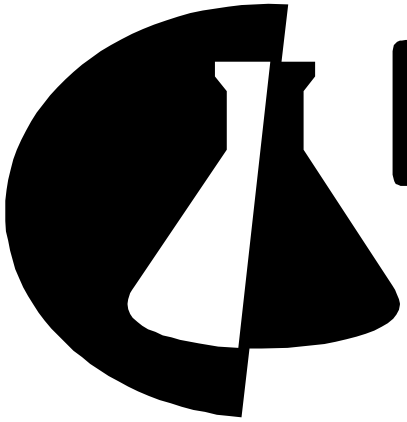


43. International Chemistry Olympiad Turkey 2011

National German Competition

Volume 17

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 high schools. 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

This booklet including the problems of the 43rd IchO and the latest statistics is available as of September 2011 from
http://www.ipn.uni-kiel.de/abt_chemie/icho/icho.html (chapter:"Aufgaben")

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

Contact addresses:

IPN, University of Kiel. z.H. PD Dr. Sabine Nick
Olshausenstraße 62
D-24098 Kiel
tel: +49-431-880-3116
fax: +49-431-880-5468
E-mail: nick@ipn.uni-kiel.de

IPN, Universität Kiel, Dr. Stefan Schwarzer
Olshausenstraße 62
D-24098 Kiel
Tel: 0431-880-2158
Fax: 0431-880-5468
E-Mail: schwarzer@ipn.uni-kiel.de

IPN, University of Kiel. z.H. Monika Barfknecht
Olshausenstraße 62
D-24098 Kiel
tel: +49-431-880-3168
fax: +49-431-880-5468
E-mail: barfknecht@ipn.uni-kiel.de

Wolfgang Hampe
Habichtweg 11
D-24222 Schwentinental
tel: +49-431-79433
E-mail: Hampe@t-online.de

Association to promote the IChO
(Association of former participants and friends of the IChO)
Förderverein Chemie-Olympiade e.V. (FChO)

Dr. Timo Gehring
Hauptstraße 59
D-65760 Eschborn
tel: +49-171-543 55 38
E-mail: gehring@fcho.de

Internet : www.icho.de
www.fcho.de

Part 1

The problem set of the four rounds

First Round

Problem 1–1 Water

Water is a very special substance with a lot of unusual properties.

a) Draw the structural formula of water, write down the structural parameters (such as bond angle, bond length) and mark the positive and negative partial charges of the molecule with $\delta'+$ and $\delta''-$.

The shape of the water molecule can be formally derived from a tetrahedron, yet the H-O-H bond angle is considerably smaller than an ideal tetrahedron angle. This phenomenon can be explained in a simplified way by the Valence Shell Electron-Pair Repulsion (VSEPR) theory.

b) Which assumptions are made in this theory? Use those assumptions which apply to water to rationalize the diminished bond angle of water.

In the series of hydrogen chalcogenides the melting and the boiling temperatures of water differ considerably from those of the hydrogen compounds of the other elements of group 16 as water forms hydrogen bridge bonds O-H···O.

c) Show the preferential spatial shape of the hydrogen bridge bonds O-H···O. Sketch a water dimer for thiws purpose.

d) Give the empirical formulae and the names of the hydrogen chalcogenides.

e) Which melting and boiling temperatures (in °C) should water in the series of hydrogen chalcogenides show if their molar mass would be the only determining factor? Find the hypothetical melting and boiling temperatures of water using a graph with a line of best fit.

Element	S	Se	Te	Po
Melting point (Mp.) of the hydrogen compound in °C	-85.6	-65.7	-51.0	-36.1
Boiling point (Bp.) of the hydrogen compound in °C	-60.3	-41.3	-2.3	35.3

Water shows a so-called density anomaly.

f) What does this mean? Which consequences arise from the density anomaly in everyday life and in the environment? Give two examples!

Problem 1–2 Water Containing Substances

Many salts of metals form hydrates. The way water molecules are bound can be very different. They can be split off more or less easily.

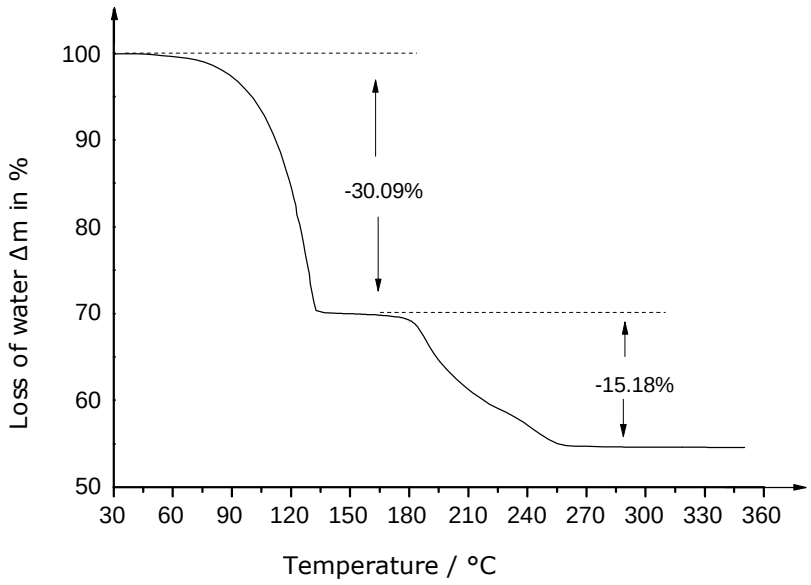
In aqueous solutions metal cations exist mostly as aqueous complexes.

a) Sketch the preferential coordination polyhedrons of $[Cr(H_2O)_6]^{3+}$ and $[Li(H_2O)_4]^{+}$.

An aqueous solution of Fe(III) chloride is acidic.

b) Give a simple explanation!

The splitting off of water molecules (dehydration) of hydrates can be analysed by a thermogravimetric measurement. Using this method the change of mass of a sample as a function of temperature is determined.
Nickel chloride was recrystallised in water, the solid filtered off and dried in air. The thermogravimetric measurement of the solid shows the following TG-graph (experimental mass losses):



c) Use the TG-graph to determine the formula of the compound which formed after recrystallisation. Which compounds do you expect after the first and after the second step of the TG? Calculate the mass loss of each step and compare the results with the experimental values of mass loss.

Water can have a strong effect on the properties of materials, e.g. the water content of a powder which is used to form tablets is crucial to their state, crumbly or solidified.
Therefore the determination of water content is very important in analytical chemistry.

A very old procedure is the reaction of a water containing sample with calcium carbide. The gas which forms in this reaction is led through an alkaline copper(I) solution. The precipitate is filtered off, dried at maximal 100 °C and weighed.

d) Which gas forms in this reaction? Write the reaction equation.

e) Which compound forms when the gas is lead through the copper containing solution? Write the reaction equation. Why should this method be used for safety reasons only when small amounts of water shall be determined?

Karl Fischer published in 1935 a new method to determine water which with small variations is still used today. He let the water containing sample react with methanol, pyridine, sulfur dioxide and iodine following the equation

$$H_2O + SO_2 + 2\ C_5H_5N + I_2 \rightleftharpoons SO_3 + 2\ HI \cdot C_5H_5N.$$

The end point of the titration is reached when a permanent brown colour occurs.

f) Apply oxidation numbers to the atoms in all iodine and sulfur containing compounds in the reaction equation above. What is the reason for the brown colour at the end of the titration?

The reaction above turned out to proceed in two steps. In the first step sulfur dioxide and methanol form an ester which then in a second step reacts with water and iodine.

1. Step: $SO_2 + H_3COH + C_5H_5N \rightleftharpoons C_5H_5NH^+ + X$
2. Step: $X + H_2O + I_2 + 2\ C_5H_5N \rightleftharpoons Y + 2\ C_5H_5NH^+ + 2\ I^-$

g) Give the formulae of X and Y! What is the function of pyridine in this reaction?

To determine the water content, a sample is added to sulfur dioxide and methanol. The mixture is then titrated with a solution of iodine in alcohol.
As it is difficult to detect the end point visually nowadays the Karl-Fischer-method is performed electrochemically. The titer is given in water equivalent in mg/mL.

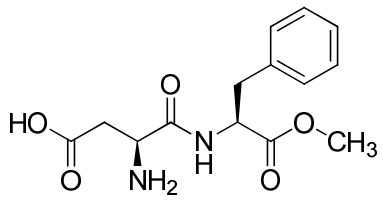
The titer of a Karl-Fischer-solution is 4.8 mg/mL. In a special apparatus samples of 10 g each of two cooking oils were analysed. The results of the titration are given in the table below.

	Sample 1	Sample 2	Sample 3	Sample 4
A	1.65 mL	1.62 mL	1.41 mL	1.62 mL
B	1.45 mL	1.43 mL	1.44 mL	1.44 m

h) Calculate the mass percentage of water in each cooking oil.

Problem 1-3 Amino acids: Chemical Jack-of-all-Trades in Nature

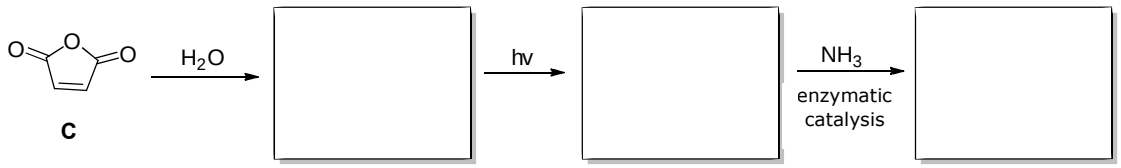
In 1965 fortune provided assistance to the American chemist James M. Schlatter. Schlatter had synthesized a compound **A** in the course of producing an antiulcer drug candidate. He accidentally discovered its sweet taste when he licked his finger, which had become contaminated with **A**. This was the hour of birth of a well-known artificial sweetener with the following structure:



A

*a) Mark all functional groups of **A** and write down their names. What is the commonly known name of compound **A**.*

A can be derived from a dipeptide which is formed by two naturally occurring amino acids, phenyl alanine and **B**. Amino acid **B** is produced industrially in the following way



C **D** **E** **B**

Anhydride **C** is hydrolysed to form **D**. When exposed to UV radiation **D** rearranges to **E**. Addition of ammonia to **E** leads in an enzymatically catalysed reaction to **B**, the wanted amino acid.

*b) Give the structural formulae of **B**, **D** and **E**. Which are the trivial names of these compounds?*

*c) In which stereochemical relationship is **D** with **E**?*

*d) Which purpose serves the enzymatic catalysis in the reaction of **E** to **B**?*

In nature proteins are based on 23 amino acids and play an important role in biochemistry. The great variety of proteins is due to the different properties of the individual amino acids.

e) Assign a fitting statement to each of the following amino acids:

Glutamic acid	contains an acid amide
Cysteine	may form disulphide bridges
Glycine	contains two stereogenic centres
Arginine	contains an indole ring
Tryptophan	is used as flavour enhancer
Alanine	contains a saturated five-membered ring
Methionine	contains four nitrogen atoms per molecule
Proline	is achiral
Threonine	forms by decarboxylation of compound **B**.
Asparagine	plays a specific role in the film "Jurassic Park"
Lysine	contains a thioether

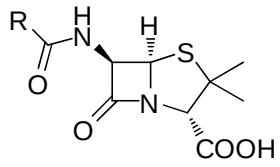
Phenyl alanine, the second amino acid from which **A** can be derived, belongs to the essential amino acids i.e. humans are not able to synthesize them. They must be obtained through our diet.

In the human body phenyl alanine is used as a starting compound to form a lot of important compounds such as the hormone adrenaline and another amino acid **F**.

An elementary analysis of 100 mg of **F** results in the following combustion products: 219 mg of CO_2, 54.8 mg of H_2O and 7.73 mg of N_2.

*f) Determine the smallest possible empirical formula of **F**. Give the structural formula and the name of **F**.*

Many other creatures use amino acids as reagents to form among other things highly complicated natural compounds e.g. the antibiotic **G** which is formed by yeast. Its medical effect was also discovered by accident.



G

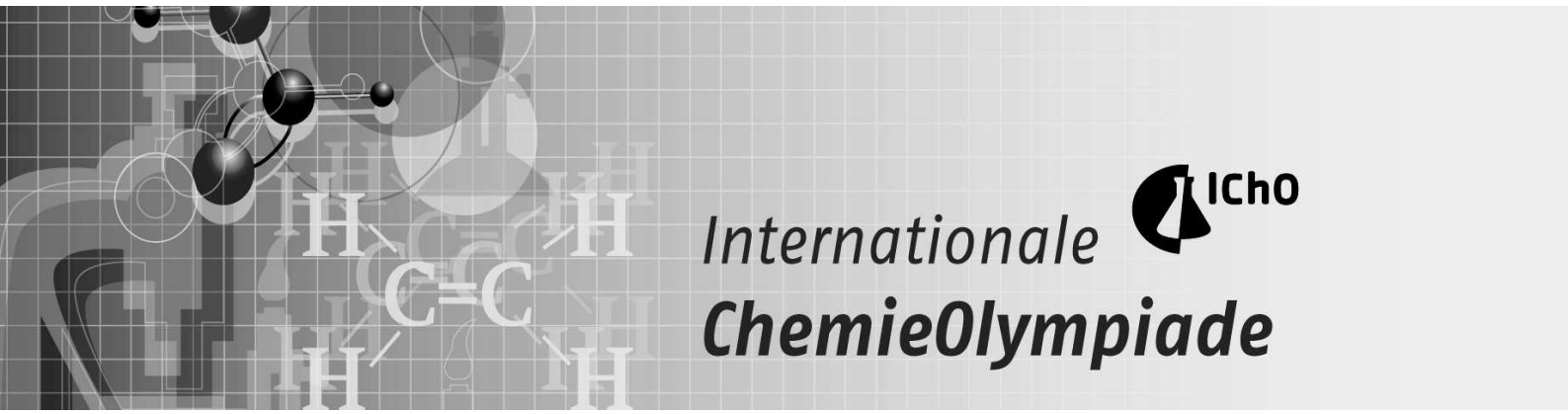
g) Which are the two amino acids to form G? Mark the corresponding fragments by circling.

*h) Give the name of **G** and the name of the group of compounds it belongs to.*

The antibiotic **G** blocks the bacterial growth by inhibiting an enzyme important for cell wall biosynthesis. Humans cells are surrounded only by a plasma membrane and don't have additional cell walls. Therefore they lack this enzyme. After inhibition the enzyme looses the ability to crosslink polysaccharide chains with peptides. Without crosslinking the cell wall is destabilized and the bacteria burst. Proteins of all organisms are exclusively composed of L-amino acids. The bacterial cell wall is one of the few examples of naturally occurring D-amino acids with D-alanine in the above mentioned linker peptides.

i) Draw the Fischer projections of L-alanine and D-alanine and determine their R,S stereochemical designations!

Hint: **A** to **G** are abbreviations of compounds, not codes of amino acids.



Problems Round 3

Test 1 Göttingen 2011: Problems 3-01 to 3-10

Test 2 Göttingen 2011: 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 compounds gives a basic solution when dissolved in water?

A	Na_2CO_3	**B**	Na_2SO_4	**C**	NaCl	**D**	HCl	**E**	NH_3

b) An aqueous solution contains only sodium ions (c = 0.5 mol/L), magnesium ions (c = 1 mol/L) und nitrate ions. What is the concentration of the nitrate ions?

A	1.5 mol/L	**B**	2.0 mol/L	**C**	2.5 mol/L	**D**	3.0 mol/L	**E**	4.0 mol/L

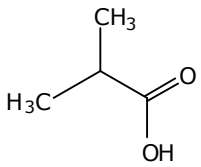
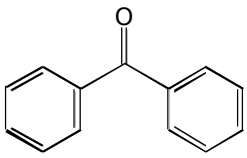
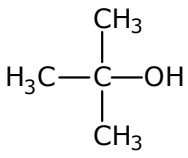
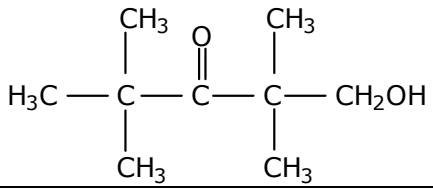
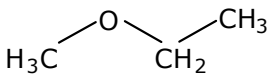
c) Which of the following elements has the largest third ionization energy?

A	B	**B**	C	**C**	N	**D**	Ca	**E**	Al

d) Which of the following conversions are oxidations?

A	$VO_3^- \rightarrow VO_2^+$	**B**	$SO_3 \rightarrow SO_4^{2-}$	**C**	$NO_2^- \rightarrow NO_3^-$	**D**	$MnO_4^- \rightarrow MnO_2$	**E**	$CrO_2^- \rightarrow CrO_4^{2-}$

e) One and only one of the following compounds reacts with $Na_2Cr_2O_7$ in an acidic solution. Which one?

A 	**B** 	**C** 
D 	**E** 	

f) Which of the given compounds has the highest boiling point?

A	CH_4	**B**	CH_3Br	**C**	CH_3-CH_3	**D**	CH_3F	**E**	C_3H_8

g) The bond angle O-Cl-O in ClO_3^- is

A	109.5°	**B**	little more than 109.5°	**C**	a little less than 109.5°	**D**	120°	**E**	little more than 120°	**F**	a little less than 120°

Problem 3-02 Binary Hydrogen Compounds

Almost all elements form binary (i.e. consisting of two different elements) compounds with hydrogen. However, these compounds differ strongly from each other in the type of bonding and in their behaviour concerning redox reactions and acid/base reactions in aqueous solutions.

a) *In the following tables insert the formulae of the hydrogen compounds of the elements of the 2nd and 3rd period of the periodic table of the elements. Complete the missing indications in the tables (acid/base: consider the Brönsted definition only)*

Compound	LiH_s	BeH_2	BH_3 (B_2H_6)	CH_4	NH_t	H_2O	H_uF
State of aggregation		s					
Type of bonding	ion/cov	cov					
Redox		red	n			n	ox
Acid/base		b	a			n	

Compound	NaH_v	MgH_w	AlH_3	SiH_x	PH_y	H_zS	HCl
State of aggregation							
Type of bonding		ion/cov	cov				
Redox							ox
Acid/base			b	(a)	n		

Abbreviations:

State of aggregation (1013 hPa, 25 °C): **s** = solid, **l** = liquid, **g** = gaseous

Type of bond: **cov** = covalent, **ion** = ionic, **met** = metallic

Redox : **red** = reducing agent, **ox** = oxidizing agent, **n** = ambiguous

Acid/base (in aqueous solution): **a** = acid, **b** = base, **n** = ambiguous

b) *How do the hydrogen compounds of the elements of the 2nd period react with oxygen? Write reaction equations!*

c) *How do the hydrogen compounds of the elements of the 2nd period react with water? Write reaction equations!*

Electronegativities:

H 2.2						
Li 0.97	Be 1.47	B 2.01	C 2.5	N 3.07	O 3.5	F 4.10
Na 1.01	Mg 1.23	Al 1.47	Si 1.74	P 2.06	S 2.44	Cl 2.83

Problem 3-03 El Pozolero

A "gentleman" with the nickname "El Pozolero" acted on behalf of a Mexican drug syndicate. He was arrested by the police in 2009.

He confessed that he had dissolved three dead bodies in a barrel filled with a mixture of hot concentrated sulfuric and nitric acid.

This barrel was confiscated. It was important for the conservation of evidence and the conviction in the following law suit to know how many victims had actually been dissolved.

As there were no other witnesses who could confirm the statement of the delinquent the content of the barrel had to be analysed to find its composition.

It was assumed that the dead bodies had a mean mass of 70 kg each and that the human body contains about 6.0 g of phosphor per kg weight.

A sample of 100 mL was taken from the barrel which was filled with 4000 L of the mixture.

a) *Calculate the mass of phosphor in the 100 mL sample if actually only three corpses had been dissolved.*

In order to determine the amount of phosphor in the token sample molybdate reagent was added in order to form ammonium molybdatophosphate ($(NH_4)_3[P(Mo_3O_{10})_4]\cdot 12\ H_2O$) as precipitate. The first step of the reaction could proceed similar to the chromate/dichromate reaction as polycondensation.

b) *Write a reaction equation for the formation of a dimolybdato ion ($Mo_2O_7^{2-}$) in an acidic solution with molybdato ions (MoO_4^{2-}) as reagent using line dot structures.*

The precipitated ammonium molybdatophosphate was heated for several hours to remove the water of hydration completely, and then it was heated to constant weight: yield 4.2880 g of $P_2O_5\cdot 24\ MoO_3$.

To get a blind a fresh mixture of hot concentrated sulfuric and nitric acid was analysed. 100 mL of this mixture contained 0.0481 g of $P_2O_5 \cdot 24\ MoO_3$.

c) *Clarify how many residues of human bodies could be detected. Calculate the number of persons who had fallen prey to "El Pozolero".*

Generally there are more possibilities to detect phosphor, e.g. precipitation reactions with $AgNO_3$, $BaCl_2$ or $ZrOCl_2$.

d) Write down the equations for these detecting reactions under the conditions in the barrel.
Account for the stability of the generated compounds in the mixture in the barrel. Which one is the most readily and which one the most sparingly soluble compound. (Hint: Use the HSAB principle for argumentation)

Problem 3-04 Benzoic Acid

Benzoic acid (C_6H_5COOH) is used as a food preservative (represented by the E-number 210) for sausages, ketchup, mustard, other sauces, margarine and a lot of more products. It inhibits the growth of mold, yeast and some bacteria. Benzoic acid is not dangerous to the human body as an accumulation is inhibited by catabolism to hippuric acid which is excreted. Cowberries, cranberries and cloudberries are examples of berries which contain relatively large amounts of benzoic acid. The preservative effect occurs when the pH is below 5.

Give all results of this problem with three significant figures.

a) Write down the reaction equation of the protolysis of benzoic acid.

b) Calculate the pH value of a solution with c(benzoic acid) = 0.012 mol/L. K_a(benzoic acid) = $6.31 \cdot 10^{-5}$

c) Determine the ratio of the concentrations of benzoate ions and benzoic acid in fruit juices with pH = 4.00 and pH = 6.00, respectively.

d) At which pH value does a solution of benzoic acid have the best buffering ability?

25 cm^3 of benzoic acid (c = 0.0150 mol/L) are added to 17 cm^3 of a solution of sodium hydroxide (c = 0.0120 mol/L).

e) Calculate the pH of the resulting solution.

Problem 3-05 Copper Sulfat Hydrates

1.36 g copper sulfate (contains no water of crystallization) are placed on a balance in an evacuated vessel at 25 °C. At this temperature water vapor is slowly led in the vessel. Thereby the pressure increases to 1.5 kPa.
The correlation between the mass of the sample and the vapor pressure is shown in the diagram below.
When point A is reached the pressure does not change for a certain time though more water vapor is led in the vessel.

a) Account for the constancy of the pressure.

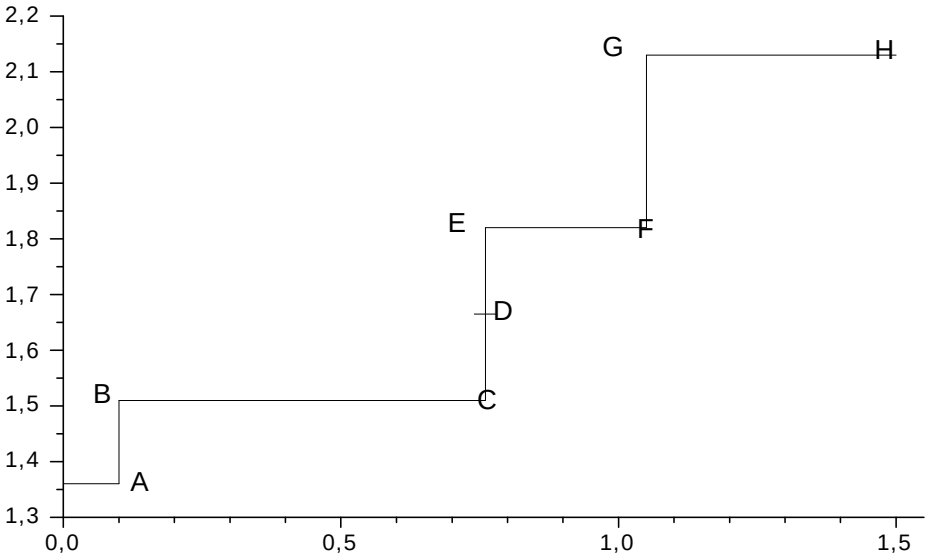
Different hydrates of copper sulfate ($CuSO_4 \cdot x\ H_2O$) are stable at different pressures of water vapor.

b) Calculate thevalues of x from the data of the diagram

Half way between C and E a point D is marked.

c) Which phase(s) exist at this point? Give the formula(e) and the composition (in percentage of mass).

d) How does the diagram change when the temperature is increased, e.g. to 30 °C?



Problem 3-06 Avogadro's Number

Avogadro's number N_A can be determined in different ways. Let's have a look on two of these ways.
At first the determination is performed electrolytically in a school experiment.
Two copper electrodes are used to electrolyse dil. sulfuric acid (c = 0.50 mol/L).

a) Write the reactions at both the anode and cathode

Experimental results

decrease in electrode mass:	0.3554 g
constant current	0.601 A
time of electrolysis	1802 s

Data

charge of an electron	$1.602 \cdot 10^{-19}$ C
molar mass (Cu)	63.546 g/mol

b) Determine Avogadro's number (result with 3 significant figures)!

The exact determination of the Avogadro constant is important for both, theoretical and practical considerations. CODATA (Committee on Data for Science and Technology) recommended in 2002 N_A = 6.0221415 (10) mol^{-1} and in 2006 N_A = 6.02214179 (30) mol^{-1} where the number in parenthesis represents one standard deviation in the last two digits.

One of the most accurate methods is using very pure silicon single crystals.

The density of pure silicon is ρ = 2.3290354 g/cm^3.

Silicon crystallises in the diamond lattice with a cubic unit cell having an edge length of a = 543.10209 pm. There are 8 atoms in a unit cell.

The molar masses and abundances of the silicon isotopes are:

	molar mass in g/mol	abundance h in %
^{28}Si	27.976926	92.238328
^{29}Si	28.976494	4.6588057
^{30}Si	29.973770	3.1028663

c) Calculate the Avogadro constant N_A based on these data. (result with 9 significant figures)!

Problem 3-07 Redox

There are elements which exist in different oxidation states in different compounds. Performing redox reactions, these oxidation states can change.
Each redox reaction has a specific standard potential E^0. If you know some of them it might be possible to determine others.

a) Determine the half-cell potential E^0 of $VO_2^+ + 4\ H^+(aq) / V^{2+} + 2\ H_2O$

Standard potentials:
$(V^{2+}/V(s))$: $E°_1 = -1.20$ V $\quad (VO^{2+} + 2\ H^+_{(aq)}/V^{3+} + H_2O)$: $E°_2 = +0.34$ V
$(V^{3+}/V(s))$: $E°_3 = -0.89$ V $\quad (VO_2^+ + 2\ H^+_{(aq)}/VO^{2+} + H_2O)$: $E°_4 = +1.00$ V

You may write a cell reaction in different ways:

$$A + B \rightleftarrows C + D \qquad (1)\ \text{with } K_1 \text{ and } E°_1$$
$$2\ A + 2\ B \rightleftarrows 2\ C + 2\ D \qquad (2)\ \text{with } K_2 \text{ and } E°_2$$

b) How differ the values of E° and K, respectively, of the presentations (1) and (2)? Account for your answer.

You may use the standard potentials to determine the equilibrium constants of redox reactions.

c) Determine the equilibrium constant at 298 K for

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H_3O^+ \rightleftarrows 6\ Fe^{3+} + 2\ Cr^{3+} + 21\ H_2O$$

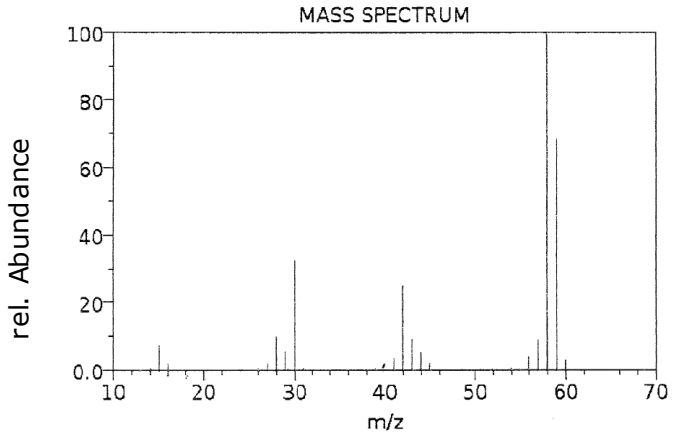
Standard potentials:
$E°_5\ (Cr_2O_7^{2-} + 14\ H_3O^+ / 2\ Cr^{3+} + 21\ H_2O) = 1.33$ V
$E°_6\ (Fe^{3+} / Fe^{2+}) = 0.770$ V

Problem 3-08 A Dash of Lemon on the Fish

Certain members of the hawthorn family produce a smell which also comes from fish. The fish smell can be hidden by lowering the pH value since the compound is an organic base. This is probably one of the reasons why lemon is served with fish.
The analysis of the smelling compound showed that it contains only carbon, hydrogen and nitrogen. Combustion of 0.125 g of the compound resulted in the formation of 0.172 g of H_2O and 0.279 g of CO_2.

a) Determine the ratio of the amounts n(C):n(H):n(N).

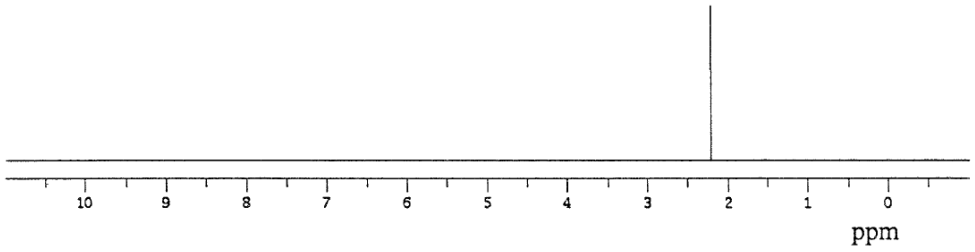
b) Use the mass spectrum below to determine the molecular formula of the compound. Show your reasoning.



There are 4 isomers with this molecular formula.

c) Draw their structures and give their names.

d) Which of the isomers of part c) has the following ^{1}H-NMR spectrum? Account for your decision.



The boiling point of the 4 isomers of part c) is in the range from 2 °C to 48 °C.

e) State which isomer has the lowest boiling point and which the highest one. Account for your decision.

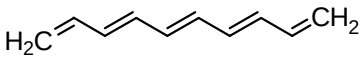
Problem 3-09 Aromatic or not?

a) Check whether the statements below are true or not.

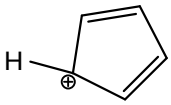
Statements	yes	no
At rt* benzene is inert when combined with Br_2, H_2, acids and $KMnO_4$		
Planar cyclic systems with 4n (n = 0, 1, 2, …) electrons are called antiaromatic		
Non aromatic cyclic polyenes can form aromatic dianions and dications		
Aromatic carbon hydrates are referred to as arenes as well.		
Nucleophilic aromatic substitutions proceed in a three-step mechanism		
Benzene undergoes at 25 °C substitution reactions rather than addition reactions		
Planar cyclic conjugated systems with 4n + 2 (n = 0, 1, 2, …) delocalized electrons are called aromatic		
Losing aromaticity means that the aromatic smell of a compound is lost by evaporating		

(*rt = room temperature)

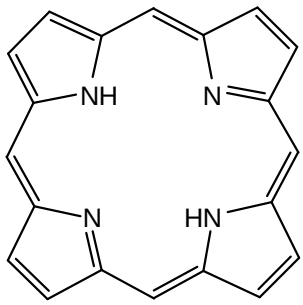
b) Mark those of the compounds A to L which are aromatic and antiaromatic, respectively.



A

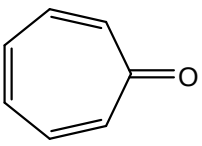


B

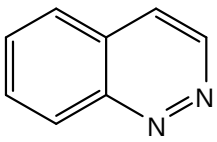


C

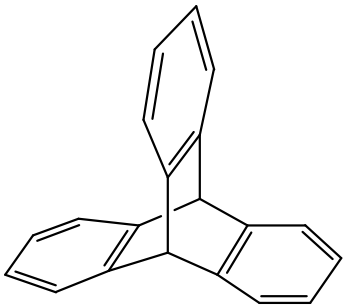
D



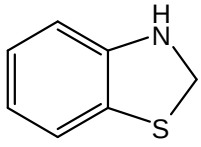
E



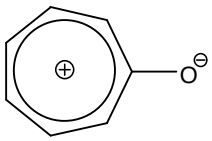
F



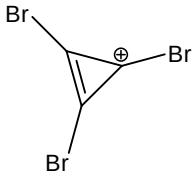
G



H

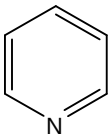


I



J

K



L

Problem 3-10 Reactions of ? (Hydralin, Adronal)

Compound A serves as parent compound to form the compounds E1 and E2 as well as F.

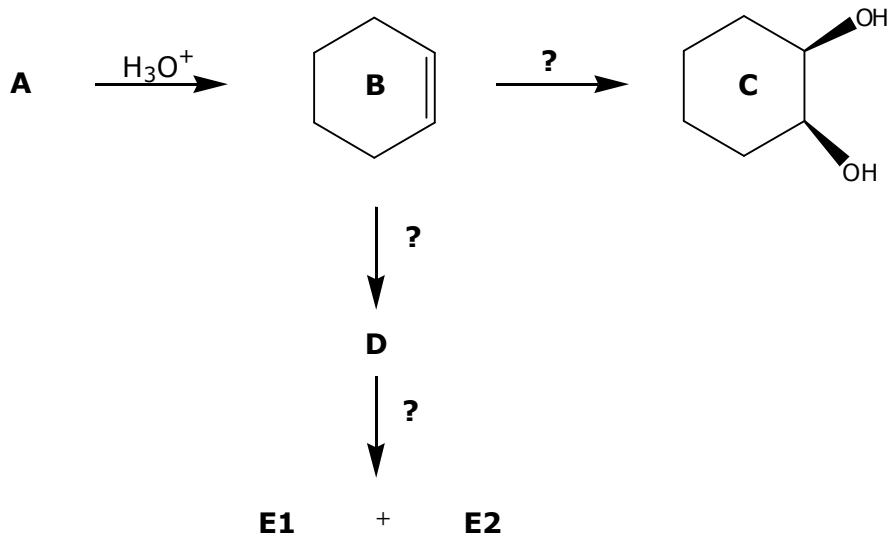
a) Complete the following reaction schema by giving the structural formulae of A, D, E1 and E2.

Write the names of all the compounds A to E2.

Add the additionally needed reagents at the places marked with "?".

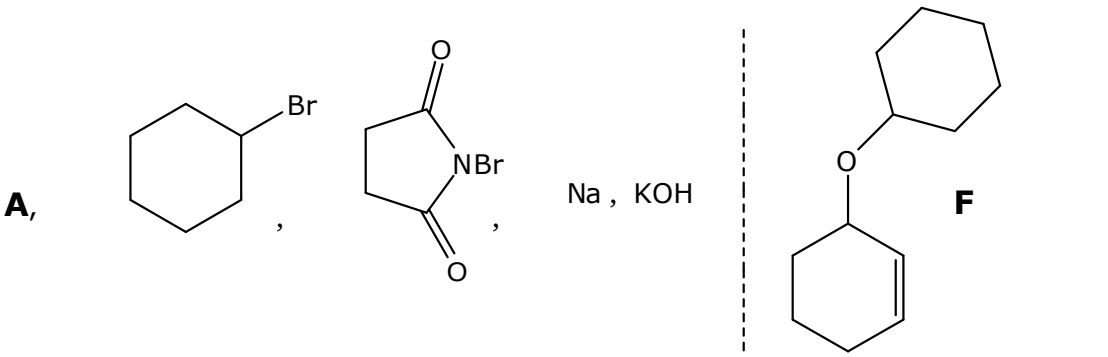
Mark all stereogenic centres with a star (*).

(Hint: The compounds E1 and E2 form in a 1:1 ratio as trans-diols).



b) What is the name of an equimolar mixture of E1 und E2? Assign R or S configuration to the stereogenic centres of E1 and E2.

c) With A and the following chemicals compound F can be produced. Suggest a way of synthesis as detailed as possible.



3-(Cyclohexoxy)cyclohexene

Compound A, methylbenzoate ($C_8H_8O_2$), maleic acid diethylester ($C_8H_{12}O_4$) and benzyl alcohol (C_7H_8O) were used in the past in devices to draw up an account of fuel costs in flats let for rent. They were directly affixed to the radiators and worked on the basis of vaporisation.

According to the climate conditions liquids with different boiling points were used. The fuel bill was calculated on the basis of the amount of the evaporated liquid.

d) Draw the structural formulae of the four compounds mentioned above.
Rank the compounds from 1 to 4 according to the height of their boiling point (1: lowest bp., 4 highest bp.). Account for your decision.
If the ranking of two compounds is not clear give a short explanation.

Third Round Test 2

Problem 3-11 Multiple Choice

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

a) The complete electrolysis of 1 mol of water requires the following amount of electric charge (F is the Faraday constant):

A F	**B** $\frac{4}{3}\cdot F$	**C** $\frac{3}{2}\cdot F$	**D** $2\cdot F$	**E** $4\cdot F$

b) Which formulae represent more than one compound?

A CH_4O	**B** $C_2H_2Cl_2$	**C** $Pt(NH_3)_2Cl_2$	**D** $Cu(SO_4)\cdot 5H_2O$	**E** C_2H_6O

c) When methylamine (CH_3NH_2) reacts with an excess of gaseous oxygen the gases N_2, O_2 and CO_2 form. Which amount of oxygen is necessary for a complete reaction of 1 mol of methylamine?

A 2.25 mol O_2	**B** 2.50 mol O_2	**C** 3.00 mol O_2	**D** 4.50 mol O_2	**E** 4.75 mol O_2

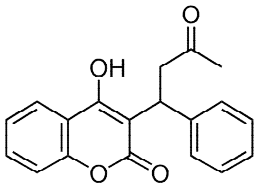
d) The ionic product of water at 45 °C is $4.0\cdot 10^{-14}$. Which is the pH-value of water at this temperature?

A 6.7	**B** 6.4	**C** 7.0	**D** 7.3	**E** 13.4

e) Given the transition pH of some indicators. Which of them should be used if a weak base is titrated with a strong acid?

A 2,4-Dinitrophenol: 3,5	**B** Bromothymol blue: 7,0	**C** Cresol red: 8,0	**D** Alizarin yellow: 11,0

f) Warfarin is a rat poison. How many stereogenic centres are present in this molecule?



A 0	**B** 1	**C** 2	**D** 3	**E** 4

g) Which of the following reactions proceed with the largest rise in entropy? (Reactants and products under standard conditions.)

A $Br_2(g) + Cl_2(g) \longrightarrow 2\ BrCl(g)$	**B** $2\ NO(g) \longrightarrow N_2(g) + O_2(g)$
C $2\ CO(g) + O_2(g) \longrightarrow 2\ CO_2(g)$	**D** $H_2O(g) \longrightarrow H_2O(l)$
E $2\ H_2O(l) \longrightarrow 2\ H_2(g) + O_2(g)$	**F** $2\ Na(s) + Cl_2(g) \longrightarrow 2\ NaCl(g)$

Problem 3-12 Gold

In 1940 the Hungarian chemist George de Hevesy dissolved the gold bearing Nobel Prize Medals of Max von Laue and James Franck in a certain solution to keep them from being confiscated by German authorities during the occupation of Denmark.

After the war the „hidden" gold was retrieved, delivered to the Royal Swedish Academy of Sciences and the Nobel Foundation generously presented Laue and Frank with new Nobel medals.

a) In which solution did George de Hevesy dissolve the medals? Give the exact composition!

b) Write the reaction equations of the formation of the solvent and of the dis-sol-ving process of gold.

Gold as one of the noblest metals dissolves only in this solvent because its disso-lution is strongly favoured.

c) Give the reasons for this favouritism qualitatively (Tip: Au/Au^{3+}: $E° = 1.50V$).

There are different operations of exploitation to obtain gold. The oldest one is the method of prospecting which is not used at large scale any longer. Nowadays gold is produced by cyanidation of gold ore. Air is blown into and mixed with gold containing sludge and potassium cyanide solution is added. At the end of the process zinc powder is given into the mixture.

d) Write the reaction equations of the cyanidation and of the reaction when zinc powder is added. Assume the formation of Au(I) in the cyanidation process!

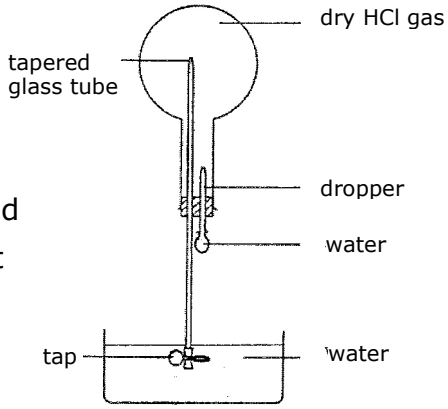
A number of comon gold compounds were characterised in a first step as gold(II) compounds, such as $CsAuCl_3$. This assumption turned out to be wrong.

e) How do these gold(II) compounds really exist?

f) Suggest a structure of the compound $CsAuCl_3$! Hint: Assume a complex compound.

Problem 3-13

In the laboratory of a highschool the hydrochloric acid fountain experiment is carried out with the equipment shown in the picture.
A flask is filled with dry HCl gas. A drop of water is added with the dropper. Then the tap is opened and the water enters the flask like a fountain and fills it totally. (p = $1.020 \cdot 10^5$ Pa, T = 295 K)



a) Determine the pH of the solution at the end of the experiment.

The same experiment was repeated with ammonia (pK_b = 4.75) instead of HCl.

b) Determine again the pH value of the solution.

Problem 3-14

a) Write down the reaction equations together with additional needed reagents for the following changes:

$Mg(s) \longrightarrow MgO(s) \longrightarrow MgSO_4(aq) \longrightarrow Mg(OH)_2(s) \longrightarrow MgCl_2(aq) \longrightarrow MgCO_3(s) \longrightarrow MgO(s)$

In a chemical plant 90000 m^3/day of waste water with pH = 1.2 accumulate. This solution is neutralised with $CaCO_3$.

b) Calculate the mass of calcium carbonate needed and the volume of the generated carbon dioxide (25 °C, 1013 hPa).

Problem 3-15 Kinetics

The reaction $2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$ obeys the following rate equation: $r = k \cdot c(NO)^2 \cdot c(O_2)$.

a) Explain how the rate of the reaction changes when the following concentration changes are made:

i. $c(O_2)$ is quadrupled,
ii. c(NO) is quadrupled,
iii. c(NO) is halved,
iv. $c(O_2)$ is halved and c(NO) is quadrupled,
v. c(NO) is halved and $c(O_2)$ is quadrupled.

The initial rate of the above reaction remains the same when the temperature is raised from 460 °C to 600 °C, with all the initial concentrations halved.

b) Determine the activation energy*.*

The first-order decay of a compound was followed spectrophotometrically (Lambert-Beer law). After loading a solution with an initial concentration of c_0 = 0.015 mol/dm^3 into a cuvette with a path-length of d = 1.00 cm, its absorbance A (at a wavelength where only this species absorbs light) was recorded as a function of time:

t in s	0	20	40	60	80	100	125	150	175	200	250
A	0.141	0.111	0.084	0.069	0.051	0.047	0.031	0.023	0.015	0.013	0.007

c) Show graphically that the reaction is really of first order.

d) Determine the molar absorption coefficient ε.

e) Determine the initial rate and the rate constant k.

f) Calculate the half-life t_{12} from the rate constant.
(If you could not solve e) take k = 9.50·10^{-3} s^{-1})

g) Calculate the time required to consume 99 % and 99.99 %, respectively, of the compound.

Problem 3-16 Silver Nitrate as an Explosive?

Tollens` reagent for detecting aldehydes is produced in the following way:
Drops of ammonia are added to an aqueous solution of silver nitrate. A puce (brownish-red) residue (1) forms which dissolves when more ammonia is added (2).
An aqueous solution of a compound which is to be tested for aldehyde groups is heated up to 70 °C. Tollens` reagent is added. If the test is positive the solution turns black and the walls of the container are covered by a shiny coating (3).

a) Suggest reaction equations which clarify the observations 1 to 3.
Use RCHO in your equations as formula of an aldehyde.

A German teacher worked with Tollens` reagent.
A short summary of an article in the German newspaper "Hamburger Abendblatt" reports what happened then:

"**Large Scale Rescue Operation at a School in the town of Wedel.**

A failed chemical experiment at a school in Wedel led to a night time large scale rescue operation. During a lesson of chemistry silver nitrate was liberated followed by a deflagration, reported the local fire department. They informed that under certain circumstances silver nitrate might be flammable and explosive.

The teacher did not inform the fire department before the evening when he became anxious of further reactions. Betwenn 10 pm and the next morning up to 60 firemen partially under breathing protection were employed to stop possible further reactions with other chemicals. At 0.30 am a special military unit usually defusing warfare agents was alarmed. ... "

Fact is: If not used for a long time black-brown flocs form in Tollens` reagent.

b) *Which chemical were they really dealing with? Account for your assumption by a reaction equation.*
Hint: The black-brown flocs contain more than 90 % of the mass of silver and decompose exposed to friction or beats into its elements.)

An excess of Tollens` reagent has to be disposed. Copper sulfate, glucose, aluminium chloride, copper shavings, glucose, potassium iodide and ascorbic acid are available.

c) *Which of these substances is appropriate and which is not? Account for your decisions.*

If potassium cyanide is added to an aqueous solution of silver nitrate silver cyanide is formed which in solid can be described at the same time as cyanide and isocyanide

d) *Which assembling should silver cyanide have in solid?*
Draw an image of a possible arrangement of the components.

Silver fluoride is very soluble in water contrary to other silver halides. Similar ionic radii of the two kinds of ions may be a reason.

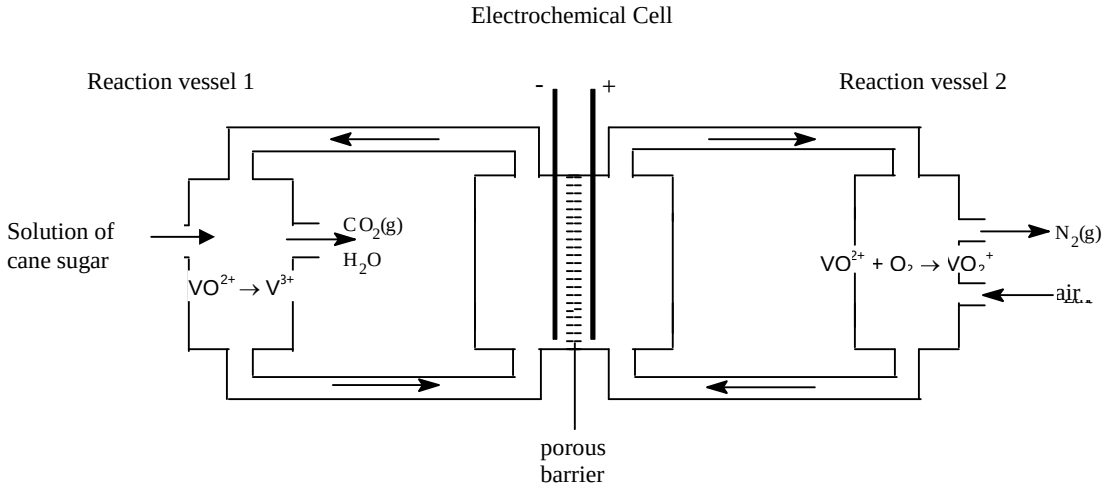
The density of silver fluoride amounts to ρ = 5.851 kg · m^{-3}. It crystallises in the sodium chloride structure.

e) *Describe the sodium chloride structure by drawing it.*

f) *Evaluate the ionic radii of both types of ions in silver fluoride by calculating.*

Problem 3-17 Electric Current from Sugar

A fuel cell is composed of two reaction vessels which contain, among others, catalysers and an electrochemical cell as shown in the figure below:



In the beginning both reaction vessels contain VO^{2+} ions in a strongly acidic solution.
In vessel 1 VO^{2+} is reduced to form V^{3+}, cane sugar is oxidised to CO_2 and H_2O.
In vessel 2 VO^{2+} is oxidised by oxygen to form VO_2^+.
The solutions of V^{3+} and VO_2^+ are pumped into the half cells of the electrochemical cell. There they react as electrolytes at the inert electrodes. If an electrical current is flowing VO^{2+} ions are formed again which are pumped back into the reaction vessels.

a) Write down a balanced equation for the reaction in vessel 1.

b) Calculate the volume of the air (15 °C, 101 kPa) which is at least necessary to be pumped into vessel 2 if in the same time 10 g of cane sugar in vessel 1 are consumed (air contains 20.95 % of volume oxygen).

Let us assume for the parts c) and d) that in the beginning VO^{2+} ions (c = 2.00 mol/L) are the only vanadium species present, that the vessels are of the same size and that a temperature of 15 °C is retained.

c) Which cell potential do you expect if the VO^{2+}concentrations in both half cells are halved?
Calculate $\Delta G°$ for the cell reactions as well as ΔG as a function of the concentrations of the vanadium species.

Equivalent amounts of cane sugar and air react in both vessels which are equal. The cell potential amounts to 0.32 V.

d) Determine the concentrations of V^{3+} and VO_2^+, respectively, in the corresponding half cells. (If you could not solve part c) use E°(cell) = + 0,65 V)

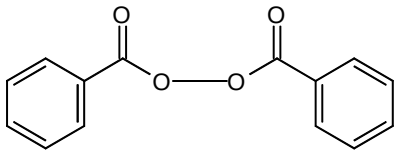
Standard potentials: $VO^{2+} + 2\ H^+_{(aq)} + e^- \rightleftharpoons V^{3+} + H_2O$ $E°_1 = + 0.34$ V

$VO_2^+ + 2\ H^+_{(aq)} + e^- \rightleftharpoons VO^{2+} + H_2O$ $E°_2 = + 1.00$ V

Problem 3-18 Synthetic Polymers

The analysis of a synthetic polymer leads to C_3H_6 as the empirical formula of the monomer.

On addition of benzoyl peroxide to this monomer a polymer forms.



Benzoyl peroxide

a) Record the single steps of the polymerisation

Write reaction equations for

i) initiation (two reaction equations)

ii) propagation (one reaction equation)

iii) termination (two reaction equations)

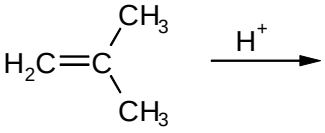
This polymerisation can lead to three different types of polymerisation products with respect to the arrangement of the CH_3-groups.

b) Draw a carbon-carbon backbone of six carbon atoms of the polymer for each of the three types and show the spatial position of the substituents.

c) What is the effect of Ziegler-Natta catalysts in the field of polymer chemistry?

d) Do you expect one of the three different types of compounds (from part b)) to rotate plane-polarized light? Explain.

In the industrial production proton donors play an important role, e.g. in the reaction to form polyisobutene.

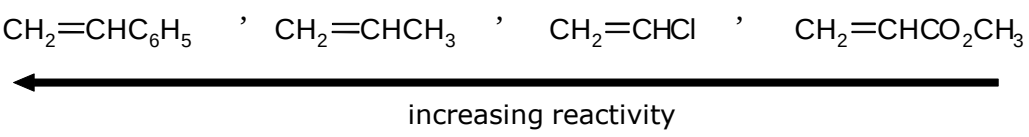


Polyisobutene

.

e) Give an equation for the initiation reaction and for the propagation reaction of the formation of polyisobutene.

If different monomers are tested for their reactivity with respect towards cationic polymerisation the following order is found:

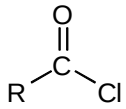


f) Account for this order of reactivity of the monomers. Use the formation of polyisobutene as an example.

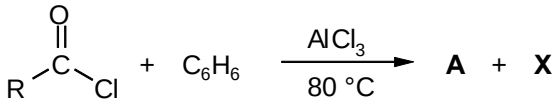
g) Integrate isobutene in the above given order of increasing reactivity.

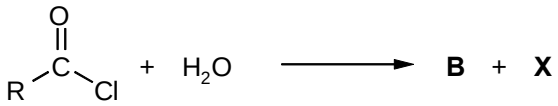
Problem 3-19 Reactions of Acid Halides

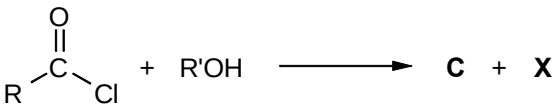
Acid halides are among the most reactive of carboxylic acid derivates and can be converted into many other kinds of compounds.

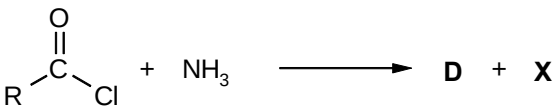


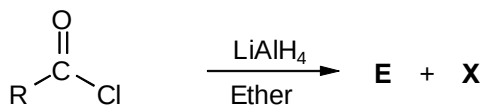
*a) Determine the reaction products **A** to **F** as well as **X** and **Y** which were prepared from an acid halide.*

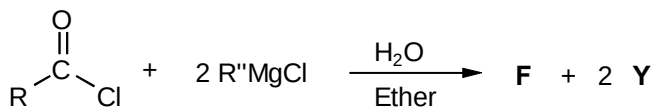




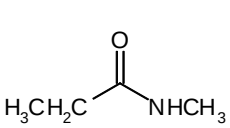




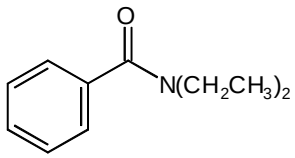




The two amides shown in the drawing are to be synthesised from an acid chloride and an amine, respectively.

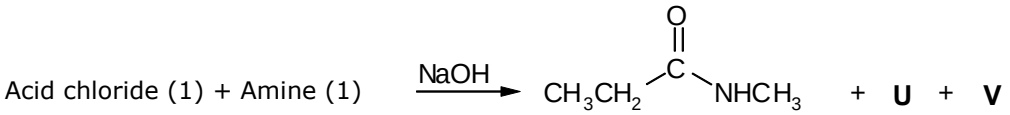


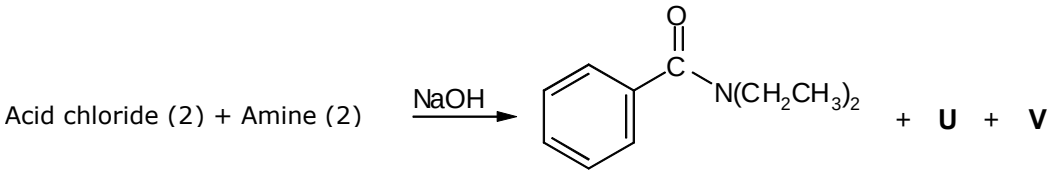
Amide 1



Amide 2

*b) Find in the equations below the acid chlorides 1 and 2, the amines 1 and 2 as well as **U** and **V**.*





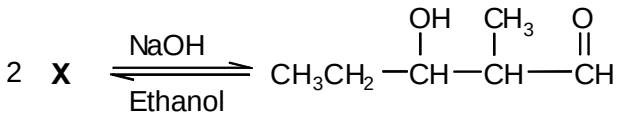
c) Give the IUPAC names of both amines.

Problem 3-20 Aldol Reactions

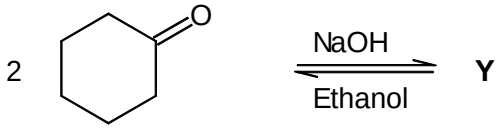
Aldol reactions take place between two cabonyl partners. One example is the dimerisation of aldehydes and ketones.

a) Determine in the following examples the structural formulae of X, Y and Z.

i)

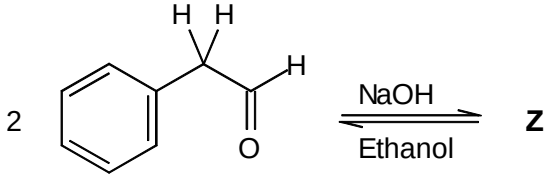


ii)



Cyclohexanon

iii)



Reaction a) iii leads to a racemate.

b) Mark all stereogenic centres in Z with a star (*).

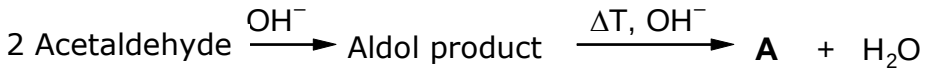
If there is only one stereogenic centre, draw the structural formulae of both enantiomers of Z. Assign R or S configuration to the enantiomers.
If there are more stereogenic centres, choose one of them and draw the structural formulae of the R and S compound according to the chosen centre. If doing so do not consider further stereogenic centres. Assign R or S configuration to the chosen centre.
(Instructions: *in front of the paper plane*
 behind the paper plane)

Aldol reactions are catalysed by bases. The used carbonyl compound forms a nucleophilic electron donor and an electrophilic electron acceptor.

c) *Propose the reaction mechanism of the dimerisation of ethanal (H_3CCHO) catalysed by a base.*
Consider the following steps:

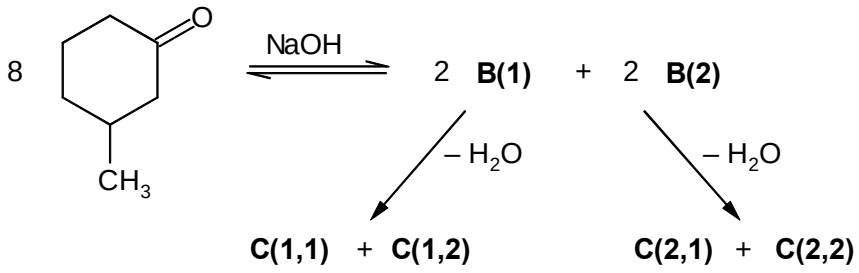
step 1: *Formation of an enolate ion*
step 2: *Nucleophilic addition*
step 3: *Formation of a neutral aldol*

The product of an aldol reaction often reacts in a following step e.g. if the temperature is increased. In this case water is eliminated (aldol condensation).



d) *Draw the structural formula of **A** und write down its name. What is the reason for the high stability of compound **A**?*

e) *Complete the following schema of an aldol reaction and aldol condensations.*



Fourth Round (theoretical problems)

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

Problem 4–01 Nitrogen group – plain and easy

The formulae of the oxo acids and the oxides of the elements of group 15 can be derived by an easy formalism:
The hydrogen atoms in the hydrogen compounds are step by step replaced by OH groups. From the empirical formulae the ortho (rich in water) or the meta (poor in water) forms are formed. The formulae of the oxides can be obtained by a (formal) total cleavage of all water.

An example: If all hydrogen atoms in the phosphonium cation PH_4^+ are replaced by OH groups the empirical formula is $P(OH)_4^+$ or $H_4PO_4^+$, respectively. By subtraction of a proton ($-H^+$) you get H_3PO_4 (phosphoric acid)

a) *Starting with the hydrogen compounds NH_3 and AsH_3 find the possible hydrogen-oxygen compounds of these elements using the formalism from the paragraph above.*

b) *Draw the Lewis structures of all arsenic containing species. Take possible isomers into account, too. Which molecular structures do you expect applying the VSEPR model?*

The respective anhydride of an acid is formed by a (formal) total cleavage of all water. Using phosphoric acid as an example you get
$2 \times H_3PO_4 \rightarrow H_6P_2O_8$ minus $3 \times H_2O \rightarrow P_2O_5$ (this is the anhydride of the phosphoric acid, which exists as dimer P_4O_{10}).

c) *Find all nitrogen oxides which may be formed by the (formal) combination of all compounds containing nitrogen, hydrogen and oxygen, found in a).*

Problem 4-02 Electrochemistry of Silver Halides

The following experiment was performed in order to determine the solubility product of silver bromide:
20.0 mL of a solution of potassium bromide (c = 0.0100 mol/L) and 20.0 mL of a solution of silver nitrate (c = 0,0100 mol/L) are mixed in a beaker. A calomel reference electrode and an ion-selective silver electrode are dipped into the solution in the beaker. The potential between these electrodes is measured: 0,199 V.

a) Account for the fact that the silver electrode is the cathode in this galvanic cell by a calculation.

b) Find the solubility product of silver bromide using the measured potential.

Data:

$Ag^+(aq) + e^- \longrightarrow Ag(s)$ $\quad E° = 0.800$ V

calomel reference electrode $\quad E = 0.241$ V

$K_s(AgCl) \approx 1.6 \cdot 10^{-10}$ $\quad K_s(AgI) = 8{,}12 \cdot 10^{-17}$

T = 298.15 K for the total problem

c) Calculate ΔG for the reaction $AgBr(s) \longrightarrow Ag^+(aq) + Br^-(aq)$

using $AgBr(s) + e^- \longrightarrow Ag(s) + Br^-(aq)$ $\quad E° = 0.071$ V.

If silver ions are added to a solution of sodium iodide a precipitate of silver iodide with $K_L(AgI) = 8.12 \cdot 10^{-17}$forms.

d) Determine the standard potential of the reduction of AgI to Ag.

Problem 4-03 The Electron in the 1-D Box

The first major expansion of the chemical industry occurred in the 19th century particularly in the production of dyes.
In those days it was not understood why the compounds prepared were so highly coloured. In the meantime quantum mechanics has developed a simple model which gives an amazingly good explanation of the colouring.
Thereunder parts of some molecules can be considered as a 1-D box over which the electrons are distributed. According to quantum mechanics these electrons can be considered to be standing waves with the wavelength λ.
Each wavelength corresponds to a specific energy. When light is absorbed by a molecule an electron makes a transition from a lower to a higher energy state.
For the energy difference ΔE you find $\Delta E = \frac{h \cdot c}{\lambda}$ (c: speed of light, h: Planck's constant, λ: wavelength of the light absorbed). When this wavelength occurs in the visible part of the spectrum (400 to 750 nm) the molecule appears coloured.

a) In the figure on the answer sheet the waves of the lowest energy electrons have been drawn (g and ①). Draw the wave of the next higher energy level.

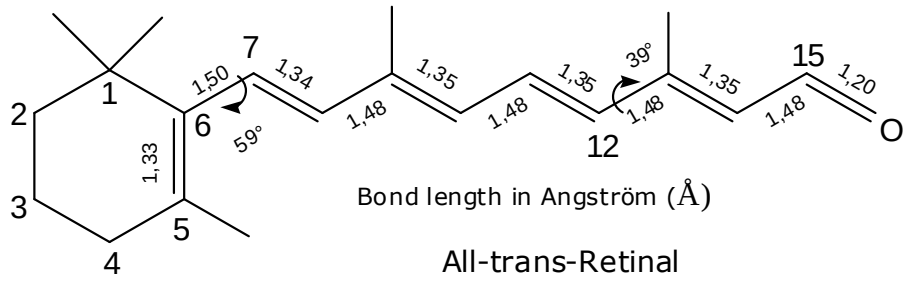
b) Give a general expression for the possible wavelengths of the electron as a function of the box length L.

In the ”particle in a box“ model only the variation in the kinetic energy is considered ($E_{kin} = ½ \cdot m \cdot v^2$).

c) Show that the possible energies of electrons in a molecule are given by $E = \frac{h^2 n^2}{8 m L^2}$ *(n: quantum number). Hint: momentum p = m·v = h/λ, m: mass of electron, v: speed of electron).*

d) Give an expression for the number z of possible energy states (orbitals) k (k even) π electrons in a conjugated system occupy in the ground state.

The retina of the human eye contains the light absorbing substance rhodopsin. It contains a protein (opsin) with the substance retinal bound to it. The structure of the molecule, together with the bond lengths, is given in the following figure.



Bond length in Angström (Å)

All-trans-Retinal

The C atoms 7 through 12 are in one plain. The curved arrows indicate that the bonds C5-C6 (about 59°) and C13-C14 (about 39°) protrude from this plain.

e) Give the number k of delocalized electrons in the box between C7 and C12 and draw the energy scheme of them in ground level.

When the theory of the “particle in the box” is applied to the fragment C7 through C12 the answer for the absorption with the lowest energy is found to be λ = 231 nm.

*f) Determine the box length which is basis of this calculation. Which length in the molecule is used as box length?*Actually the absorption turns out to be at 380 nm.

g) Using the “particle in the box” model give a reason for this longer wavelength.

When retinal is bound to opsin to form rhodopsin the absorption turns out to be at a wavelength over 550 nm.

If one wants to explain this with the "particle in the box" model some atoms have to be forced into the plain.

h) Which is (are) this (these) atom(s)? Account for your decision by calculating the exact wavelengths when additional relevant atoms are incorporated into the conjugated system of the box. Calculate step by step (atom by atom).

List of constants:
$c = 2.9979 \cdot 10^{8}$ ms^{-1}
$h = 6.6261 \cdot 10^{-34}$ Js
m(electron) $= 9.1094 \cdot 10^{-31}$ kg

Problem 4-04 A Deceptive Mineral - Apatite

Phosphorus is found in nature in apatite, a complex inorganic phosphate. The mineral we are dealing with in this problem is composed of calcium phosphate, calcium sulfate, calcium carbonate and calcium fluoride.
In preparation for the use as fertilizer apatite is processed to form water- soluble calcium dihydrogen phosphate. In doing this a mixture of phosphoric acid and sulfuric acid is added.
The elementary analysis of a sample of apatite gives the following results. Thereby the content of the elements – except for fluorine – is given as the ratio of their oxides.

	CaO	P_2O_5	SiO_2	F	SO_3	CO_2
Mass ratio	0.5269	0.3913	0.0274	0.0179	0.0323	0.0118

A sample of m_0 of the mineral is given into 50.0 mL of a solution which contains 0.500 mol/L of phosphoric acid and 0.100 mol/L of sulfuric acid. The mixture is totally evaporated at a temperature ≤ 60 °C under the hood. The yield is m_1 of a solid which is composed of gypsum (calcium sulfate dihydrate) and silicon dioxide.

a) Write down complete equations for all reactions in the reaction vessel. Explain why the reaction is performed under a hood and at a temperature ≤ 60 °C.

b) Calculate the maximal theoretical mass m_0 of apatite which can react with the acid mixture used.

c) Which mass m_1 is formed from the theoretical mass m_0 calculated in b)?

Problem 4-05 The Industrial Preparation of Hydrogen

Hydrogen can be prepared in an industrial process by heating hydrocarbons together with steam:

$CH_4(g) + H_2O(g) \longrightarrow 3\ H_2(g) + CO(g)$

[In this problem you may assume that all these gases are ideal and that ΔH and ΔS are independent of temperature.]

The equilibrium constants of this reaction at two different temperatures are known:

at 298.15 K $K_p = 1.450 \cdot 10^{-25}$, at 1580 K $K_p = 26640$.

a) Give the number of significant figures of results based on this data.

b) Determine ΔH, ΔS as well as ΔG and K_p for this reaction at 1000 K.

There are 1,000 mol of CH_4 and 1,000 mol H_2O at 400 K in a sealed vessel of constant volume. The total pressure is 1.600 bar.

The temperature is raised to 1100 K. At this temperature the equilibrium constant is 28.50.

c) Calculate the pressure in the vessel when the equilibrium is reached. Determine the amount of conversion (in %) of methane.

Performing the reaction with the same amount of reactants at 1100 K in a vessel with constant pressure (1.600 bar) the amount of conversion of methane will not have the same value.

d) How does the conversion change? Explain your statement.

In a reaction under these conditions the volume will change from V_{begin} to $V_{equilibrium} = 1.750 \cdot V_{begin}$.

e) Determine the amount of conversion under these conditions.

f) How can CO be removed from a mixture of H_2 and CO?

Problem 4-06 Silver in Photography - A Relic

Ten years ago the beneficiation of silver containing residue from the photo industry was of great commercial interest. Nowadays it does no longer play an

important role apart from some special applications. It was nearly totally pushed aside in the course of the develoment of digital photography.
In the process of fixation of a developed photo the unexposed silver halide was dissolved by complexation. Ag^+ ions form with different ligands stable complexes of the coordination number 2. Below you find the solubility product (K_{sp}) of silver chloride and the complex-formation constants (K_K) of some silver complexes.

$K_{sp}(AgCl) \approx 1.6 \cdot 10^{-10}$, T = 298.15 K in the total problem

Ligand	K_K
NH_3	$1.4 \cdot 10^{7}$
$S_2O_3^{2-}$	$3.2 \cdot 10^{13}$
CN^-	$3.2 \cdot 10^{20}$

a) *Write down the equations for the dissolving reactions with the three ligands.*

b) *Calculate the solubility of silver chloride in mol/L in the three complex solutions. Assume that the concentration of the ligands in the solution which is saturated with silver chloride is 0,100 mol/L in each case.*

c) *Which of the three fixatives was actually used? Account for your answer.*

In the qualitative inorganic analysis complexation often inhibits the formation of a desired precipitate. Silver is precipitated preferentially as chloride, however it may form the complex $[AgCl_2]^-$ if the concentration of Cl^- is high enough.

20.0 mL of a solution of Ag^+ (c = 0,100 mol/L) are treated with 100.0 mL of hydrochloric acid (c = 6.00 mol/L).

d) *Decide whether the formation of the silver complex $[AgCl_2]^-$ inhibits the precipitation of silver chloride. Account for your decision by a calculation.*

Equilibrium constant $K_{eq} = 1.00 \cdot 10^{-5}$ for $AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^-$.

Problem 4-07 Kinetics

It is possible that the gas phase reaction between NO and O_2 to give NO_2 ($2\ NO + O_2 \longrightarrow 2\ NO_2$) proceeds via the following mechanism:

$$2\ NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad \text{(fast equilibrium)}$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2\ NO_2 \quad \text{(slow)}$$

a) *Derive a rate law such as*

$$\text{rate of formation of } NO_2 = \frac{d[NO_2]/2}{dt} = k \cdot [NO]^a \cdot [O_2]^b \cdot [NO_2]^c$$

which is consistent with this mechanism and express k through the rate constants given above.

To prove whether this reaction follows this rate law you have do perform experiments. If the reaction takes place in a sealed container the total pressure will change if the reaction proceeds. There are many devices which are capable of measuring the pressure rather precisely. The difficulty is that you can measure only the total pressure whereas you want to know the partial pressure (and hence the concentration) of each of the species present.
For this reaction it is possible to relate the overall pressure to the required partial pressures for instance if you start with a 2:1 mixture of NO_2 and O_2
$n(NO):n(O_2) = V(NO):V(O_2) = 2:1$.

b) *Show that under this condition the partial pressure of oxygen ($p(O_2)$) can be derived from the total pressure (p_{total}) measured as*

$$p(O_2) = p_{total} - 2/3 \cdot p_{0,\,total}$$

$p_{0,\,total}$: initial total pressure.

Denote in your calculation the initial partial pressure of oxygen as $p_0(O_2)$, the fall of this partial pressure as Δp.

The reaction above is thought to have the following rate law

$$\frac{d[O_2]}{dt} = -k_3 \cdot [NO]^2 \cdot [O_2].$$

If the initial concentrations are again $[NO]:[O_2] = 2:1$ you can simplify the rate law and write it as a function of $[O_2]$.

c) *Show that in this case the equation can be simplified to* $\frac{d[O_2]}{dt} = -k_3' \cdot [O_2]^x$. *Determine x and give the relation between k_3 and k_3'.*

d) *Integrate this rate law to show that the concentration of O_2 varies with time in the following way:* $\frac{1}{[O_2]^2} = \frac{1}{[O_2]_0^2} + 2\,k_3' \cdot t$

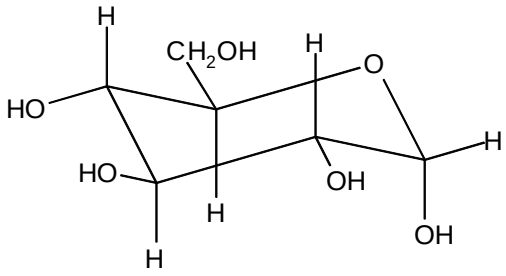
The following data was obtained at 298 K for a mixture of NO and O_2 in the ration 2:1:

t / s	0	60	120	180	240	300	360	420	480
$P_{total}/10^4$ Pa	1.350	1.120	1.060	1.035	1.015	1.005	0.995	0.985	0.980

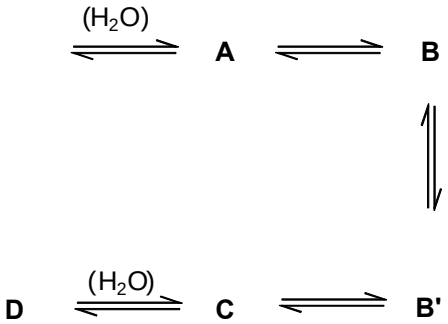
e) By plotting a suitable graph, show that this data is consistent with the rate law found in c) and obtain a value of the rate constant k_3', stating its units. (You can either use the pressure directly as a unit of concentration or convert the pressures to concentrations in mol/dm^3 using the ideal gas law)

Problem 4-08 Stereospecific Reactions

a) By means of structures in chair conformation outline the following reaction mechanism starting with α-D-glucopyranose.
Give the name of the product D.



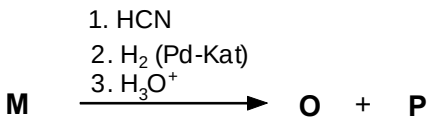
α-D-glucopyranose



The reactant of the following reaction is a D-aldopentose M with the empirical formula $C_5H_{10}O_5$.
Oxidation of M with nitric acid leads to an optically inactive product N.

b) By means of Fischer projections sketch the reaction scheme.

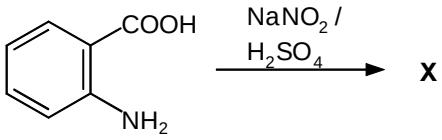
Compound M reacts in the following way:



Both compounds **O** and **P** are oxidized by nitric acid, too. Compound O gives an optically active compound O' while compound P forms an optically inactive product P'.

*c) Draw the Fischer projections of the compounds **O** and **P**.*
(If there is more than one possibility for M choose one of them.)

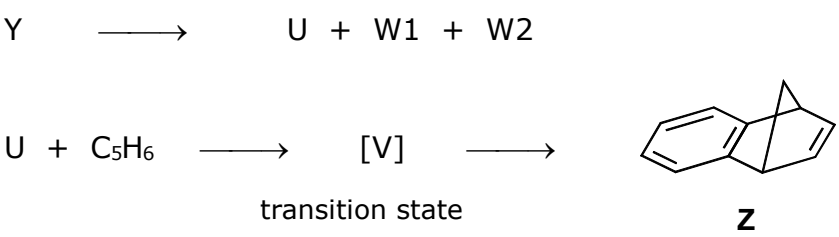
o-Aminobenzoic acid reacts with sodium nitride and sulfuric acid to form a diazonium salt X.



The reaction of X with a base results in compound Y.

*d) Draw the structural formulae of **X** and **Y**.*

When compound Y is heated vigorously it reacts with cyclopentadiene (C_5H_6). Compound Z is formed:



e) Draw the structural formulae of the intermediates U and V as well as of the compounds W1 and W2. What is the name of the reaction between U and cyclopentadiene?

Problem 4-09 Nuclear Magnetic Resonance Spectroscopy (NMR-Spectroscopy)

The following table shows a selection of chemical shifts δ of ^{13}C in different chemical surroundings.

Tab. 1: Chemical shift δ of ^{13}C in ppm:

Aldehyde / Ketone	170 – 200
Alkene	100 – 150
Bromoalkane	25 - 65
Chloroalkane	35- 80
Methyl group	8 - 30
Nitrogen- / carbon compounds	30 - 65

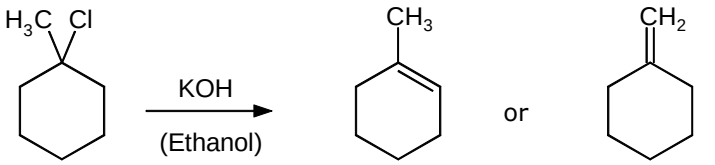
The ^{13}C-NMR spectrum of dichloroacetic acid shows to signals, δ_1 = 175 ppm and δ_2 = 65 ppm.

a) Assign the shifts δ_1 and δ_2 to the carbon atoms of dichloroacetic acid.

A second ^{13}C NMR-spectrum *of dichloroacetic acid* shows the fine structure of the spectrum.

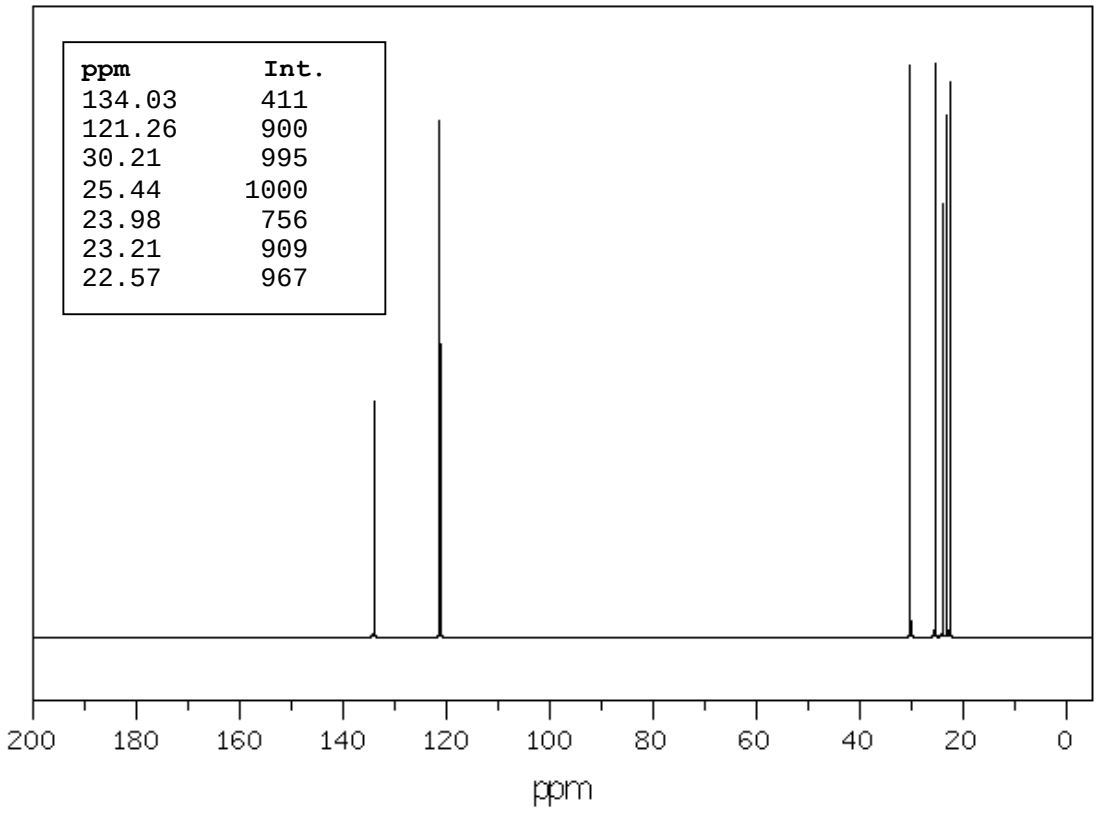
b) What do you expect to observe? Explain!

KOH is added to 1-chloro-1-methylcyclohexane.



product 1 product 2

c) Use the ^{13}C NMR spectrum on the next page to determine which product is formed. Rationalize your decision.



The following problems refer to ^{1}H NMR spectroscopy.

d) How many signals do you expect in a ^{1}H-NMR spectrum of the following compounds? Give a short explanation.

1. 2,3-Dimethyl-2-buten 2. 2-Methyl-2-buten.

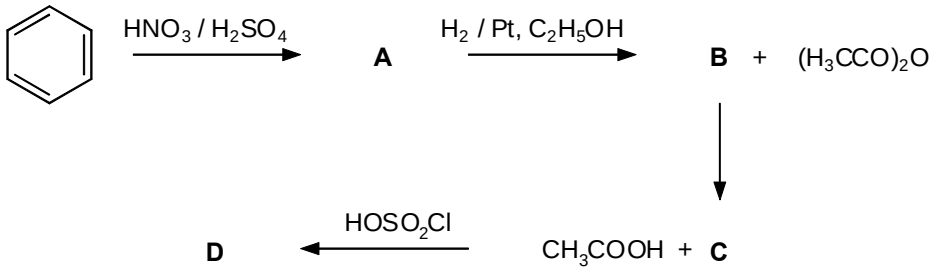
The fine structures of ^{1}H NMR spectra of two compounds are detected:
(1) $ClCH_2 - CH_2Cl$ und (2) CH_3CH_2Cl .

e) How many signals of compound (1) do you expect, how many of compound (2)? Account for your decision.

Problem 4-10 Selected Syntheses

Synthesis 1

Sulfathiazole (compound **F**) can be synthesized in the following way:

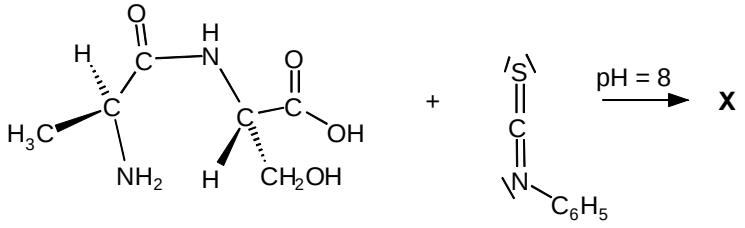


Compound **D** has the empirical formula $C_8H_8O_3NSCl$.

a) Find the structural formulae of the compounds A to F. What is the function of the reaction step B + $(CH_3CO)_2O$?

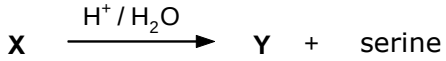
Synthesis 2

H – Ala – Ser – OH (alanylserine) reacts with Phenylisothiocyanate (PITC) under weak basic conditions to form compound X. It is a nucleophilic addition of the amino group to PITC.



b) Draw the structural formula of X.

The addition of acid leads to the formation of a ring Y and the elimination of serine.



c) Draw the structural formula of Y.

d) What can this reaction be used for?

Fourth Round (practical problems)

Problem 4-11 Synthesis and Analysis of Potassium Trioxlatoferrate(III)-Hydrate, $K_3[Fe(C_2O_4)_3] \cdot n\ H_2O$

In this experiment you are required to synthesize potassium trioxalatoferrate(III)-hydrate. Thereafter the exact content of water has to be found out by a quantitative determination of the content of oxalate.

Safety precautions:
Wear eye protection and protective clothing!

Equipment:
100 mL beaker, 50 mL beakers for weighing in (2x), plastic bowl, vacuum pump, suction flask, Büchner funnel with rubber seal, filter paper (2x) for Büchner funnel, balanced and labeled 100 mL beaker for the product, volumetric flask (100 mL) with stopper, volumetric pipette (20 mL), pipette control, 50 mL measuring cylinder, 300 mL conical beaker (wide mouth, 2x), spatula, burette (25 mL) with funnel and clamp, stand with boss and clamps, magnetic stirrer plate with stirring bar, glass rod, thermometer

Substances:
Iron(III) chloride hexahydrate, $FeCl_3 \cdot 6\ H_2O$ (5.3 g already weighed in in a beaker)
Potassium oxalate monohydrate, $K_2C_2O_4 \cdot H_2O$ (12.0 g already weighed in in a beaker)
Standard solution of potassium permanganate, $c(KMnO_4) = 0.02$ mol/L
Sulfuric acid, $w(H_2SO_4) = 25$ %, (corrosive, C)
Sulfuric acid, $c(H_2SO_4) = 1$ mol/L, (corrosive, C)
Ethanol (highly flammable, R 11, harmful to health, Xn)
Demineralized water, Ice

Procedures
<u>Synthesis of potassium trioxalatoferrate(III)-hydrate:</u>

Add a solution of 5.3 g (~ 20 mmol) $FeCl_3 \cdot 6\ H_2O$ in 8 mL of water to a warm (35 – 40 °C) solution of 12 g (~ 65 mmol) $K_2C_2O_4 \cdot H_2O$ in approx. 25 mL of water. The mixture is cooled down in an ice bath to 0 °C and kept at this temperature until total crystallization.

Decant the mother liquor and dissolve the salt in approx. 20 mL of warm (35 to 40 °C) water. Cool down again to 0 °C to crystallize the salt.
The solid has to be filtered off with the help of a Büchner funnel, at first washed twice with 10 mL of ice water each time, then washed with 10 mL of ethanol.
Allow to stand at air until it is dry.

a) *Determine the yield in % referring to iron(III) chloride hexahydrate. Assume in this case that your product is existent without water of crystallization.*

b) *Give the equation of the formation reaction.*

Determination of the content of oxalate in potassium trioxalatoferrate(III)-hydrate with the help of potassium permanganate:

Approx. 0.6 g of the prepared product are accurately weighed in into a small beaker and then completely transferred to a volumetric flask. By adding demineralized water the salt dissolves. Then the flask has to be filled up to 100 mL. The solution is mixed well to form your test solution.
20 mL of the test solution are transferred to a conical beaker with the help of the volumetric pipette.
Add 10 mL of sulfuric acid ($w(H_2SO_4) = 25$ %).
The solution is filled up to approx. 100 mL, heated up to a temperature of 70 – 80 °C and then titrated with the standard solution of potassium permanganate ($c(KMnO_4) = 0.02$ mol/L) until it turns lightly pink.

c) *Write down the equation for the reaction between oxalate und permanganate.*

d) *Write down the mean consumption on the answer sheet and calculate the mass concentration β in mg/L of oxalate in your test solution.*

e) *Calculate the water content on the basis of your titration results and give the correct empirical formula.*

f) *Give your product in the labeled beaker to the lab assistant after you determined the yield and took away approx. 0.6 g in order to determine the water content. Write the number of your beaker on the answer sheet.*

Disposal:
Liquid substances and solutions have to be poured into the provided disposal container. The filter papers can be given into the domestic waste.

Problem 4-12 Cerimetric Determination of Nitrite

In this experiment the mass concentration of nitrite in a test solution has to be determined. In this process cerium(IV) is reduced to cerium(III).

Safety precautions:
Wear eye protection and protective clothing!
The cerium containing standard solution is very acidic.
Precaution when working with conc. nitric acid.

Equipment:
Volumetric flask (100 mL) with stopper, volumetric pipette (20 mL), pipette control, 250 mL beaker (2 x), spatula, 25 mL burette with funnel and clamp, magnetic stirrer plate with stirring bar

Substances:
Nitrite containing sample in a 100 mL volumetric flask
Standard solution of cerium(IV) sulfate, $c(Ce(SO_4)_2)$ = 0.1 mol/L (titer: 1.024)
Conc. nitric acid, $w(HNO_3)$ = 65 % (corrosive, C)
Solution of ferroin, $c([C_{36}H_{24}FeN_6]SO_4)$ = 0.025 mol/L
demineralized water

Procedures:
The test solution (100 mL volumetric flask) has to be filled up to exactly 100 mL and mixed well.
20 mL of the standard solution of cerium(IV) sulfate are transferred to a 250 mL beaker using a volumetric pipette. The solution is diluted with approx. 50 mL of demineralized water and 5 mL of conc. nitric acid are added.
The solution is heated on the magnetic stirrer plate up to 50 °C.
The nitrite containing test solution is filled into the burette. The burette is lowered until its tip is just dipping into the solution of cerium sulfate.
Titrate with the test solution until the intense yellow colour of the solution of cerium sulfate has nearly disappeared.
2 or 3 drops of the ferroin solution are added. Then the titration is slowly continued until the colour changes from blue-grey to slightly pink.

Disposal:

Liquid substances and solutions have to be poured into the provided disposal container.

a) Write down the equation for the reaction of nitrite with cerium(IV) sulfate.

b) Write down the mean consumption on the answer sheet and calculate the mass concentration β in mg/L of nitrite in your test solution.

Part 2

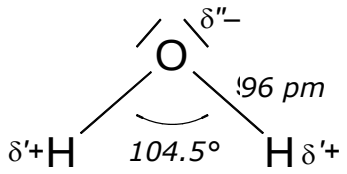
The answers to the problems of the four rounds

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)



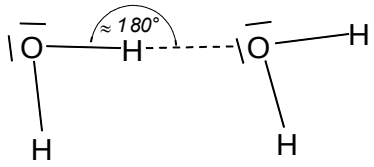
b) The VSEPR theory is a model in chemistry used to predict the shape of individual molecules based upon the extent of electron-pair electrostatic repulsion.

Atoms in a molecule are bound together by electron pairs. These are called bonding pairs. More than one set of bonding pairs of electrons may bind any two atoms together (multiple bonding).

1. Electron pairs surrounding an atom mutually repel each other, and will therefore adopt an arrangement that minimizes this repulsion. They will get as far apart from each other as possible.
2. Lone pairs occupy more space than bonding electron pairs.
3. Double bonds occupy more space than single bonds.
4. The multiple electron pairs in a multiple bond are treated as though they were a single pair.
5. Electronegative substituents attract electron pairs more strongly and diminish their required space.

The H_2O molecule has four electron pairs in its valence shell: two lone pairs and two bond pairs. The four electron pairs are spread so as to point roughly towards the apices of a tetrahedron. However, the bond angle between the two O-H bonds is only 104.5°, rather than the 109.5° of a regular tetrahedron, because the two lone pairs (whose density or probability envelopes lie closer to the oxygen nucleus) exert a greater mutual repulsion than the two bond pairs.

c) Linear, the angle O-H···O is near to 180°



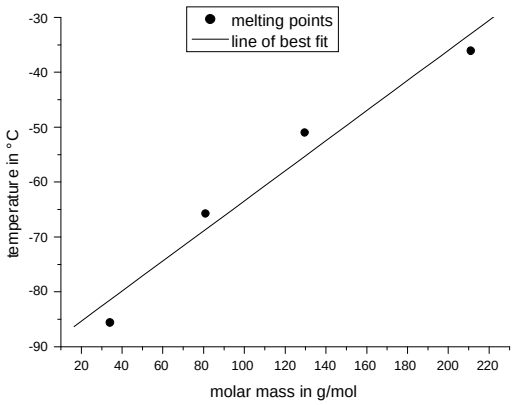
d) H_2O dihydrogen monooxide, water

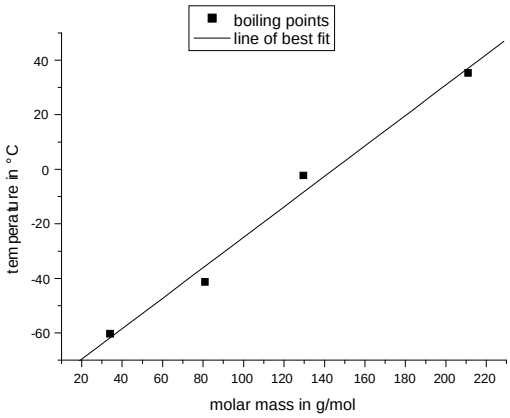
H_2S	hydrogen sulfide,	dihydrogen monosulfide,	(mono)sulphane
H_2Se	hydrogen selenide,	dihydrogen monoselenide.	(mono)selane
H_2Te	hydrogen telluride,	tellurium hydride	
H_2Po	polonium hydride		

e)

	H_2O	H_2S	H_2Se	H_2Te	H_2Po
Mp. in °C	Fp_{H2O}	-85.6	-65.7	-51.0	-36.1
Bp. in °C	Kp_{H2O}	-60.3	-41.3	-2.3	35.3
M in g/mol	18.01	34.08	80.98	129.62	211.02

(Note: 209 g/mol were used as molar mass of polonium.)





$$Y = A + B \cdot X$$

Melting point: Boiling point:

$Mp = -90.82\ °C + 0.274°C{\cdot}mol/g \cdot M$ $Bp = -80.78\ °C + 0.5585°C{\cdot}mol/g \cdot M$

$M = 18.01$ g/mol

$Mp_{H2O} = -85.9\ °C$ $Bp_{H2O} = -70.7\ °C$

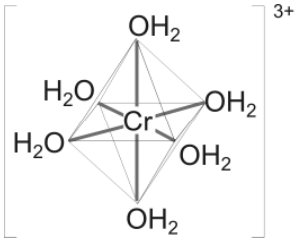
Using Kelvin you get A = 182.33 K and 192.37 K respectively,
and 187.3 K and 202.4 K respectively.

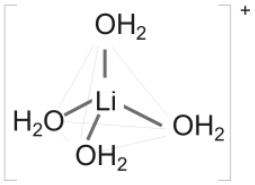
f) Anomalies:
When freezing solid the density of water decreases. A bulking of about 9 % occurs.
In liquid water the density increases with increasing temperature up to 4 °C. Then it decreases continuously with increasing temperature.
Examples of consequences:

- Closed vessels/pipes etc. which contain water/aqueous solutions may burst when water is freezing.
- Erosion of rocks at deep temperatures.
- Damage to streets and pavement in winter time.
- Fish/other animals can survive in winter as water sinks down with a temperature of 4 °C.
- Ice floats on water.
- Water freezes from the top.

Solution to problem 1-2

a) Chromium (III): Octahedron, Lithium(I): Tetrahedron





b) Iron(III) forms in an aqueous solution the aquo complex $[Fe(H_2O)_6]^{3+}$. The water molecules may act as proton donors and so cause the acidic reaction

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+ \quad (K_s = 6 \cdot 10^{-3})$$

and further steps of protolysis.

c) You may assume that at the end of the measurement the compound has lost all water of crystallisation. Thus you can calculate the number of H_2O per $NiCl_2$ unit:
$M(NiCl_2) = 129.60$ g/mol

Molar mass of the starting compound: $M = \frac{129.60\ \text{g/mol}}{1 - 0.3009 - 0.1518} = 236.80$ g/mol

$\Delta = (236.80 - 129.60)$ g/mol = 107.2 g/mol

Δ refers to 6 molecules of H_2O (108.06 g/mol).

The compound which formed on recrystallisation is $NiCl_2 \cdot 6\ H_2O$

with $M(NiCl_2 \cdot 6\ H_2O) = 237.68$ g/mol

1. Step: $NiCl_2 \cdot 2\ H_2O$ has formed
   Loss of mass 30.09 % (experimental)
   Loss of 4 H_2O: [4 x $M(H_2O)$ / 237.68 g/mol] · 100 % = 30.31 % (theo.)
2. Step: $NiCl_2$ has formed
   Loss of mass 15.18 % (experimental)
   Loss of 2 H_2O: [2 x $M(H_2O)$ / 237.68 g/mol] · 100 % = 15.15 % (theo.)

d) Acetylene (ethine): $CaC_2 + 2\ H_2O \rightleftharpoons Ca(OH)_2 + H_2C_2$

e) Copper acetylide forms. This compound is highly explosive and has to be handled with maximal caution. Only small amounts should be synthesised.

$$2\ [Cu(NH_3)_2]^+ + H_2C_2 \rightleftharpoons Cu_2C_2 + 2\ NH_3 + 2\ NH_4^+$$

f) $\overset{+IV,\,-II}{H_2O} + \overset{0}{SO_2} + 2\ C_5H_5N + \overset{0}{I_2} \rightleftharpoons \overset{+VI,\,-II}{SO_3} + 2\ \overset{+I,\,-I}{HI} \cdot C_5H_5N$

At the end point additional iodine does no longer react. Thus the colour turns brown.

g) 1. Step: $SO_2 + H_3COH + C_5H_5N \rightleftharpoons C_5H_5NH^+ + {}^-O_2SOCH_3$

2. Step: ${}^-O_2SOCH_3 + H_2O + I_2 + 2\ C_5H_5N \rightleftharpoons {}^-O_3SOCH_3 + 2\ C_5H_5NH^+ + 2\ I^-$

Pyridine functions as a base and shifts the equilibrium towards the products. Furthermore it's a very good solvent of sulfur dioxide.

h) Sample 3 of oil A was ignored.
Average consumption of oil A: 1.63 mL, of oil B: 1.44 mL

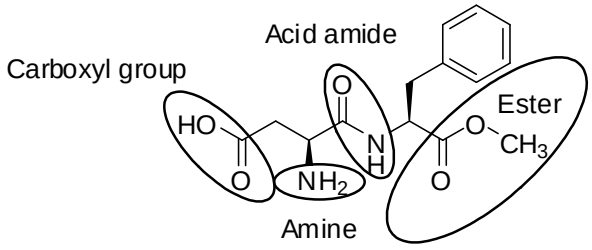
$$\text{Mass percentage of water} = \frac{\text{mass of water}}{\text{mass of the sample}} \cdot 100\ \% = \frac{\text{consumption} \cdot \text{titer}}{\text{mass of the sample}} \cdot 100\ \%$$

$$\text{Mass percentage of water in oil A} = \frac{1.63\,\text{mL} \cdot 4.8\,\text{mg/mL}}{10000\,\text{mg}} \cdot 100\ \% = 0.078\ \%$$

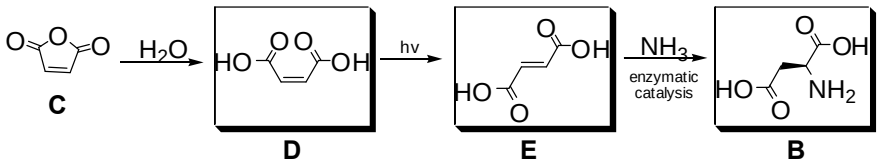
$$\text{Mass percentage of water in oil B} = \frac{1.44\,\text{mL} \cdot 4.8\,\text{mg/mL}}{10000\,\text{mg}} \cdot 100\ \% = 0.069\ \%$$

Solution to problem 1-3

a) **A** is called „Aspartam". Its molecule contains four functional groups:



b)



D: Maleic acid **E**: Fumaric acid **B**: L-Aspartic acid

c) **D** and **E** are cis/trans isomers (E/Z isomers).

d) The reaction of **E** to **B** is catalysed by the enzyme L-aspartase. On the one hand it controls the regioselectivity of the reaction with ammonia (i.e. it avoids the formation of an ammonium salt or an acid amide). On the other hand this enzyme is especially important because it controls the strereochemistry of this reaction: Only a single product is formed, L-aspartic acid (Compound **B**).

e)

Glutamic acid	is used as flavour enhancer
Cysteine	may form disulphide bridges
Glycine	is achiral
Arginine	contains four nitrogen atoms per molecule
Tryptophan	contains an indole ring
Alanine	forms by decarboxylation of compund **B**
Methionine	contains a thioether

Proline	contains a saturated five-membered ring
Threonine	contains two stereogenic centres
Asparagine	contains an acid amide
Lysine	plays a specific role in the film "Jurassic Park"

f) $n(C) = \frac{m(CO_2)}{M(CO_2)} = \frac{219\,mg}{44.01\,g/mol}$ = 4.98 mmol

$n(H) = \frac{m(H_2O)}{M(H_2O)} = \frac{54.8\,mg}{18.02\,g/mol}$ = 6.08 mmol

$n(N) = \frac{m(N_2)}{M(N_2)} = 2 \cdot \frac{7.73\,mg}{28.01\,g/mol}$ = 0.552 mmol

$$n(O) = \frac{m(O)}{M(O)} = \frac{m(F) - m(C) - m(H) - m(N)}{M(O)} = \frac{m(F) - m(C)\cdot M(C) - m(H)\cdot M(H) - m(N)\cdot M(N)}{M(O)}$$

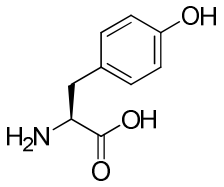
$$= \frac{100\,mg - 4.98\,mmol\cdot 12.01\,g/mol - 6.08\,mmol\cdot 1.01\,g/mol - 0.552\,mmol\cdot 14.01\,g/mol}{16.00\,g/mol}$$

n(O) = 1.64 mmol

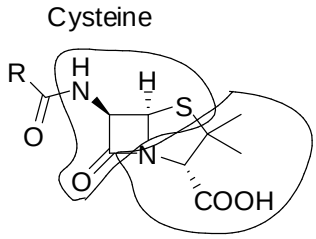
n(C) : N(H) : N(N) : N(O) = 4.98 : 6.08 : 0.552 : 1.64

= 9 : 11 : 1 : 3

Smallest empirical formula of **F:** ($C_9H_{11}NO_3$), tyrosine



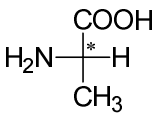
g)



G Valine

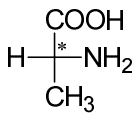
h) **G** is a penicillin which belongs to the β-lactam-antibiotics (annulated rings or heterocycles correct , too).

j)



(*S*)

L-Alanine



(*R*)

D-Alanine

Answers Round 3 Test 1

Solution to problem 3-01

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

Solution to 3-02

a)

Compound	LiH	BeH_2	BH_3 (B_2H_6)	CH_4	NH_3	H_2O	HF
State of aggregation	s	s	g	g	g	l	g*
Type of bonding	ion/cov	cov	cov	cov	cov	cov	cov
Redox	red	red	n	red	red	n	ox
Acid/base	b	b	a	n	b	n	a

* g (>19.5 °C)

Compound	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl
State of aggregation	s	s	s	g	g	g	g
Type of bonding	ion	ion/cov	cov	cov	cov	cov	cov
Redox	red	red	red	red	red	red	ox
Acid/base	b	b	b	(a)	n	a	a

b) $4\ LiH + O_2 \rightleftharpoons 2\ Li_2O + 2\ H_2$

$2\ BeH_2 + O_2 \rightleftharpoons 2\ BeO + 2\ H_2$

$2\ BH_3\ (B_2H_6) + 3\ O_2 \rightleftharpoons B_2O_3 + 3\ H_2O$

$CH_4 + 2\ O_2 \rightleftharpoons CO_2 + 2\ H_2O$

$4\ NH_3 + 3\ O_2 \rightleftharpoons 2\ N_2 + 6\ H_2O$

$H_2O + O_2 \rightleftharpoons$ no reaction

$4\ HF + O_2 \rightleftharpoons 2\ F_2 + 2\ H_2O$ (Equilibrium on the side of the reactants)

c) $NaH + H_2O \rightleftharpoons NaOH + H_2$

$MgH_2 + 2\ H_2O \rightleftharpoons Mg(OH)_2 + 2\ H_2$

$AlH_3 + 3\ H_2O \rightleftharpoons Al(OH)_3 + 3\ H_2$

$SiH_4 + 4\ H_2O \rightleftharpoons H_4SiO_4 + 4\ H_2$

$PH_3 + H_2O \rightleftharpoons PH_4^+ + OH^-$ (Equilibrium on the side of the reactants)

$H_2S + H_2O \rightleftharpoons HS^- + H_3O^+$

$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$

Solution to problem 3-03

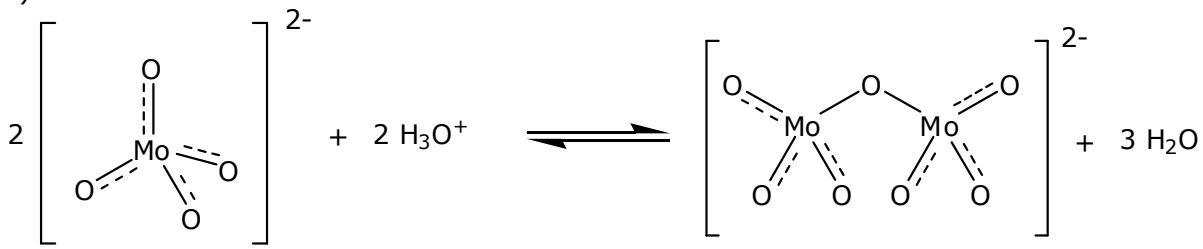
a) Content of phosphor of 1 person: $6.0\ g \cdot 70 = 420\ g$

Mass of phosphor in the barrel: 420 g / 4000 L

Mass of phosphor in 100 ml: 420 g · 0.1 L / 4000 L = 10.5 mg

Mass of phosphor of 3 persons: 10.5 mg · 3 = 31.5 mg

b)



c) Actual mass of $P_2O_5 \cdot 24\ MoO_3$:

4.2880 g – 0.0481 g = 4.2399 g

mass of phosphor in 100 ml solution

$$2 \cdot M(P) \cdot n(P_2O_5 \cdot 24\ MoO_3) = 2 \cdot 30.97\ \text{mg/mol} \cdot \frac{4.2399\ \text{g}}{3596.5\ \text{g/mol}}$$

m(P) ≈ 73.0 mg

number of victims

73.0 mg / 10.5 mg = 6.95 to match with 7 persons

d) Strongly acidic conditions: PO_4^{3-} exists as H_3PO_4

$AgNO_3$: $3\ AgNO_3 + H_3PO_4 \longrightarrow Ag_3(PO_4) + 3\ HNO_3$

$BaCl_2$: $3\ BaCl_2 + 2\ H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3\ HCl$

$ZrOCl_2$: $3\ ZrOCl_2 + 4\ H_3PO_4 \longrightarrow Zr_3(PO_4)_4 + 6\ HCl + 3\ H_2O$

Ag_3PO_4:	not stable:	soft cation / hard anion; most readily soluble
$Ba_3(PO_4)_2$:	not stable:	relatively soft cation / hard anion
$Zr_3(PO_4)_4$:	stable:	hard cation / hard anion; most sparingly soluble

Solution to problem 3-04

a), b) $C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$

Conc. at begin in mol/L	0.012	0	≈ 0
Conc. at equil. in mol/L	0.012-x	x	x

$$6.31 \cdot 10^{-5} = \frac{x^2}{0.012 - x} \quad \Rightarrow \quad x^2 + 6.31 \cdot 10^{-5}\, x - 0.012 \cdot 6.31 \cdot 10^{-5} = 0$$

$x_1 = 8.39 \cdot 10^{-4}$ ($x_2 < 0$) pH = 3.08

or with the approximation for weak acids:

$pH = 1/2 \cdot (pKs - \lg [c_0(C_6H_5COOH))/c^0]$

$pH = ½ \cdot (-\lg(6.31 \cdot 10^{-5}) - \lg 0.012) = 3.06$

c) $$\frac{c(\text{benzoate anions})}{c(\text{benzoic acid})} = \frac{K_S}{c(H_3O^+)/c^0}$$

pH = 4: $\frac{c(\text{benzoate anions})}{c(\text{benzoic acid})} = \frac{6.31 \cdot 10^{-5}}{10^{-4}}$ $\frac{c(\text{benzoate anions})}{c(\text{benzoic acid})} = 0.631$

pH =6: $\frac{c(\text{benzoate anions})}{c(\text{bezoic acid})} = 63.1$

d) The best buffering ability against acids and bases occurs if $\frac{c(\text{benzoate anions})}{c(\text{benzoic acid})} = 1$

$\Rightarrow$ pH = pK_s pH = - lg $6.31 \cdot 10^{-5}$ = 4.20

e) n(benzoic acid) = $25 \cdot 10^{-3} \cdot 0.0150$ mol = $3.75 \cdot 10^{-4}$ mol

n(sodium hydroxide) = $17 \cdot 10^{-3} \cdot 0.0120$ mol = $2.04 \cdot 10^{-4}$ mol

benzoic acid exists in excess ($\Delta = 1.71 \cdot 10^{-4}$ mol) thus we can assume in the beginning that all NaOH is reacted with benzoic acid to form benzoate anions.

c_0(benzoic acid) = $\frac{1.71 \cdot 10^{-4}\ \text{mol}}{42 \cdot 10^{-3}\ \text{L}} = 4.07 \cdot 10^{-3}$ mol/L

c_0(benzoate anions) = $\frac{2.04 \cdot 10^{-4}\ \text{mol}}{42 \cdot 10^{-3}\ \text{L}} = 4.86 \cdot 10^{-3}$ mol/L

Assuming the solution to be a buffer with approximately c = c_0:

$pH = pK_s + \lg \frac{c_0(\text{benzoate})}{c_0(\text{benzoic acid})}$ $pH = -\lg(6.31 \cdot 10^{-5}) + \lg \frac{4.86 \cdot 10^{-3}}{4.07 \cdot 10^{-3}} = 4.28$

Exact calculation:

Whether protolysis of benzoic acid takes place can be derived from the fraction

$Q = \frac{c(\text{benzoate anions}) \cdot c(H_3O^+)}{c(\text{benzoic acid})}$, $Q = \frac{4.86 \cdot 10^{-3} \cdot 10^{-7}}{4.07 \cdot 10^{-3}} = 1.19 \cdot 10^{-7} < K_s = 6.31 \cdot 10^{-5}$

$\Rightarrow$ benzoic acid has to deprotonate.

$C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$

Conc. at begin in mol/L	$4.07 \cdot 10^{-3}$	$4.86 \cdot 10^{-3}$	$10^{-7} \approx 0$
Conc. at equil. in mol/L	$4.07 \cdot 10^{-3}$-x	$4.86 \cdot 10^{-3}$+x	x

$6.31 \cdot 10^{-5} = \frac{(4.86 \cdot 10^{-3} + x) \cdot x}{4.07 \cdot 10^{-3} - x}$ $\Rightarrow$ $x^2 + 4.92 \cdot 10^{-3}\, x - 2.57 \cdot 10^{-7} = 0$

$x_1 = 5.169 \cdot 10^{-5}$ ($x_2 < 0$) pH = 4.29

Sollution to problem 3-05

a) 0.1 kPa is the pressure of water vapor of the first hydrate. incoming water vapor is incorporated as water of crystallization. Thereby the pressure is not increased.

b) 1.36 g of $CuSO_4$ are $\frac{1.36\ \text{g}}{159.62\ \text{g/mol}}$ = $8.52 \cdot 10^{-3}$ mol of $CuSO_4$

Δm(A-B) = 0.15 g that are $8.33 \cdot 10^{-3}$ mol of H_2O $\Rightarrow$ $x_1 = 1$

Δm(C-E) = Δm(F-G) = 2 · Δm(A-B) $\Rightarrow x_2 = 3$ und $x_3 = 5$

c) Δm(C-D) = Δm(D-E)

$\Rightarrow$ an equimolar mixture of $CuSO_4 \cdot H_2O$ and $CuSO_4 \cdot 3\ H_2O$ is existent

$M(CuSO_4 \cdot H_2O)$ = 177.64 g/mol

$M(CuSO_4 \cdot 3\ H_2O)$ = 213.67 g/mol

$CuSO_4 \cdot H_2O$: $\frac{177.64}{177.64+213.67} \cdot 100\% = 45.4\%$

$CuSO_4 \cdot 3\ H_2O$: $\frac{213.67}{177.64+213.67} \cdot 100\% = 54.6\%$

d) The horizontal distances are prolonged (the equilibrium pressures rise), the mass increase does not change.

Solution to problem 3-06

a) Anode: $Cu \longrightarrow Cu^{2+} + 2\ e^-$ Cathode $2\ H^+ + 2\ e^- \longrightarrow H_2$

after a certain time at the cathode additionally $Cu^{2+} + 2\ e^- \longrightarrow Cu$

b) Current = 0.601·1802 As, that are $\frac{0.601 \cdot 1802\ As}{1.602 \cdot 10^{-19}\ C}$ electrons

amount of ionised copper $n(Cu) = \frac{0.3554\ g}{63.546\ g/mol}$

number of electrons released during electrolysis $2 \cdot N_A \cdot n(Cu) = 2 \cdot N_A \cdot \frac{0.3554}{63{,}546}\ mol$

$$\Rightarrow \quad \frac{0.601 \cdot 1802\ As}{1.602 \cdot 10^{-19}\ C} = 2 \cdot N_A \cdot \frac{0.3554}{63.546}\ mol$$

$$N_A = \frac{0.601 \cdot 1802 \cdot 63.546}{1.602 \cdot 10^{-19} \cdot 2 \cdot 0.3554\ mol} \qquad N_A = 6.04 \cdot 10^{23}\ mol^{-1}$$

c) $\rho = \frac{m}{V}$ $\rho = \frac{8 \cdot [m(^{28}Si) \cdot h(^{28}Si) + m(^{29}Si) \cdot h(^{29}Si) + m(^{30}Si) \cdot h(^{30}Si)]}{a^3 \cdot N_A} \Rightarrow$

$$N_A = \frac{8 \cdot [m(^{28}Si) \cdot h(^{28}Si) + m(^{29}Si) \cdot h(^{29}Si) + m(^{30}Si) \cdot h(^{30}Si)]}{a^3 \cdot \rho}$$

with the given data $N_A = 6.02214091 \cdot 10^{23}$

Solution to problem 3-07

a) The standard potentials are valid for half-cell reactions with the electron acceptor on the left.

(1) $V^{2+} + 2\ e^- \rightleftarrows V(s)$ $E°1 = -1.20\ V$ $\Delta G°_1 = -2 \cdot E°_1 \cdot F$

(2) $VO^{2+} + 2\ H^+_{(aq)} + e^- \rightleftarrows V^{3+} + H_2O$ $E°_2 = +0.34\ V$ $\Delta G°_2 = -1 \cdot E°_2 \cdot F$

(3) $V^{3+} + 3\ e^- \rightleftarrows V(s)$ $E°_3 = -0.89\ V$ $\Delta G°_3 = -3 \cdot E°_3 \cdot F$

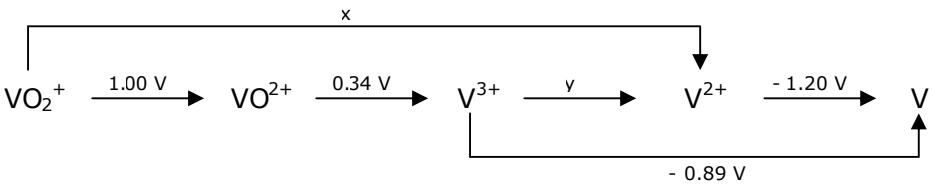
(4) $VO_2^+ + 2\ H^+_{(aq)} + e^- \rightleftarrows VO^{2+} + H_2O$ $E°_4 = +1.00\ V$ $\Delta G°_4 = -1 \cdot E°_4 \cdot F$

(5) $VO_2^+ + 4\ H^+_{(aq)} + 3\ e^- \rightleftarrows V^{2+} + 2\ H_2O$ $\Delta G°_5 = \Delta G°_4 + \Delta G°_2 - \Delta G°_1 + \Delta G°_3$

$\Delta G°_5 = -1 \cdot F \cdot (E°_4 + E°_2 - 2 \cdot E°_1 + 3 \cdot E°_3)$ $\Delta G°_5 = -1 \cdot F \cdot 1.07\ V$

$\Delta G°_5 = -3 \cdot F \cdot E°_5$ $E°_5 = \Delta G°_5/(-3 \cdot F)$ $E°_5 = 0.36\ V$

or more elegant



$1 \cdot y + 2 \cdot (-1.20\ V) = 3 \cdot (-0.89\ V)$ $\quad Y = -0.27\ V$

$1 \cdot 1.00\ V + 1 \cdot 0.34\ V + 1 \cdot (-0.27\ V) = 3 \cdot x$ $\quad x = 0.36\ V$

b) The standard potentials are valid for half-cell reactions with the standard concentration of 1 mol/L $\quad \Rightarrow E°_1 = E°_2$

$\Delta G_1 = - z \cdot F \cdot E°_1 \qquad K_1 = e^{\frac{z \cdot F \cdot E_1^0}{R \cdot T}}$

$\Delta G_2 = - 2 \cdot z \cdot F \cdot E°_1 \qquad K_2 = e^{\frac{2 \cdot z \cdot F \cdot E_1^0}{R \cdot T}} = \left(e^{\frac{z \cdot F \cdot E_1^0}{R \cdot T}}\right)^2 \qquad \Rightarrow K_2 = K_1^2$

or

$K_1 = \frac{[C] \cdot [D]}{[A] \cdot [B]} \qquad K_2 = \frac{[C]^2 \cdot [D]^2}{[A]^2 \cdot [B]^2} \qquad \Rightarrow K_2 = K_1^2$

c) $Cr_2O_7^{2-} + 14\ H_3O^+ + 6\ e^- \rightleftarrows 2\ Cr^{3+} + 21\ H_2O \qquad E°_5 = 1.33\ V \quad \Delta G°_5 = -6 \cdot F \cdot 1.33\ V$

$Fe^{3+} \rightleftarrows Fe^{2+} \qquad E°_6 = 0.770\ V \quad \Delta G°_6 = -F \cdot 0.770\ V$

$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H_3O^+ \rightleftarrows 6\ Fe^{3+} + 2\ Cr^{3+} + 21\ H_2O \qquad \Delta G°_R$

$\Delta G°_R = \Delta G°_5 - 6 \cdot \Delta G°_6 \qquad \Delta G°_R = -6 \cdot F \cdot 0.56\ V \qquad \Delta G°_R \approx -324\ kJ/mol$

$\Delta G°_R = - R \cdot T \cdot \ln K \qquad \ln K = \frac{324000\ J/mol}{8.314\ J mol^{-1} K^{-1} \cdot 298\ K} \qquad \ln K \approx 130.8$

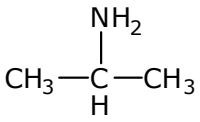
$K \approx 6.39 \cdot 10^{56}$

Solution to problem 3-08

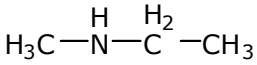
a) 0.172 g of H_2O correspond to $0.172 \cdot 2/18$ mol of H = $19.1 \cdot 10^{-3}$ mol of H,
that are $19.3 \cdot 10^{-3}$ g of H
0.279 g CO_2 correspond to 0.279/44 mol of C = $6.34 \cdot 10^{-3}$ mol of C,
that are $76.1 \cdot 10^{-3}$ g of C
$m(N) = (125 - 19.3 - 76.1) \cdot 10^{-3}$ g = $29.6 \cdot 10^{-3}$ g
$29.6 \cdot 10^{-3}$ g N correspond to $29.6 \cdot 10^{-3}/14$ mol of N = $2.11 \cdot 10^{-3}$ mol of N
n(C):n(H):n(N) = 6.34 : 19.1 : 2.11 = 3.00 : 9.05 : 1 ≈ 3 : 9 : 1

b) Molecular formula: $(C_3H_9N)_n$ with a molar mass of $n \cdot 59$ g/mol.
There should exist a fragment with m/z > 59 if n>1. Such a fragment is not existent
$\Rightarrow$ m/z = 59 and n = 1. Formula: C_3H_9N

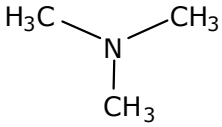
c) $H_3C - CH_2 - CH_2 - NH_2$ 1-Aminopropane



2-Aminopropane



Ethyl-methylamine



Trimethylamine

d) The isomer is trimethylamine since the ^{1}H-NMR spectrum shows only equivalent protons (three CH_3 groups), which are not coupling with one another (singlet) because there is a nitrogen atom between them.

e) Lowest boiling temperature: Trimethylamine (smallest surface. lowest van der Waals forces)

Highest boiling temperature: 1-Aminopropane (largest surface similar to ethyl-methylamineand thus highest intermolecular attraction and compared with ethyl-methylamine significant better possibility to form hydrogen bridges)

Note specifying the boiling temperatures:

Trimethylamine	2.87 °C
2-Aminopropane	32.4 °C
Ethylmethylamine	36.6 °C
1-Aminopropane	47.8 °C

Solution to problem 3-09

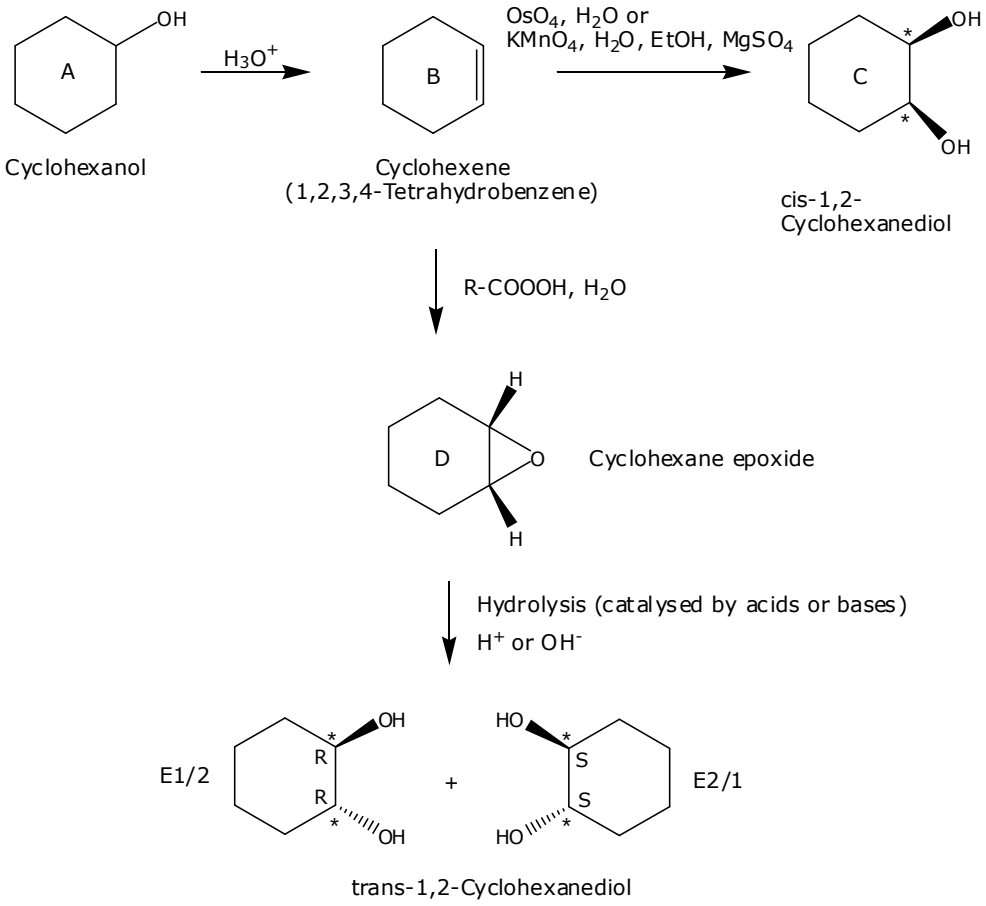
a)

Statements	yes	no
At rt* benzene is inert when combined with Br_2, H_2, acids and $KMnO_4$	x	
Planar cyclic systems with 4n (n = 0, 1, 2, …) electrons are called anti-aromatic		x
Non aromatic cyclic polyenes can form aromatic dianions and dications	x	
Aromatic carbon hydrates are referred to as arenes as well.	x	
Nucleophilic aromatic substitutions proceed in a three-step mechanism		x
Benzene undergoes at 25 °C substitution reactions rather than addition reactions	x	
Planar cyclic conjugated systems with 4n + 2 (n = 0, 1, 2, …) delocalized electrons are called aromatic	x	
Losing aromaticity means that the aromatic smell of a compound is lost by evaporating		x

b) A: - B: antiaromatic C: aromatic
D: - E: - F: aromatic
G: aromatic H: - I: aromatic
J: aromatic K: antiaromatic L: aromatic

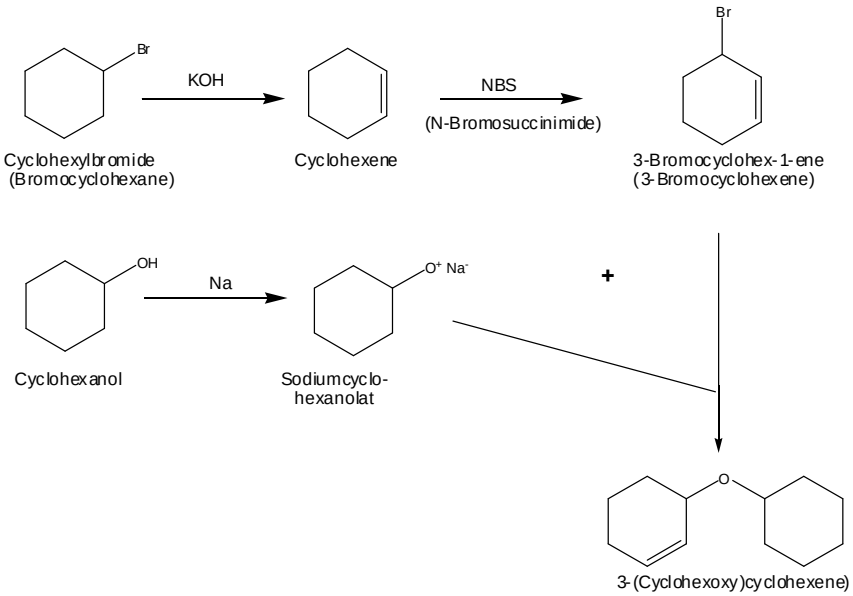
Solution to problem 3-10

a)



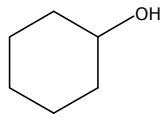
b) Racemate, the absolute configuration of the stereogenic centres of E1 and E2 is given in a).

c)



d) The height of the boiling point depends on the molar mass and on the polarity of a compound: "The higher the molar mass the higher the boiling point" and "The higher polarity the higher the boiling point".
Thus position 1 and 4 are fixed.
The positions of methylbenzoate and benzylalcohol are not clear. Benzylalcohol has a lower molar mass but it can form hydrogen bonds. You cannot predict which influence prevails.

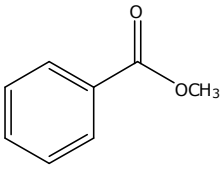
1



Cyclohexanol,
Bp.: 161 °C

100.16 g/mol

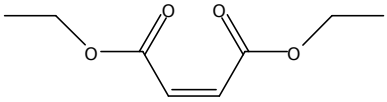
2/3



Methylbenzoate,
Bp.: 199 °C

136.15 g/mol

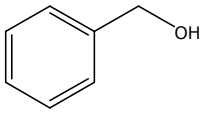
4



Malenic acid diethylester,
Bp.: 226 °C

172.18 g/mol

3/2



Benzylalcohol,
Bp.: 206 °C

108.14 g/mol

Answers of Round 3 Test 2

Solution to problem 3-11

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

Solution to problem 3-12

a) Aqua regia. Composition: 3 parts by volume of conc. hydrochloric acid and 1 part by volume of nitric acid.

b) Formation of aqua regia: $HNO_3 + 3\ HCl \longrightarrow 2\ H_2O + NOCl + 2\ Cl^-$
Dissolving of gold: $2\ Au + 6\ Cl^{\cdot} + 2\ Cl^- \longrightarrow 2\ [AuCl_4]^-$

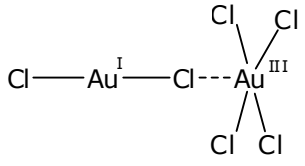
c) The reason for the favouritism is the formation of the stable complex ion $[AuCl_4]^-$. This process decreases $c_{Au^{3+}}$ and thus the redox potential of (Au/Au^{3+}).

d) Addition of potassium cyanide solution:
$2\ Au + H_2O + 0{,}5\ O_2 + 4\ KCN \longrightarrow 2\ K[Au(CN)_2] + 2\ KOH$

Addition of zinc powder:
$2\ K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2\ Au$

e) Gold(II) compounds exist as double compounds of gold(I) and gold(III), e.g. $CsAuCl_3 \equiv Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$

f)



$[AuCl_2^- \cdot AuCl_4^-]_x \equiv [AuCl_3^-]_{2x}$

Solution to problem 3-13

$n(HCl) = p \cdot V/(R \cdot T)$

$c(HCl) = n/V$ $c(HCl) = p \cdot/(R \cdot T)$

[1 Pa = 1 N/m^2 = 1 Nm/m^3 = 1 J/m^3]

$$c(HCl) = \frac{1.020 \cdot 10^5\ Pa}{8.314 J K^{-1}\ mol^{-1} \cdot 295 K} = \frac{1.020 \cdot 10^5\ J/m^3}{8.314 J\ mol^{-1} \cdot 295}$$

$c(HCl) = 41.6\ mol/m^3$ $c(HCl) = 0.0416\ mol/L$ pH = 1.4

b) $c_0(NH_3) = 0.0416\ mol/L$

	$NH_3 + H_2O \rightleftarrows$	$NH_4^+ +$	OH^-
Concentration in mol/L	0.0416-x	x	x

$$10^{-4.75} = \frac{x^2}{0.0416 - x}$$

$x^2 + x \cdot 10^{-4.75} - 10^{-4.75} \cdot 0.0416 = 0$

$x_1 = 8.51 \cdot 10^{-4}$ $(x_2 = -8.69 \cdot 10^{-4})$

$pOH = -\ lg\ 8.51 \cdot 10^{-4} = 3.07$ pH = 10.9

Solution to problem 3-14

a) $2\ Mg\ (s) + O_2\ (g) \longrightarrow 2\ MgO\ (s)$

$MgO\ (s) + H_2SO_4\ (aq) \longrightarrow MgSO_4\ (aq) + H_2O\ (l)$

$MgSO_4\ (aq) + 2\ NaOH\ (aq) \longrightarrow Mg(OH)_2\ (s) + Na_2SO_4\ (aq)$

$Mg(OH)_2\ (s) + 2\ HCl\ (aq) \longrightarrow MgCl_2\ (aq) + 2\ H_2O\ (l)$

$MgCl_2\ (aq) + Na_2CO_3\ (aq) \longrightarrow MgCO_3\ (s) + 2\ NaCl\ (aq)$

$MgCO_3\ (s) \xrightarrow{\Delta T} MgO\ (s) + CO_2\ (g).$

b) $pH = 1.2$ ™ $c(H_3O^+) = 0.063\ mol/L$

$n(H_3O^+) = 0.063\ mol \cdot L^{-1} \cdot 90000\ m^3$ $\quad n(H_3O^+) = 5.68 \cdot 10^6\ mol$

$n(CaCO_3) = ½ \cdot n(H_3O^+)$ $\quad n(CaCO_3) = 2.84 \cdot 10^6\ mol$

$m(CaCO_3) = n(CaCO_3) \cdot M(CaCO_3)$

$m(CaCO_3) = 2.84 \cdot 10^6 \cdot 100.09\ g$ $\quad m(CaCO_3) = 284\ t$

$n(CO_2) = n(CaCO_3)$

$$V(CO_2) = \frac{2.84 \cdot 10^6 \cdot 8.314 \cdot 298}{1.013 \cdot 10^5} \qquad V(CO_2) \approx 69{,}5 \cdot 10^3\ m^3$$

Solution to problem 3-15

a) The rate will
- i increase by the factor 4,
- ii increase by the factor 16,
- iii decrease by the factor ¼,
- iv increase by the factor 8,
- v not change.

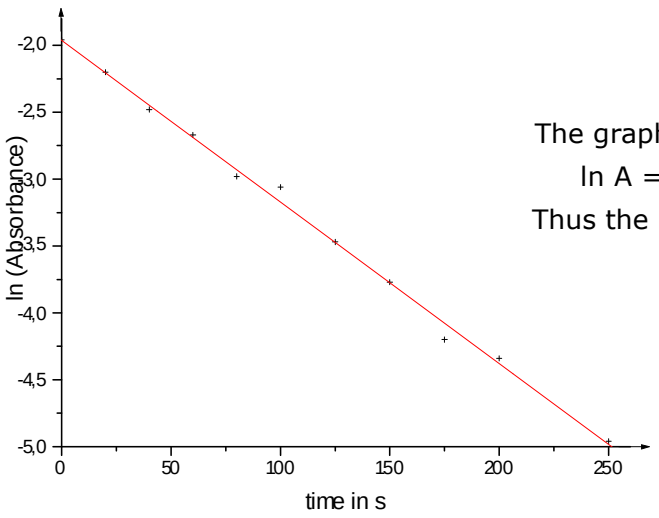
b) Halving all concentrations reduces the rate to 1/8 if the temperature is not changed. If the rate remains constant if the temperature is raised, k must be increased by the factor 8.

$k = A \cdot e^{-Ea/(R \cdot T)}$ $\quad \ln k = \ln A - E_a/(R \cdot T)$

$$E_a = -R \cdot \ln\frac{k_2}{k_1} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1} \qquad E_a = -R \cdot \ln 8 \cdot \left(\frac{1}{873} - \frac{1}{733}\right)^{-1} \qquad E_a \approx 79\ kJ/mol$$

c) ln c = f(t) is a straight line for a reaction of 1. order. Since the absorbance is proportional to the concentration you may plot ln A = f(t) and check whether it is a straight line.

t in s	0	20	40	60	80	100	125	150	175	200	250
A	0.141	0.111	0.084	0.069	0.051	0.047	0.031	0.023	0.015	0.013	0.007
ln A	- 1.96	- 2.20	-2.48	- 2.67	- 2.98	- 3.06	- 3.47	- 3.77	- 4.20	- 4.34	- 4.96



The graph shows a straight line
ln A = - 0.0121·t – 1.96.
Thus the rate law is of 1. order.

d) $A = \varepsilon \cdot c \cdot d$ t = 0 s, c = 0.0150 mol/L, A = 0.141, d = 1 cm

$\Rightarrow \varepsilon = \frac{0{,}141}{0{,}0150\,\text{mol/L} \cdot 1\,\text{cm}}$ ε = 9.40 L·mol^{-1}·cm^{-1}

e) $c_{20} = A_{20}/(\varepsilon \cdot d)$ c_{20} = 0.111/(9.40 L·mol^{-1}·cm^{-1}·1 cm) c_{20} =0.0118 mol/L

$c_{20} = c_0 \cdot e^{-k \cdot t}$ $\Rightarrow$ k = - ln(0.0118/0.0150) / 20 s k = 12.0·10^{-3} s^{-1}

Rate equaion: $c(t) = 0.0150\ \text{mol/L} \cdot e^{-12{,}0 \cdot 10^{-3}\ s^{-1} \cdot t}$.

$v = -dc/dt = -0.015\ \text{mol/L} \cdot (-12.0 \cdot 10^{-3}\ s^{-1}) \cdot e^{-12{,}0 \cdot 10^{-3}\ s^{-1} \cdot t}$

$v_{initial} = -dc/dt$ für t = 0 $v_{initial}$ = 0.015 mol/L·12.0·10^{-3} s^{-1}·e^0

$v_{initial}$ = 1.8·10^{-4} mol/(L·s)

Solution to problem 3-16

a) (1) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$2\ Ag^+ + 2\ OH^- \rightleftharpoons (2\ AgOH) \rightleftharpoons Ag_2O + H_2O$

(2) $Ag_2O + 4\ NH_3 + H_2O \rightleftharpoons 2\ [Ag(NH_3)_2]^+ + 2\ OH^-$

(3) $2\ [Ag(NH_3)_2]^+ + 2\ OH^- + RCHO \rightleftharpoons 2\ Ag + RCOOH + H_2O$

b) Silver nitride forms: $3\ [Ag(NH_3)_2]^+ \rightleftharpoons Ag_3N + 2\ NH_3 + 3\ NH_4^+$

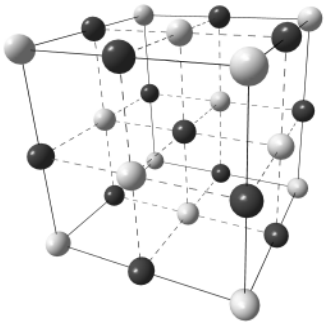
c) Not appropriate are copper sulfate and aluminium chloride. Copper sulfate would decrease the ammonia concentration and thus favour the forming of silver nitride. Aluminium chloride would form silver chloride which precipitates but is dissolved again an ammine complex.

Appropriate are copper shavings, glucose, ascorbic acid and potassium iodide. Iodide anions form silver iodide which is insoluble under these conditions, the other three chemicals reduce the silver ions.

d) The cyanide ions form bridges between the metal centres. They bind with carbon and with nitrogen to silver. A kind of chain structure is formed.

$$\text{—Ag–C}\equiv\text{N—Ag–C}\equiv\text{N—Ag–C}\equiv\text{N—}$$

e)



f) There are Z = 8 · $^1/_8$ + 6 · ½ = 4 silver and the same amount of fluoride ions in a unit cell with the edge length a.

ρ = 5.85 kg · m^{-3} and $\rho = \dfrac{Z \cdot M(Ag) + Z \cdot M(F))}{N_A \cdot a^3}$

$$a^3 = \frac{Z \cdot M(Ag) + Z \cdot M(F)}{N_A \cdot \rho} = \frac{4 \cdot 107.9\,g\,mol^{-1} + 4 \cdot 19.00\,g\,mol^{-1}}{6.022 \cdot 10^{23}\ mol^{-1} \cdot 5.851\,g\,cm^{-3}} = 1.441 \cdot 10^{-22}\ cm^3$$

$a = \sqrt[3]{1.441 \cdot 10^{-22}\ cm^3}$ a = 5.243·10^{-8} cm

a = 2 x radius of silver ions + 2 x radius fluoride ions

$\Rightarrow$ r = a/4 r = 131.1 pm

Solution to problem 3-17

a) $C_{12}H_{22}O_{11} + 48\ H_3O^+ + 48\ VO^{2+} \longrightarrow 12\ CO_2 + 83\ H_2O + 48\ V^{3+}$

or $C_{12}H_{22}O_{11} + 48\ H^+_{(aq)} + 48\ VO^{2+} \longrightarrow 12\ CO_2 + 35\ H_2O + 48\ V^{3+}$.

b) 1 mol of cane sugar provides 48 mol of electrons, 1 mol of O_2 consumes 4 mol of electrons

$\Rightarrow$ n(O_2) = 12·10 g/(342.3 g/mol) n(O_2) = 0.351 mol

V(O_2) = 0.351 mol · 8.314 J/(K·mol) · 288 K / (1.01·10^5 Pa) = 8.321 L O_2.

This corresponds to 8.311 L · 100/20.95 = 39.72 L of air**.**

c) Under these conditions all relevant species have the concentration of 1 mol/L thus you may use the standard potentials.

E°(cell) = E°$_2$ – E°$_1$ E°(cell) = + 0.66 V ($\Rightarrow$ ΔG°(cell) = - 63.7 kJ/mol)

Für die Zellreaktion $VO_2^+ + V^{3+} \rightleftarrows 2\ VO^{2+}$ ist

$E_1 = 0.34\ V + \dfrac{R \cdot T}{F} \cdot \ln \dfrac{c(VO^{2+})}{c(V^{3+})}$ and $E_2 = 1.00\ V + \dfrac{R \cdot T}{F} \cdot \ln \dfrac{c(VO_2^+)}{c(VO^{2+})}$

$E(cell) = E_2 - E_1 = E°(cell) + \dfrac{R \cdot T}{F} \cdot \ln \dfrac{c(VO_2^+) \cdot c(V^{3+})}{c^2(VO^{2+})}$ /·(-F) (1)

with $\Delta G = -1 \cdot F \cdot \Delta E$ $\quad \Delta G(cell) = \Delta G^{o}(cell) - R \cdot T \cdot \ln \frac{c(VO_2^+) \cdot c(V^{3+})}{c^2(VO^{2+})}$

with T = 288 K $\quad \Delta G(cell) = -63.7\ kJ/mol - 2.39\ kJ/mol \cdot \ln \frac{c(VO_2^+) \cdot c(V^{3+})}{c^2(VO^{2+})}$

d) $E(cell) = E°(cell) + \frac{R \cdot T}{F} \cdot \ln \frac{c(VO_2^+) \cdot c(V^{3+})}{c^2(VO^{2+})}$ (1)

Let be $c(VO_2^+) = c(V^{3+}) = x$ and $c(VO^{2+}) = 2.00\ mol/L - x$:

$E(cell) = E°(cell) + \frac{R \cdot T}{F} \cdot \ln \frac{x^2}{(2\,mol/L - x)^2}$

$\ln \frac{x^2}{(2\,mol/L-x)^2} = \frac{(E(cell) - E^{o}(cell)) \cdot F}{R \cdot T} = \frac{(0.32\ V - 0.66\ V) \cdot 96485\ Cmol^{-1}}{8.314 Jmol^{-1}K^{-1} \cdot 288\ K} = -13.7$

$\frac{x^2}{(2\,mol/L-x)^2} = 1.12 \cdot 10^{-6}$ $\qquad \frac{x}{(2\,mol/L-x)} = \sqrt{1.12 \cdot 10^{-6}} = 1.058 \cdot 10^{-3}$

$x = c(VO_2^+) = c(V^{3+}) = 2.11 \cdot 10^{-3} mol/L$

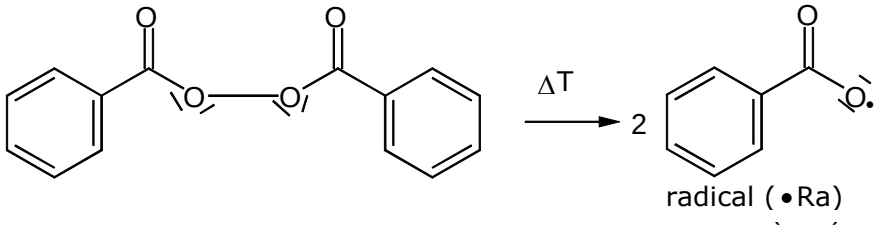
With E°(cell) = 0,65 V 8

$\ln \frac{x^2}{(2\,mol/L-x)^2} = -13.3$ $\qquad \frac{x^2}{(2mol/L-x)^2} = 1.67 \cdot 10^{-6}$ $\qquad \frac{x}{(2\,mol/L-x)} = 1.292 \cdot 10^{-3}$

$x = c(VO_2^+) = c(V^{3+}) = 2.58 \cdot 10^{-3}$ mol/L

Solution to problem 3-18

a) i) Initiation:



$\bullet Ra + H_2C{=}CHCH_3 \longrightarrow Ra{-}CH_2{-}CH(CH_3)\bullet$
propene

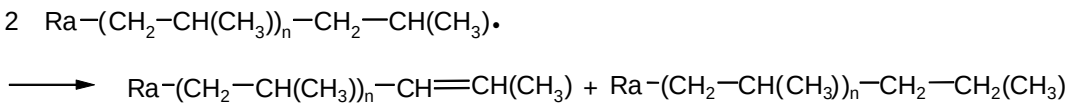
ii) Propagation:

$Ra{-}CH_2{-}CH(CH_3)\bullet + H_2C{=}CHCH_3 \longrightarrow Ra{-}CH_2{-}CH(CH_3){-}CH_2{-}CH(CH_3)\bullet$
propene

iii) Termination:

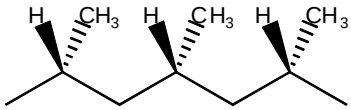
$2\ Ra{-}(CH_2{-}CH(CH_3))_n{-}CH_2{-}CH(CH_3)\bullet$

$\longrightarrow Ra{-}(CH_2{-}CH(CH_3))_n{-}CH_2{-}CH(CH_3){-}(CH_3)HC{-}CH_2{-}((CH_3)HC{-}CH_2)_n{-}Ra$

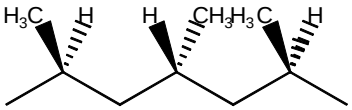


b)

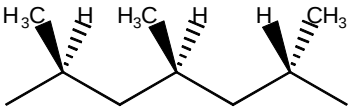
Methyl groups on the same side: isotactic



Methyl groups alternate regularly on opposite sides: syndiotactic



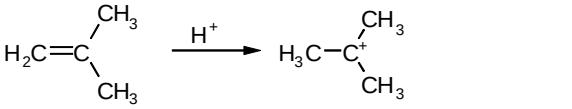
Methyl groups randomly orientated: atactic



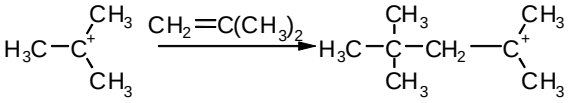
c) 1. The resultant polymers are linear with practically no chain branching
2. The reaction is stereochemically controllable. Isotactic, syndiotactic and atactic forms can be produced, depending on the catalyst system used.

d) No, the polymers are racemic.

e) Polymerisation of isobutene

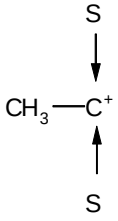


Initiation



Propagation

f) In the polymerisation process cations are formed. They are stabilised by electron rich substituents (S) such as CH_3 groups or a phenyl ring. On the other hand substituents such as halogens or a -$COOCH_3$ group remove electrons and thus prevent the stabilisation of the polymer cation.



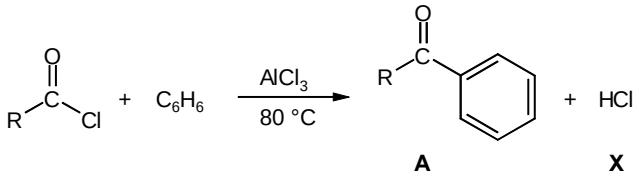
g)

$CH_2{=}CHC_6H_5$, $\boxed{CH_2{=}C(CH_3)_2}$, $CH_2{=}CHCH_3$, $CH_2{=}CHCl$, $CH_2{=}CHCO_2CH_3$

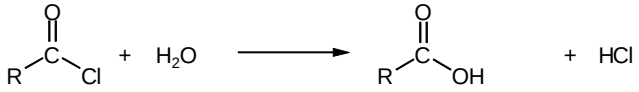
Isobutene

Solution to problem 3-19

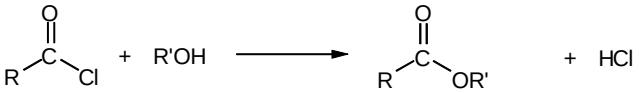
a)



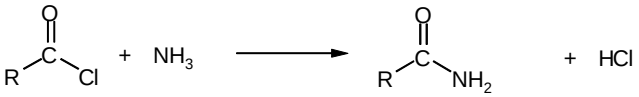
A **X**



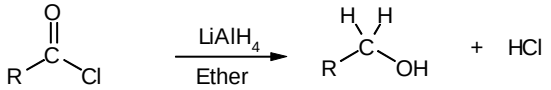
B **X**



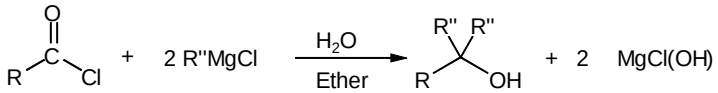
C **X**



D **X**

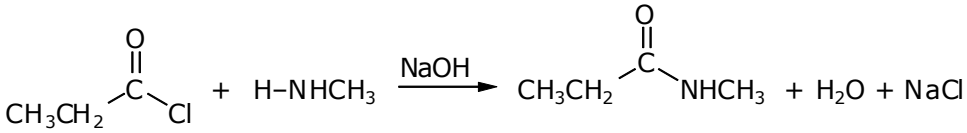


E **X**

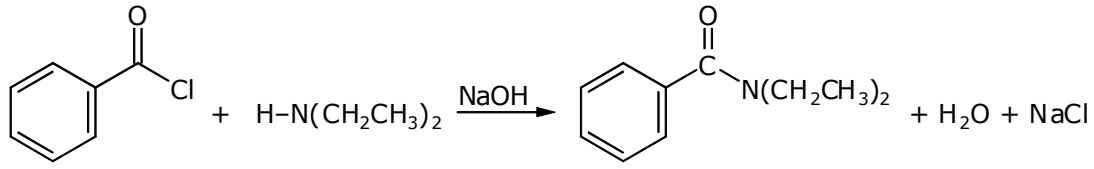


F **Y**

b)



Acid chloride (1) **Amine (1)** **U** **V**



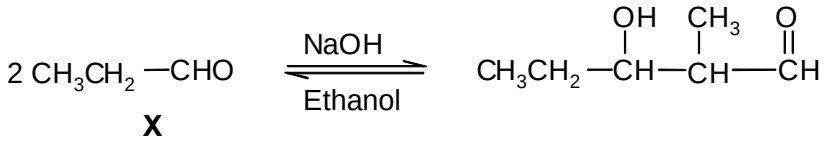
Acid chloride (2) **Amine (2)** **U** **V**

c) Amide 1: N-Methylpropanamide

Amide 2: N,N-Diethylbenzamide

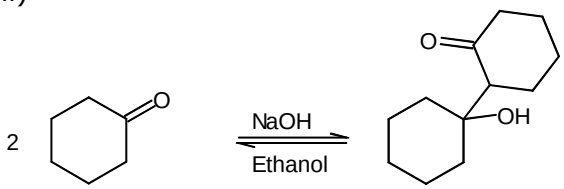
Solution to problem 3-20

a) i)



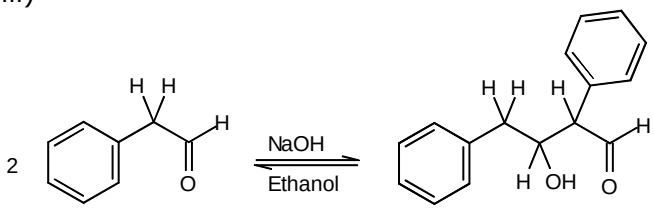
X

ii)



Cyclohexanone **Y**

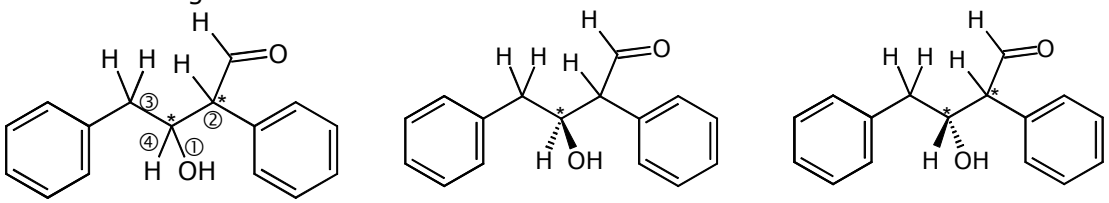
iii)



Z

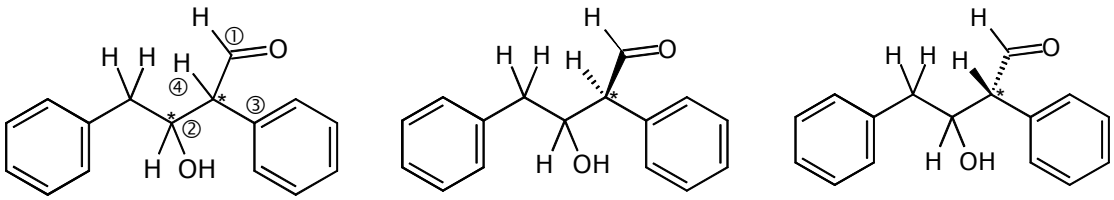
b) Enantiomere von Z

the left stereogenic centre



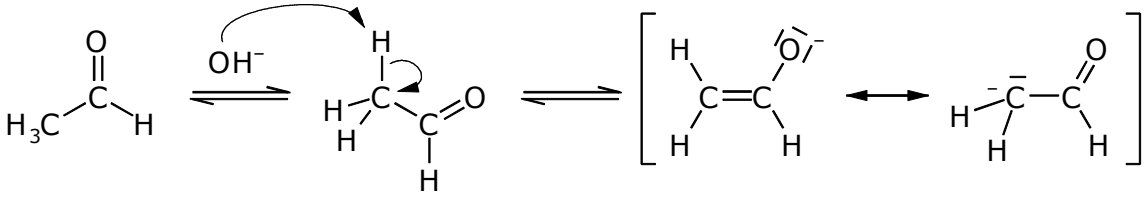
Priorities S-configuration R-Configuration

or the right stereogenic centre

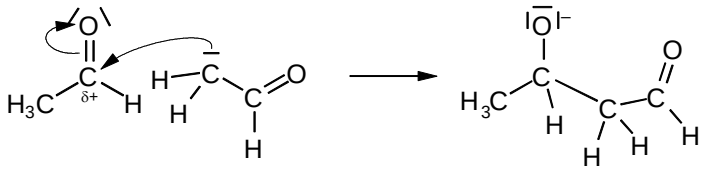


Priorities S-Configuration R-Configuration

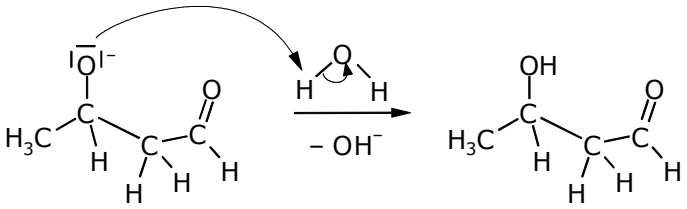
c) Step 1: Formation of the enolate ion



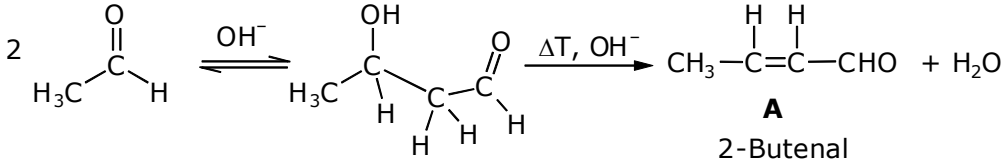
Step 2: Nucleophilic addition



Step 3: Formation of a neutral aldol

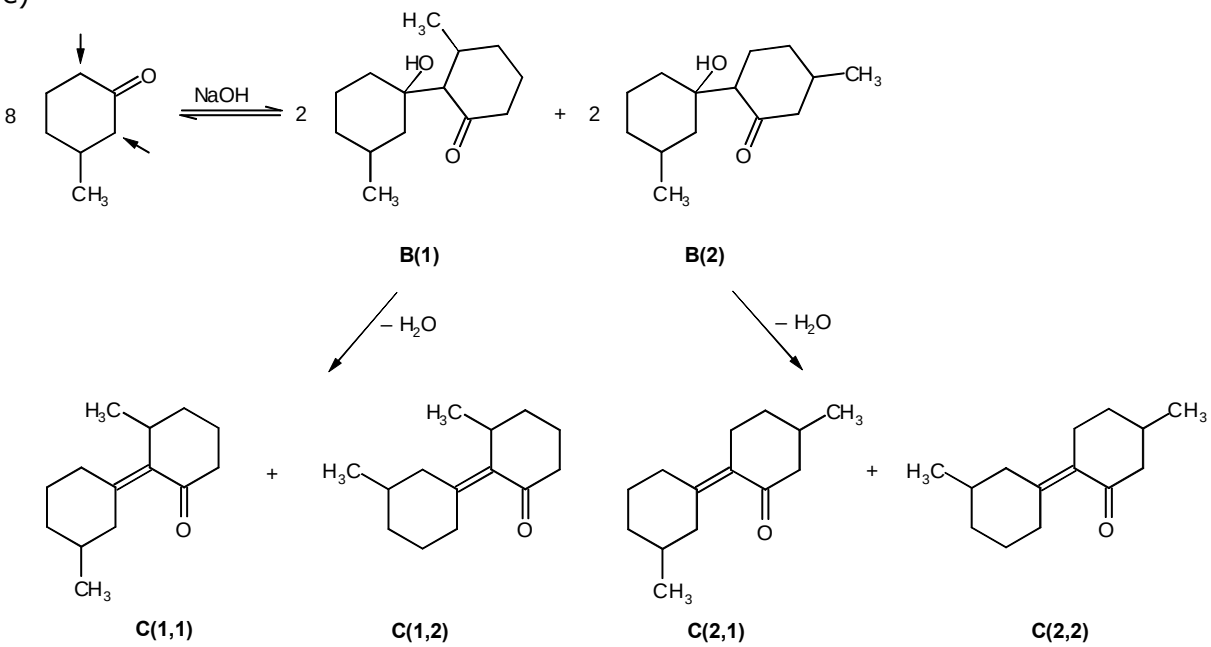


d)



2-Butenal is stable due to the conjugated double bond (α,β-unsaturated).

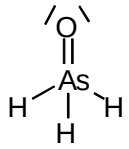
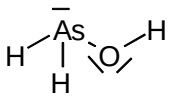
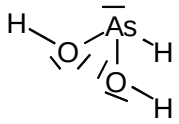
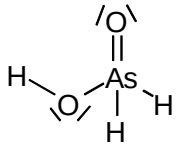
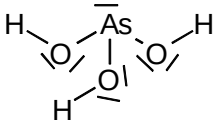
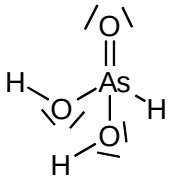
e)



Answers Round 4 (theoretical)

Solution to problem 4-01

a) + b) **NH_3** NH_2OH / H_3NO
$NH(OH)_2$ / H_3NO_2 / HNO / $H_2N_2O_2$
$N(OH)_3$ / H_3NO_3 / HNO_2

AsH_3	**Name**	**Structural formula**	**Molecular structure**
	H_3AsO		(distorted) tetrahedral
	AsH_2OH		trigonal pyramidal
	$AsH(OH)_2$		trigonal pyramidal
	H_3AsO_2		(distorted) tetrahedral
	$As(OH)_3$/ H_3AsO_3		trigonal pyramidal
	$AsH(OH)_2O$		(distorted) tetrahedral

c) possible compounds: ① H_3NO, ② H_3NO_2, ③ H_3NO_3

possible combinations:

① + ①	$H_6N_2O_2$	./.
① + ②	$H_6N_2O_3$	./.
① + ③	$H_6N_2O_4$	N_2O
② + ②	$H_6N_2O_4$	N_2O
② + ③	$H_6N_2O_5$	N_2O_2 (NO)
③ + ③	$H_6N_2O_6$	N_2O_3 (NO_2 / NO, N_2O_4 / N_2O_2)

Solution to problem 4-02

a) The solubility of AgBr lies in the range between that of AgCl and AgI:
$K_L(AgCl) > K_L(AgBr) > K_L(AgI)$.
In a solution with a precipitate of AgI: $c(Ag^+) \approx \sqrt{8 \cdot 10^{-17}}$ mol/L = $8.94 \cdot 10^{-9}$ mol/L

in the respective half cell: $E = E°(Ag^+/Ag) + R\cdot T\cdot F^{-1}\cdot \ln\sqrt{K_L(AgI)}$.

$E \approx 0.800\ V + 8.314\ J\cdot K^{-1}mol^{-1}\cdot 298.15\ K\cdot(96485\ C/mol)^{-1}\cdot \ln 8.94\cdot 10^{-9}$

$E \approx 0.324\ V$

$c(Ag^+)$ in a solution of AgBr> $c(Ag^+)$ in al solution of AgI

$\Rightarrow$ E(AgBr half cell) > E(AgI half cell) > E(reference electrode)

The electrode with the higher potential is the cathode, so in this case the silver electrode.

b) $\Delta E = E(cathode) - E(anode) \quad \Rightarrow \quad E(cathode) = \Delta E + E(anode)$

$E(AgBr\ half\ cell) = 0.199\ V + 0.241\ V = 0.440\ V$

$0.440\ V = 0.800\ V + R\cdot T\cdot F^{-1}\cdot \ln c(Ag^+)/c° \qquad (c° = 1\ mol/L)$

$c(Ag^+) = e^{-0.360\ V\cdot R^{-1}\cdot T^{-1}\cdot F}$ $\qquad c(Ag^+) = c(Br^-) = 8.21\cdot 10^{-7}\ mol/L$

$K_L(AgBr) = (8.21\cdot 10^{-7})^2 = 6.74\cdot 10^{-13}$

c) $AgBr(s) + e^- \longrightarrow Ag(s) + Br^-(aq) \qquad E°_1 = 0.071\ V \qquad (1)$

$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E°_2 = 0.800\ V \qquad (2)$

(1) – (2): $AgBr(s) \longrightarrow Ag^+(aq) + Br^-(aq) \qquad E° = E°_1 - E°_2 = -0.729\ V$

$\Delta G° = - n\cdot F\cdot E° \qquad \Delta G° = -96485\ C/mol \cdot (-0.729\ V) \qquad \Delta G° = 70.3\ kJ$

d) The half-cell potential of $AgI(s) + e^- \longrightarrow Ag(s) + I^-(aq)$ under standard conditions (i.e. $c(I^-) = 1\ mol/L$) is asked.

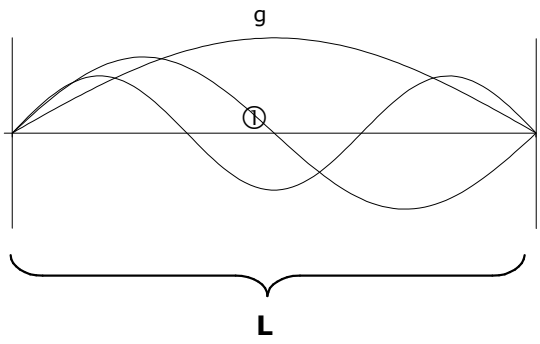
$E°(AgI/Ag) = E°(Ag^+/Ag) + R\cdot T\cdot F^{-1}\cdot \ln (c^*(Ag^+)/c°)$

$c(I^-) = 1\ mol/L \quad \Rightarrow \quad c^*(Ag^+) = K_L(AgI)$

$E°(AgI/Ag) = 0.800\ V + R\cdot T\cdot F^{-1}\cdot \ln 8.12\cdot 10^{-17} \qquad E°(AgI/Ag) = -0.152\ V$

Solution to problem 4-03

a)



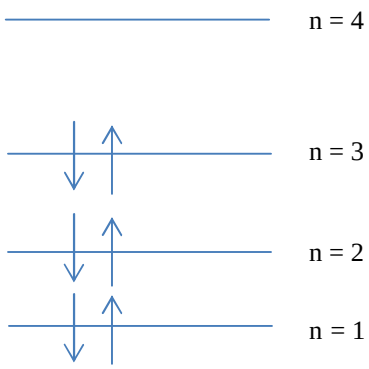
b) $L = n\cdot\frac{\lambda}{2}$ bzw. $\lambda = \frac{2L}{n}$ für n = 1, 2, 3, …

c) $E = ½\cdot m\cdot v^2$ und $m\cdot v = h/\lambda \quad v^2 = \frac{h^2}{m^2\cdot\lambda^2}$

$\Rightarrow \quad E = ½\,\frac{h^2}{m\lambda^2}$ mit $\lambda = \frac{2L}{n}$: $\quad E = \frac{h^2 n^2}{8mL^2}$ q.e.d.

d) $n = ½\cdot k$

e) k = 6



f) Transition with the lowest energy: n = 3 $\longrightarrow$ n = 4

$\Delta E = \frac{h^2}{8\,m\,L^2}\,(4^2 - 3^2) = \frac{7\,h^2}{8\,m\,L^2}$ and $\Delta E = \frac{h\,c}{\lambda}$

$\Rightarrow$ $L = \sqrt{\frac{7\,h\,\lambda}{8\,m\,c}}$ with λ = 231 nm: L =

$$\sqrt{\frac{7 \cdot 6.6261 \cdot 10^{-34}\,Js \cdot 231 \cdot 10^{-9}\,m}{8 \cdot 9.1094 \cdot 10^{-31}\,kg \cdot 2.9979 \cdot 10^{8}\,ms^{-1}}}$$

$L = 7.00 \cdot 10^{-10}$ m L = 7 Å = (1.34 + 2·1.35 + 2·1.48) Å ,

i.e. the sum of the bond lengths between the atoms C7 and C12.

g) The angles between C5-C6 and C13-C14 and the plane are 59° and 39°, respectively. Only if they were 90° you could completely neglect the effect of the double bonds between C5 and C6, C13 and C14 and C15 and O. The overlap still occurs (as the angle is ≠ 90°) and makes the box bigger. A larger L leads to a larger wavelength.

h) $\lambda = \frac{h\,c}{\Delta E}$ $\lambda = \frac{8\,m\,c}{h} \cdot \frac{L^2}{(0.5\,k+1)^2 - (0.5\,k)^2}$ $\lambda = 3.30 \cdot 10^{12}\,m^{-1} \cdot \frac{L^2}{k+1}$

Only C5 and C6 are forced into the plane:

L = (7.00 + 1.50 + 1.33) Å = 9.83 Å k = 8 λ = 354 nm

this is not sufficient as well as if only C13 and C14 are forced into the plane.

C5, C6, C13 und C14 are forced into the plane:

L = (9.83 + 1.48 + 1.35) Å = 12.66 Å k = 10 λ = 481 nm

$\Rightarrow$ not enough.

C5, C6, C13, C14, C15 and O are forced into the plane:

L = (12.66 + 1.48 + 1.20) Å = 15.34 k = 12 λ = 597 nm

Experimentally 602 nm are found.

In accordance with this model the atoms C5 through O are forced into the plane.

Solution to problem 4-04

a) $Ca_3(PO_4)_2 + 4\,H_3PO_4 \longrightarrow 3\,Ca(H_2PO_4)_2$ (1)

$Ca_3(PO_4)_2 + 2\,H_2SO_4 + 4\,H_2O \longrightarrow Ca(H_2PO_4)_2 + 2\,CaSO_4 \cdot 2\,H_2O$ (2)

(or $Ca_3(PO_4)_2 + 3\,H_2SO_4 + 6\,H_2O \longrightarrow 3\,CaSO_4 \cdot 2\,H_2O + 2\,H_3PO_4$ (2')

and H_3PO_4 reacts furthermore as in (1) or (5))

$CaF_2 + 2\ H_3PO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\ HF$ (3)

$CaF_2 + H_2SO_4 + 2\ H_2O \longrightarrow CaSO_4 \cdot 2H_2O + 2\ HF$ (4)

$CaCO_3 + 2\ H_3PO_4 \longrightarrow Ca(H_2PO_4)_2 + CO_2 + H_2O$ (5)

$CaCO_3 + H_2SO_4 + H_2O \longrightarrow CaSO_4 \cdot 2\ H_2O + CO_2$ (6)

Working under a hood: HF forms which is a poisonous gas.

Temperature ≤ 60 °C : At higher temperature anhydrite ($CaSO_4$) forms.

b) 1 g of apatite contains:

0.3913 g P_2O_5 ⇒ $5.51 \cdot 10^{-3}$ mol PO_4^{3-} resp. $2.76 \cdot 10^{-3}$ mol $Ca_3(PO_4)_2$

0.0179 g F ⇒ $9.42 \cdot 10^{-4}$ mol F^- resp. $4.71 \cdot 10^{-4}$ mol CaF_2

0.0118 g CO_2 ⇒ $2.68 \cdot 10^{-4}$ mol CO_3^{2-} resp. $2.68 \cdot 10^{-4}$ mol $CaCO_3$

Consumption of acid:

H_3PO_4:		H_2SO_4	
$11.03 \cdot 10^{-3}$ mol	from reaction (1)	$5.51 \cdot 10^{-3}$ mol	from reaction (2)
$9.42 \cdot 10^{-4}$ mol	from reaction (3)	$4.71 \cdot 10^{-4}$ mol	from reaction (4)
$5.36 \cdot 10^{-4}$ mol	from reaction (5)	$2.68 \cdot 10^{-4}$ mol	from reaction (6)
$12.51 \cdot 10^{-3}$ mol	for 1 g of apatite	$6.25 \cdot 10^{-3}$ mol	for 1 g of apatite

50.0 mL solution: $c_{H_3PO_4} = 0.500$ mol/L; $c_{H_2SO_4} = 0.100$ mol/L

n H_3PO_4 = $25.00 \cdot 10^{-3}$ mol ⇒ $m_{apatite} = 1.998$ g

n H_2SO_4 = $5.00 \cdot 10^{-3}$ mol ⇒ $m_{apatite} = 0.800$ g

$m_{apatite} = 2.798$ g ≈ 2.80 g react

c) 1) $Ca(H_2PO_4)_2$

2.80 g of apatite contain $2.80 \cdot 5.51 \cdot 10^{-3}$ mol = $15.43 \cdot 10^{-3}$ mol of PO_4^{3-}

from the added acid $25.00 \cdot 10^{-3}$ mol of PO_4^{3-}

in total $40.43 \cdot 10^{-3}$ mol of PO_4^{3-}

resp. $20.21 \cdot 10^{-3}$ mol of $Ca(H_2PO_4)_2$

resp. 4.730 g of $Ca(H_2PO_4)_2$

2) $CaSO_4 \cdot 2\ H_2O$

2.80 g apatite contain $2.80 \cdot \frac{0.0323}{80.07}$ mol = $1.13 \cdot 10^{-3}$ mol of SO_4^{2-}

from the added acid $5.00 \cdot 10^{-3}$ mol of SO_4^{2-}

in total $6.13 \cdot 10^{-3}$ mol of SO_4^{2-}

resp. $6.13 \cdot 10^{-3}$ mol of $CaSO_4 \cdot 2\ H_2O$

resp. 1.055 g of $CaSO_4 \cdot 2\ H_2O$

3) SiO_2

2.80 g of apatite contain $2.80 \cdot 0.0274$ g = 0.0767 g of SiO_2.

⇒ $m_1 = 4.730$ g + 1.055 g + 0.0767 g ≈ 5.862 g

The results may differ a little bit due to different rounding.

Solution to problem 4-05

a) 4 significant figures in the results, intermediate values may have more of them.

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

$\Delta H^0 = - 8.314 \cdot \ln (1.450 \cdot 10^{-25} / 26640) \cdot (298.15^{-1} - 1580^{-1})^{-1}$ J

$\Delta H^0 = 205.9$ kJmol^{-1}

$\Delta G^0 = - R \cdot T \cdot \ln K_p$ $\Rightarrow$ $\Delta G^0_{1580\ K} = - 8.314$ J/mol $\cdot 1580 \cdot \ln 26640$

$\Delta G^0_{1580\ K} = - 133.9$ kJ/mol

$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0$ $\Rightarrow$ $\Delta S^0 = (205.9 + 133.9)$ kJmol^{-1} / 1580 K

$\Delta S^0 = 215.1$ JK^{-1}mol^{-1}

$\Delta G^0_{1000\ K} = 205.9$ kJmol^{-1} – 1000 K · 215.1 JK^{-1}mol^{-1}

$\Delta G^0_{1000\ K} = - 9200$ kJmol^{-1}

$\ln K_{p.\ 1000\ K} = - 9200$ kJmol^{-1}/(- 8.314 Jmol^{-1}K^{-1}·1000 K) $\ln K_{p.\ 1000\ K} = 1.107$

$K_{p,\ 1000\ K} = 3.025$

c) At constant volume $p_1/T_1 = p_2/T_2$ $\Rightarrow$ $p_2 = T_2 \cdot p_1/T_1$

	CH_4	H_2O	H_2	CO
begin at 400 K	0.800 bar	0.800 bar	0 bar	0 bar
begin at1100 K	2.200 bar	2.200 bar	0 bar	0 bar
Equilibrium at 1100 K	(2.200-x) bar	(2.200-x) bar	3·x bar	x bar

$K_p = \frac{x \cdot (3x)^3}{(2.200-x)^2}$ $\Rightarrow$ $\frac{\sqrt{27} \cdot x^2}{(2.200-x)} = \sqrt{28.50/27}$

$x^2 + \sqrt{28.50/27} \cdot x - 2.200 \cdot \sqrt{28.50/27} = 0$ $x_1 = 1.075$ ($x_2 = - 2.102$)

total pressure in equilibrium = (4.400 + 2·x) bar **$p_{total,\ 1100\ K} = 6.550$ bar**

ratio of amounts = ratio of partial pressures $\Rightarrow$

conversion(methane) = x/2.200 · 100% **conversion(,ethane) ≈ 49 %**

d) The conversion will be higher. This is a reaction with a yield of substances. Coming from a higher pressure (6.550 bar) to a lower one (1.6 bar) the system shifts in order to oppose the change (Le Chatelier`s principle) which means in this case to shift to the side of the products.

e)

	CH_4	H_2O	H_2	CO	Σ
begin at 1100 K	1 mol	1 mol	0	0	2 mol
equilibrium at 1100 K	(1-a) mol	(1-a) mol	3·a mol	a mol	2·(1+a) mol

amount and volume are proportional at same pressure and temperature

$\Rightarrow$ 2·(1+a) = 2·1.750 a = 0.750

conversion(methane) = a/1 · 100% **Conversion(methane) = 75 %**

f) Conversion of CO to CO_2 with additional steam:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Under high pressure CO_2 can be washed out easily with water or it can be absorbed by methanol or by bases (such as K_2CO_3 or organic amines):

$$CO_2 + H_2O + K_2CO_3 \longrightarrow 2\ KHCO_3$$

Solution to problem 4-06

a) $AgCl + 2\ NH_3 \longrightarrow [Ag(NH_3)_2]^+ + Cl^-$

$AgCl + 2\ S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Cl^-$

$AgCl + 2\ CN^- \longrightarrow [Ag(CN)_2]^- + Cl^-$

b) $AgCl \rightleftharpoons Ag^+ + Cl^-$ $\quad K_L$

$Ag^+ + 2\ Lig^* \rightleftharpoons [Ag(Lig)_2]^+$ $\quad K_B$ $\quad$ *Lig = ligand

$AgCl + \underbrace{2\ Lig}_{0.100} \rightleftharpoons \underbrace{[Ag(Lig)_2]^+}_{x} + \underbrace{Cl^-}_{x}$ $\quad L = K_{sp} \cdot K_K$

$x = c_{(AgCl,\ dissolved)}$ $\qquad L = \dfrac{x^2}{0{,}100^2}$ $\qquad x = 0.100 \cdot \sqrt{K_{sp} \cdot K_k}$

ligand	x (mol/L)
NH_3	$4.73 \cdot 10^{-3}$
$S_2O_3^{2-}$	7.15
CN^-	$2.26 \cdot 10^4$

c) Thiosulfate is used. The complex with ammonia is too weak and cyanide is too poisonous.

d) Think of an experiment arranged the following way:

1. At first HCl is given to 20 mL of the solution of Ag^+ in such a quantity so that as a resujlt all Ag^+ is precipitated as AgCl.
2. Then the rest of HCl is added. A small part of AgCl will dissolve. You calculate the maximal amount of dissolved AgCl.
Is this amount smaller than the amount determined in 1. the residue stays or there will form a residue when both solutions are mixed, respectively.

As to 1.: 20 mL of a solution of Ag^+ contain 0.100 mol/L · 0.020 L = 0.002 mol Ag^+. 0.002 mol of AgCl are formed.
Originally there were 6.00 mol/L · 0.100 L = 0.600 mol Cl^-.
After forming AgCl 0.600 mol - 0.002 mol = 0.598 mol Cl^- remain.

As to 2.: Without any further reaction these 0.598 mol Cl^- cause a concentration of $c_0(Cl^-) = 0.598$ mol/0.120 L ≈ 5 mol/L in the solution of 120 mL after mixing.
A part of it reacts to form $[AgCl_2]^-$ $\quad \Rightarrow c(Cl^-) < 0.598/0.120$ mol/L < 5 mol/L

$K_{eq} = \dfrac{c([AgCl_2]^-)}{c(Cl^-)}$ $\quad \Rightarrow$ $\quad c([AgCl_2]^-) = K_{eq} \cdot c(Cl^-) < 1.00 \cdot 10^{-5} \cdot 5$ mol/L.

Then the amount of $[AgCl_2]^-$ in 120 mL is: $\quad n([AgCl_2]^-) < 5.0 \cdot 10^{-5}$ mol/L · 0.120 L

$n([AgCl_2]^-) < 6.0 \cdot 10^{-6}$ mol.

$\Rightarrow$ maximal $6.0 \cdot 10^{-6}$ mol of the existing 0.002 ($= 2000 \cdot 10^{-6}$) mol of AgCl dissolve, the preponderant amount of AgCl will precipitate when the solutions are mixed.

Solution to problem 4-07

a) $\frac{d[NO_2]/2}{dt} = ½ \cdot k_2 \cdot [N_2O_2] \cdot [O_2]$

$K_{equilibrium} = k_1/k_{-1} = \frac{[N_2O_2]}{[NO]^2} \quad \Rightarrow \quad [N_2O_2] = [NO]^2 \cdot k_1/k_{-1}$

$\Rightarrow \frac{d[NO_2]/2}{dt} = ½ \cdot k_2 \cdot k_1/k_{-1} \cdot \quad [NO]^2 \cdot [O_2]$

$\Rightarrow$ a = 2 b = 1 c = 0 $k = ½ \cdot k_2 \cdot k_1/k_{-1}$

b) At the start: $p(O_2) = p_0(O_2)$. $p(NO) = 2 \cdot p_0(O_2)$. $p(NO_2) = 0$

$\Rightarrow \quad p_{o,total} = 3 \cdot p_0(O_2)$

total pressure $p_{total} = \underbrace{2 \cdot p_0\,(O_2) - 2\Delta p}_{NO} + \underbrace{p_0(O_2) - \Delta p}_{O_2} + \underbrace{2\Delta p}_{NO_2}$

$p_{total} = 3 \cdot p_0\,(O_2) - \Delta p$

$p(O_2) = p_0\,(O_2) - \Delta p \quad \Rightarrow \quad p(O_2) = p_0\,(O_2) - (3 \cdot p_0\,(O_2) - p_{total})$

with $p_0(O_2) = 1/3 \cdot p_{o,total}$ $\quad p(O_2) = 1/3 \cdot p_{o,total} - (p_{o,total} - p_{total})$

$p(O_2) = p_{total} - 2/3 \cdot p_{o,total}$ q.e.d

c) $[NO] = 2 \cdot [O_2] \quad \Rightarrow \quad \frac{d[O_2]}{dt} = -k_3 \cdot (2 \cdot [O_2])^2 \cdot [O_2] = -k_3` \cdot [O_2]^3$

x = 3 $\quad k_3` = 4 \cdot k_3$

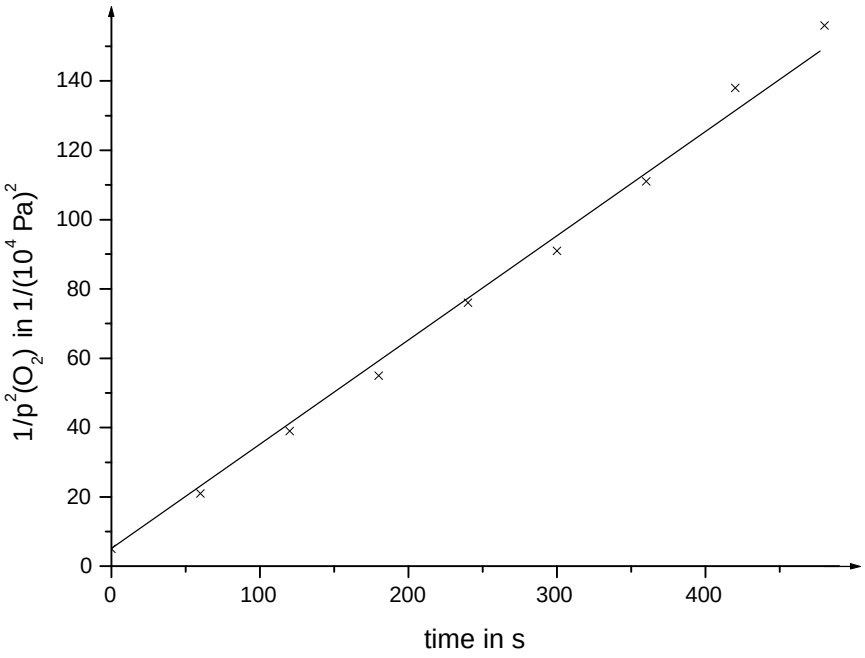
d) $\frac{d[O_2]}{dt} = -k_3` \cdot [O_2]^3 \qquad d[O_2] \cdot [O_2]^{-3} = -k_3` \cdot dt$

$\int_{[O_2]_0}^{[O_2]} [O_2]^{-3} \cdot d[O_2] = -\int_0^t k_3` \cdot dt$

$-½ \cdot ([O_2]^{-2} - [O_2]_0^{-2}) = -k_3` \cdot t \quad \Rightarrow \quad \frac{1}{[O_2]^2} = \frac{1}{[O_2]_0^2} + 2\,k_3` \cdot t$

e) Since $\frac{1}{[O_2]^2} = \frac{1}{[O_2]_0^2} + 2\,k_3` \cdot t$ a plot of $\frac{1}{[O_2]^2}$ as function of time should give a straight line with the slope $2\,k_3`$. As pressure and concentration differ only by a factor pressure p is used as a unit of concentration. As shown in b) the partial pressure of O_2 is given by $p(O_2) = p_{total} - 2/3 \cdot p_{o,total}$.

t / s	0	60	120	180	240	300	360	420	480
p_{total} / 10^4 Pa	1.350	1.120	1.060	1.035	1.015	1.005	0.995	0.985	0.980
$p(O_2)$ / 10^4 Pa	0.450	0.220	0.160	0.135	0.115	0.105	0.095	0.085	0.080
$1/p^2(O_2)$/ $1/(10^4\ Pa)^2$	4.94	20.66	39.06	54.87	75.61	90.70	110.80	138.41	156.25
rounded	5	21	39	55	76	91	111	138	156

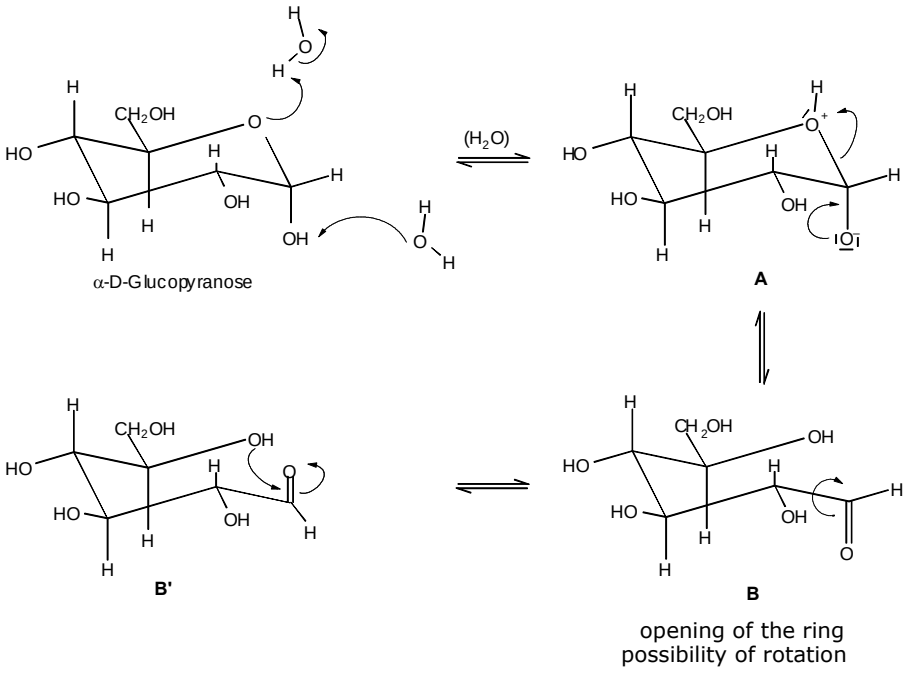


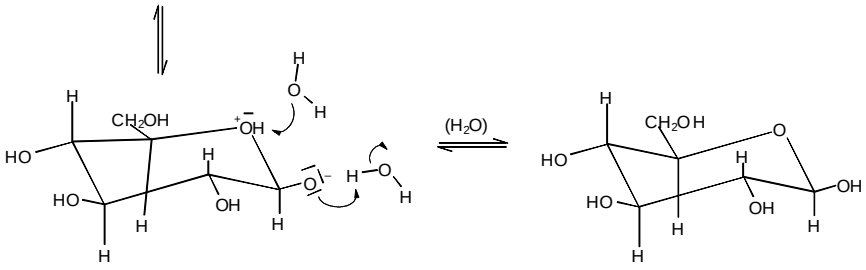
The plot shows approximately a straight line with a slope of ≈ 0.3

$\Rightarrow 2 \cdot k_3' \approx 0.3\ (s \cdot (10^4\ Pa)^2)^{-1}$ $\quad k_3' \approx 0.15 \cdot 10^{-8}\ s^{-1}\ Pa^{-2}$.

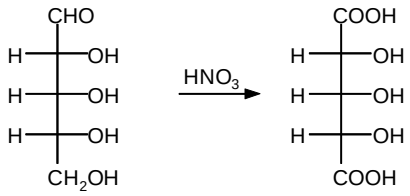
Solution to problem 4–08

a)





b)

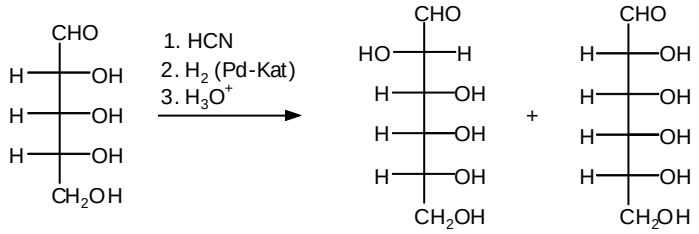


meso compound, optically inactive

M **N**

The aldopentose with the OH group at C3 on the left hand side matches the stipulated conditions, too.

c) The reaction leads to a chain extension

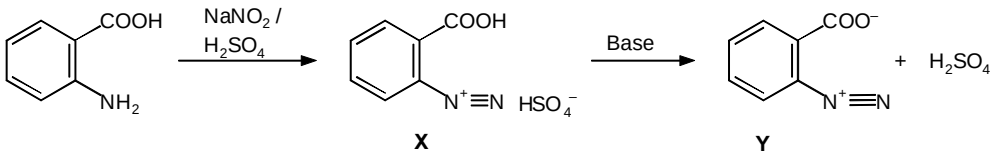


M **O** **P**

The oxidation with nitric acid leads to the respective D-carboxylic acids of O' and P'. O' is optically active and P’ optically inactive.

The second possibility leads to an analogous solution.

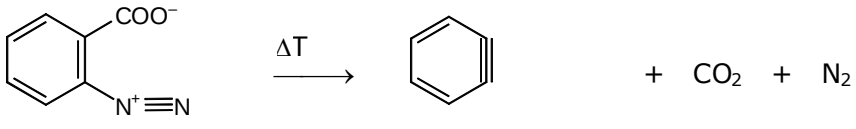
d)



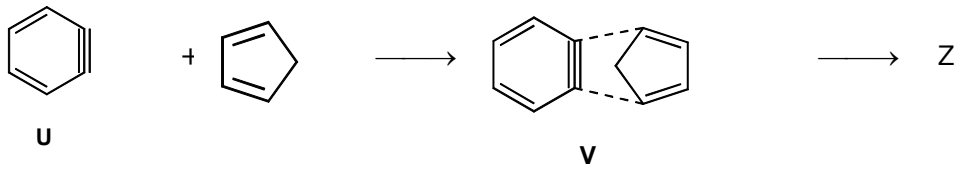
X **Y**

diazonium salt

e)



Y **U**

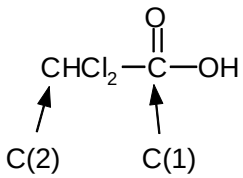


Diels-Alder reaction

Solution to 4-09

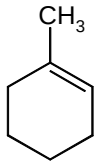
a) $\delta_2 \sim 65$ ppm $\rightarrow$ C(2)

$\delta_1 \sim 175$ ppm $\rightarrow$ C(1)

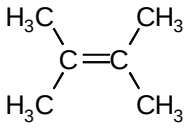


b) Spin-spin coupling in dichloroacetic acid $CHCl_2COOH$.
Instead of one signal δ_2 you will find two. The reason is the spin-spin coupling of ^{13}C with the proton of the $CHCl_2$ group. The two different spin states of the concerned hydrogen affect the local magnetic field experienced by the carbon atom (2). One spin state slightly increases the local magnetic field, the other slightly reduces it. This leads to two different signals.
The signal δ_1 does not change.

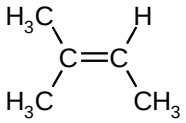
c) Product 1 is formed according to the 7 signals in the spectrum.
Product 1 has 7 C atoms with different chemical surroundings, product 2 only 5.



d) 1. 2,3-Dimethyl-2-buten
All CH_3 groups (i.e. all 12protons) are chemically equivalent $\Rightarrow$ 1 signal.

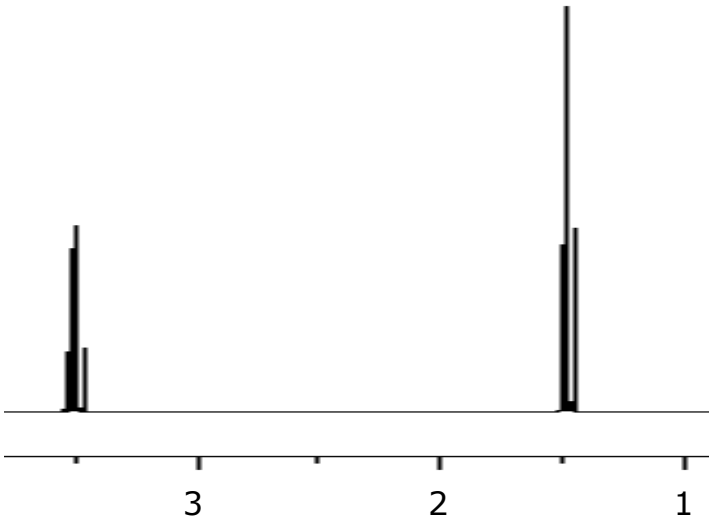


2. 2-Methyl-2-buten
The three CH_3 groups have different chemical surroundings. There are 4 signals in total, 3 signals of the protons of the 3 CH_3 groups and 1 signal of the proton of the $=CH(CH_3)$ group.



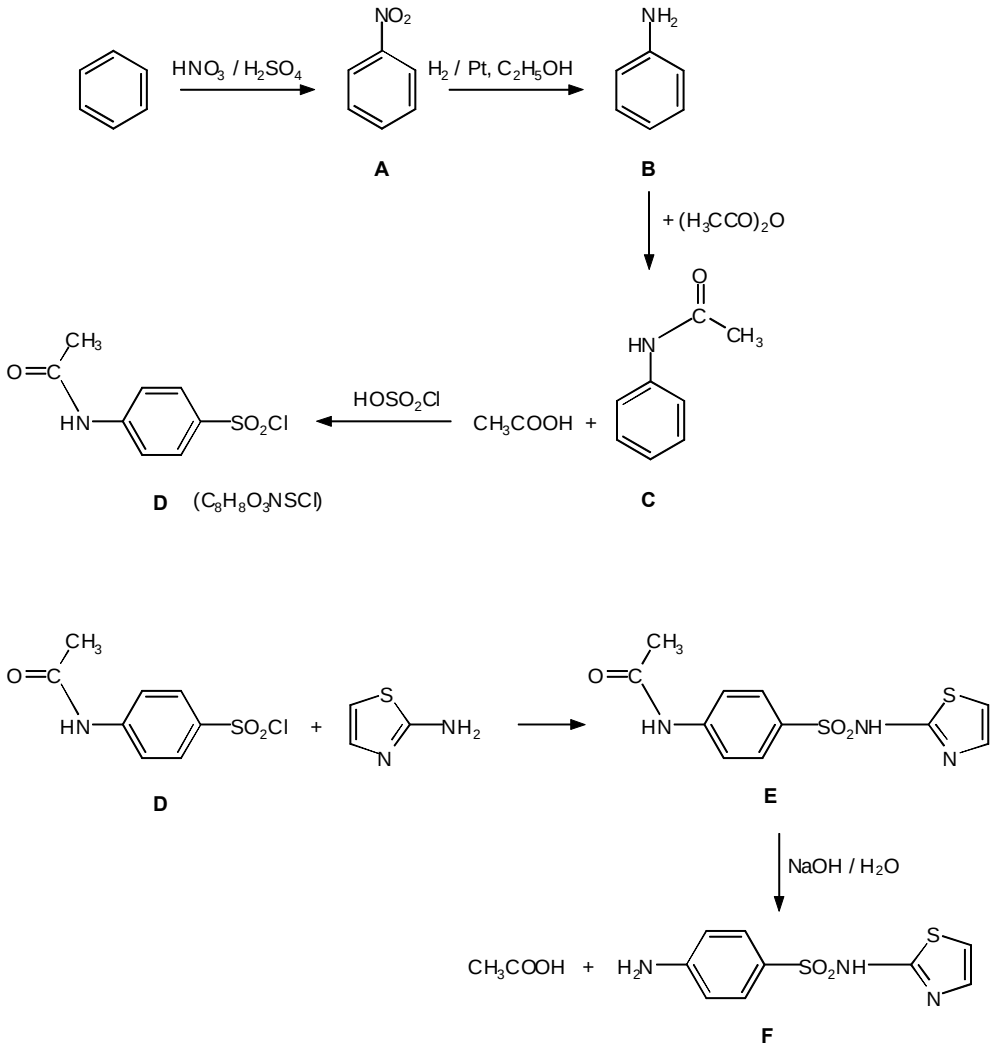
e) (1) $ClCH_2 - CH_2Cl$ All 4 protons are equivalent, no splitting by spin-spin coupling. Expected: 1 signal.

(2) CH_3CH_2Cl Spin-spin coupling of adjacent groups: The CH_3 groups splits into a triplet due to 2 adjacent protons. The CH_2 group splits into a quartet caused by 3 adjacent protons of the CH_3- group.
In total 7 signals in the ^1H NMR spectrum are expected.
<u>The spectrum is shown for information:</u>



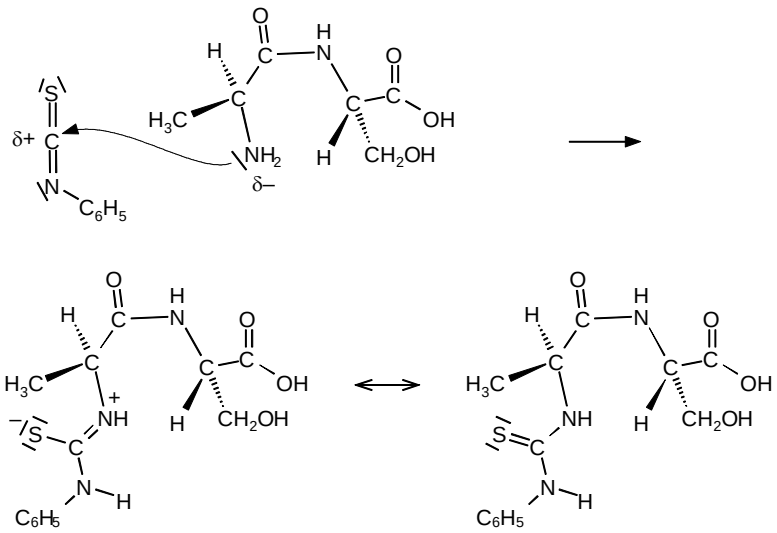
Hz	ppm	Int.
1062,42	3,541	159
1055,20	3,517	486
1047,96	3,493	496
1040,74	3,469	172
453,60	1,512	506
446,38	1,488	1000
439,14	1,464	482

Solution to problem 4–10



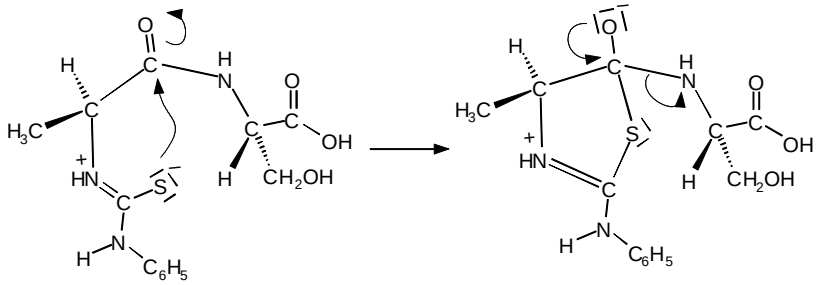
Step B → C is a reaction with the free NH_2 group and leads to a protection of this group in the following reactions. In step E → F the protecting group is removed.

b) 1. Step: Nucleophilic addition of the terminal NH_2 group of the peptide to PITC:

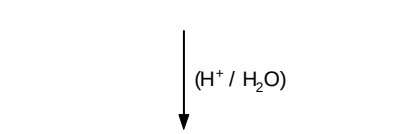


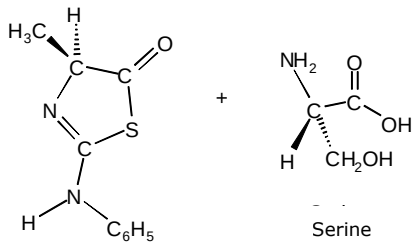
X

c) 2. Step: Formation of a ring and elimination of serine



X





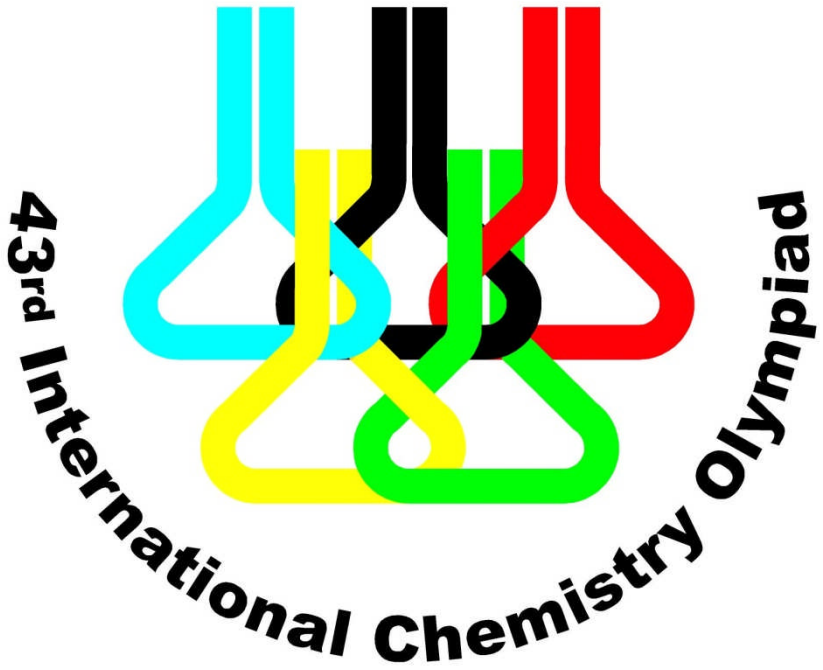
Ring **Y**

Serine

d) The reaction can be used to sequence a peptide by cleaving one amino acid at a time from the end of the peptide chain. The terminal amino acid is then separated and identified, and the cleavage reactions are repeated on chain-shortened peptide e.c.t. ("Edman degradation").

Part 3

2011 Ankara, TURKEY



Theoretical and Practical Problems

14. + 12. July 2011

Constants and Formulae

Avogadro constant:	$N_A = 6.0221\times10^{23}$ mol^{-1}	Ideal gas equation:	$PV = nRT$
Gas constant:	R =8.314 J·K^{-1}·mol^{-1} =0.08205 atm·L·K^{-1}·mol^{-1}	Energy of a photon:	$E = \frac{hc}{\lambda}$
Faraday constant:	F = 96485 C·mol^{-1}	Gibbs free energy:	$G = H - TS$
Planck constant:	$h = 6.6261\times10^{-34}$ J·s		$\Delta_r = - RT\cdot ln\ K = -nFE°_{cell}$ $\Delta H = \Delta E + \Delta nRT$
Speed of light:	$c = 3.000\times10^{8}$ m·s^{-1}	Faraday equation:	Q = it
Zero of Celsius scale:	273.15 K	Arrhenius equation:	$k = A e^{-E_a/RT}$
1 N = 1 kg m s^{-1}	1 eV = 1.602×10^{-19} J	K_w = = 1.0×10^{-14}	at 25 °C

1 atm = 760 torr = 1.01325×10^5 Pa

Integrated rate law for the zero order reaction: $[A] = [A]_o - kt$

Integrated rate law for the first order reaction: $\ln [A] = \ln [A]_o - kt$

Periodic Table of Elements with Relative Atomic Masses

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.941	4 Be 9.012											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 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	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 [98]	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 La 138.91	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 (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac (227)	104 Rf (261)	105 Ha (262)													

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	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
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (256)	102 No (254)	103 Lr (257)

Problem 1

Nitrogen oxides, common pollutants in the ambient air, are primarily nitric oxide, NO, and nitrogen dioxide, NO_2. Atmospheric nitric oxide is produced mainly during thunderstorms and in the internal combustion engines. At high temperatures NO reacts with H_2 to produce nitrous oxide, N_2O, a greenhouse gas.

$$2\ NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$$

To study the kinetics of this reaction at 820 °C, initial rates for the formation of N_2O were measured using various initial partial pressures of NO and H_2.

Exp.	Initial pressure, torr		Initial rate of production of N_2O, torr·s^{-1}
	P_{NO}	P_{H_2}	
1	120.0	60.0	8.66×10^{-2}
2	60.0	60.0	2.17×10^{-2}
3	60.0	180.0	6.62×10^{-2}

Throughout this problem do not use concentrations. Use units of pressure in torr and time in seconds.

a) Determine the experimental rate law and calculate the rate constant.

b) Calculate the initial rate of disappearance of NO, if 2.00×10^2 torr NO and 1.00×10^2 torr H_2 are mixed at 820 °C. (*If you do not have the value for the rate constant then use $2\times10^{\square 7}$ in appropriate unit*.)

c) Calculate the time elapsed to reduce the partial pressure of H_2 to the half of its initial value, if 8.00×10^2 torr NO and 1.0 torr of H_2 are mixed at 820 °C. (*If you do not have the value for the rate constant then use $2\times10^{\square 7}$ in appropriate unit*.)

d) A proposed mechanism for the reaction between NO and H_2 is given below:

$$2\ NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$

$$N_2O_2(g) + H_2(g) \xrightarrow{k_2} N_2O(g) + H_2O(g)$$

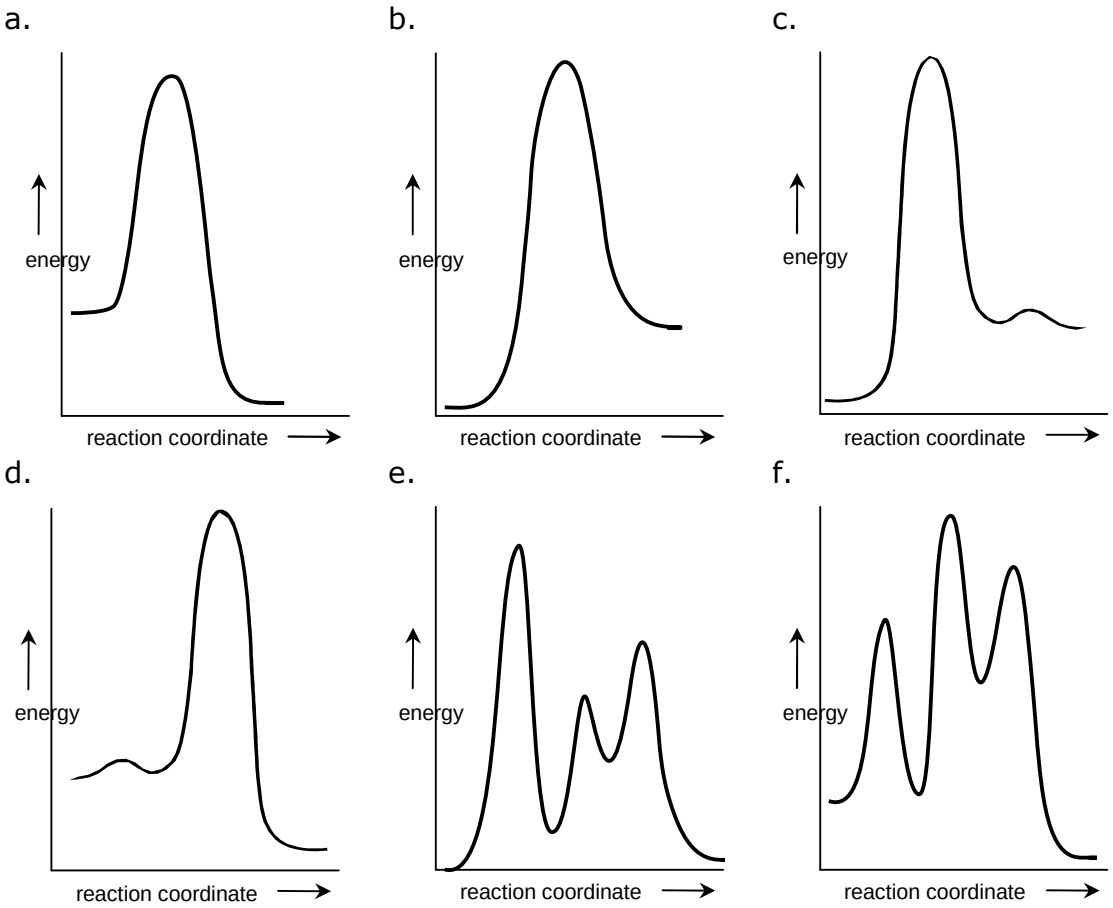
i. Derive the rate law for the formation of N_2O from the proposed mechanism using the steady-state approximation for the intermediate.

ii. Under what condition does this rate law reduce to the experimentally determined rate law found in Part a? If

$k_{-1} \ll k_2 \cdot p(H_2)$ $k_{-1} \gg k_2 \cdot p(H_2)$ $k_{-1} > k_2$ $k_1 > k_{-1}$

iii. Express the experimentally determined rate constant k in terms of k_1, k_{-1} and k_2.

e) Select the schematic energy diagram that is consistent with the proposed reaction mechanism and experimental rate law.



Problem 2

Anhydrous ammonia is an ultra-clean, energy-dense alternative liquid fuel. It produces no greenhouse gases on combustion.

In an experiment, gaseous NH_3 is burned with O_2 in a container of fixed volume according to the equation given below.

$$4\ NH_3(g)\ +\ 3\ O_2(g) \longrightarrow 2\ N_2(g)\ +\ 6\ H_2O(l)$$

The initial and final states are at 298 K. After combustion with 14.40 g of O_2, some of NH_3 remains unreacted.

a) Calculate the heat given out during the process.

Given: $\Delta_f H°(NH_3(g))$ = -46.11 kJ·mol^{-1} and $\Delta_f H°(H_2O(l))$ = -285.83 kJ·mol^{-1}

b) To determine the amount of NH_3 gas dissolved in water, produced during the combustion process, a 10.00 mL sample of the aqueous solution was withdrawn from the reaction vessel and added to 15.0 mL of 0.0100 M H_2SO_4 solution. The resulting solution was titrated with 0.0200 M standard NaOH solution and the equivalence point was reached at 10.64 mL.
($K_b(NH_3) = 1.8 \times 10^{-5}$; $K_a(HSO_4^-) = 1.1 \times 10^{-2}$)

i. Calculate pH of the solution in the container after combustion.

ii. At the end point of titration, NH_4^+ and SO_4^{2-} ions are present in the solution. Write the equations for the relevant equilibria to show how the presence of these two ions affect the pH and calculate their equilibrium constant(s).

iii. Circle the correct statement for the pH of solution at the equivalence point.

pH > 7.0 pH =7.0 pH <7.0

Problem 3

At 0 K, the total energy of a gaseous diatomic molecule AB is approximately given by $E = E_o + E_{vib}$ where E_o is the electronic energy of the ground state, and E_{vib} is the vibrational energy.
Allowed values of the vibrational energies are given by the expression:

$E_{vib} = (v + \frac{1}{2})\,\varepsilon$ v = 0, 1, 2,… $\varepsilon = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$ $\mu(AB) = \frac{m_A m_B}{m_A + m_B}$

where h is the Planck's constant, v is the vibrational quantum number, k is the force constant, and μ is the reduced mass of the molecule. At 0 K, it may be safely assumed that v is zero, and E_o and k are independent of isotopic substitution in the molecule.

a) Calculate the enthalpy change, ΔH, in kJ·mol^{-1} for the following reaction at 0 K.

$$H_2(g) + D_2(g) \rightarrow 2\ HD(g)$$

Deuterium, D, is an isotope of hydrogen atom with mass number 2. For the H_2 molecule, k is 575.11 $N \cdot m^{-1}$, and the isotopic molar masses of H and D are 1.0078 and 2.0141 $g \cdot mol^{-1}$, respectively. Given: ε_{H_2} = 1.1546 ε_{HD} and ε_{D_2}= 0.8167 ε_{HD} at 0 K.

b) Calculate the frequency in s^{-1} of infrared photons that can be absorbed by HD molecule. (*If you do not have the value for* ε_{HD} *then use* 8.000×10^{-20} *J for the calculation.)*

c) The allowed electronic energies of H atom are given by the expression

$E = -\frac{R_H}{n^2}, \quad n = 1, 2, \ldots$ where R_H = 13.5984 eV, 1 eV = 1.602×10^{-19} J

i. The total energy of H_2 molecule in its ground state is -31.675 eV, relative to the same reference as that of hydrogen atom. Calculate the dissociation energy in eV of a hydrogen molecule in its ground state such that both H atoms are produced in their ground states

ii. A H_2 molecule in the ground state dissociates into its atoms after absorbing a photon of wavelength 77.0 nm. Determine all possibilities for the electronic states of H atoms produced. In each case, what is the total kinetic energy in eV of the dissociated hydrogen atoms?

d) Calculate the electron affinity of H_2^+ ion in eV if its dissociation energy is 2.650 eV. (*If you do not have the value for the dissociation energy for* H_2 *then use 4.500 eV for the calculation.)*

Problem 4

For sustainable energy, hydrogen appears to be the best energy carrier. The most efficient way of using hydrogen is generation of electrical energy in a fuel cell. However, storing hydrogen in large quantities is a challenge in fuel cell applications. Among the chemical hydrides considered as solid hydrogen storage materials, sodium borohydride ($NaBH_4$), being nontoxic, stable and environmentally benign, appears to be the most promising one. The hydrolysis of sodium borohydride that releases H_2 gas is a slow reaction at ambient temperature and, therefore, needs to be catalyzed.

$$NaBH_4(aq) + 2\,H_2O(l) \xrightarrow{\text{catalyst}} Na^+(aq) + BO_2^-(aq) + 4\,H_2(g)$$

Colloidal ruthenium(0) nanoclusters are the most active catalysts in this hydrolysis even at room temperature and lead to a complete H_2 release from sodium

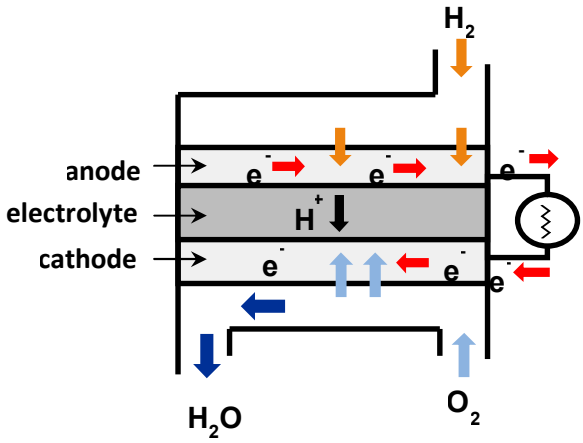
borohydride. Kinetic studies show that the catalytic hydrolysis of $NaBH_4$ is first order with respect to the catalyst, but zero order with respect to the substrate. The rate of hydrogen production per mole of ruthenium is
92 mol H_2·(mol Ru)$^{-1}$·min^{-1} at 25 °C.

a) Calculate the amount of ruthenium catalyst (in mg) which must be added to 0.100 L solution of 1.0 mol·L^{-1} $NaBH_4$ to supply the hydrogen gas at a rate of 0.100 L·min^{-1} at 25 °C and 1.0 atm, that is required for a portable fuel cell.

b) For how many minutes will this system supply hydrogen gas at this rate?

c) The Arrhenius activation energy for this catalytic hydrolysis of sodium borohydride is E_a = 42.0 kJ·mol^{-1}. Calculate the temperature required to achieve the same rate of hydrogen evolution by using half the amount of ruthenium catalyst used at 25.0 °C.

d) A fuel cell is made up of three segments sandwiched together: the anode, the electrolyte, and the cathode. Hydrogen is used as fuel and oxygen as oxidant. Two chemical reactions occur at the interfaces of the three different segments.



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

$H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$

The net result of the two reactions is
$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$
The hydrogen for the fuel cell is supplied from the hydrolysis of sodium borohydride.
Calculate the standard potential for the cathode half reaction if the standard reduction potential for the anode half reaction is □0.83 V and $\Delta_f G°$ ($H_2O(l)$) is -237 kJ·mol^{-1}.

e) Calculate the volume of air at 25 °C and 1.0 atm needed to generate a constant current of 2.5 A for 3.0 h in this fuel cell. Assume that air contains 20% by volume O_2(g).

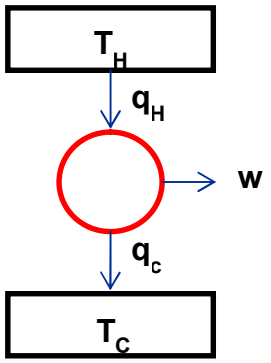
f) The efficiency of a fuel cell is given by the ratio of the work produced to the heat dissipated by the cell reaction. Thus, the maximum efficiency for a fuel cell is given by:

$\eta_{\text{fuel cell}} = \frac{\text{work}}{\text{heat}}$

Calculate the maximum efficiency for the fuel cell using the data given below at 25 °C and standard pressure.

	$H_2(g)$	$O_2(g)$	$H_2O(l)$
$S°$ ($J \cdot mol^{-1} \cdot K^{-1}$)	130.7	205.2	70.0

g) The second law of thermodynamics states that it is impossible to convert all of the heat, q_H, from a high-temperature reservoir at T_H into work. At least, some of the energy, q_C, must be transferred to a low-temperature reservoir at T_C. Thus, a heat engine with 100% efficiency is thermodynamically impossible. When the heat engine is working reversibly, as in a Carnot cycle, the efficiency will be maximum.



For a heat engine working reversibly between two reservoirs the following relations applies:

$$q_H = w + q_C$$

and

$$\frac{q_H}{T_H} = \frac{q_C}{T_C}$$

What should be the temperature of the hot reservoir, T_H, of a Carnot heat engine to maintain the efficiency of the fuel cell calculated in part (f), if the temperature of cold reservoir T_C is 40 °C? (*If you do not have the value for the efficiency then use 0.80*)

Aufgabe 5

Polynitrogen compounds have great potential for being used as high energy density materials. They are thermodynamically unstable. Huge amount of energy is released from their decomposition or reactions leading to more stable products. The only known polynitrogen species are N_2, N_3^- and N_5^+, isolated in 1772, 1890 and 1999, respectively, and the recently reported cyclic anion, N_5^-.

a) (i) Write the Lewis structure for N_5^+ with three energetically favorable resonance forms. Indicate the lone pairs and formal charges. Draw the molecular geometry of N_5^+.

(ii) Write the Lewis structures for cyclic N_5^- with five energetically favorable resonance forms. Indicate the lone pairs and formal charges. Draw the molecular geometry of cyclic N_5^-.

b) The synthesis of $[N_5^+][AsF_6^-]$, a white ionic solid, was achieved by reacting $[N_2F^+][AsF_6^-]$ with hydrazoic acid, HN_3, in liquid HF at -78 °C. Write the balanced chemical equation for this reaction.

The preparation of $[N_2F^+][AsF_6^-]$ requires the reaction of N_2F_2 with strong Lewis acid, AsF_5, as follows:

$$x\ C(\text{graphite}) + AsF_5 \longrightarrow C_x{\cdot}AsF_5 \quad (\text{graphite intercalate with } x = 10\text{-}12)$$

$$2\ C_x{\cdot}AsF_5 + N_2F_4 \longrightarrow 2\ [C_x^+][AsF_6^-] + \textit{trans}\text{-}N_2F_2$$

$$\textit{trans}\text{-}N_2F_2 + AsF_5 \longrightarrow [N_2F^+][AsF_6^-]$$

In the synthesis of N_2F_2, the *trans* isomer is formed, which is thermodynamically less stable than *cis*-N_2F_2. However, conversion of *trans*-N_2F_2 to *cis*-N_2F_2 requires surmounting a high energy barrier of 251 kJ/mol, so that equilibration between the *cis* and the *trans* isomers does not significantly take place without a suitable catalyst.

When *trans*-N_2F_2 is maintained in a closed container for 6 days at room temperature, in the presence of a small amount of SbF_5 as a catalyst, *cis-trans* thermal equilibrium is established.

$$\textit{trans}\text{-}N_2F_2 \underset{}{\overset{25\ ^\circ C}{\rightleftharpoons}} \textit{cis}\text{-}N_2F_2$$

The standard enthalpies of formation of *trans*- and *cis*-N_2F_2 are 67.31 and 62.03 kJ/mol, respectively, and their standard entropies at 25 °C are 262.10 and 266.50 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, respectively.

c) Find the ratio of the number of *cis*-N_2F_2 molecules over that of the *trans*-N_2F_2 molecules in an equilibrium mixture at 25 °C.

d) Write the Lewis structures showing the geometry of the N_2F^+ ion and of the *trans*- and *cis*-isomers of N_2F_2. Include all lone pairs and formal charges. Suggest an appropriate hybridization for each nitrogen atom in N_2F_2 and N_2F^+.

Solid $[N_5^+][AsF_6^-]$ is marginally stable at room temperature but reacts explosively with water to produce arsenic pentafluoride, hydrogen fluoride, molecular nitrogen and oxygen.

e) Write a balanced equation for the reaction between $[N_5^+][AsF_6^-]$ and water.

Conversion of $[N_5^+][SbF_6^-]$ into other N_5^+ salts can be achieved by a metathesis reaction:

$$[N_5^+][SbF_6^-] + [M^+][X^-] \longrightarrow [N_5^+][X^-] + [M^+][SbF_6^-]$$

$M^+ = Na^+, K^+, Cs^+$; X^- = large anion such as SnF_6^{2-} and $B(CF_3)_4^-$.

Since $[Cs^+][SbF_6^-]$ has a low solubility in anhydrous HF, and $[K^+][SbF_6^-]$ has a low solubility in SO_2, these two solvents were used extensively to carry out metathesis reactions at -78 °C and -64 °C, respectively.

f) Write the balanced equation for the preparation of $[N_5^+]_2[SnF_6^{2-}]$ and $[N_5^+][B(CF_3)_4^-]$ in solution starting with $[Cs^+]_2[SnF_6^{2-}]$ and $[K^+][B(CF_3)_4^-]$, respectively. Indicate the appropriate solvent.

When $[N_5^+]_2[SnF_6^{2-}]$ decomposes under carefully controlled conditions at 25-30 °C, $[N_5^+][SnF_5^-]$ and N_5F are formed. The $[N_5^+][SnF_5^-]$ salt is a white solid and has a thermal stability comparable to that of $[N_5^+][SbF_6^-]$ (50 – 60 °C). The solution ^{119}Sn NMR spectrum has shown that the SnF_5^- anion in this compound is, in fact, a mixture of dimeric and tetrameric polyanions. In both of these polyanions the coordination number of Sn atom is 6 and there are bridging fluorine atoms.

g) Draw the structures of dimeric and tetrameric polyanions.

Problem 6

Extraction of gold using sodium cyanide, a very poisonous chemical, causes environmental problems and gives rise to serious public concern about the use of this so called "cyanide process". Thiosulfate leaching of gold has been considered as an alternative. In this process, the main reagent is ammonium thiosulfate, $(NH_4)_2S_2O_3$, which is relatively nontoxic. Although this process appears to be environmentally benign, the chemistry involved is very complex and needs to be studied thoroughly. The solution used for leaching gold contains $S_2O_3^{2-}$, Cu^{2+}, NH_3, and dissolved O_2. The solution must have a pH greater than 8.5 to allow free ammonia to be present.
According to the proposed mechanism, a local voltaic micro-cell forms on the surface of gold particles during the leaching process and operates as follows:

Anode:

$Au(s) + 2\ NH_3(aq) \longrightarrow [Au(NH_3)_2]^+(aq) + e^-$
$[Au(NH_3)_2]^+(aq) + 2\ S_2O_3^{2-}(aq) \longrightarrow [Au(S_2O_3)_2]^{3-}(aq) + 2\ NH_3(aq)$

Cathode:

$[Cu(NH_3)_4]^{2+}(aq) + e^- \longrightarrow [Cu(NH_3)_2]^+(aq) + 2\ NH_3(aq)$
$[Cu(NH_3)_2]^+(aq) + 3\ S_2O_3^{2-}(aq) \longrightarrow [Cu(S_2O_3)_3]^{5-}(aq) + 2\ NH_3(aq)$

a) Write the overall cell reaction for this voltaic cell.

b) In the presence of ammonia, O_2 oxidizes $[Cu(S_2O_3)_3]^{5-}$ back to $[Cu(NH_3)_4]^{2+}$. Write a balanced equation for this oxidation-reduction reaction in basic solution.

c) In this leaching process, the $[Cu(NH_3)_4]^{2+}$ complex ion functions as catalyst and speeds up the dissolution of gold. Write the net overall oxidation-reduction reaction for dissolution of the gold metal, which is catalyzed by $[Cu(NH_3)_4]^{2+}$ complex ion.

d) Draw the coordination geometries of the metal in $[Au(NH_3)_2]^+$ and $[Au(S_2O_3)_2]^{3-}$ complex ions, indicating the coordinating atoms.

e) The formation constants, K_f, of $[Au(NH_3)_2]^+$ and $[Au(S_2O_3)_2]^{3-}$ complexes are 1.00×10^{26} and 1.00×10^{28}, respectively. Consider a leaching solution, in which the equilibrium concentrations of the species are as follows:

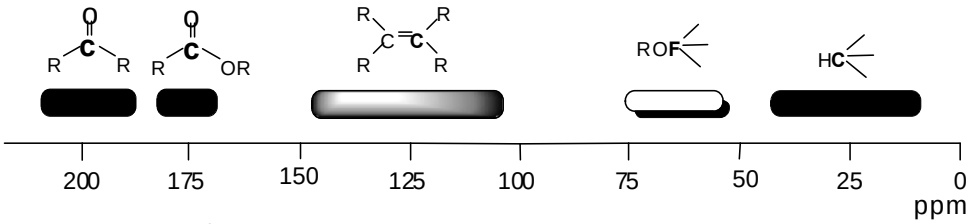
$[S_2O_3^{2-}] = 0.100$ M; $[NH_3] = 0.100$ M;
total concentration of gold(I) species = 5.50×10^{-5} M.

Calculate the percentage of gold(I) ion, which exists in the form of thiosulfate complex.

f) When the concentration of O_2 is not high enough and pH>10, $S_2O_3^{2-}$ reduces $[Cu(NH_3)_4]^{2+}$ to $[Cu(S_2O_3)_3]^{5-}$ with the formation of tetrathionate ion, $S_4O_6^{2-}$:
$2\ [Cu(NH_3)_4]^{2+}(aq) + 8\ S_2O_3^{2-}(aq) \longrightarrow 2\ [Cu(S_2O_3)_3]^{5-}(aq) + S_4O_6^{2-}(aq) + 8\ NH_3(aq)$
In basic solution tetrathionate disproportionates to trithionate, $S_3O_6^{2-}$, and thiosulfate. Write a balanced equation for this disproportionation reaction.

g) When the O_2 concentration is too high it oxidizes $S_2O_3^{2-}$ to yield trithionate and sulfate ions. Write a balanced equation for this reaction.

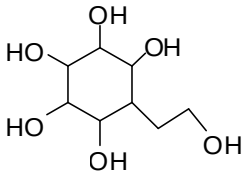
Problem 7 Synthesis of a carbasugar



^{13}C-NMR chemical shift ranges of typical functional groups

Carbohydratesare essential components of living cells and a source of energy for animals. They include simple sugars with small molecules as well as macromolecular substances.When the ring oxygen (endocyclic oxygen) in sugars is replaced by a methylene group, the compounds formed are called as ***pseudosugars*** or***carbasugars***. Since carbasugars are hydrolytically stable towards acidsand enzymes, several carbasugars have found application in the field of glycosidase inhibition.

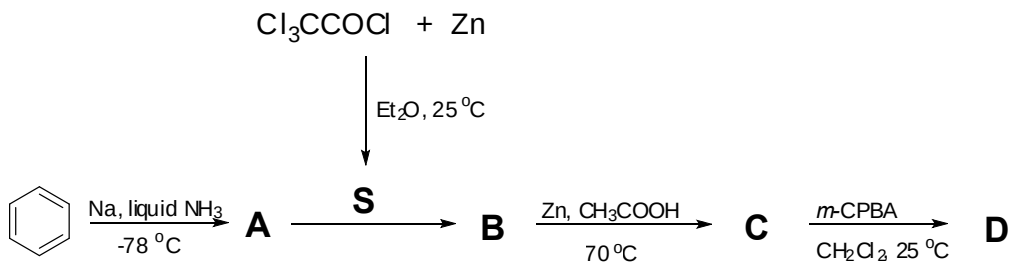
The total syntheses of two isomeric carbasugarshaving skeleton **1** are described below.



1

The total synthesis of **1** starts with a reduction of benzene by sodium in liquid ammonia to give **A**. The C-13 NMR spectrum of **A** consists of two signals at 124.0 and 26.0 ppm.

Trichloroacetyl chloride in the presence of Zn gives a reactive species **S**.One equivalent of **S** undergoes[2+2] cycloaddition with **A** to form a racemic product **B**. The reaction of **B** with Zn in acetic acid gives **C**. Compound **C** contains only carbon, hydrogen and oxygen: The C-13 NMR spectrum of **C** exhibits three sp^2 carbon signals at 210.0, 126.5 and 125.3 ppm.



The reaction of **C** with one equivalent *m*-chloroperbenzoic acid (*m*-CPBA) in methylene chloride gives **D** as a major product. The C-13 NMR spectrum of **D** exhibits also three signals in the sp^2 region at 177.0, 125.8, 124.0 ppm.

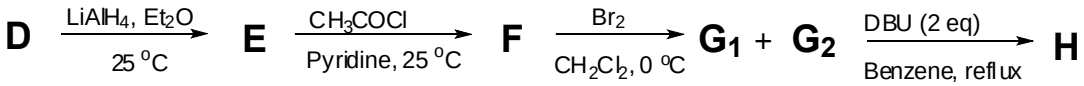
Draw the structures of **A**, **B**, **C**, **D**, and the intermediate **S**.

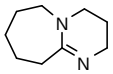
Reduction of **D** with $LiAlH_4$ yields **E**, which reacts with excess acetyl chloride in pyridine to give **F**. Draw the structures (use one enantiomer) of **E** and **F** using dashed-wedged line notation. Assign the configurations (*R* or *S*) at the asymmetric carbon atoms in **E**.

The compound **F** (use the drawn enantiomer) is reacted with bromine to give the stereoisomers $\mathbf{G_1}$and $\mathbf{G_2}$. Draw the structures of $\mathbf{G_1}$and $\mathbf{G_2}$ using dashed-wedged line notation.

A mixture of $\mathbf{G_1}$ and $\mathbf{G_2}$is reacted with two equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which is a strong amine base, to afford **H**.

Draw the structure of **H** using dashed-wedged line notation.



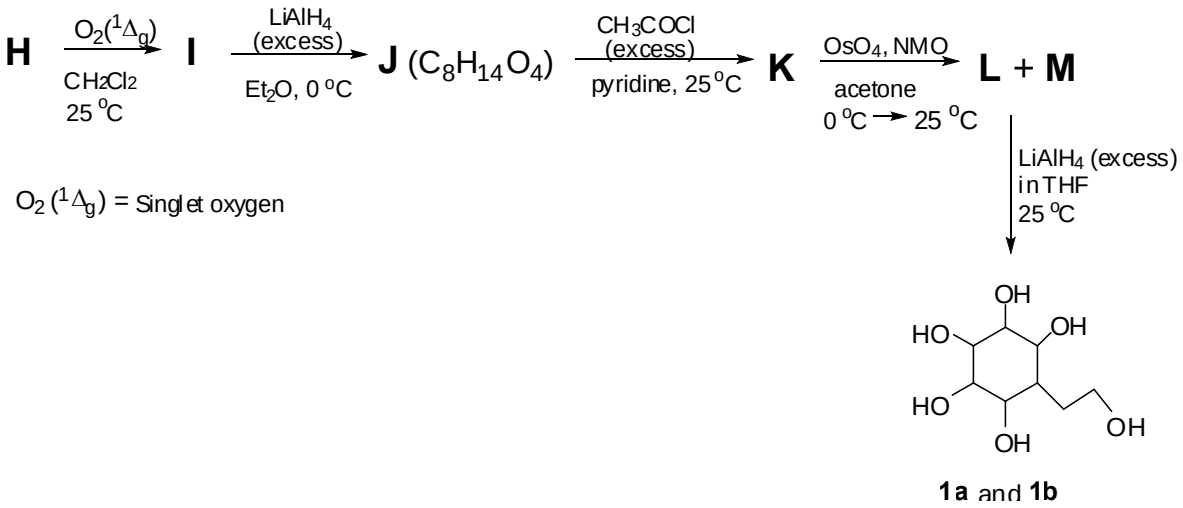
DBU = 

Reaction of **H** with singlet oxygen (in situ generated) affords **I**. Although two isomers are theoretically possible, **I** is formed as the single isomer due to steric hindrance and electronic repulsion.

The reaction of **I** with excess $LiAlH_4$ results in the formation of **J**. The C-13 NMR spectrum of **J** shows 8 signals, two in the sp^2region.

Reaction of **J** with excess acetyl chloride in the presence of pyridine yields **K**. Subsequent reaction of **K** with OsO_4 in the presence of 4-methylmorpholine 4-oxide (NMO) gives stereoisomers **L** and **M.**

Upon reduction with excess $LiAlH_4$, **L** and **M** give the stereoisomers **1a** and **1b**, respectively.



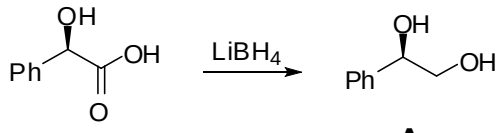
1a and **1b**

Draw the structures of **I, J, K, L, M, 1a**, and **1b** using dashed-wedged line notation.

Problem 8

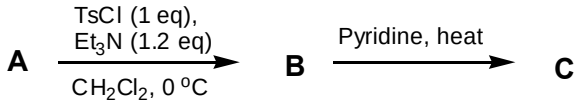
Click chemistry is a chemical concept introduced by K. B. Sharpless in 2001 and describes a setof chemical reactions that generate substances quickly, reliably and quantitatively by joining molecules through small units under mild conditions. This methodology has recently been applied as a key step in the following synthesis of bicyclic compounds.

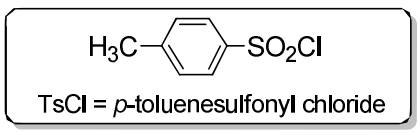
Mandelic acid is a versatile natural compound and widely used as a "chiral pool" in synthesis. The reduction of (*R*)-mandelic acid with $LiBH_4$ affords **A**.



(*R*)-Mandelic acid **A**

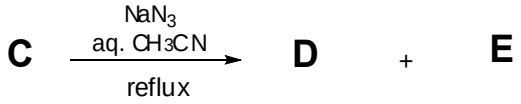
Reaction of **A** with 1 equivalent *p*-toluenesulfonyl chloride gives **B**. Heating **B** in pyridine yields **C**. During this transformation, compounds **B** and **C** retain their absolute configurations.

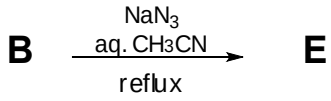




Draw the structures of **B** and **C** with the correct stereochemistry. Use dashed-wedged line notation throughout this problem.

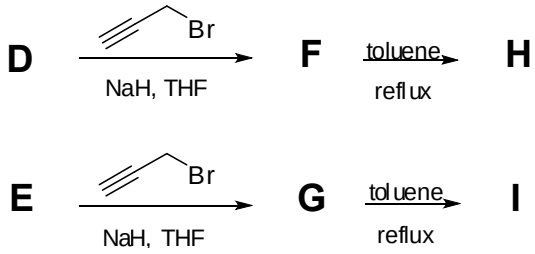
Reaction of **C** with sodium azide in aqueous acetonitrile gives a mixture of enantiopure regioisomers **D** and **E** in a ratio of 3:1. On the other hand, the compound **B** affords **E** as the sole product under the same condition.





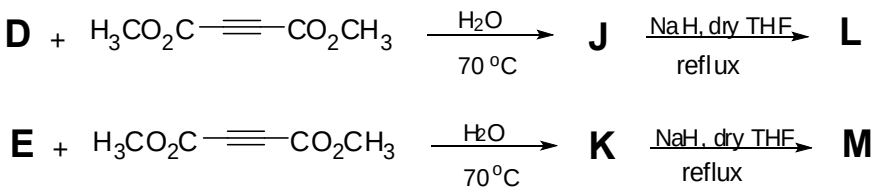
Draw the structures of **D** and **E** with the correct stereochemistry.

Part I: Compounds **D** and **E** are separately subjected to NaH mediated reaction with 3-bromoprop-1-yne to afford **F** and **G**, respectively. Heating **F** and **G** separatelyin toluene gives the bicyclic products **H** and **I**, respectively.



Draw the structure of compounds **F**,**G**,**H** and **I** with the correct stereochemistry.

Part II: Reaction of **D** and **E** separately with dimethyl acetylenedicarboxylate in water at 70°C forms the optically active monocyclic regioisomers **J** and **K**, respectively. Subsequent treatment of**J** and **K** with NaH gives final bicyclic products **L** and **M**, respectively, both having the formula $C_{13}H_{11}N_3O_4$.



Draw the structures of compound **J**,**K**,**L** and **M** with the correct stereochemistry.

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

Problem 1

Analysis of a mixture of chlorides

Composition of a solution containing only $MgCl_2$ and NaCl can be determined by an indirect titration method by performing a precipitation titration to determine the total amount of chloride present, followed by a complex formation titration to determine the amount of magnesium ions. A common precipitation titration technique used to determine the amount of chloride ions present in a solution is the Fajans method. In this argentometric procedure, silver nitrate is used as the titrant to precipitate the chloride ions present in the solution. The end point is detected through the use of an adsorption indicator, typically dichlorofluorescein, a weak organic acid. Prior to the end point, silver chloride particles are negatively charged because of the adsorption of excess chloride ions present in solution. The indicator anions are repelled by the negatively charged surface of the silver chloride particles imparting a yellow-green color to the solution. Beyond the equivalence point, however, silver chloride particles adsorb silver ions. Thus a positively charged layer is formed and it attracts the dichlorofluoresceinate ions displaying a pink-red color. Dextrin is used to stabilize the silver chloride particles against the coagulation.

On the other hand, the amount of magnesium ions present in a solution can be determined by complexometric titration with ethylenediaminetetraacetic acid, EDTA. As a hexadentate ligand, EDTA forms chelates with all metal ions, except alkali metal ions, in a 1:1 ratio regardless of the charge of the cation. Eriochrome Black T (EBT) is a common indicator used for EDTA titrations. When pH > 7.00 EBT imparts a blue color to the solution in the absence of metal ions and forms a red color when coordinated to metal ions.

In this experiment the chloride content of the solution containing $MgCl_2$ and NaCl will be determined by Fajans method. Magnesium ion concentration will be determined by EDTA titration.

A 100 mL solution prepared by dissolving $MgCl_2$ and NaCl in water is given as the unknown sample. The objective is to determine the concentration of $MgCl_2$ and NaCl in g/100 mL.

A. Determination of total chloride by Fajans Method

1. Using a 10-mL pipette, transfer 10.0 mL aliquot from the bottle labeled as **unknown solution** into a 250-mL Erlenmeyer flask. Complete the volume to approximately 100 mL by adding distilled water.
2. Take one of the Eppendorf tubes given in the zipper bag labeled as **dextrin** and transfer all its content into the Erlenmeyer flask.
3. Add 5 drops of dichlorofluorescein indicator solution.
4. Record the exact concentration of $AgNO_3$ in standard solution.
5. Fill one of the burettes with the standard $AgNO_3$ solution.
6. Titrate the unknown solution until the whole solution has pink-red color.
7. Record the volume of $AgNO_3$ used, in mL.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the **Aqueous Waste** container and rinse it twice with distilled water.

B. Determination of Mg^{2+} by direct titration with EDTA

1. Fill the second burette with the standard EDTA solution.
2. Record the exact concentration of EDTA in standard solution.
3. Using a 25-mL pipette, transfer a 25.0 mL aliquot of unknown solution into a 250-mL Erlenmeyer flask. Complete the volume to approximately 100 mL by adding distilled water.
4. Using a 1-mL pipette, add 1.0 mL of pH 10 buffer.
5. Add 3-4 drops of EBT indicator solution.
6. Titrate the unknown solution with standard EDTA solution until the color changes from red to blue.
7. Record the volume of EDTA solution used, in mL.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the **Aqueous Waste** container and rinse it twice with water.

Treatment of Data

1. Determine the amount of Cl^- ion in millimoles in 100 mL unknown solution.
2. Determine the amount of Mg^{2+} ion in millimoles100 mL unknown solution.
3. Calculate the concentration of $MgCl_2$ and NaCl in the unknown solution, in g/100 mL.

Problem 2

Preparation of hydrogen from ammonia borane

Hydrogen has been considered as a clean and environmentally benign new energy carrier in the way towards a sustainable energy future. An effective and safe storage of hydrogen is one of the key issues of the hydrogen economy. Among the chemical hydrides, considered as potent solid hydrogen storage materials, ammonia-borane ($H_3N{\cdot}BH_3$) has been attracting a great deal of attention due to its high hydrogen content and stability under fuel cell operating conditions. It can release hydrogen upon hydrolysis:

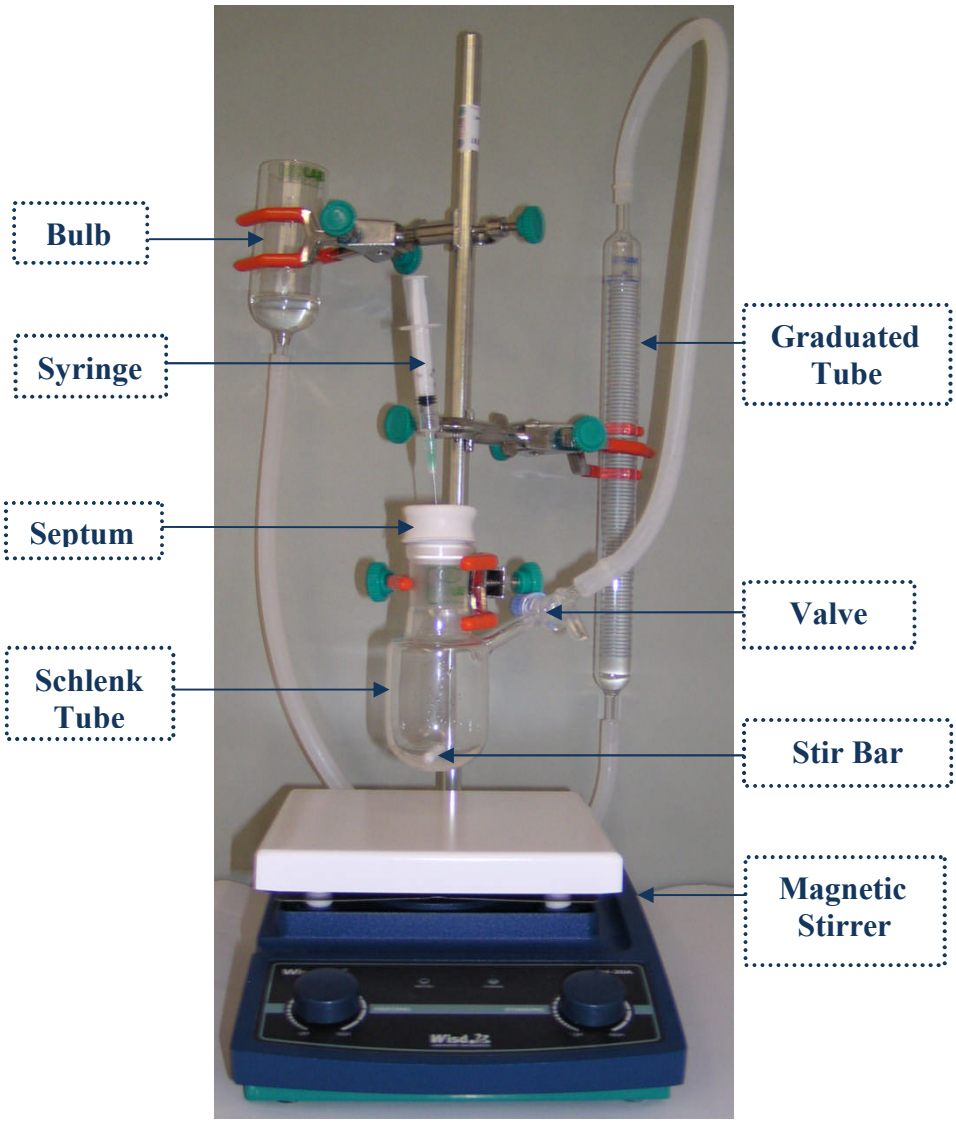
$$H_3N{\cdot}BH_3(aq) + 2\ H_2O(l) \longrightarrow NH_4BO_2(aq) + 3\ H_2(g) \qquad (1)$$

Aqueous solution of ammonia borane is stable and its hydrolysis occurs only in the presence of a suitable catalyst. Recent studies have shown that palladium(0) nanoclusters stabilized by water soluble polymers are highly active catalyst in the hydrolysis of ammonia borane. Palladium(0) nanoclusters are generated in situ by the reduction of potassium tetrachloropalladate(II) with ammonia borane in the presence of poly(4-styrenesulfonic acid-co-maleic acid).

In this experiment, the catalytic hydrolysis of ammonia borane will be carried out starting with potassium tetrachloropalladate(II) in a solution containing poly(4-styrenesulfonic acid-co-maleic acid). Potassium tetrachloropalladate(II) will be used as precatalyst, which will be reduced by ammonia borane and palladium(0) nanoclusters will be formed and stabilized by poly(4-styrenesulfonic acid-co-maleic acid). These nanoclusters will catalyze the hydrolysis of ammonia borane.

I. Preparation of the Experimental Set-up

1. Check that the experimental setup, shown below, is held on a support, the graduated tube is connected to the Schlenk tube by Tygon tubing, and a stir bar is in the Schlenk tube.
2. Make sure that the septum is off and the valve is open.
3. By changing the bulb height adjust the water level in the graduated tube to zero.
4. Close the valve on the Schlenk tube.



Experimental Set-up

II. Hydrolysis of ammonia borane

A. In the absence of catalyst

1. Transfer all of the ammonia-borane solution (**Solution-A**) from the glass vial to the Schlenk tube through the funnel,
2. Add the polymer solution (**Solution-B**) from the glass vial to the Schlenk tube through the funnel.
3. Close the Schlenk tube with the septum, turn the stirring on at 600 rpm (as marked on the stirrer), and open the valve connecting to the graduated tube. Record the water level as $\mathbf{V_o}$ at time zero. Start the timer.

4. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

B. In the presence of catalyst

1. While stirring, transfer all of the potassium tetrachloropalladate(II) solution (**Solution-C**) from the glass vial to the Schlenk tube by injecting through the septum using a 2.0 mL syringe. Keep the syringe inserted in the septum throughout the experiment. Start the timer.
2. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

Treatment of Data

A. Reaction of ammonia-borane without catalyst

1. Plot the volume of gas recorded versus time in Graph 1.
2. Report the volume of gas evolved as $V_{\text{uncatalyzed}}$.

B. Reaction of ammonia-borane with catalyst

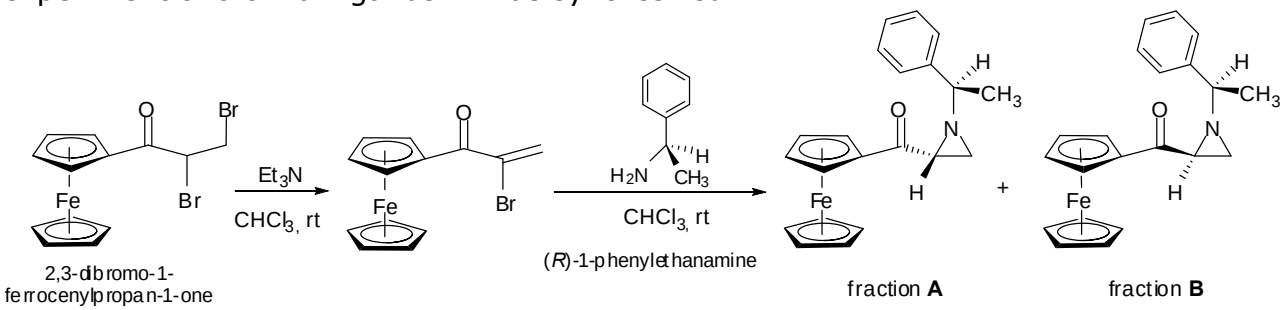
1. Plot the volume of gas generated versus time in Graph 2.
2. Calculate the maximum number of moles and the maximum volume (mL) of hydrogen gas which will be evolved theoretically from the hydrolysis of 29.5 mg ammonia borane with a purity of 97% w/w at 25 °C. The atmospheric pressure is 690 torr.
3. Calculate the rate of hydrogen generation in your experiment
   i) in mL H_2/ min.
   ii) in mmol H_2/ min by assuming that the temperature is 25 °C. The atmospheric pressure is 690 torr.
4. Calculate the rate of hydrogen production per mole of palladium in (mol H_2)·(mol Pd)$^{-1}$·(min)$^{-1}$ in your experiment. The purity of potassium tetrachloropalladate(II) is 98% w/w.

Propblem 3

Synthesis, purification and separation of a diastereomeric mixture

Nature has many compounds in the form of a single enantiomer or diastereomer such as sugars, amino acids, steroids, etc. Some of these compounds are biologically active and used as drugs. Therefore, the asymmetric synthesis of organic compounds is important. One of the methods for the asymmetric

synthesis of organic compounds employes a metal-catalyst, in which the metal is coordinated to a chiral organic molecule named as chiral ligand. In this experiment two chiral ligands will be synthesized.



A. Synthesis

1. Transfer the triethylamine solution in vial 1 (**V1**) using a syringe to the 10 mL round bottom reaction flask (**Rxn RB**) containing 0.50 mmol 2,3-dibromo-1-ferrocenylpropan-1-one through the septum.
2. Stir the mixture at room temperature for 30 min using the magnetic stirrer at 600 rpm (as marked on the stirrer).
3. At the end of 30 min, transfer the (*R*)-1-phenylethanamine solution in vial 2 (**V2**) to the reaction flask using the same syringe through the septum.
4. Stir the mixture for additional 60 min at room temperature.
5. At the end of 60 min turn off the magnetic stirrer and perform a Thin Layer Chromatography, TLC, analysis as follows:
   i) Check your TLC plates before use. Damaged plates will be replaced upon request without penalty.
   ii) Draw a start line on the lower portion of TLC plate with a pencil (Fig. 2.1).
   iii) Apply starting material from the vial labeled as **SM** two times to the spot on the left and then two times to the spot in the middle of plate. To the same plate, apply the reaction mixture (**RM**) taken from the reaction flask once to the spot on the right and then once to the spot in the middle as shown in Figure 2.1 (use a different capillary tube for each sample).
   iv) Develop TLC plate in the TLC chamber with the eluent. Mark the solvent front with the pencil.
   v) When the TLC plate is dry, place it in a zipper storage bag marked as **TLC1**.

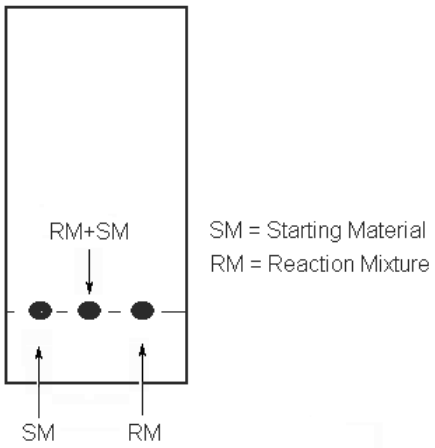


Figure 2.1. A TLC plate

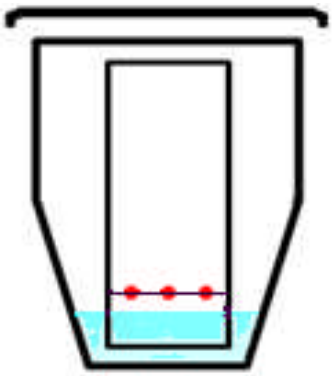


Fig. 2.2 A TLC plate placed in the TLC developing chamber

B. Flash Column Chromatography

1. Remove the stopper, open the valve, and bring the eluent level at top of column to the upper level of silica gel.
2. Close the valve and load the content of reaction flask on the top of flash column using a Pasteur pipette (Fig. 2.3)

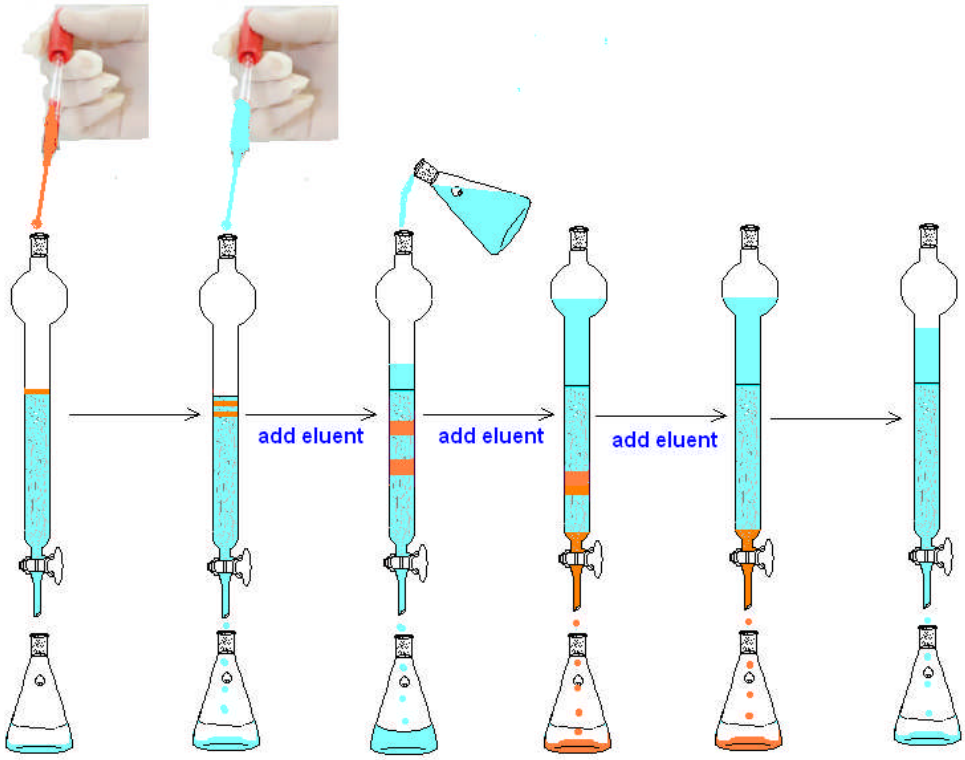


Figure 2.3. Flash Column Chromatography

3. Rinse the reaction flask with 0.5 mL eluent taken from the bottle labeled as **ELUENT** using a clean syringe. Using the same Pasteur pipette, load the washings also on the top of column.
4. Open the valve of the column and let the solvent run down to the upper level of silica gel.
5. Close the valve and add 1.0 mL eluent by a Pasteur pipette. Open the valve. When the eluent is at the upper level of silica gel, add 2-3 mL eluent slowly without closing the valve.
6. Fill the column by adding more eluent. **CAUTION: Be careful during the addition of eluent; do not disturb silica gel.**
7. In order to speed up the purification, apply little pressure by connecting the pressure applying bulb with an adapter on top of the column. **CAUTION: Be careful not to apply too much pressure. Add eluent time to time to avoid silica gel run dry.**
8. You are expected to collect two major fractions **A** and **B**. Discard any material which elutes before major fraction **A** and between **A** and **B** into the container labeled as **Organic Waste**.
9. Collect the first major fraction into a 100 mL Erlenmeyer flask and label it as fraction **A**.
10. Collect the second major fraction into a 250 mL Erlenmeyer flask and label it as fraction **B**.
11. After collecting fraction **B** stop the elution by closing the valve.

C. Analysis

1. Perform another TLC by applying the starting material (**SM**) two times to the spot on the left, apply fraction **A** two times to the spot in the middle, and then fraction **B** five times to the spot on the right. After development, when the TLC plate is dry, place it in a zipper storage bag marked **TLC2**.
2. Measure the volume of fraction **A** using 50 mL graduated cylinder and record the volume to your answer sheet.
3. Measure the volume of fraction **B** using 250 mL graduated cylinder and record the volume to your answer sheet.
4. Using a 2-mL pipette transfer 2.0 mL of fraction **A** into the 10 mL volumetric flask and complete the volume to 10 mL by adding eluent. After shaking the flask, fill out the UV-visible cell (at least ¾ of its volume) by using a Pasteur pipette. Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.

5. Using fraction **B**, fill out (at least ¾ of its volume) the other UV-visible cell by a Pasteur pipette (no need for dilution). Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.

Treatment of Data

1. Copy (sketch) the TLC1 plate on your answer sheet.
2. Copy (sketch) the TLC2 plate on your answer sheet.
3. Calculate and record the R_f values of the spots (fraction **A**, fraction **B**, and starting material **SM**) using the TLC2 plate.
4. The molar extinction coefficient, □, is 404 $Lmol^{-1}cm^{-1}$ for **A** and 400 $Lmol^{-1}cm^{-1}$ for **B** at 450 nm. Calculate:
   i) The percent yield of fraction **A** based on the starting material.
   ii) The percent yield of fraction **B** based on the starting material.

The Answers to the Theoretical Problems of the IChO

Solution to problem 1

a) Rate $R = k \cdot p(NO)^a \cdot p(H_2)^b$ a= 2 b = 1

$k = \frac{8.66 \cdot 10^{-2}\ Torr \cdot s^{-1}}{(120\ Torr)^2 \cdot 60\ Torr}$ $k = 1.00 \cdot 10^{-7}\ Torr^{-2} \cdot s^{-1}$

b) $R = \frac{\Delta p(N_2O)}{\Delta t} = -\frac{1}{2} \cdot \frac{\Delta p(NO)}{\Delta t} = 1.00 \cdot 10^{-7}\ Torr^{-2} \cdot s^{-1} \cdot (200\ Torr)^2 \cdot 100\ Torr$

$R = 0.40\ Torr \cdot s^{-1}$ $-\frac{\Delta p(NO)}{\Delta t} = 0.80\ Torr \cdot s^{-1}$

c) $p(NO) \gg p(H_2)$ $\Rightarrow$ $R = k' \cdot p(H_2)$ mit $k' = k \cdot p(NO)^2$

$k' = 1.00 \cdot 10^{-7}\ Torr^{-2} \cdot s^{-1} \cdot (8.00 \cdot 10^2\ Torr)^2 = 0.064\ s^{-1}$

$t_{1/2} = \ln 2 / k'$ $t_{1/2} = 10.8\ s$

d) i. $\frac{\Delta p(N_2O)}{\Delta t} = k_2 \cdot p(N_2O_2) \cdot p(H_2)$ steady state for N_2O_2:

$\frac{\Delta p(N_2O_2)}{\Delta t} = k_1 \cdot p(NO)^2 - k_{-1} \cdot p(N_2O_2) - k_2 \cdot p(N_2O_2) \cdot p(H_2) = 0$

$\Rightarrow p(N_2O_2) = \frac{k_1 \cdot p(NO)^2}{k_{-1} + p(H_2)}$ $\frac{\Delta p(N_2O)}{\Delta t} = k_2 \cdot p(H_2) \cdot \frac{k_1 \cdot p(NO)^2}{k_{-1} + k_2 \cdot p(H_2)}$

Rate law $\frac{\Delta p(N_2O)}{\Delta t} = k_1 \cdot k_2 \cdot p(H_2) \cdot \frac{p(H_2) \cdot p(NO)^2}{k_{-1} + k_2 \cdot p(H_2)}$

ii. $k_{-1} \gg k_2 \cdot p(H_2)$ iii. $k = (k_1 \cdot k_2)/k_{-1}$

e) Diagram d

Solution to problem 2

a) $q_V = \Delta E = \Delta H - \Delta n_g \cdot R \cdot T$

for 1 mol of NH_3: $\Delta H = 1.5 \cdot (-285.83\ kJ \cdot mol^{-1}) - (46.11\ kJ \cdot mol^{-1}) = -382.64\ kJ \cdot mol^{-1}$

$\Delta n_g = -1.25\ mol$

$\Delta E = -382.64\ kJ \cdot mol^{-1} - (-1.25\ mol \cdot 8.314\ JK^{-1}mol^{-1})$

$\Delta E = -379.5\ kJmol^{-1}$

$n(O_2) = 14.40\ g/(32\ g/mol) = 0.450\ mol$

$(4/3) \cdot 0.450\ mol = 0.600\ mol$ of NH_3 react

$q_V = \Delta E = 0.600\ mol \cdot (-379.5\ kJmol^{-1}) = -228\ kJ$

b) i. $c_0(H_2SO_4) = 15.0\ mL \cdot 0.0100\ mol/L = 0.150\ mmol$

H_2SO_4 reacted = ½ · consumption of NaOH

$= \frac{1}{2} \cdot 10.64\ mL \cdot 0.0200\ mol/L = 0.01064\ mmol\ H_2SO_4$

H_2SO_4 reacted with NH_3: $0.150\ mmol - 0.01064\ mmol = 0.0436\ mmol\ H_2SO_4$

$n(NH_3) = 2 \cdot n(H_2SO_4) = 2 \cdot 0.0436\ mmol = 8.72 \cdot 10^{-2}\ mmol$

$c(NH_3) = \frac{8.72 \cdot 10^{-2} mmol}{10\ mL} = 8.72 \cdot 10^{-3}\ mol/L$

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$c_0(NH_3) - x$ x x x

$K_b = 1.8 \times 10^{-5} = \frac{x^2}{0.00872 - x}$ $\Leftrightarrow$ $x^2 + 1.8 \times 10^{-5} \cdot - 1.584 \cdot 10^{-7} = 0$

$x = 3.96 \cdot 10^{-4}$ $pH = 14 - p(OH) = 14 - \log 3.96 \cdot 10^{-4} = 10.59$

ii. $SO_4^{2-}(aq) + H_2O(l) \rightleftharpoons HSO_4^-(aq) + OH^-(aq)$

$k_b = K_w/K_s = 1.0 \cdot 10^{-14}/1.1 \cdot 10^{-2} = 9.1 \cdot 10^{-13}$

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

$K_s = K_w/K_b = 1.0 \cdot 10^{-14}/1.8 \cdot 10^{-5} = 8.6 \cdot 10^{-10}$

iii. pH > 7

Solution to problem 3

a) $H_2(g) + D_2(g) \longrightarrow 2\ HD$ $\Delta H = \Delta E + n_g \cdot RT$ $n_g = 0$ $\Rightarrow$ $\Delta H = \Delta E$

$\Delta E = 2 \cdot E(HD) - E(H_2) - E(D_2)$

as v = 0 at 0 K $\Rightarrow$ $E_{vib} = \frac{1}{2} \cdot \varepsilon$

$\Delta E = 2 \cdot (E_0 + \frac{1}{2} \cdot \varepsilon_{HD}) - (E_0 + \frac{1}{2} \cdot \varepsilon_{H_2}) - (E_0 + \frac{1}{2} \cdot \varepsilon_{D_2}) = \varepsilon_{HD} - \frac{1}{2} \cdot (\varepsilon_{H_2} + \varepsilon_{D_2})$

$\Delta E = \varepsilon_{HD} \cdot (1 - \frac{1}{2} \cdot (1.1546 + 0.8167 = 0.01435 \cdot \varepsilon_{HD}$

$\mu(HD) = \frac{m_H \cdot m_D}{m_H + m_D} = \frac{1.0078 \cdot 10^{-3}\ kgmol^{-1} \cdot 2.0141 \cdot 10^{-3}\ kgmol^{-1}/N_A^2}{(1.0078 \cdot 10^{-3}\ kgmol^{-1} - 2.0141 \cdot 10^{-3}\ kgmol^{-1})/N_A} = 1.1154 \cdot 10^{-27}$ kg

$\varepsilon_{HD} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{6.6261 \cdot 10^{-34}\ J \cdot s}{2 \cdot \pi} \cdot \sqrt{\frac{575.11\ N \cdot m^{-1}}{1.1154 \cdot 10^{-27}\ kg}} = 7.5724 \cdot 10^{-20}$ J

$\varepsilon_{HD} = 7.5724 \cdot 10^{-20}$ J $\cdot N_A = 45600$ kJ/mol

$\Delta E = 0.01435 \cdot \varepsilon_{HD} = 0.6544$ kJ/mol

b) $h \cdot \nu = \Delta E$ $\Delta E = E(\nu 1) - E(\nu 0) = \varepsilon_{HD}$ $\Rightarrow$ $\nu = \varepsilon_{HD}/h$ with $\varepsilon_{HD} = 7.5724 \cdot 10^{-20}$ J

$\nu = \frac{7.5724 \cdot 10^{-20}\ J}{6.6261 \cdot 10^{-34}\ J \cdot s} = 1.1428 \cdot 10^{14}\ s^{-1}$

c) i. $H_2 \longrightarrow 2\ H$ n = 1: $\Delta E = 2 \cdot (-13.5984\ eV) - (-31.675\ eV)$

$\Delta E = 4.478$ eV

ii. $H_2 + h \cdot \nu \longrightarrow H + H$ $(n_1/n_2) \in \{(1/1), (1/2), (2/1), (2/2), \ldots\}$

The energy of an H_2 molecule in ground state is – 31.675 eV. $\lambda = 77.0$ nm

$E/photon) = h \cdot \nu/c = \frac{6.6261 \cdot 10^{-34}\ J \cdot s \cdot 3.00 \cdot 10^8\ m s^{-1}}{77 \cdot 10^{-9}\ m} = 2.58 \cdot 10^{-18}$ J = 16.105 eV

$\Delta E = E(n_1) + E(n_2) - E(H_2) = -\frac{R_H}{n_1^2} - \frac{R_H}{n_2^2} - (-31.675\ eV) < 16.105$ eV

$(n_1/n_2) = (1/1)$:

$\Delta E = -\frac{13.5984\ eV}{1^2} - \frac{13.5984\ eV}{1^2} + 31.675\ eV = 4.448$ eV

kinetic energy = 16.105 eV - 4.448 eV ≈ 11.7 eV

$(n_1/n_2) = (2/1)$ oder $(n_1/n_2) = (1/2)$:

$\Delta E = -\frac{13.5984\ eV}{1^2} - \frac{13.5984\ eV}{2^2} + 31.675\ eV = 14.677$ eV

kinetic energy = 16.105 eV – 14.677 eV ≈ 1.43 eV

$(n_1/n_2) = (2/2)$

$\Delta E = -\frac{13.5984\ eV}{2^2} - \frac{13.5984\ eV}{2^2} + 31.675\ eV = 24.880\ eV > 16.105\ eV$

Thus possibilities are $(n_1/n_2)\ \varepsilon\ \{(1/1).(1/2).(2/1)\}$

d) Ionisation ernergy of H: $IE(H) = -\frac{13.5984\ eV}{\infty^2} - \frac{-13.5984\ eV}{1^2} = 13.598\ eV$

$H_2^+ + e^- \longrightarrow H_2$		$EA(H_2^+) = -IE(H_2)$
$H_2^+ \longrightarrow H^+ + H$		$DE(H_2^+) = 2.650\ eV$
$H \longrightarrow H^+ + e^-$		$IE(H) = 13.598\ eV$
$H_2 \longrightarrow H + H$		$DE(H_2) = 4.478\ eV$

$EA(H_2^+) = DE(H_2^+) - IE(H) - DE(H_2) = (2.650 - 13.598 - 4.478)\ eV = -15.426\ eV$

Solution to problem 4

a) $n(H_2) = \frac{100\cdot10^{-3}\ L\cdot min^{-1}\cdot 1.0\ atm}{0.082\ atm\cdot L\cdot K^{-1}\cdot L^{-1}\cdot 298\ K} = 4.09\cdot10^{-3}$ mol H_2/min

$\frac{4.09\cdot10^{-3}\ mol\ H_2/min}{92\ mol\ H_2\cdot(mol\ Ru)^{-1}\cdot min^{-1}} = 4.45\cdot10^{-5}$ mol Ru

$4.45\cdot10^{-5}$ mol Ru · 101.07 g/mol = 4.50 mg Ru

b) $n(NaBH_4) = 0.10$ mol

$n(H_2$, released$) = 4\cdot n(NaBH_4) = 0.40$ mol $\quad t = \frac{0.40\ mol\ H_2}{4.1\cdot10^{-3} mol\ H_2/min} = 98$ min

c) $v = k\cdot c(Ru) = A\cdot e^{-E_a/RT}\cdot c(Ru)$ $\quad \frac{e^{-E_a/R298}}{e^{-E_a/RT}} = ½$

$\frac{E_a}{R}\cdot\left(\frac{1}{298} - \frac{1}{T}\right) = \ln ½$ $\quad \frac{42.0\cdot10^3\ J\cdot mol^{-1}}{8.314\ J\cdot K^{-1}\cdot mol^{-1}}\cdot\left(\frac{1}{298} - \frac{1}{T}\right) = \ln 2$

T = 311 K or 38 °C

d) $\Delta G° = -n\cdot F\cdot E°$ $\quad 2\cdot-2.37\cdot10^5$ J/mol = - 4 mol·96485 C /mol · E°

E° = 1.23 V $\quad 1.23\ V = E°_{cathode} - (-8.83\ V)$ $\quad E°_{cathode} = 0.40$ V

e) 2.5 A · 3.0 h · 3600 s/h = 27000 C

$n(O_2) = 27000\ C/(4\cdot96485\ C) = 0.0700$ mol

$V(O_2) = \frac{0.070\ mol\cdot0.082\ atm\cdot L\cdot K^{-1}\cdot mol^{-1}\cdot 298\ K}{1.0\ atm} = 1.71$ L $\quad V_{Luft} = 8.55$ L

f) $\Delta G = -n\cdot F\cdot E°$ $\quad \Delta G = -4\cdot96485\cdot1.23$ J/mol = 474.7 kJ/mol

$\Delta G° = \Delta H° - T\cdot\Delta S°$ $\quad \Delta H° = \Delta G° + T\cdot\Delta S°$

$\Delta S° = -326.6\ J\cdot mol^{-1}\cdot K^{-1}$ $\quad \Delta H° = -474\ kJ/mol + 298\ K\cdot 326.6\cdot10^{-3}\ kJ\cdot mol^{-1}\cdot K^{-1}$

$\Delta H° = -571.4$ kJ/mol $\quad w_{max} = \Delta G° = -474.7$ kJ/mol

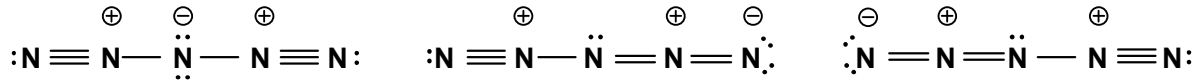
$\eta = \frac{w_{max}}{\Delta H^0}$ $\quad \eta = \frac{-474.7\ kJ/mol}{-571.4\ kJ/mol} = 0.83$

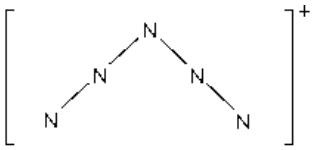
g) $\eta = \frac{w}{q_H} = \frac{q_H - q_C}{q_H} = 1 - \frac{q_C}{q_H}$ $\quad \frac{q_H}{T_H} = \frac{q_C}{T_C} \Rightarrow \frac{T_C}{T_H} = \frac{q_C}{q_H}$

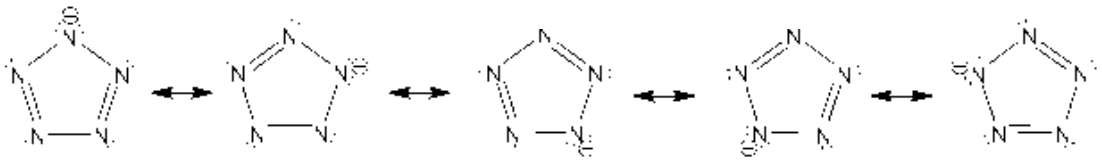
$\Rightarrow \eta = 1 - \frac{T_C}{T_H}$ $\quad 0.83 = 1 - \frac{313\ K}{T_H}$ $\quad T_H = 1841$ K or 1568 °C

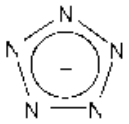
Solution to problem 5

a)



molecular geometry 



molecular geometry 

b) $[N_2F^+][AsF_6^-] + HN_3 \xrightarrow[\text{in HF(l)}]{} [N_5^+][AsF_6^-] + HF$

c) The desired ratio is the value of the equilibrium constantof the trans $\rightleftharpoons$ cis reaction

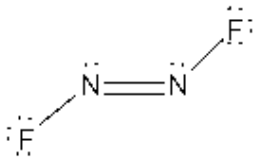
K = cis/trans $\quad \Delta G° = - RT \cdot \ln K \quad \Delta G° = \Delta H° - T \cdot \Delta S°$

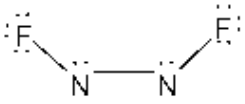
$\Delta H° = (62.03 - 67.31)\ kJ/mol = - 5.28\ kJ \cdot mol^{-1}$

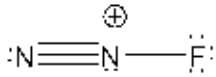
$\Delta S° = (266.50 - 262.10)\ J \cdot mol^{-1} \cdot K^{-1} = 4.40\ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta G° = - 5.28 \cdot 10^3\ J \cdot mol^{-1} - 298\ K \cdot 4.40\ J \cdot mol^{-1} \cdot K^{-1} = -6.59 \cdot 10^3\ J \cdot mol^{-1}$

$K = e^{-\Delta G°/RT} = e^{-(-6590\ J/mol)/(8.314 \cdot 298\ J/mol)} = 14.3$

d) trans N_2F_2  $sp^2 \quad sp^2$

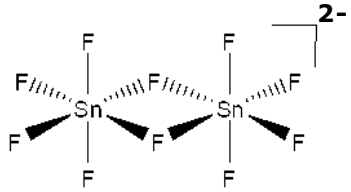
cis- N_2F_2  $sp^2 \quad sp^2$

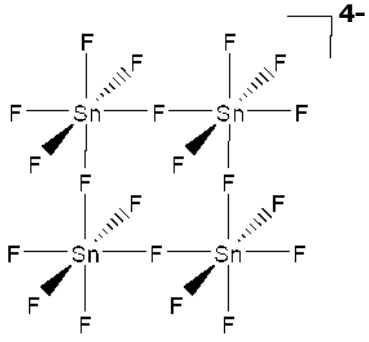
N_2F^-  $sp \quad sp$

e) $4\ [N_5^+][AsF_6^-] + 2\ H_2O \longrightarrow 4\ AsF_5 + 4\ HF + 10\ N_2 + O_2$

f) $2\ [N_5^+][SbF_6^-] + [Cs^+]_2[SnF_6^{2-}] \xrightarrow{HF,\ -78\ °C} [N_5^+]_2[SnF_6^+] + 2\ [Cs^+]_2[SbF_6^-]$

$[N_5^+][SbF_6^-] + [K^+][B(CF_3)_4^-] \xrightarrow{SO_2,\ -64\ °C} [N_5^+][B(CF_3)_4^-] + [K^+][SbF_6^-]$

g)  **2-**

 **4-**

Solution to problem 6

a) Anode $Au(s) + 2\ NH_3(aq) \longrightarrow [Au(NH_3)_2]^+(aq) + e^-$

$\underline{[Au(NH_3)_2]^+(aq) + 2\ S_2O_3^{2-}(aq) \longrightarrow [Au(S_2O_3)_2]^{3-}(aq) + 2\ NH_3(aq)}$

$Au(s) + 2\ S_2O_3^{2-}(aq) \longrightarrow [Au(S_2O_3)_2]^{3-}(aq) + e^-$

Cathode $[Cu(NH_3)_4]^{2+}(aq) + e^- \longrightarrow [Cu(NH_3)_2]^+(aq) + 2\ NH_3(aq)$

$\underline{[Cu(NH_3)_2]^+(aq) + 3\ S_2O_3^{2-}(aq) \longrightarrow [Cu(S_2O_3)_3]^{5-}(aq) + 2\ NH_3(aq)}$

$[Cu(NH_3)_4]^{2+}(aq) + 3\ S_2O_3^{2-}(aq) + e^- \longrightarrow [Cu(S_2O_3)_3]^{5-}(aq) + 4\ NH_3(aq)$

total reaction $Au(s) + [Cu(NH_3)_4]^{2+}(aq) + 5\ S_2O_3^{2-}(aq) \longrightarrow$

$[Au(S_2O_3)_2]^{3-}(aq) + [Cu(S_2O_3)_3]^{5-}(aq) + 4\ NH_3(aq)$

b) Oxidation

4×/ $[Cu(S_2O_3)_3]^{5-}(aq) + 4\ NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq) + 3\ S_2O_3^{2-}(aq) + e^-$

Reduction

1×/ $4\ e^- + O_2(g) + 2\ H_2O(l) \longrightarrow 4\ OH^-(aq)$

Redoxreaction

$4\ [Cu(S_2O_3)_3]^{5-}(aq) + 16\ NH_3(aq) + O_2(g) + 2\ H_2O(l) \longrightarrow$

$4\ [Cu(NH_3)_4]^{2+}(aq) + 12\ S_2O_3^{2-}(aq) + 4\ OH^-(aq)$

c) 4×/ $Au(s) + [Cu(NH_3)_4]^{2+}(aq) + 5\ S_2O_3^{2-}(aq) \longrightarrow$

$[Au(S_2O_3)_2]^{3-}(aq) + [Cu(S_2O_3)_3]^{5-}(aq) + 4\ NH_3(aq)$

$4\ [Cu(S_2O_3)_3]^{5-}(aq) + 16\ NH_3(aq) + O_2(g) + 2\ H_2O(l) \longrightarrow$

$\underline{4\ [Cu(NH_3)_4]^{2+}(aq) + 12\ S_2O_3^{2-}(aq) + 4\ OH^-(aq)}$

$4\ Au(s) + 8\ S_2O_3^{2-}(aq) + O_2(g) + 2\ H_2O(l) \longrightarrow 4\ [Au(S_2O_3)_2]^{3-}(aq) + 4\ OH^-(aq)$

d) $[H_3N\text{-}Au\text{-}NH_3]^+$ $[O_3S\text{-}S\text{-}Au\text{-}S\text{-}SO_3]^{3-}$

e) (-1)×/ $Au^+(aq) + 2\ NH_3(aq) \longrightarrow [Au(NH_3)_2]^+(aq)$ $Kf\ (1) = 1.00\times10^{26}$

1×/ $\underline{Au^+(aq) + 2\ S_2O_3^{2-}(aq) \longrightarrow [Au(S_2O_3)2]^{3-}(aq)}$ $\underline{Kf\ (2) = 1.00\times10^{28}}$

$[Au(NH_3)_2]^+(aq) + 2\ S_2O_3^{2-}(aq) \longrightarrow [Au(S_2O_3)_2]^{3-}(aq) + 2\ NH_3(aq)$

$K_{eq} = K_f(2)/K_f(1) = 1.00\times10^2$

$[Au(NH_3)_2^+] + [Au(S_2O_3)_2^{3-}] = 5.50\times10^{-5}$ mol/L

$K_{eq} = \frac{0.100^2\ x}{(5.50\cdot10^{-5} - x)\cdot0.100^2} = 1.00\cdot10^2$ $x = 5.445\cdot10^{-5}$

$\frac{5.445\cdot10^{-5}}{5.50\cdot10^{-5}}\cdot 100\ \% = 99.0\ \%$ are in the form of $[Au(S_2O_3)_2]^{3-}(aq)$.

f) 5×/ $S_4O_6^{2-}(aq) + 2e^- \longrightarrow 2\ S_2O_3^{2-}(aq)$

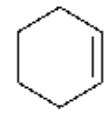
1×/ $\underline{12\ OH^-(aq) + 3\ S_4O_6^{2-}(aq) \longrightarrow 4\ S_3O_6^{2-}(aq) + 6\ H_2O(l) + 10\ e^-}$

$4\ S_4O_6^{2-}(aq) + 6\ OH^-(aq) \longrightarrow 5\ S_2O_3^{2-}(aq) + 2\ S_3O_6^{2-}(aq) + 3\ H_2O(l)$

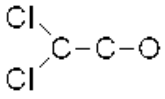
g) $2\ S_2O_3^{2-}(aq) + 2\ O_2(g) \rightarrow SO_4^{2-}(aq) + S_3O_6^{2-}(aq)$

Solution to problem 7

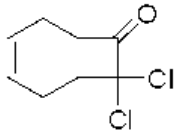
A



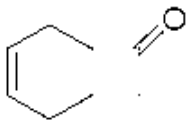
S



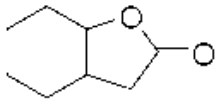
B



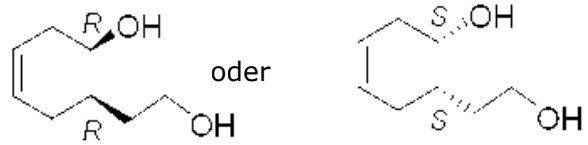
C



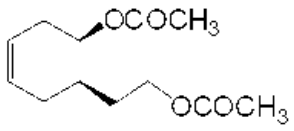
D



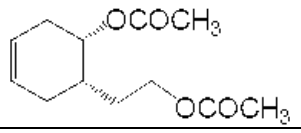
E



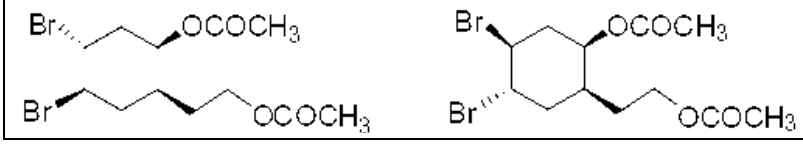
F



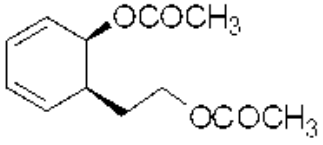
or



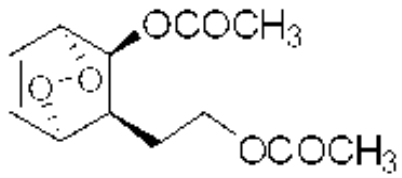
G_1 and G_2



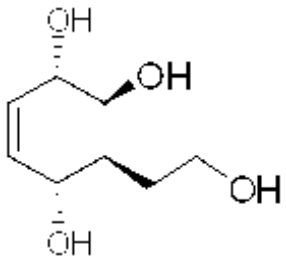
H



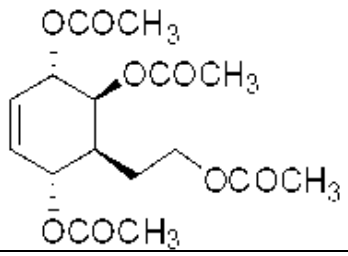
I



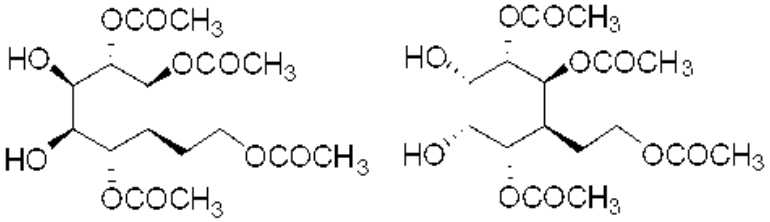
J



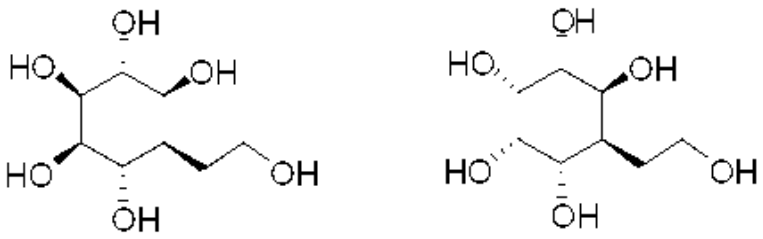
K



L and M

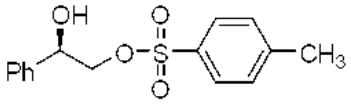


1a and 1b

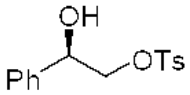


Solution to problem 8

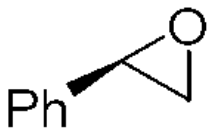
B



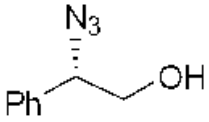
oder



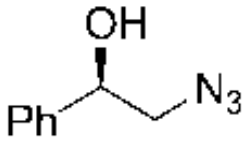
C



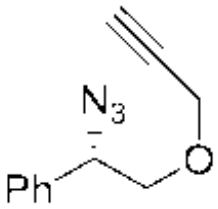
D



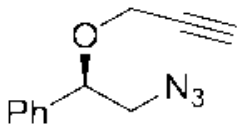
E



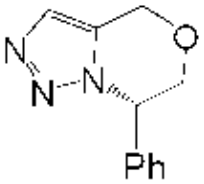
F



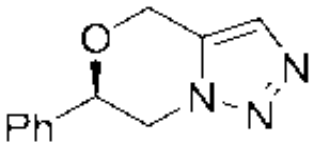
G



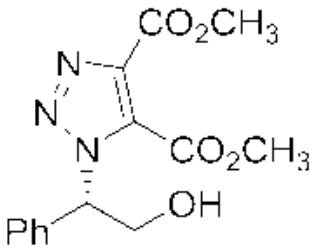
H



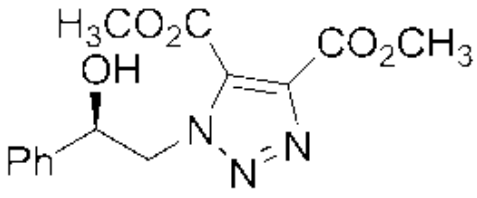
I



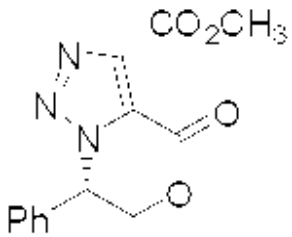
J



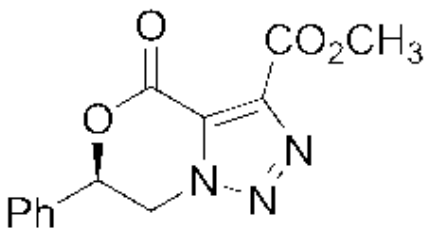
K



L



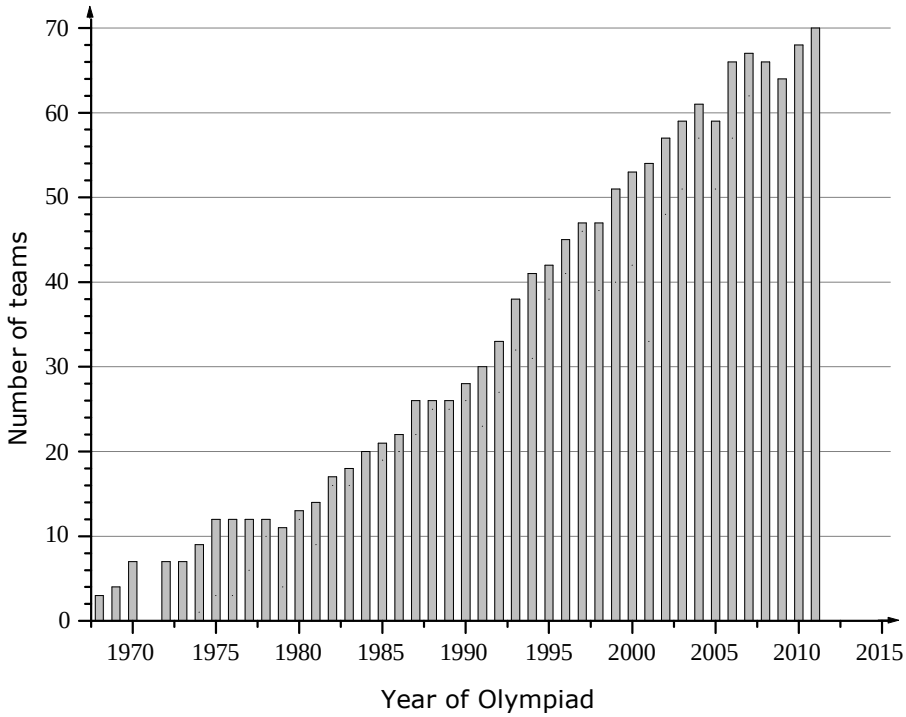
M



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 attentding the IChO in the following years are shown in the plot below.

Number of teams attending the IChO



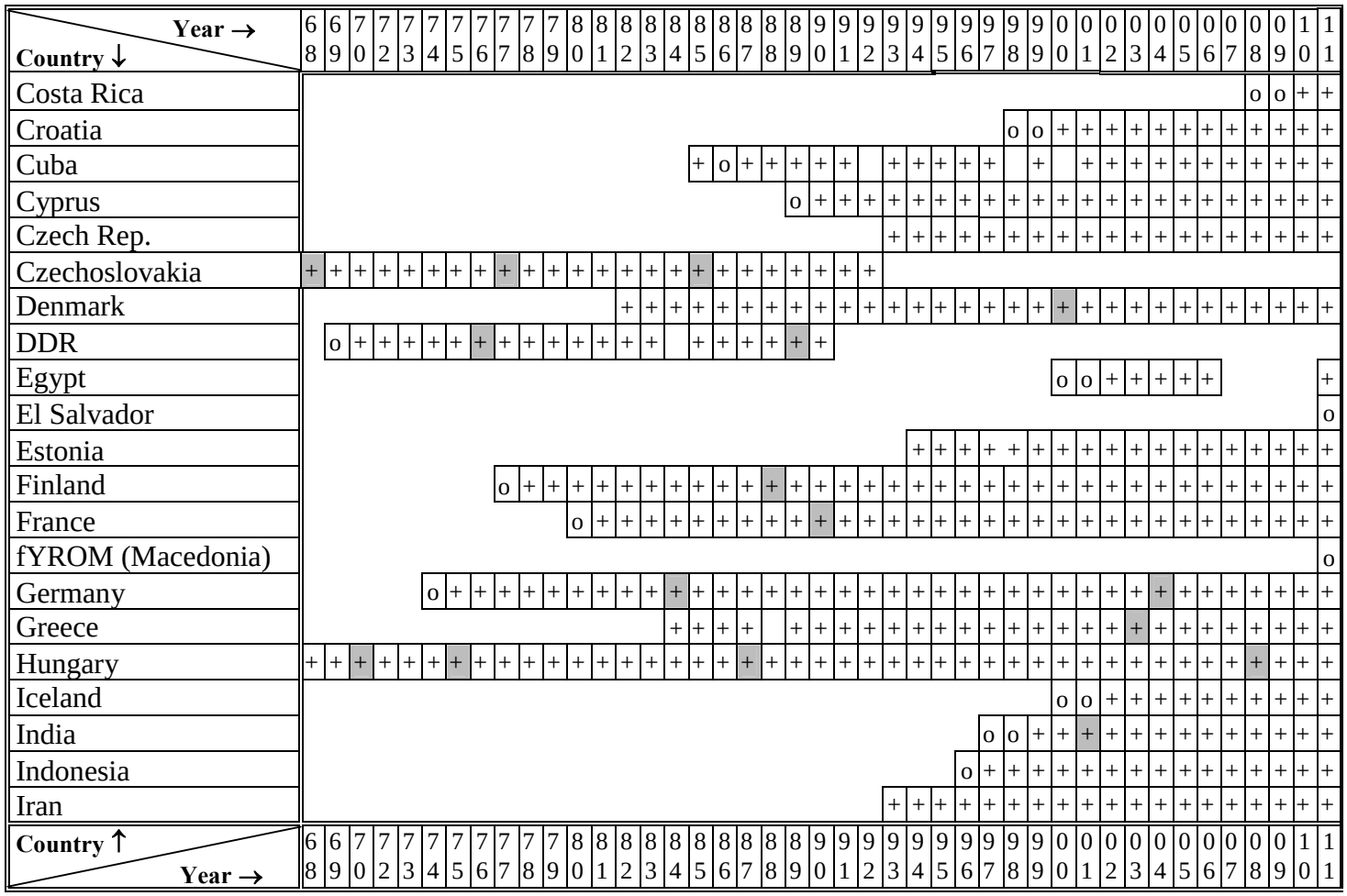
The participating countries are shown in the following table.

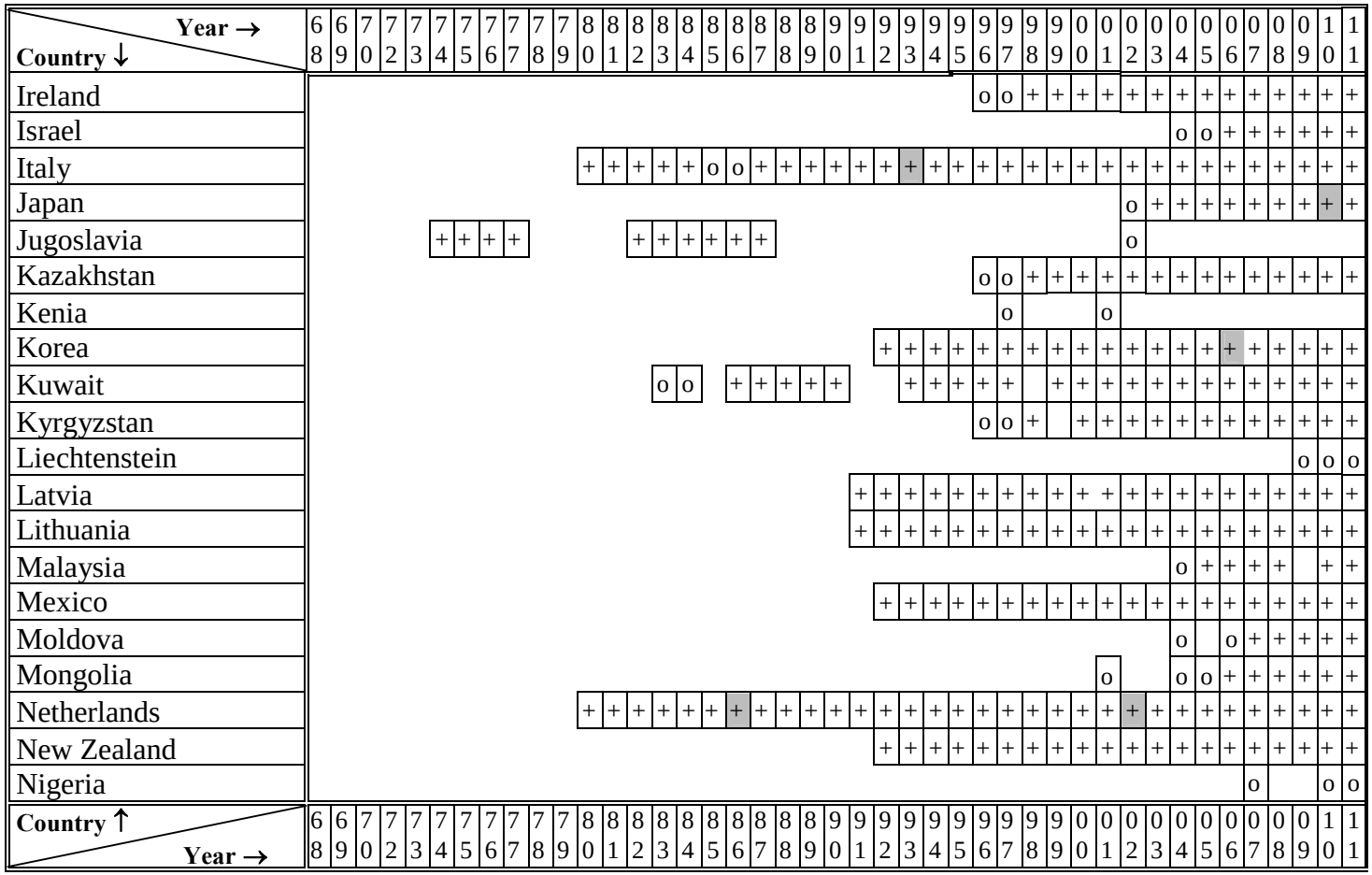
Participating Delegations

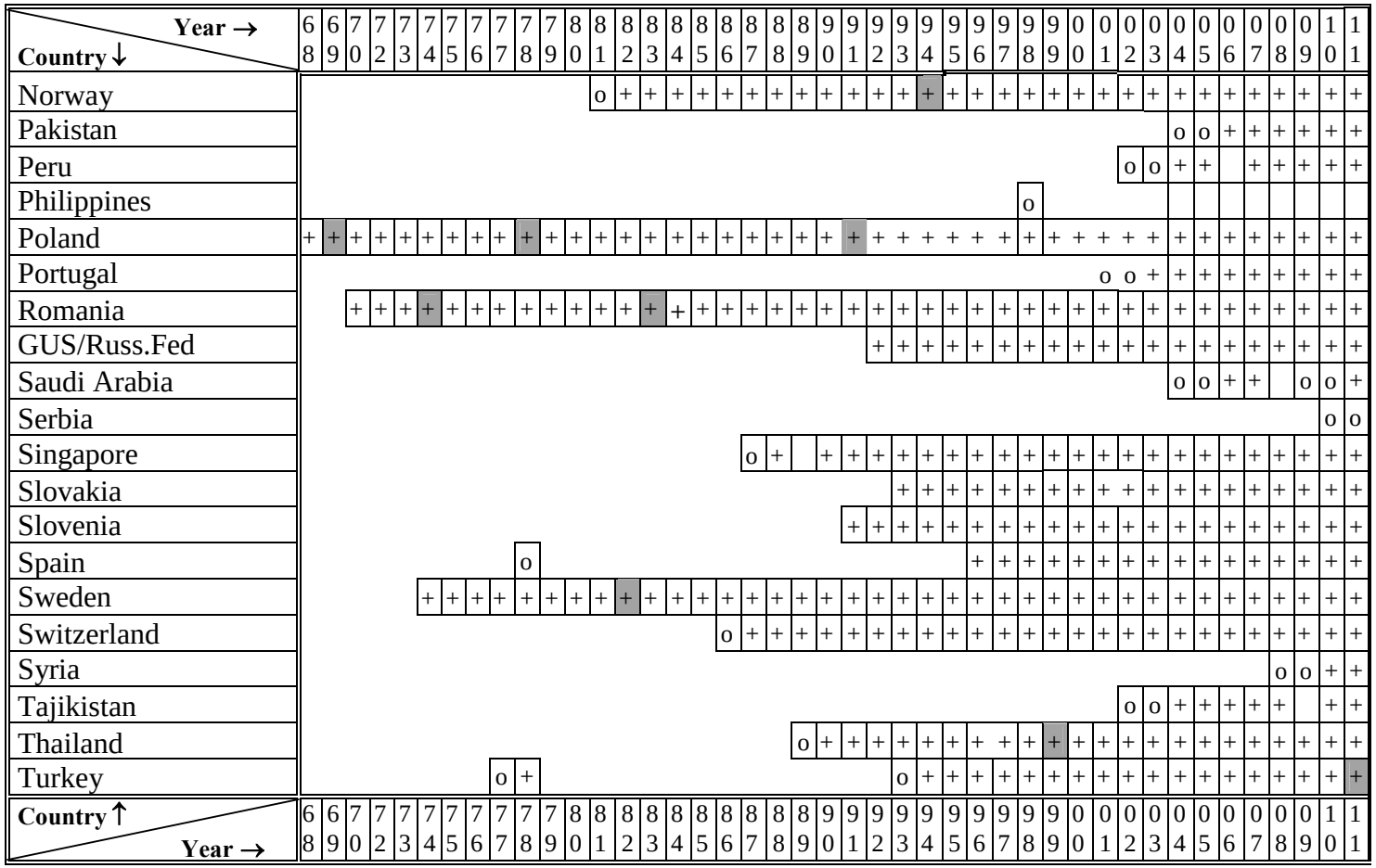
in alphabetical order

+ = host. + = participant. o = observer

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	11
Argentina																											+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Armenia																																				o	o	+	+	+	+	+	+	+	+
Australien																			o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Austria							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Azerbaijan																													o	o		+	+	+	+	+	+	+	+	+	+	+	+	+	+
Belarus																											+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Brasil																													o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Bulgaria		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Canada																	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
China																			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Chinese Taipei																								+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
↑ 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	11


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 11
Costa Rica
Croatia
Cuba
Cyprus
Czech Rep.
Czechoslovakia
Denmark
DDR
Egypt
El Salvador
Estonia
Finland
France
fYROM (Macedonia)
Germany
Greece
Hungary
Iceland
India
Indonesia
Iran
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 11
Ireland
Israel
Italy
Japan
Jugoslavia
Kazakhstan
Kenia
Korea
Kuwait
Kyrgyzstan
Liechtenstein
Latvia
Lithuania
Malaysia
Mexico
Moldova
Mongolia
Netherlands
New Zealand
Nigeria
Country ↑
Year →


Year →
Country ↓
Norway
Pakistan
Peru
Philippines
Poland
Portugal
Romania
GUS/Russ.Fed
Saudi Arabia
Serbia
Singapore
Slovakia
Slovenia
Spain
Sweden
Switzerland
Syria
Tajikistan
Thailand
Turkey
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	11
Turkmenistan																															o	o	o	+	+	+		+	+	+	+	+	+	
UdSSR			+	+	+	+	+	+	+	+	+		+	+	+	+	+	+	+	+	+		+																					
Ukraine																											+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United Kingdom												o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United States													o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Uruguay																													o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Usbekistan																																												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	11
Number of countries	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	64	68	70

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 page 127)

	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 page 127)

	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	RC	
.	ROK	T	IR	ROK	VN	TPE	RUS	RUS	RC	T	ROK	
.	USA	TPE	ROK	RUS	IR	ROK	TPE	UA	ROK	ROK	RUS	
.	RUS	ROK	T	UA	RUS	RUS	PL	ROK	RUS	J	RI	
5	IR	A	BY	D	AZ	VN	ROK	T	SGP	TPE	USA	
.	TR	UA	RUS	PL	TPE	T	D	BY	J	H	T	
.	IND	USA	IND	TPE	T	J	T	VN	USA	CZ	SGP	
.	AUS	PL	SGP	H	RA	Pl	IND	TPE	H	SGP	CDN	
.	TPE	IND	D	TR	D	IND	H	H	IR	**USA**	H	
10	T	D	TPE	VN	IND	D	SK	SGP	GB	IR	IR	
.	SGP	IR	UA	IND	A	SK	LT	KZ	RO	RUS	TR	
.	PL	H	PL	IR	CZ	DK	USA	A	T	TR	IND	
.	RO	RUS	CDN	RO	UA	SGP	VN	PL	D	LT	CZ	
.	F	CDN	CZ	LT	PL	BR	GB	IR	IND	D	F	
15	SK	TR	RO	CZ	AUS	CDN	BY	IND	PL	PL	J	
.	H	AUS	KZ	USA	TR	AZ	EST	RO	AUS	GB	TPE	
.	VN	GB	VN	SGP	H	UA	UA	AUS	A	IND	D	
.	CZ	SGP	EST	CDN	SK	USA	RI	D	BY	RI	SK	
.	RA	E	GB	AZ	USA	H	IR	SK	VN	RO	KZ	
20	BY	SK	AUS	AUS	GB	CZ	RO	TR	F	A	AUS	
.	C	BY	H	KZ	RO	AUS	AUS	LT	RI	VN	VN	
.	D	VN	SK	GB	BY	IRL	A	EST	TR	SK	RO	
.	GB	FIN	USA	J	SGP	F	KZ	I	LT	CDN	GB	
.	UA	F	YV	A	J	IR	SGP	GB	UA	EST	BY	
25	A	LT	IND	BY	RI	A	NZ	CDN	EST	AUS	PL	
.	MEX	CZ	F	SK	LV	TR	CZ	NZ	CZ	UA	A	
.	DK	KZ	A	T	BG	RI	F	BR	SK	F	LT	
.	CDN	LV	I	RA	HR	GB	TR	USA	CDN	RA	EST	
.	EST	NL	TR	EST	MEX	RO	J	LV	I	NZ	RA	
30	RI	RO	AZ	F	KZ	NL	ARM	RI	RA	BY	UA	
.	HR	RA	MEX	NZ	LT	HR	SLO	F	NZ	KZ	FIN	
.	I	EST	LT	SLO	F	LT	RA	CZ	TM	BR	SLO	
.	N	HR	NL	HR	EST	KZ	BR	J	MEX	IL	I	
.	BG	BG	FIN	LV	CDN	SLO	CDN	DK	KZ	HR	BR	
35	CY	NZ	HR	NL	I	EST	I	RA	IL	SLO	HR	
.	KZ	I	J	I	DK	RA	MAL	MEX	BR	FIN	NZ	
.	B	DK	DK	CH	SLO	BR	IL	SLO	HR	DK	TM	
.	LT	SLO	RA	FIN	FIN	TJ	IRL	IL	AZ	NL	LV	
.	NZ	N	GR	RI	NL	LV	NL	AZ	DK	E	S	
40	CH	YV	LT	S	IRL	MAL	CH	HR	S	I	NL	
.	E	MEX	E	BG	GR	S	S	TM	LV	LV	PE	
.	FIN	BR	TM	KS	NZ	IRL	LV	BG	IRL	BG	PK	
.	SLO	S	BR	E	KS	IL	DK	MGL	FIN	CR	TJ	
.	NL	RI	BG	GR	S	FIN	MD	IRL	N	CH	E	
45	LV	TM	CH	BR	B	IS	E	MAL	E	IRL	MEX	
.	BR	B	NZ	TM	BR	I	BG	E	NL	MEX	CH	
.	S	IRL	IS	CY	CH	CY	TM	S	MGL	MGL	MGL	
.	YV	CH	IRL	YVA	P	N	HR	NL	PE	MAL	IL	
.	IRL	C	CY	IRL	IS	TM	PK	CH	PK	N	CY	
50	GR	CY	KS	IS	N	CH	N	ROU	SLO	S	BG	

(List of abbreviations see page127)

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