+		o	o
Singapore																			o	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Slovakia																									+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Slovenia																							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Spain										o																	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Sweden					+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Switzerland																		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Syria																																									o	o	+
Tajikistan																																		o	o	+	+	+	+	+		+
Thailand																					o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Turkey										o	+														o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Turkmenistan																															o	o	o	+	+	+		+	+	+	+	+	+
UdSSR			+	+	+	+	+	+	+	+	+			+	+	+	+	+	+	+	+	+	+																					
Ukraine																										+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United Kingdom												o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United States													o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Uruguay																													o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Venezuela														o		o									+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Vietnam																												+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Country ↑ / Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10
Number of participating teams →	3	4	7	7	7	9	12	12	12	12	11	13	14	17	18	20	21	22	26	26	26	28	30	33	38	41	42	45	47	47	51	53	54	57	59	61	59	66	67	66		

Inofficial ranking since 1974

(set up by adding the points of the teams. up to position 50)

	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988
IChO held in	**RO**	**H**	**DDR**	**CS**	**PL**	**SU**	**A**	**BG**	**S**	**RO**	**D**	**CS**	**NL**	**H**	**FIN**
1	SU	SU	DDR	CS	SU	PL	PL	H	CS	RO	D	SU	NL	SU	RC
.	RO	H	SU	SU	PL	SU	D	CS	D	SU	CS	CS	PL	RC	D
.	CS	PL	H	H	D	RO	DDR	PL	PL	D	SU	D	D	RO	USA
.	H	BG	PL	PL	DDR	CS	H	BG	NL	CS	H	A	SU	CS	PL
5	PL	RO	A	S	CS	A	A	A	A	H	A	NL	A	D	GB
.	DDR	DDR	RO	A	H	S	RO	D	SU	A	GB	H	USA	F	DDR
.	BG	S	BG	D	A	H	BG	DDR	H	F	PL	DDR	H	GB	N
.	YU	CS	CS	DDR	RO	D	CS	RO	BG	DDR	USA	PL	BG	PL	RO
.	S	A	S	RO	S	BG	S	SU	DDR	PL	RO	USA	F	H	H
10	D*	D	D	BG	BG	FIN	FIN	NL	S	NL	DK	F	RO	DDR	SU
.		YU	YU	YU	TR	DDR	NL	FIN	F	BG	S	GB	CS	NL	I
.		B	B	B	FIN		I	S	FIN	GB	NL	RO	GB	USA	NL
.							B	F	N	N	FIN	BG	S	BG	BG
.								I	RO	DK	F	N	DDR	A	CS
15			* hors concours						DK	FIN	BG	S	CDN	S	AUS
.									YU	S	N	FIN	N	FIN	SGP
.									I	I	I	YU	DK	N	F
.										YU	GR	B	B	DK	A
.											YU	GR	FIN	I	FIN
20											B	DK	GR	GR	CDN
.												C	KWT	C	DK
.													YU	B	C
.														YU	S
.														CDN	B
25														CH	CH
.														KWT	KWT

(List of abbreviations see 143)

	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
IChO held in	**DDR**	**F**	**PL**	**USA**	**I**	**N**	**RC**	**RUS**	**CDN**	**AUS**	**T**	**DK**
1	DDR	RC	RC	RC	RC	RC	RC	IR	H	SGP	USA	RC
.	D	PL	RO	H	TPE	GB	IR	RC	D	USA	ROK	RUS
.	RC	D	H	PL	USA	USA	RO	RUS	TR	ROK	RC	USA
.	BG	USA	PL	USA	I	A	A	A	TPE	RC	IR	H
5	SU	CS	NL	A	GUS	SGP	D	D	IR	H	RO	TPE
.	H	RO	USA	GUS	H	ROK	GB	USA	RUS	RA	H	A
.	PL	F	I	D	D	TPE	SK	UA	ROK	RUS	TPE	SK
.	RO	A	D	RO	CDN	CZ	TPE	CZ	RC	AUS	UA	BY
.	CS	DDR	N	F	SGP	GUS	I	H	SGP	D	PL	VN
10	I	H	GB	I	CZ	IR	CZ	RO	PL	GB	AUS	TR
.	NL	GB	CS	SGP	A	D	RUS	GB	USA	PL	VN	SGP
.	GB	I	SU	CS	RO	H	H	TPE	UA	A	D	D
.	A	AUS	A	AUS	P	RO	AUS	BY	AUS	RO	RA	ROK
.	USA	SGP	AUS	NL	NZ	DK	SGP	SGP	CDN	TPE	BY	IR
15	S	NL	DK	DK	ROK	I	F	RA	RO	SK	T	CZ
.	F	N	SGP	ROK	LV	T	TR	TR	A	NL	F	FIN
.	N	DK	CDN	GB	IR	NZ	PL	F	T	IR	TR	T
.	AUS	T	BG	CH	DK	UA	USA	I	EST	UA	SGP	MEX
.	CDN	FIN	F	T	AUS	AUS	DK	AUS	CZ	VN	IND	GB
20	DK	CDN	S	LV	NL	F	RA	ROK	VN	LT	GB	AUS
.	FIN	BG	T	NZ	LT	PL	ROK	EST	F	TR	RUS	IND
.	B	C	CH	S	SK	NL	UA	CDN	S	BY	MEX	CDN
.	C	S	LV	LT	F	SK	LT	T	BY	F	A	RA
.	GR	CH	LT	N	C	CDN	T	VN	NZ	I	IRL	UA
25	CH	B	FIN	CDN	GB	LT	NL	SK	LV	T	NZ	PL
.	KWT	GR	C	SLO	T	S	CH	CH	RA	FIN	I	NZ
.		KWT	GR	BG	BG	N	BG	NL	SLO	CZ	CDN	BG
.		CY	B	TPE	B	BG	S	NZ	GB	CDN	LT	F
.			CY	B	S	FIN	NZ	DK	SK	S	NL	DK
30			SLO	FIN	FIN	EST	EST	PL	LT	BG	SK	NL
.				GR	SLO	LV	CDN	SLO	I	N	BG	B
.				CY	GR	CH	MEX	MEX	DK	MEX	KZ	RO
.				MEX	MEX	MEX	N	LV	NL	CH	DK	KZ
.					N	SLO	SLO	N	IRL	SLO	CH	LT
35					CH	B	LV	CY	N	EST	CZ	CH
.					YV	CY	CY	BG	MEX	CY	FIN	SLO
.					CY	GR	B	S	CH	LV	B	EST
.					KWT	TR	GR	LT	CY	DK	S	S
.						YV	FIN	E	E	NZ	CY	YV
40						C	YV	B	FIN	GR	EST	CY
.						KWT	KWT	GR	BG	KZ	LV	HR
.							C	FIN	YV	E	SLO	I
.								YV	GR	IRL	YV	RI
.								C	B	B	BR	N
45								KWT	RI	KS	E	AZ
.									KWT	YV	N	IRL
.									C	RI	RI	E
.											GR	LV
.											ROU	GR
50											C	BR

(List of abbreviations see 143)

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
IChO held in	**IND**	**NL**	**GR**	**D**	**TPE**	**ROK**	**RUS**	**H**	**GB**	**J**	**TR**	**USA**
1	RC	RC	RC	RC	ROK	RC	RC	RC	TPE	RC		
.	ROK	T	IR	ROK	VN	TPE	RUS	RUS	RC	T		
.	USA	TPE	ROK	RUS	IR	ROK	TPE	UA	ROK	ROK		
.	RUS	ROK	T	UA	RUS	RUS	PL	ROK	RUS	J		
5	IR	A	BY	D	AZ	VN	ROK	T	SGP	TPE		
.	TR	UA	RUS	PL	TPE	T	D	BY	J	H		
.	IND	USA	IND	TPE	T	J	T	VN	USA	CZ		
.	AUS	PL	SGP	H	RA	Pl	IND	TPE	H	SGP		
.	TPE	IND	D	TR	D	IND	H	H	IR	**USA**		
10	T	D	TPE	VN	IND	D	SK	SGP	GB	IR		
.	SGP	IR	UA	IND	A	SK	LT	KZ	RO	RUS		
.	PL	H	PL	IR	CZ	DK	USA	A	T	TR		
.	RO	RUS	CDN	RO	UA	SGP	VN	PL	D	LT		
.	F	CDN	CZ	LT	PL	BR	GB	IR	IND	D		
15	SK	TR	RO	CZ	AUS	CDN	BY	IND	PL	PL		
.	H	AUS	KZ	USA	TR	AZ	EST	RO	AUS	GB		
.	VN	GB	VN	SGP	H	UA	UA	AUS	A	IND		
.	CZ	SGP	EST	CDN	SK	USA	RI	D	BY	RI		
.	RA	E	GB	AZ	USA	H	IR	SK	VN	RO		
20	BY	SK	AUS	AUS	GB	CZ	RO	TR	F	A		
.	C	BY	H	KZ	RO	AUS	AUS	LT	RI	VN		
.	D	VN	SK	GB	BY	IRL	A	EST	TR	SK		
.	GB	FIN	USA	J	SGP	F	KZ	I	LT	CDN		
.	UA	F	YV	A	J	IR	SGP	GB	UA	EST		
25	A	LT	IND	BY	RI	A	NZ	CDN	EST	AUS		
.	MEX	CZ	F	SK	LV	TR	CZ	NZ	CZ	UA		
.	DK	KZ	A	T	BG	RI	F	BR	SK	F		
.	CDN	LV	I	RA	HR	GB	TR	USA	CDN	RA		
.	EST	NL	TR	EST	MEX	RO	J	LV	I	NZ		
30	RI	RO	AZ	F	KZ	NL	ARM	RI	RA	BY		
.	HR	RA	MEX	NZ	LT	HR	SLO	F	NZ	KZ		
.	I	EST	LT	SLO	F	LT	RA	CZ	TM	BR		
.	N	HR	NL	HR	EST	KZ	BR	J	MEX	IL		
.	BG	BG	FIN	LV	CDN	SLO	CDN	DK	KZ	HR		
35	CY	NZ	HR	NL	I	EST	I	RA	IL	SLO		
.	KZ	I	J	I	DK	RA	MAL	MEX	BR	FIN		
.	B	DK	DK	CH	SLO	BR	IL	SLO	HR	DK		
.	LT	SLO	RA	FIN	FIN	TJ	IRL	IL	AZ	NL		
.	NZ	N	GR	RI	NL	LV	NL	AZ	DK	E		
40	CH	YV	LT	S	IRL	MAL	CH	HR	S	I		
.	E	MEX	E	BG	GR	S	S	TM	LV	LV		
.	FIN	BR	TM	KS	NZ	IRL	LV	BG	IRL	BG		
.	SLO	S	BR	E	KS	IL	DK	MGL	FIN	CR		
.	NL	RI	BG	GR	S	FIN	MD	IRL	N	CH		
45	LV	TM	CH	BR	B	IS	E	MAL	E	IRL		
.	BR	B	NZ	TM	BR	I	BG	E	NL	MEX		
.	S	IRL	IS	CY	CH	CY	TM	S	MGL	MGL		
.	YV	CH	IRL	YVA	P	N	HR	NL	PE	MAL		
.	IRL	C	CY	IRL	IS	TM	PK	CH	PK	N		
50	GR	CY	KS	IS	N	CH	N	ROU	SLO	S		

(List of abbreviations see 143)

List of abbreviations

A	Austria
AUS	Australia
AZ	Azerbaijan
B	Belgium
BG	Bulgaria
BR	Brazil
BY	Belarus
C	Cuba
CDN	Canada
CH	Switzerland
CS	Czechoslovacia
CY	Cyprus Republic
CZ	Czech Republic
D	Germany
DDR	German Democratic Republic
DK	Denmark
E	Spain
EAK	Kenya
EST	Estonia
ET	Egypt
F	France
FIN	Finland
GB	United Kingdom
GR	Greece
GUS	Commonwealth of Independent States
H	Hungary
HR	Croatia
I	Italy
IL	Israel
IND	India
IR	Iran
IRL	Ireland
IS	Iceland
J	Japan
KS	Kyrgistan
KWT	Kuwait
KZ	Kasakhstan
LV	Latvia
LT	Lithuania
MAL	Malaysia
MD	Moldova
MEX	Mexico
MGL	Mongolei
N	Norway
NL	Netherlands
NZ	New Zealand
P	Portugal
PE	Peru
PL	Polen
RA	Argentina
RI	Indonesia
RC	China
RO	Romania
ROK	South Korea
ROU	Uruguay
RUS	Russian Federation
S	Sweden
SGP	Singapore
SK	Slovakia
SLO	Slowenia
SU	Sowjet Union
T	Thailand
TJ	Tadschikistan
TM	Turkmenistan
TPE	Chinese Taipei
TR	Turkey
UA	Ukraine
USA	United States of America
VN	Vietnam
WAN	Nigeria
YU	Yugoslavia
YV	Venezuela