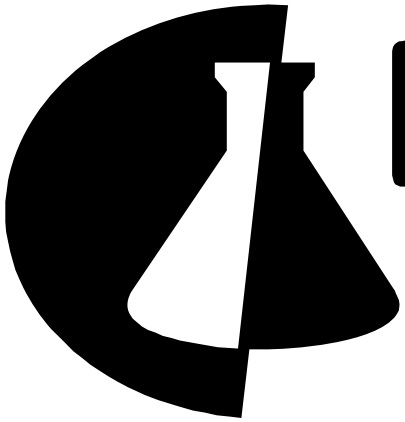

41. International ChemistryOlympiad Great Britain 2009

National German Competition

Volume 15

Preface

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

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

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

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

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

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

In the appendix you find tables of historical interest.

Wolfgang Hampe

Contents

Part 1: The problems of the four rounds

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

Part 3: The IChO in Cambridge

Part 4: Appendix

You will find these problems including the problems of the 41. IChO as pdf-file as of September 2009 in the internet: http://www.icho.de (Aufgaben)

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Association to promote the IChO
(Association of former participants and friends of the IChO)
Internet address: www.fcho.de

Part 1

The problem set of the four rounds

First Round

Problem 1-1 Hair and Colour

The packages of two hair dyeing lotions (blond and light brown) were unfortunately thrown away. Both substances look totally identical.

In order to distinguish the two lotions A and B the content of H_2O_2 is determined using potassium permanganate because the content of hydrogen peroxide in the dyeing lotion to get blond hair is expected be a little higher.

4.5 mL of lotion A are transferred into a 100 mL volumetric flask. Aliquots of 25 mL are titrated. To consume as little as possible of lotion B only 3.0 mL of it are transferred into a 100 mL volumetric flask and aliquots of 20 mL are titrated. (The density of both loltions amounts to ρ = 1.15 g/cm^3).

a) Write down the equation of the reaction of hydrogen peroxide and potassium permanganate.

The following volumes of potassium permanganate standard solution (c($KMnO_4$) = 0.020 mol/L) are needed to reach the end point of titration:

titration no.	lotion A	lotion B
1	18.95 mL	19.95 mL
2	19.20 mL	20.00 mL
3	19.15 mL	19.45 mL
4	19.65 mL	20.00 mL

b) Calculate the mass percentage of hydrogen peroxide in both lotions. Which of them is used to dye the hair blond?

Another oxidation agent to determine hydrogen peroxide is cer(IV) sulfate. This method is called cerate oxidimetry.

c) Write down the equation of the redox reaction of cer(IV) ions and hydrogen peroxide.

d) Why is the determination with cer(IV) sulfate carried out in strongly acidic medium?

Permanent hair colouration incorporates itself into the hair in the form of polymer molecules. To establish this incorporation a "developer" and a "coupling agent"

react with an oxidizing agent. Developer and coupling agent are part of the dyeing lotion, the oxidizing agent is contained in the developing emulsion.
The small molecules enter the hair and not until then they react to form the colouring polymers which can not move out of the hair again because of their size.
A dye contains 1,4-diaminobenzene as developer and resorcin as coupling agent. Hydrogen peroxide is the oxidizing agent.
Activating reaction: 1.4-diaminobenzene + $H_2O_2 \longrightarrow X + 2\ H_2O$
This activating reaction is comparable to the oxidation of hydroquinone (1,4-dihydroxybenzene) using mild conditions (e.g. with Fe^{3+} ions).

e) Give the reaction equation of the oxidation of hydroquinone with Fe^{3+} ions.

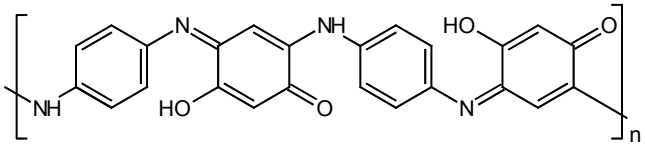
f) In which sense are the reactants and products of the oxidation of 1,4-diaminobenzene and 1,4-dihydroxybenzene comparable?

g) Show the structure of X.

One molecule of compound X reacts with one molecule of resorcin in a substitution reaction to form compound Y. Compound Y shows the empirical formula $C_{12}H_{12}N_2O_2$. Three different substitution products Y(1). Y(2). Y(3) are possible.

h) Draw the structures of Y(1). Y(2) und Y(3). Which of them will be formed preferentially? *Account for your answer.*

In the following steps of reaction between coupling agent, developer and oxidizing agent the polymer hair dye forms. The image shows a section of the structure:



i) How materialises colour in such polymer compounds?

A lot of developer and coupling agents in hair dyeing lotions for sale are toxic.

j) Indicate the R-ratings and S-provisions of 1,4-diaminobenzene, resorcin and hydrogen peroxide.

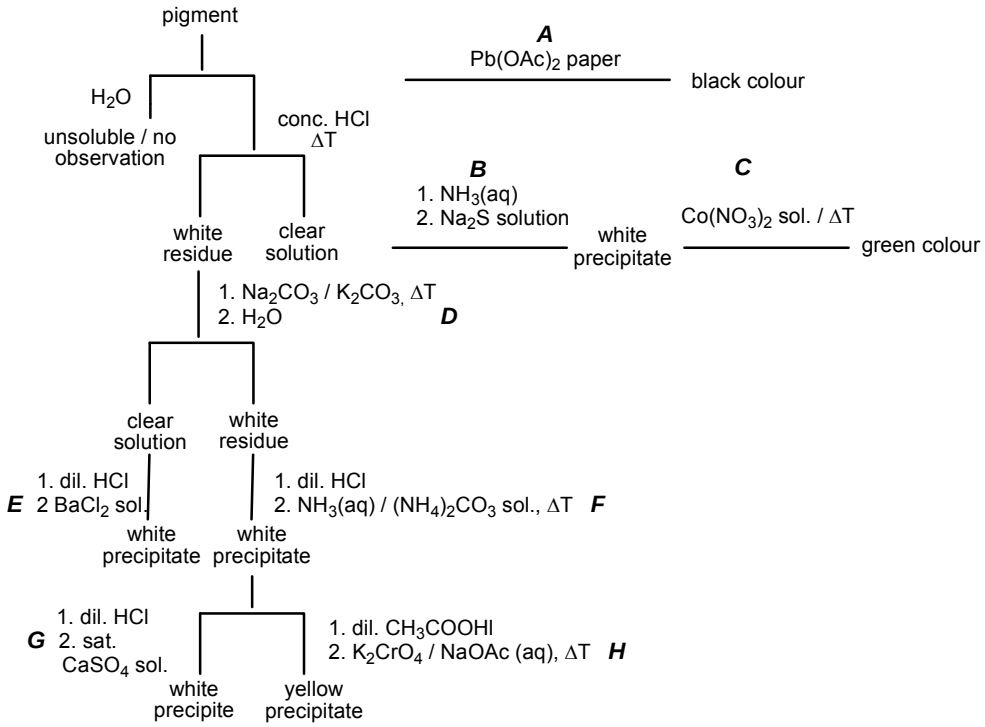
An especially strong allergenic and mutagenic impact is attributed to intermediates formed by reactions of X with itself: $3\ X \longrightarrow Z$.

k) Show the structural formula of Z (empirical formula: $C_{18}H_{18}N_6$).

l) How can the formation of these intermediates such as Z be minimized?

m) What do you have to do in order to protect your skin against the toxicity of the substances in purchasable hair dyeing lotions?

A big sack containing a white pigment was found in the stockroom of a closed pigment plant.
Unfortunately there is no hint which pigment it could be. The analysis in a laboratory showed the following results:



n) Give the composition of the pigment. Write down all equations of the reactions in the scheme above. (Be aware that there can be two step reactions.)

In 2002 hair was found in an archeological excavation which was coloured with natural dyes. In this hair the ration of amount of $n(^{14}C)/n(^{12}C)$ was $1.1034 \cdot 10^{-12}$. The halflife of the carbon isotope ^{14}C amounts to 5730 years, the natural ratio of amount of $n(^{14}C)/n(^{12}C)$ is $1.176 \cdot 10^{-12}$. This ratio is regarded to be constant in the relevant period.

o) From which time originates the hair found in the archeological excavation *presumably?*

Second Round (homework)

Problem 2-1: Distribution of an Organic Acid

A lot of organic acids dissolve partially in aromatic solvents. In doing so dimers and higher aggregates are being formed. Let us consider only dimers and disregard all other aggregates.
The constant of dimerisaton of an acid HA dissolved in toluene is $K_{Dim} = 16.4$.

a) Use acetic acid to visualise a dimer molecule. Give the reason for dimerisation.

Three solutions of 5.5 mg of acid HA in 500 mL of toluene each have been prepared to perform the following experiments.

b) Calculate the degree of dimerisation $\beta = \frac{c((HA)_2)}{c_0(HA)}$ *in these solutions. Taking into account the value of* β*, which conclusions do you draw with respect to the following calculations?*

The three solutions undergo solvent extraction either with

i) 250 mL of hydrochloric acid (c = 1.000 mol/L) or
ii) 250 mL sodium hydroxide solution (c = 1.000 mol/L) or
iii) 250 mL demineralised water .

c) Calculate the mass percentage of acid HA which was removed from the organic phase by solvent extraction. In case of i) und ii) use reasonnable simplifications and account for them.

The appropriate distribution coefficient of the acid HA between toluene and water amounts to $K_{distribution} = \frac{c(HA)_{toluol}}{c(HA)_{water}} = 2$

d) How often has a solution of 5.5 mg of acid HA in 500 mL of toluene to be extracted with 250 mL of hydrochloric acid (c = 1 mol/L) in order to pour out more acid than doing so once with demineralised water?
(Independend of your results in b)i) and b)iii) assume that pouring out once with hydroxchloric acid removes 21 %. with demineralize water 76 % of the acid HA from the organic phase.)

$pK_s(HA) = 2.97$. $M(HA) = 152.15$ g/mol

Problem 2-2 Looking for a Compound

An aqueous solution of a salt A is added to an aqueous solution of a salt B. In doing so a white product C precipitates. Product C does not dissolve in diluted acetic acid. The solutions of A and B show the following reactions:

i) If sulfuric acid is added to a solution of A a white precipitate forms.
ii) This precipitate is filtered off and then a solution of strontium chloride is added to the filtrate. Again a white precipitate forms.
iii) The solution of A shows a positive reaction with zinc/Lunge reagent .
iv) If zinc and a solution of sodium hydroxide are added to a solution of A and the mixture is heated then a moistened pH-paper held over the solution turns blue.
v) If a saturated solution of iron(II) sulfate is added to a solution of A and afterwards conc. sulfuric acid is added to form a lower layer a brown ring occurs at the boundary layer.
vi) A solution of B forms a white preciipitate with a solution of silver nitrate.
vii) A solution of B decoloures a solution of potassium permanganate.
viii) In reaction (vii) a gas is discharged which forms a white precipitate when passing through a solution of barium hydroxide.
ix) If a solution of B reacts with a conc. solution of sodium hydroxide a pungent smelling gas evolves the solution of which in water turns pink when treated with phenolphthaleine.

The elementary analysis of precipitate C to determine carbon, hydrogen and nitrogen results in: C: 16.41 %. H: 1.39 %. N: 0.11%.

a) Write the equation of the reaction of A und B to form C.

b) Check the result of the elementary analysis by calculating the theoretical mass percentage of C, H and N. Show your calculation.

c) Write the reaction equations i) – ix)!

Product C is thermal gravimetricly analysed. Thereby the mass of C is measured as a function of temperature. While heating up to 750 °C three levels of mass are monitored (Fig. 1).

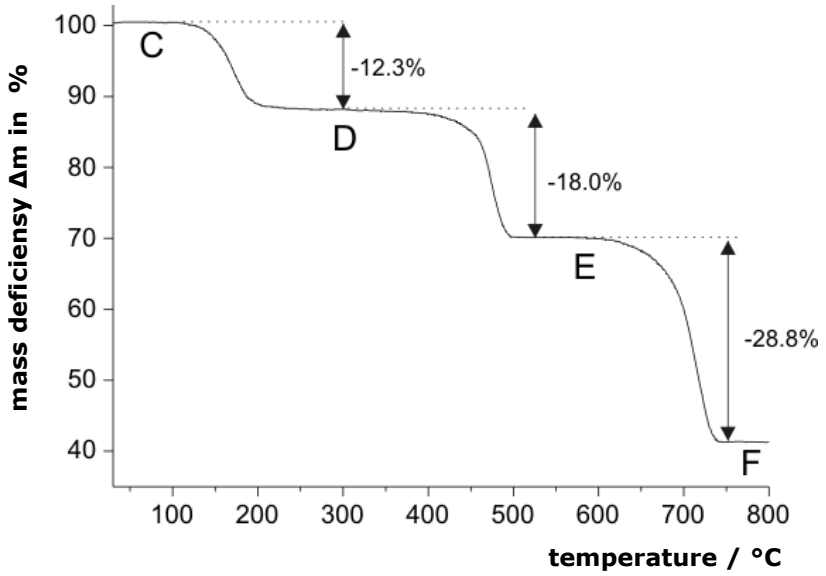


Fig. 1 Plot of thermal gravimetric analysis

d) Which gases are released in the 3 reactions? Which products D, E and F form? Give the equations of the thermal decomposition of C to from D, E and F.

Product E occurs in three different polymorphic modifications.

e) Which are the names of these three modifications?

f) Which of these modifications is the thermodynamically most stable at room temperature?

g) What is the property called when chemical elements occur in different modifications?

To identify E reliably an X-ray powder diffraction photograph has been taken. The analysis of the diffraction pattern results in a trigonal (rhombohedral) unit cell with a = b = 4.984 Å. c = 17.121. $\alpha = \beta = 90°$ and $\gamma = 120°$.

h) Which of the three different polymorphic modifications of E forms in the second reaction of the thermal gravimetric analysis?

i) Calculate the volume of the unit cell!

j) Calculate the density of E assuming that the number of formula units per unit cell is Z =6.

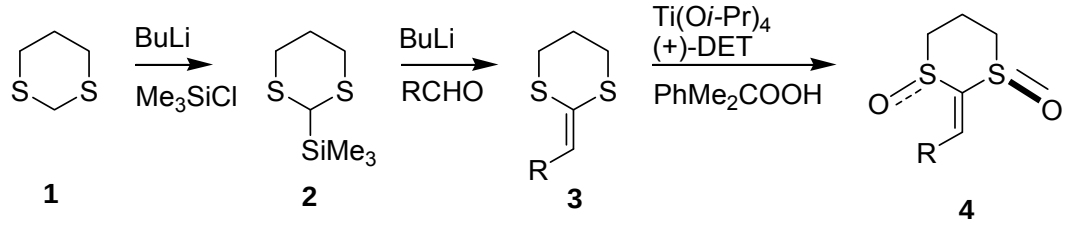
Product F is given into water. In this solution carbon dioxide is fed in. A white precipitate forms which dissolves when the feeding in of carbon dioxide is continued.

k) Which precipiate forms in the beginning? Why does it dissolve when more carbon dioxide is fed in? Give reaction equations.

Problem 2–3 Synthesis of a 1,4-Dicarbonyl Compound

An enantioselective synthesis of the 1,4-dicarbonyl compound **11** is described below. The information about chirality is introduced in the course of the synthesis by an asymmetric kind of Sharpless oxidation of compound **3**. A so called Peterson olefination is used to form the C=C double bond in compound **3.**
The synthesis starts as follows:

Scheme 1



bound lies in front of the paper plane

bound lies behind the paper plane

DET = diethyl tartrate = tartaric acid diethyl ester

*a) Write the IUPAC names of the compounds **1** and **2**.*

*b) Mark all stereogenic centers in compound **4** and and draw the actuelly existent structure of this compound in chair conformation. There are two possibilities of the chair conformation, draw both of them. Which of it is formed preferentially? Account for your answer.*

*c) Which change in the course of synthesis in s**cheme 1** has to be carried out in order to get the other enantiomer of compound **4**?*

*d) Explain why compounds of type **3** can also be named as ketene dithioacetals.*

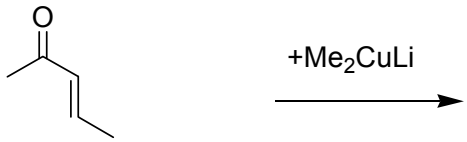
There are several name reactions in organic chemistry which give rise to a double bond.

*e) Indicate the reactants to form compound **3** by a Wittig reaction. Write a blanced reaction equation.*

f) In organic chemistry there exist so called Michael systems. What kind of systems are these? At which position in the molecule are attacks of nucleophiles possible?

*g) You can conduct a 1,4-addition with a Michael system using the compound E-3-pentene-2-on (**5**) with Me_2CuLi (**scheme 2**). Specify the product.*

Scheme 2

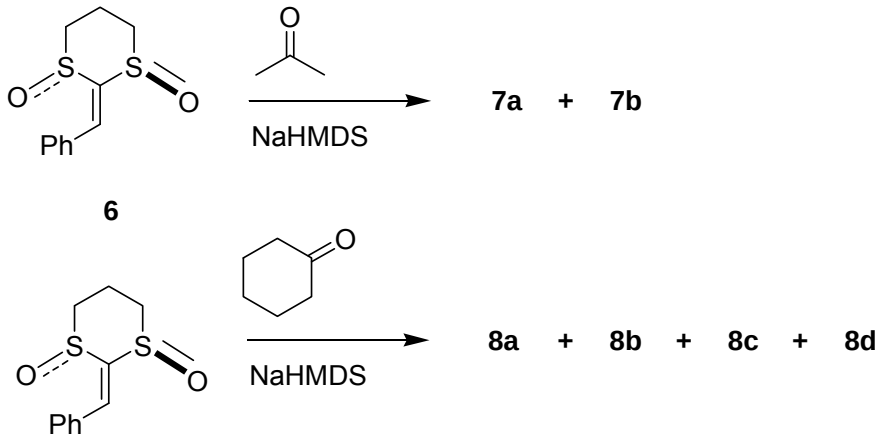


5

The C=C double bond in compound **4** is in conjugation with the S=O double bonds. There is a reactivity analog to that in a Michael system.

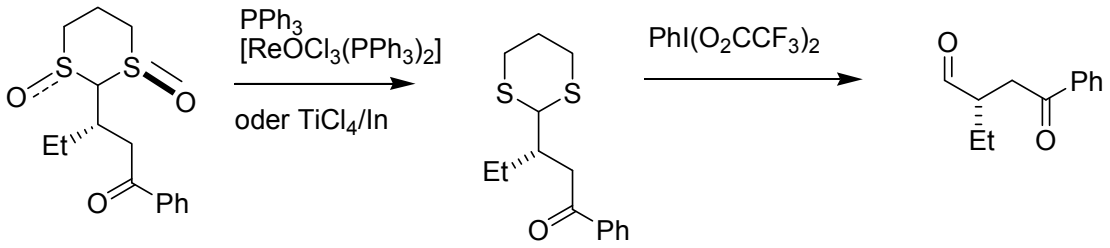
*h) Which of the feasible products **7a. 7b. 8a. 8b. 8c** and **8d** form on the addition of the enolate of acetone and cyclohexanone, respectively, to compound **6** (**scheme 3** after aqueous working-up in each case)? Which is the stereochemical relation of the products to one another?*

Scheme 3



Using the addition products the correspondent 1,4-dicarbonyl compound **11** can be formed by a reduction (e.g. catalysed by PPh_3) and a reaction with $PhI(O_2CCF_3)_2$. This sequence is shown for a special addition product in **scheme 4**.

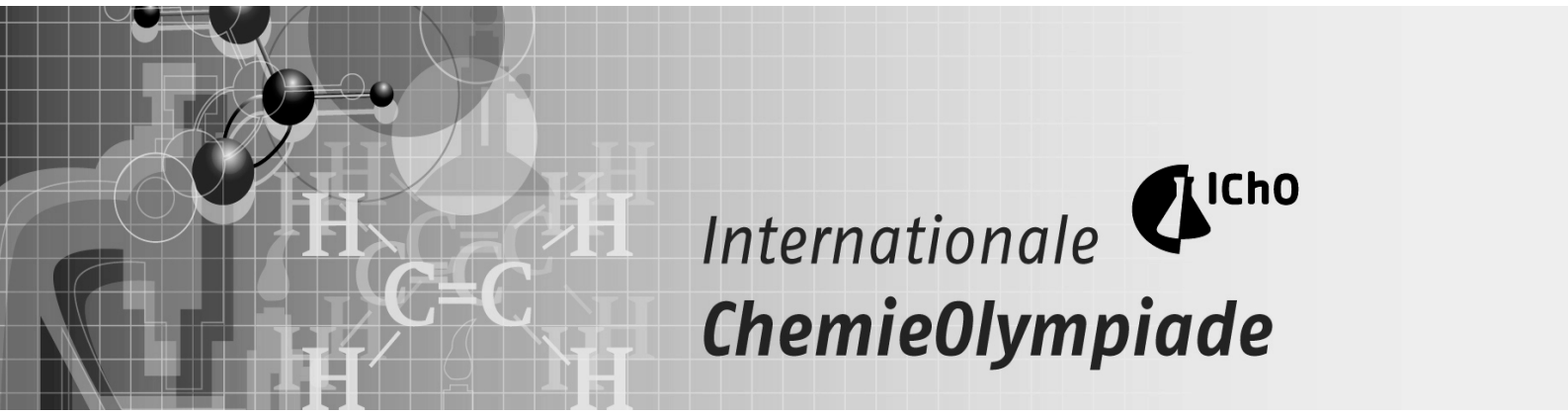
Scheme 4



9 **10** **11**

*i) Which functional groups contains compound **10**?*

*j) Bissulfoxides of type **4** (with R=H) can react well with a C=C double bond in a Diels-Alder reaction. Which products do you expect in the reaction of **4** (with R=H) with*
1) cyclopentadiene 2) butadiene?



Problems Round 3

Test 1 Göttingen 2009: Problems 3-01 to 3-10

Test 2 Göttingen 2009: 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 3-1 Multiple Choice

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

a) Natural resources of antimony consists of the two stable isotopes ^{121}Sb and ^{123}Sb, natural resources of chlorine of the two stable isotopes ^{35}Cl and ^{37}Cl, natural resources of hydrogen of the two stable isotopes ^{1}H and ^{2}H.
How many peaks of the fragment ion $SbHCl^+$ do you expect in a mass spectrum of low resolution?

A)	4	**B)**	5	**C)**	6	**D)**	7	**E)**	8	**F)**	9

b) Which volume of an iron(II)-nitrate solution (c = 0.020 mol/L) contains 0.0080 mol of nitrate ions?

A)	40 cm^3	**B)**	100 cm^3	**C)**	200 cm^3	**D)**	400 cm^3	**E)**	800 cm^3

c) The solutions of two compounds (c = 0.1 mol/L each) are mixed. Mark the cases in which a precipitate forms.

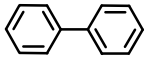
A) HCl / $AgNO_3$	**B)** NaOH / $CuSO_4$	**C)** NH_4NO_3 / K_2SO_4	**D)** $NaNO_3$ / $BaCl_2$	**E)** H_2SO_4 / $Ba(OH)_2$

d) Which of the following solutions (c = 0.1 mol/L) has the highest pH value?

A) sodium acetate	**B)** acetic acid	**C)** ammonium chloride	**D)** sodium sulfate	**E)** hydrochloric acid

e) The ^{1}H NMR spectrum of an unknown compound with the empirical formula $C_3H_5Cl_3$ shows two signals at 2.20 ppm (3H singlet) and 4.02 (2H singlet). Which of the following compounds could be involved?

A) $Cl_3C\text{-}CH_2\text{-}CH_3$	**B)** $ClH_2C\text{-}CCl_2\text{-}CH_3$	**C)** $ClH_2C\text{-}CHCl\text{-}CH_2Cl$	**D)** $ClH_2C\text{-}CH_2\text{-}CHCl_2$	**E)** $Cl_2HC\text{-}CHCl\text{-}CH_3$

f) How many dideuterated biphenyls () exist?

A)	10	**B)**	12	**C)**	14	**D)**	16	**E)**	18

g) Which of the following compounds exhibits the greatest bond length?

A)	H-O	**B)**	H-F	**C)**	H-C	**D)**	H-P	**E)**	H-I

Problem 3-2 Structures and more

The *valence shell electron pair repulsion* (VSEPR) model is a good way to predict the shapes of small molecules without using modern theories and powerful computers.

a) *Using this model predict the structures of the following compounds in the gas phase. Sketch each structure in a way that the spatial constitution can be recognised. State in each case whether or not the structure could diverge from the ideal geometric form.*
Xenon difluoride, xenon tetrafluoride, xenon trioxide, xenon tetraoxide, boron trifluoride, trimethylamine, sulfur tetrafluoride.

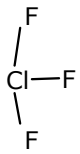
Sketch free electron pairs (if present) at the central atom, too.

b) *Suggest a way of synthesis of the xenon fluorides mentioned in a) and of xenon trioxide.*
Rationalize why the noble gases helium, neon and argon do not form such compounds under similar conditions.

In the amide CH_3-CO-NH_2 the three bonds to nitrogen lie in a plane contrary to the predictions of VSEPR.

c) *Rationalize why these three bonds lie in a plane.*

ClF_3 is a highly reactive liquid which is used (among other things) to produce UF_6 in the processing of nuclear fuels. It has the following T-shaped structure:



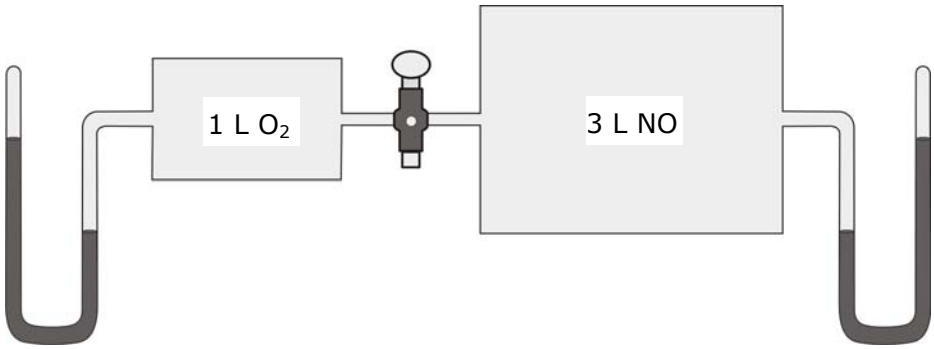
with angle (FClF) = 87°.

d) *Use the VSEPR model to show that the structure of ClF_3 can be expected to be based on a trigonal bipyramid. Draw a diagram to illustrate this and suggest why the bond angle is not 90° as it would be in a regular trigonal bipyramid.*

Problem 3-3 Dimerization

The cock between the two vessels in the figure on the next page is closed. Opening it the two gases mix to form NO_2. A part of this NO_2 will dimerize to N_2O_4.

After the system has reached equilibrium and the initial temperature appears again, the differences in height of the mercury columns in the attached manometers amount to 7.1 cm instead of 10 cm in the beginning.



difference in height in both manometers: 10 cm

Calculate the percentage of NO_2 that has dimerized to N_2O_4.

Assumptions: N_2O_4 is totally gaseous.
The vapor pressure of mercury in the closed ends of the manometers can be neglected, you may assume vacuum there.
The changes in height of the mercury columns have no influence on the total volume, it can be regarded as constant.

1898 L. N. Vauquelin found the later favorite metal of car enthusiasts, the hard, brightly shining chromium. It's an element which is used as a metal pure and in alloys as well as in compounds with different oxidation states.
The following three problems from different areas refer to this element.

Problem 3-4

A) Chromium in razor blades

An alloy of iron and chromium is used to produce razor blades.
A fraction of a razor blade with the mass of 0.1331 g reacts with an excess of diluted sulfuric acid to form among other species Fe^{2+} and Cr^{3+} ions. The resulting solution is titrated with a solution of permanganate at room temperature: Consumption 20.08 cm^3.
Under these conditions Cr^{3+} ions do not react.

10 cm^3 of a solution of oxalic acid (c = 0.0500 mol/L) are acidified with diluted sulfuric acid and then titrated with the same permanganate solution:
Consumption 9.75 cm^3.

a) Write balanced equations of all reactions mentioned.

b) Calculate the mass percentage of iron and chromium in the alloy.

B) Chromium produced by galvanisation

Galvanic coverings of chromium can be generated by electrolysis of a solution of chromic acid.
An electrolysis cell was filled with 100 L of a solution which contained 230 g/L "anhydrous chromic acid" (CrO_3). The electrolysis was performed for 10 hours with a current of 1500 A. The chromium covered objects acted as cathode, the anode did not change. The increase of mass of the cathode amounted to 670 g, additionally gases evolved at the cathode as well as at the anode.

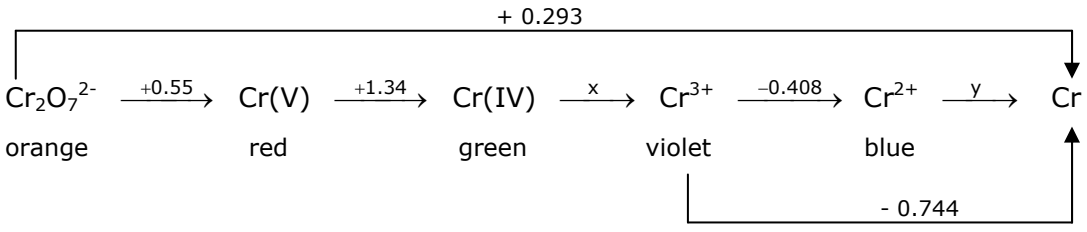
c) Name the gases which evolved at the cathode and at the anode.

d) Calculate the percentage of current efficiency of the electrodeposit of metallic chromium at the cathode.

e) Calculate the volumes of the gases which evolved at the cathode and at the anode at standard conditions (25°C, 1.00 bar).

Problem 3-5 Redox Systems

Chromium (from Greek chroma = colour) got its name from the multicoloured appearance of its compounds and ions. The different redox potentials can be represented clearly in a so-called Latimer diagram:



(All data refer to pH = 0.)

a) Calculate the missing standard potentials x and y.

b) Check by calculation whether Cr(IV) disproportionates into Cr(III) and Cr(VI).

In analytical chemistry the redox system chromium(III)/dichromate, the standard potential of which is $E°(Cr^{3+}|Cr_2O_7^{2-}) = + 1.33$ V, is often used.

c) Write down the reaction equation of this redox system.
Determine the change of voltage of the potential of this redox system if the pH value rises by 1 (T = 298 K). (Assumption: The concentrations of the chromium species do not change.)

A detection reaction of chromium is the reaction of dichromate with hydrogen peroxide. If chromium is present an intensely blue compound forms following the equation

$$Cr_2O_7^{2-} + 4\ H_2O_2 + 2\ H^+ \longrightarrow 2\ CrO_5 + 5\ H_2O\ .$$

d) Indicate what is oxidized and what is reduced in this reaction.
Assign oxidation numbers to all atoms.

Problem 3-6 Equilibria

The equilibrium constant K of the reaction

$$2\ CrO_4^{2-} + 2\ H^+ \rightleftarrows Cr_2O_7^{2-} + H_2O$$

has to be determined.
To do this you can take advantage of the different UV-extinctions of the ions CrO_4^{2-} and $Cr_2O_7^{2-}$ at λ = 345 nm. Using the law of Lambert and Beer you then can determine the concentrations.
In each case a certain amount of potassium dichromate was dissolved in water. The solution was filled up to 1 L and then buffered at the given pH value. Then the extinction was measured in a 1cm cuvette:

pH = 1.0	$n(K_2Cr_2O_7) = 2.00 \cdot 10^{-4}$ mol	E = 0.214
pH = 12.0	$n(K_2Cr_2O_7) = 2.00 \cdot 10^{-4}$ mol	E = 0.736
pH = 5.6	$n(K_2Cr_2O_7) = 4.00 \cdot 10^{-4}$ mol	E = 0.827

a) Calculate the equilibrium constant K.

The equilibrium mentioned above can also be written in another way:

$$Cr_2O_7^{2-} + 2\ OH^- \rightleftarrows 2\ CrO_4^{2-} + H_2O \quad (I)$$

In 4 tests each of the following reagents was added to a solution of potassium dichromate of moderate concentration:

(i) KOH (ii) HCl (iii) $BaCl_2$ (iv) H_2O

The solubility product of $BaCrO_4$ amounts to $1.2 \cdot 10^{-10}$. $BaCr_2O_7$ is very soluble in water.

b) In which direction does the equilibrium shift on addition of each reagent?

Problem 3-7 Equilibria in the Blood System

The transport of gases pertains to the most important functions of the human blood system. Thereby the cells are provided with oxygen, the emerging carbon dioxide is transported to the lungs where the gas exchange with the inhaled air takes place. The content of carbon dioxide affects the pH value of the blood significantly.

In text books you often find two values for the pH of blood in a human body, 7.40 and 7.37.

a) Assign these values to oxygen poor and oxygen rich blood, respectively.

The following equilibria are responsible for buffering the blood:

(1) $CO_{2(g)} \rightleftharpoons CO_{2\,(aq)}$ *

(2) $CO_{2\,(aq)} + H_2O \rightleftharpoons H_2CO_3$ $K_2 = c(H_2CO_3)/c(CO_{2\,(aq)}) = 4.68 \cdot 10^{-3}$

(3) $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$ $pK_a = 3.77$

As the adjustment of equilibrium (2) is kinetically retarded and proceeds far slower than (1) and (3), dissolved CO_2 is directly converted in the cells to form HCO_3^- by the enzyme carboanhydrase:

(4) $CO_{2(aq)} + 2\,H_2O \rightleftharpoons H_3O^+ + HCO_3^-$ K_4

b) Determine K_4 by calculation.

In blood with the pH value of 7.40 $c(HCO_3^-) = 24.0$ mmol/L was determined.

c) Calculate $c(CO_{2(aq)})$ in the equilibrium in this blood.
(If you could not solve b) take here and later on $K_4 = 8.7 \cdot 10^{-7}$)

d) Calculate the mean partial pressure of CO_2 which prevails in the lungs.
(If you could not solve c) take here and later on $c(CO_{2(aq)})$ = 2 mmol/L in blood with pH = 7.40)

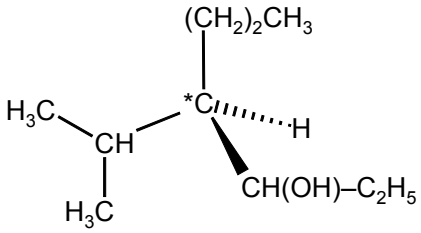
A human being exhales 274 mL CO_2 (37.0 °C, 1013 mbar) per minute. The blood flow through the lungs is 5.40 L/min at an average.

e) Which concentrations of CO_2 and HCO_3^- are existent in carbon dioxide rich blood?
(If you could not solve the previous problems take the given values as alternative.)

* The Henry law is ruling with $K_H = 3.40 \cdot 10^{-2}$ mol/(L·atm)

Problem 3-8 R/S-Nomenclature

To describe the absolute configuration at stereogenic centers (also called chirality centers) in molecules unambiguously, the R/S-nomenclature following Cahn, Ingold and Prelog (CIP) was introduced. The method used employs sequence rules to assign priorities to atoms or groups attached to the stereogenic center (in this case a C atom (*)).
The following compound shows an R configuration:



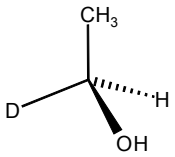
bond lies behind the paper plane

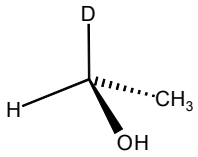
bond lies in front of it

a) Assign priorities to the four different groups (atoms). Rationalize the sequence by indicating the atomic number of the first and the second atoms away from the stereogenic center.

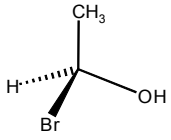
Given three pairs of stereoisomers:

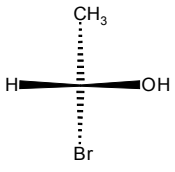
i)



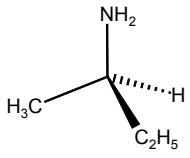


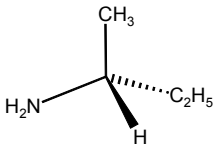
ii)





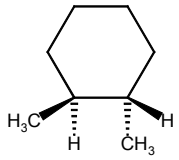
iii)





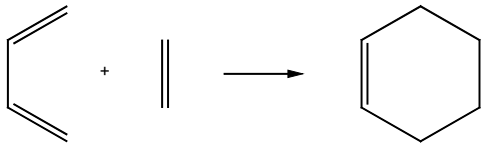
b) Assign R or S configuration to all compounds and decide which of the pairs show identical molecules, which enantiomers.

c) Give the absolute configuration (R/S) and the name of the following compound:



Problem 3-9 Diels-Alder-Reaction

A Diels-Alder reaction follows the pattern below:



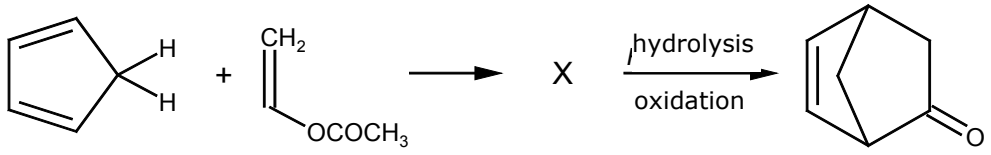
This reaction is also called (4+2) cycloaddition.

a) Rationalize this name indicating the π electrons engaged in the reaction mechanism. Explain why this reaction is exothermic.

Electron rich dienes and preferably electron-deficient dienophiles increase the reactivity of a Diels-Alder reaction.

b) Assign the following groups either to dienes or to dienophiles in a way that the reactivity is increased.
Groups: $-CH_3$, –CN, -CHO, $-OCH_3$.

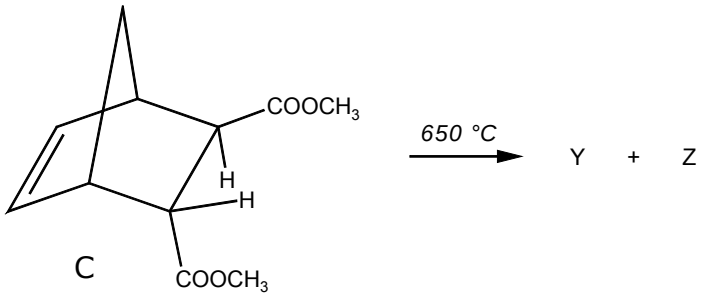
c) Determine the missing compound X in the following reaction path



A B

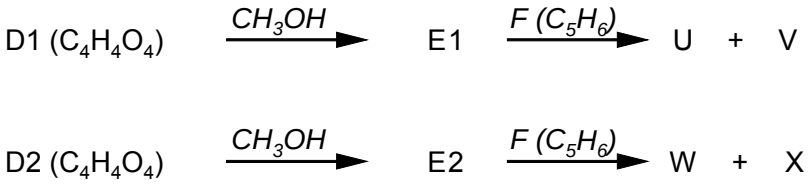
d) Give the names of the compounds A and B.

Compound C is heated up to 650°C. Two new compounds, Y and Z form.



e) Draw the structural formulas of Y and Z.

The compounds D1 and D2 are E/Z isomers with the empirical formula $C_4H_4O_4$. They react with methanol (in the ratio of amount n(D1/D2) : n(methanol) = 1:2) to form the compounds E1 and E2, respectively. E1 and E2 react with the cyclic compound F (empirical formula C_5H_6) to form different stereoisomers:



f) Determine the structures of D1, D2, E1 and E2 as well as the structure of F. Sketch the structures of U, V, W and X in a way that the spatial constitution can be recognised.

Problem 3-10 Addition to Alkenes

Propene und hydrogen chloride (HCl) react to form 2-chloropropane exclusively but not 1-chloropropane.

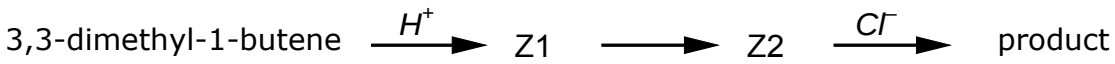
a) Show the mechanism of this reaction and account for the exclusive formation of 2-chloropropane.

b) Draw a qualitative energy diagram (y-axis: energy and x-axis: reaction progress) which shows the different courses of energy from A (propene) to both theoretically possible carbocation intermediates to the possible products.

1-Butene reacts with hydrogen bromide (HBr) to from a racemic mixture.

c) Show the mechanism of the formation of the racemate (the formation of two enantiomers). Write down full names (R/S nomenclature) of the enantiomers.

The addition of hydrogen chloride (HCl) to 3,3-dimethyl-1-butene leads to 2-chloro-2,3-dimethylbutane (product). During this process two intermediates are formed:



d) Draw the structural formulas of the organic reactant, the product and the two intermediates Z1 and Z2. Which common rule follows the formation of intermediate Z2?

Third Round Test 2

Problem 3-11 Multiple Choice

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

a) Which of the following compounds can be reduced by $NaBH_4$ to form an alcohol?

A) ketones	**B)** aldehydes	**C)** carboxylic acids	**D)** esters	**E)** ethers

b) Which value is a measure of the tendency of bonded atoms to attract electrons?

A) ionisation enthalpy
B) electron affinity
C) electronegativity
D) redox potential
E) ionisation energy

c) Which of the following elements has the lowest first ionisation energy?

A) Na	**B)** Al	**C)** Si	**D)** P	**E)** S

d) Which of the following compound pairs are isoelectric to each other?

A) CH_4 / CH_3F	**B)** H_2O / OF_2	**C)** CO / N_2	**D)** HCl / HBr	**E)** CO_2 / N_2O

e) Which of the following oxides react with water to form HNO_3 and as the case may be to other compounds?

A) N_2O	**B)** NO	**C)** N_2O_3	**D)** NO_2	**E)** N_2O_5

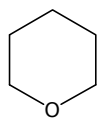
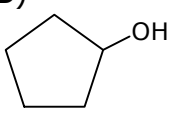
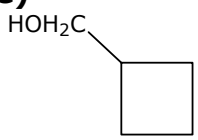
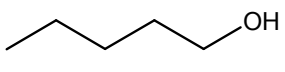
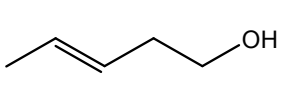
f) To which family of compounds do the products (each for itself) of the reaction of acetic acid anhydride and ethanol belong?

A) alkohols	**B)** ketons	**C)** aldehydes	**D)** esters	**E)** carboxylic acids

g) Which compound **does not** dissolve better in diluted acid than in water?

A) $CaSO_4$	**B)** $BaCO_3$	**C)** Ag_3PO_4	**D)** Mg	**E)** $NaCH_3COO$

h) The following 5 compounds possess 5 carbon atoms each. Which of them has the lowest boiling point?

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

Problem 3-12 The Search of an Unknown Element

In 1886 C. Winkler, a German chemist, was experimenting with the mineral argyrodite. He found out that argyrodite contained silver (Ag^+), sulfur (S^{2-}) and an unknown element X. After weeks of experimenting it became clear that **X** had all the properties of an element, the existence of which had been predicted by Mendelejeff 15 years earlier. 1871 Mendelejeff indicated the oxidation number +4.

1.00 g of argyrodite was heated in air until SO_2 stopped emitting and a solid residue **A** remained. SO_2 was passed through a solution of $Ba(OH)_2$, the residue **A** dissolved partly in nitric acid with a compound **B** as residue.
To determinate the amount of Ag, 100.0 cm^3 of a solution of potassium bromide (c = 0.100 mol/L) was added. By back titration an excess of 29.1 mL of KBr solution was found.
In the solution of $Ba(OH)_2$ 1.156 g of a precipitate was formed.
Compound **B**, insoluble in nitric acid, was found to be an amphoteric oxide, which was soluble in both, concentrated HCl and NaOH solutions, to form colourless solutions.

a) Calculate the masses and amounts of silver and sulfur in 1 g of argyrodite.

*b) Determine the element **X** and give the formula of argyrodite.*

*c) Write the equations of the reactions of **A** with conc. solution of HCl and conc. solution of NaOH, respectively.*

Problem 3-13 Substances and Reactions

The following reaction which is obviously a redox reaction is started by heating:

$$(NH_4)_2[PtCl_6] \longrightarrow Pt + N_2 + NH_4Cl + HCl$$

a) Specify the oxidizing agent.

b) Specify the reducing agent.

c) Balance the equation.

d) Write down the name of the complex.

Write balanced equations of the following reactions.

(Use appropriate ionic and molecular formulas for the reactants. All reactions occur in aqueous solution unless otherwise indicated.)

e) 1 mol of ammonia is bubbled into 1 L of sulfuric acid (c = 1 mol/L).

f) An excess of sodium hydroxide solution is added to a solution of nickel(II)-chloride.

g) Solutions of potassium permanganate and hydrogen peroxide are mixed in an acid solution.

h) Chlorine water is added to a solution of sodium iodide.

i) Acetic acid is added drop wise to solid sodium hydrogen carbonate.

j) An excess of concentrated ammonia is added to a solution of zinc nitrate.

k) Ethanol is heated with concentrated sulfuric acid.

Problem 3-14 Kinetics[1]

The alkaline hydrolysis of ethyl ethanoat in aqueous solution is of first order in both, ester and OH^-, and so second order overall

$$\frac{dc(OH^-)}{dt} = - k_2 \cdot c(Ester) \cdot c(OH^-)$$

In an experiment to verify this rate law a reaction mixture was prepared in which the initial concentrations of ester and OH^- were 0.025 mol/L, each.
After the reaction was initiated, samples of 10 cm^3 of the reaction mixture were withdrawn at intervals and mixed with 10 cm^3 of HCl (c = 0,050 mol/L). This amount of acid is sufficient to neutralize any unused OH^-, thus quenching the reaction. The remaining acid was then titrated with NaOH(aq) (c = 0,020 mol/L) to the end point in the usual way. This method gave the following data:

t/s	120	300	600	900	1200	1500	1800
volume of titre $V_{titr.}(NaOH)/cm^3$	13,4	14,3	15,6	16,4	17,4	18,1	18,5

Since the initial concentrations of ester and OH^- ions are equal, the rate law can be simplified to $\frac{dc(OH^-)}{dt} t = - k_2 \cdot c(OH^-)^2$

It therefore follows that a plot of $1/c(OH^-)$ against t should give a straight line.

a) Work out the concentration of OH^- in each sample. Fill in the results in the table on the answer sheet.

[1] taken from Keeler, Wothers: Chemical Structure and Reactivity, Oxford 2008

b) *Plot 1/c(OH^-) as a function of t.*
(This is real data, so some scatter is to be expected.)

c) *Use the plot to estimate the second order rate constant.*

d) *Test the data to see if they fit a first order rate law by using a corresponding plot.*

Problem 3-15 Titrations with EDTA

A solution containing Mn^{2+}, Mg^{2+} and Zn^{2+} ions was analyzed as follows:
A 25.00 mL sample was treated with 0.25 g of $[NH_3(OH)]Cl$, a reducing agent, 10 mL of ammonia buffer solution (pH = 10) and a few drops of eriochrom black T indicator and then diluted up to 100.00 mL.
This solution was warmed to 40 °C and titrated with 39.98 mL of EDTA solution (c = 0.04500 mol/L) to the blue end-point.
Then 2.5 g of NaF were added to displace Mg^{2+} from the EDTA complex. The liberated EDTA required 10.26 mL of Mn^{2+} solution (c = 0.02065 mol/L) for complete titration.
After this second end-point was reached 5 mL of 15 % (w/w) aqueous KCN solution were added to displace Zn^{2+} from the complex. This time 15.47 mL of the same Mn^{2+} solution were needed to reach the end-point.

a) *Which amount of metal ions can be complexed by 1 mol of EDTA?*

b) *Calculate the mass of Mn^{2+}, Mg^{2+} and Zn^{2+} ions respectively in the 25 mL sample of the unknown.*

c) *Which part plays ammonium chloride $[H_3N(OH)]Cl$ in this procedure?*

d) *Draw the structural formula of the anion of EDTA (ethylenediamine tetraacetic acid) and mark the positions which are responsible for the complexation.*

Problem 3-16 Thermodynamics

a) *Fill in the blanks (i) to (v) on the answer sheet all that apply from the following*

equilibrium constant	K
change of entropy	ΔS
change of enthalpy	ΔH

change of free energy ΔG

(i) ( ) is strongly dependant on temperature.

(ii) ( ) is closely related to bond strength.

(iii) ( ) is related to the quantity of reactants and products of a reaction.

(iv) ( ) is a measure of spontaneity of a reaction.

(v) ( ) is a measure of heat released or absorbed in a reaction.

The following equilibrium exists in the vapor phase dissociation of molecular addition compounds of a donor molecule D and the boron compound BMe_3 (Me = CH_3):

$$DBMe_3(g) \rightleftharpoons D(g) + BMe_3(g).$$

Dissociation constants K_p and values of ΔS of the following addition compounds at 100°C are:

Adduct 1	Me_3NBMe_3	$K_{p1} = 0.472$	$\Delta S = 191.3\ JK^{-1}mol^{-1}$
Adduct 2	Me_3PBMe_3	$K_{p2} = 0.128$	$\Delta S = 167.6\ JK^{-1}mol^{-1}$

b) Calculate ΔG of the dissociation reactions of these adducts at 100°C. Which compound is more stable regarding dissociation?

c) Calculate the standard enthalpy changes of dissociation of these adducts and state which of the bonds N-B or P-B is the stronger one.

The next problem deals with the reaction

$$2\ Ni(l) + O_2(g) \rightleftharpoons 2\ NiO(s) \text{ at } 1627°C.$$

There is a mixture of Ni(l) and NiO(s).

d) Can this reaction proceed spontaneously in the forward direction if the partial pressure of oxygen is below 150 Pa?

$\Delta G°_f(NiO)$ bei 1627°C = - 72.1 kJ/mol

(Remember that standard pressure amounts to $p_0 = 1.000 \cdot 10^5$ Pa)

Problem 3-17

Each of the following statements reflects an observation concerning acids.

(i) In aqueous solution, the strengths of the oxyacids of chlorine, HOCl, HOClO, $HOClO_2$ and $HOClO_3$, depend on the number of oxygen atoms not bonded to hydrogen.

(ii) Successive ionisation constants of polyprotic acids decrease greatly, approximately by a factor of about 10^{-5}.

(iii) HCl, HNO_3 and H_2SO_4 appear to have the same strength in water but a different strength in glacial acetic acid (pure acetic acid).

a) Use atomic and/or molecular theories to explain each of the statements.

A solution of a diprotic acid H_2A ($K_{a1} = 1.5 \cdot 10^{-4}$, $K_{a2} = 8.0 \cdot 10^{-7}$) containing 0.010 moles per 100 mL is titrated with a very concentrated solution of KOH so that the volume can be assumed to remain constant during the titration.

b) Sketch the titration curve expected for the titration of 100 mL of this solution. (x-coordinate: amount of KOH in moles, y-coordinate: pH).
To complete the sketch determine at least the pH values at the equivalence- and the half-equivalence points, the pH value of the solution in the beginning and after adding 0.025 moles of KOH.

Problem 3-18 Mass Spectrometry

An alkane was examined in a mass spectrometer.
In the mass spectrum the following data (amongst others) were noted:

i) an intensive peak at m/z = 72
ii) a smaller peak at m/z = 57
iii) a very tall peak at m/z = 43 (base peak)
iv) yet another taller peak at m/z = 29.

a) What is the meaning of "m/z" in a mass spectrum?

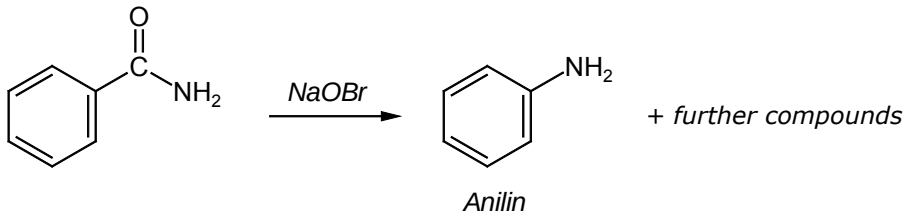
b) Which alkane was analyzed?

c) Interpret the fragments at m/z = 72, 57, 43 und 29.

Another very small peak was found at m/z = 73.

d) Interpret this peak at m/z = 73.

Benzamide reacts under the influence of sodium hypobromite ($NaOH/Br_2$) to give aniline:



It was analyzed whether the formation of aniline under these conditions is based on an **intermolecular** mechanism or an **intramolecular** one. To do this the following mixture of reactants was employed):

After the reaction a mass spectrum of the raw product was made:
It showed only one peak at m/z = 94. Thus an **intramolecular** mechanism was deduced.

e) Rationalize why the occurrance of a sole peak at m/z = 94 in the mass spectrum gives rise to such a statement.

Problem 3-19 Aromatic Substitutions

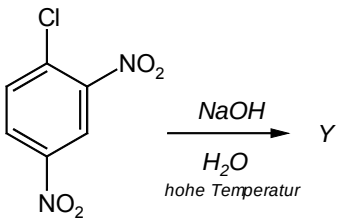
Several compounds react with benzene in an electrophilic substitution to form different products.

i) Benzene + halide (Br_2) ⟶
ii) Benzene + nitric acid ⟶
iii) Benzene + conc. sulfuric acid ⟶
iv) Benzene + alkyl halide (C_2H_5Cl) ⟶
v) Benzene + acyl halide (CH_3COCl) ⟶

a) Complete the table on the answer sheet by writing down for each reaction

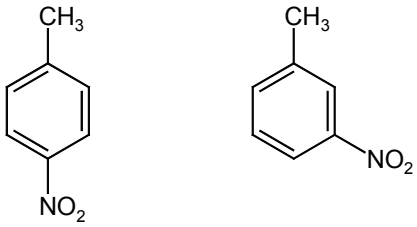
- *the reacting electrophile*
- *a potential catalyst*
- *the product.*

b) Which are the products X and Y formed by the following reactions?



c) What kind of reaction is taking place? Explain why this reaction is possible.

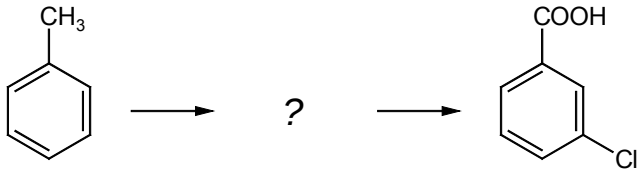
Another electrophilic substitution shall be carried out with the two compounds A and B.



A *B*

d) Show which positions at the aromatic ring are favoured and account for your decision.

Starting with toluene the following substituted benzoic acid shall be synthesised.

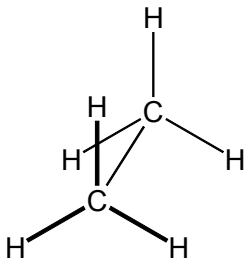


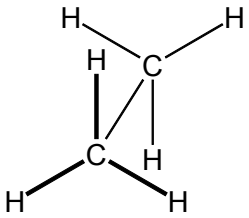
e) Show the path of synthesis and the reagents you need (two steps at most).

Problem 3-20 Conformers

Different arrangements of atoms that result from bond rotation (e.g. round a C-C bond) are called conformations, and molecules that have different arrangements are called conformers (conformational isomers). They may have different energy.

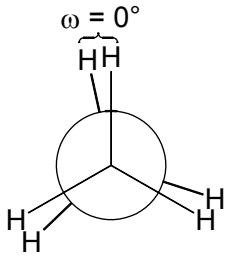
In an ethane molecule there are two special positions of the two methyl groups, staggered and eclipsed.

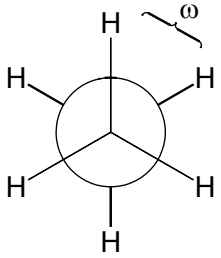




ethane: eclipsed (syn) structure *ethane: staggered (anti) structure*

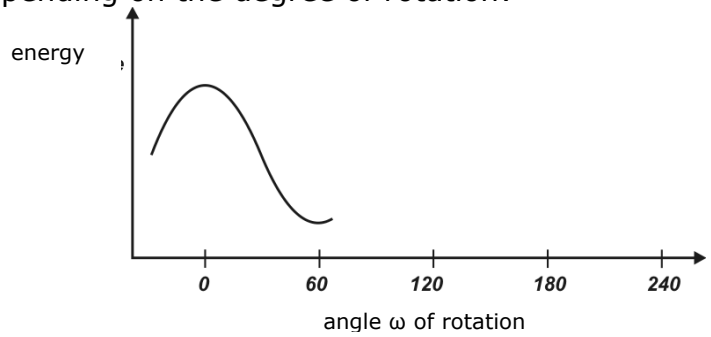
The Newman projection views the carbon-carbon bond directly end-on and represents the two carbon atoms by a circle:





eclipsed *staggered*

A graph of potential energy versus bond rotation shows the differences in torsional strain depending on the degree of rotation:



a) Complete the energy diagram up to the angle of ω = 180°.

b) Interpret the changes of torsional strain from ω = 0° to ω = 180°.

Cyclohexane exists in different conformer structures. There are two structures of the same energy in chair geometry and one structure called boat conformation having a different energy. One conformer of chair geometry can flip to the other one (ring-flip) via boat conformation.

c) Draw these three conformers and the way of a ring-flip.

d) Decide which conformer has the higher energy and account for your decision.

e) Draw the spatial structure of cis-1,4-dimethylcyclohexane in one of the chair conformations. Indicate whether the methyl groups at C1 and C4, respectively, are in axial (a-position) or equatorial (e-position).

f) Indicate how the symmetry of cis-1,4-dimethylcyclohexane and the positions of the methyl groups (a- and e-position, respectively) at C1 and C4 change when the chair conformation interconverts (ring-flip).

There are two chair conformations of 1-methylcyclohexane. In one of them the methyl group is in a-position in the other one in e-position. The distribution of these conformers is asymmetrical, one of them exists in an excess of 90 %.

g) Which of these two possible conformers – CH_3 group in a-position or in e-position – prevails? Account for your decision using a Newman projection.

Fourth Round (theoretical problems)

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

Problem 4-1 Dating Rocks

The radioactive decay of ^{238}uranium is used to determine the age of minerals. This decay leads finally to ^{206}lead with a half-life of $t_{1/2} = 4.511 \cdot 10^9$ a.

The analysis of a mineral gave the following ratios of amounts:

$$\frac{n(^{206}Pb)}{n(^{238}U)} = 0.1224 \quad \text{and} \quad \frac{n(^{206}Pb)}{n(^{204}Pb)} = 75.41.$$

As ^{204}Pb was detected, too, you have to assume, that the mineral contained natural lead from the beginning.

Ratio of isotopes in natural lead:
$n(^{204}Pb) : n(^{206}Pb) : n(^{207}Pb) : n(^{208}Pb) = 1.48\% : 23.6\% : 22.6\% : 52.3\%$

a) Write down how the atomic mass and the atomic number of an element change at an α-decay and a β-decay, respectively.

b) Determine the age of the mineral.

Problem 4-2 Kinetics

Saccharose undergoes hydrolysis in water to form two monosaccharides. The reaction is of second order. It is catalized by hydronium ions.
Measuring the reaction rate it was found to be 4.1 times higher at 35°C than at 25°C.

a) Calculate the activation energy.

Ethanal decomposes in a second-order reaction.
The rate constant has been measured as a function of temperature as follows:

T / K	700	730	760	790	810	840	910	1000
k /[(mol/L)$^{-1}$·s^{-1}]	0.011	0.035	0.105	0.343	0.789	2.17	20.0	145

b) Make an Arrhenius plot of this data and hence determine a value for the activation energy and the pre-exponential factor. State the units of each quantity.

The experimentally determined rate law of the reaction $H_2 + Br_2 \longrightarrow 2\ HBr$ is quite complex:

$$\frac{d[HBr]}{dt} = \frac{k_a \cdot [H_2] \cdot [Br_2]^{3/2}}{[Br_2] + k_b \cdot [HBr]} \ .$$

This rate law can be explained by a chain reaction involving five elementary steps:

1. $Br_2 \xrightarrow{k_1} 2\ Br\cdot$
2. $Br\cdot + H_2 \xrightarrow{k_2} HBr + H\cdot$
3. $H\cdot + Br_2 \xrightarrow{k_3} HBr + Br\cdot$
4. $H\cdot + HBr \xrightarrow{k_4} Br\cdot + H_2$
5. $Br + Br\cdot \xrightarrow{k_5} Br_2$

c) List each reaction as initiation (S), propagation (P), inhibition (I) or termination (T).

To simplify the problem we will look at the rate of reaction in an early stage of the process when the concentration of HBr is low.[2]

d) State how the rate equation is simplified by this approach. Which of the steps 1) to 5) of the reaction mechanism can be ignored under this condition?

Assume that the intermediate radicals $H^{\cdot}$ and $Br^{\cdot}$ are in the steady state.

e) Write down the equations resulting as a consequence of this assumption. Derive the rate law found in d).

Problem 4-3 Thermodynamics

a) Calculate the thermodynamic properties (reaction enthalpy, entropy, Gibbs energy and the equilibrium constant K_p) of the formation of ammonia according to the Haber-Bosch Process under standard conditions.

[2] following Keeler, Wothers: Chemical Structure and Reactivity, Oxford 2008, page 436

Under standard temperature this reaction proceeds scarcely because of the high activation energy (≈ 230 kJ·mol^{-1}). Thus higher temperature and higher pressure are chosen in the technical process. At a higher temperature and a pressure of 200 bar e.g. the amount of ammonia in an equilibrium mixture is 18 % of volume.
Assume in b) and c) that all gases behave ideally and ΔH and ΔS are constant.

b) Calculate K_p under these conditions.

c) Calculate the temperature at which this yield was obtained.

Compared to the temperature calculated in c) the actual temperature which leads to such a result (18 % of vol. NH_3) lies lower.

d) Give reasons for this deviation.

e) Calculate the bond dissociation enthalpy $\Delta_bH°$ of an N-H bond in NH_3.

f) Estimate the standard enthalpy of formation $\Delta_fH°$ of the radical $\cdot NH_2$ by calculation.
Here take $\Delta_bH°(H\text{-}NH_2)$ = 380 kJ·mol^{-1} independently of the result in e).

Data:
Standard pressure p^0 = 1.000 bar = 1.000·10^5 Pa

	$H_2(g)$	$N_2(g)$	$NH_3(g)$
$\Delta_fH°$ in kJ·mol^{-1}	0	0	- 45,9
$\Delta_fS°$ in J·mol^{-1}·K^{-1}	130.7	191.6	192.8

	N ≡ N	N = N	N - N	H - H
bond dissociation enthalpy $\Delta_bH°$ in kJ·mol^{-1}	945	466	159	436

Problem 4-4 Electrochemistry

Concider the following electrochemical cell:

Pt (s)|H_2(g, p = 1 bar)|H_2SO_4(aq))|| H_2SO_4(aq)|$PbSO_4$(s)|Pb(s).
c (H_2SO_4) = 10^{-2} mol/L

a) Determine the concentration of the SO_4^{2-} ions in the sulfuric acid and the pH value of the solution. Be aware of $pK_{a2}(H_2SO_4)$!

b) Write down the conventional cell reactions.
(Regardless of the direction of the actual process, the half cell reactions are always specified as reductions.)

The potential of the cell mentioned above is – 0.188 V at 298.15 K.
Assume in c) and d) $c(SO_4^{2-}) = 5 \cdot 10^{-3}$ mol/L and $c(H_3O^+) = 15 \cdot 10^{-3}$ mol/L regardless of your result in a).

c) Calculate the solubility product of $PbSO_4$.

d) By how much would the potential of the cell change if the pressure of hydrogen was halved?

Gold does not dissolve (better: does not react) in nitric acid but does in aqua regia, a 3:1 mixture of concentrated hydrochloric acid and concentrated nitric acid, which was developed by alchemists to „dissolve" gold.
In a reaction with aqua regia the complex $[AuCl_4]^-$ forms.

e) Using the given standard potentials calculate the complex formation constant of $[AuCl_4]^-$, $K_b = \frac{c([AuCl_4]^-)/c_0}{(c(Au^{3+})/c_0)\cdot(c(Cl^-)/c_0))^4}$.

Data: $pK_{a2}(H_2SO_4) = pK_a(HSO_4^-) = 1.92$

$E°(Pb^{2+}/Pb) = - 0.126$ V
$E°(Au^{3+}/Au) = + 1.50$ V
$E°([AuCl_4]^- / Au + 4\ Cl^-) = + 1.00$ V

Problem 4-5 Oxygen on Collision Course

In an ideal gas, the collision frequency with a surface is given by

$$Z_{surface} = \frac{p}{\sqrt{2\pi \cdot m \cdot k_b \cdot T}}$$

where p = pressure and T = temperature of the gas in K, m = mass of the gas particles, $k_b = 1.3806 \cdot 10^{-23}$ JK^{-1} Boltzmann's constant.

a) Determine the unit of $Z_{surface}$ using SI units in the formula given above.

In cases of emergency patients are given artificial respiration using oxygen.

Human lungs have a surface area of approximately 75 m^2. The average human breath takes around 5 s, the mean temperature in a hospital is 20°C. You should assume that the pressure in the lungs remains constant at atmospheric pressure (1,013 bar) while breathing. Actually it changes by less than 1 % during each respiratory cycle.

b) Estimate the number of collisions of oxygen molecules with the surface of the lungs during a single breath.

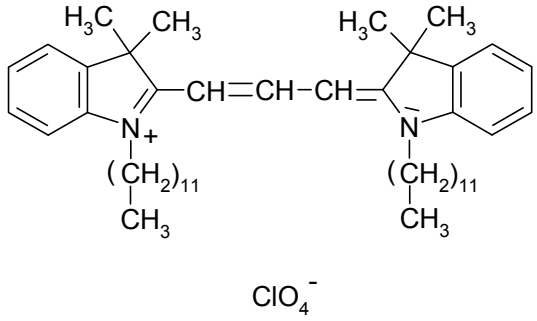
A human being exhales about 270 mL of CO_2 (37°C, 1.013 bar).

c) How many collisions of oxygen lead to an exchange with CO_2? Which ratio of collisions was „successful"?
Assume the number of oxygen collision to be $Z = 9 \cdot 10^{31}$, regardless of your result in b).

Problem 4-6 Observing Single Molecules

The detection of single molecules can be demonstrated with the carbocyanine dye (F) the structure of which is shown below. In this experiment dye molecules are spread on a sample surface and localized according to their fluorescence signals.

F:



The surface density of the molecules have to be sufficiently low if you want to observe them as individual fluorescent spots under a microscope. No more than 10 molecules per μm^2 on a sample surface is a good value.

10 µL of a solution of **F** in methanol were deposited on a very clean glass cover slide. The drop covered a circular area having a diameter of 4 nm.

a) Calculate the molar concentration of the solution necessary to obtain the value of 10 molecules per μm^2.
(You may assume that the distribution of the dye molecules on the sample surface after evaporation of the solvent was homogeneous on the whole wetted area.)

The sample was illuminated with the 543.5 nm line of a green He-Ne laser. The excitation power was adjusted so that the illuminated area (100 nm in diameter) is hit by $3 \cdot 10^{10}$ photons per second.

b) Calculate the excitation power that has been used.

The absorption cross section is the effective area of the molecule that captures all incoming photons under low illuminating conditions (like an idealized solar cell that would capture all light photons hitting its surface).

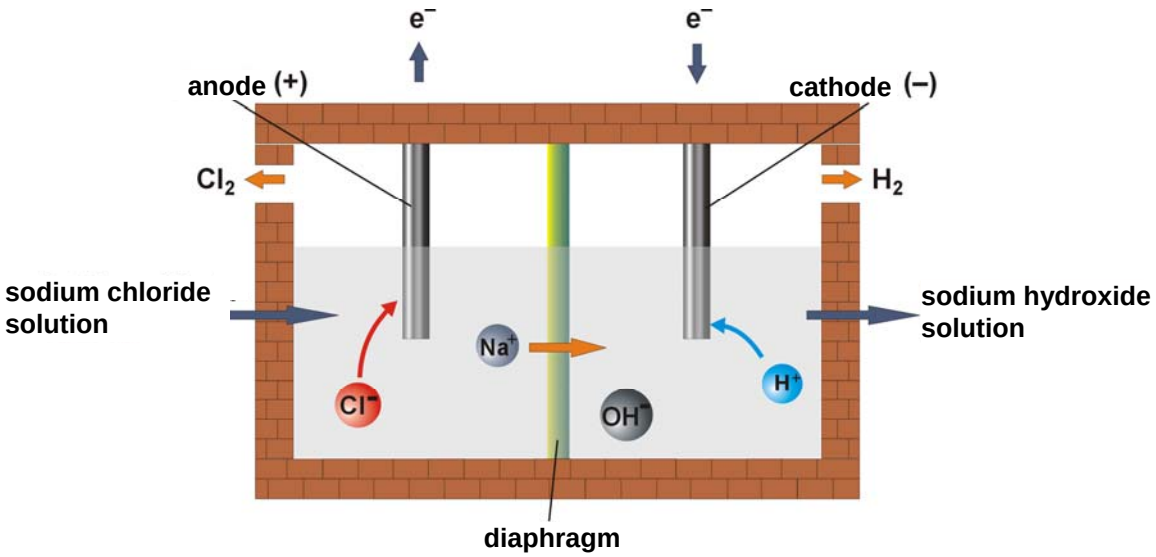
c) Calculate the area one dye molecule occupies statistically.

An illuminated dye molecule absorbs $2.3 \cdot 10^5$ photons/s under the described conditions.

d) Calculate the absorption cross section of one molecule of F.

Problem 4-7 About Chlorine

The picture shows a schematic representation of the diaphragm process to produce chlorine, hydrogen and sodium hydroxide solution from a solution of sodium chloride (chlorine-alkali electrolysis).



In this process it is of importance that the two reaction sites are separated from each other. Otherwise a further product ***A*** would form by a reaction of chlorine

and sodium hydroxide solution besides the mixture of chlorine and hydrogen (which will react at daylight to form hydrogen chloride).

*a) Write down the reaction equation for the formation of **A**.*

In other cases compound **A** is produced systematically. You can buy it as a 1.5 % aqueous solution to use as bleach. Sales promotion promises: „...decomposes to form sodium chloride and oxygen and thus is no hazard to the environment...". Is this advertisement correct?

*b) Write down the reaction equation of the decomposition of an aqueous solution of **A** which is propagated by the consumer advertisement.*

Concentrated aqueous solutions of **A** often turn yellow.

c) Which compound is responsible for the yellow colour? Write down the reaction equation for the formation of this compound.

If an aqueous (better even alkaline) solution of compound **A** is heated (e.g. as bleach in a hot wash program) besides sodium chloride a compound **B** forms which is hazardous to the environment.

*d) Write down the reaction equation for the formation of **B**.*

If a barium nitrate solution is added to an aqueous solution of **B** a white precipitate separates, which on heating forms barium chloride and a white solid **D**.

*e) Write down the reaction equation for the formation of **C**.*

*f) Write down the reaction equation for the formation of **D**.*

Elemental chlorine reacts with nearly all elements exept noble gases, nitrogen and oxygen.
If chlorine is introduced into molten sulfur at a temperature of 240°C e.g. a binary compound **E** forms which turns with more chlorine slowly (in the presence of Fe(III) or iodine quickly) to a red coloured liquid **F**. This binary compound **F** contains 68,9 percent of mass of chlorine. It always is in equilibrium with a small amount of compound **E** and chlorine.

*g) Write down the reaction equation for the formation of **E**.*

*h) Write down the equation of the equilibrium between **E** and **F**.*

The oxidation of compound **F** leads to an oxygen poor compound **G** and an oxygen rich compound **H**.

*i) Write down the reaction equation for the formation of **G** and **H** starting with **F**.*

The compounds **G** and **H**, which are liquids at standard conditions, react vehemently with water. Hence compound **G** is perfectly suited to remove marginal hints of water from chemical equipment. You simply reflux **G**, the gaseous products of the reaction with water discharge. The amount of **G** which did not react can be removed by heating under vacuum.

*j) Write down the equation of the reaction for **G** with water.*

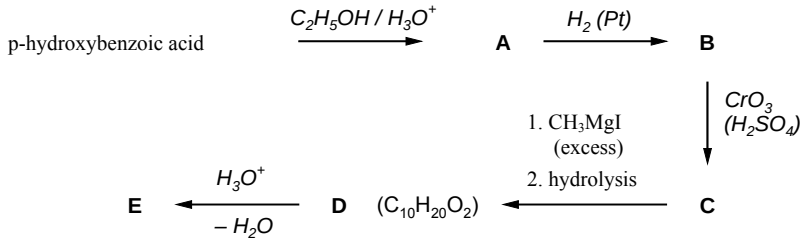
*k) Plot the Lewis formulae of the compounds **E**, **F**, **G** and **H**. Which structures of **F**, **G** and **H** do you expect following the VSEPR model? Draw sterical images of the structures considering free electron pairs and name each structure.*

*l) Which oxygen containing acids can be derived formally from **G** and **H**?*

Problem 4-8 Organic Synthesis

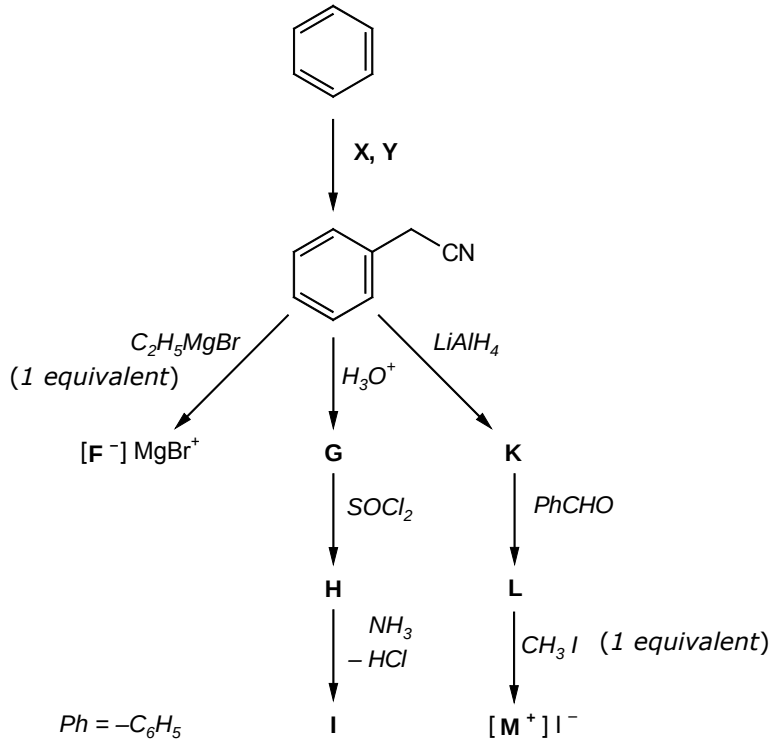
Identify the missing compounds in the following scheme by plotting their structural formulae.

a)



Compound **C** shows a sharp IR absorption band at ca. 1700 cm^{-1}.
Compound **E** contains no C = C double bond.

b)



Problem 4-9 NMR Spectroscopy and Structure

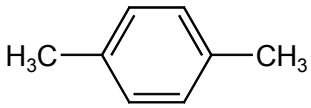
The following compounds are to be inspected by ^{1}H NMR and ^{13}C NMR:

I) $(H_3C)_2C{=}C(CH_3)_2$

II) Cyclohexane

III) $H_3C{-}O{-}CH_3$

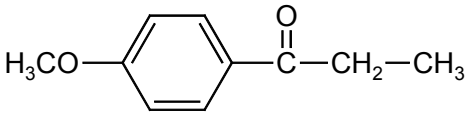
IV) $(H_3C)_3C{-}\overset{\overset{O}{\|}}{C}{-}CH_3$

V) 

VI) 1,1-Dimethylcyclopropane

VII) 2-Chloropropene

a) How many signals do you expect in both spectra (^{1}H und ^{13}C) of the different compounds I) to VII) (measured at room temperature)?

The ^{1}H NMR of  shows five signals.

Chemical shifts (δ) are found at

δ_1 = 6.98 (doublet) δ_2 = 8.0 (doublet)

δ_3 = 3.90 (singlet) δ_4 = 2.95 (quartet)

δ_5 = 1.2 (triplet)

b) Assign the 5 signals to their particular protons.

c) The ^{1}H NMR spectrum of the compound with the empirical formula $C_4H_8Cl_2O$ shows only two triplets. Plot the structural formula. Account for your proposal.

Problem 4-10 Analysis and Synthesis of Peptides

A peptide consists of the six amino acids Arg, Gly, Leu and 3 x Pro. Proline was found in an N-terminal as well as in a C-terminal position. Partial hydrolysis lead to the following fragments:

a) H – Gly – Pro – Arg – OH

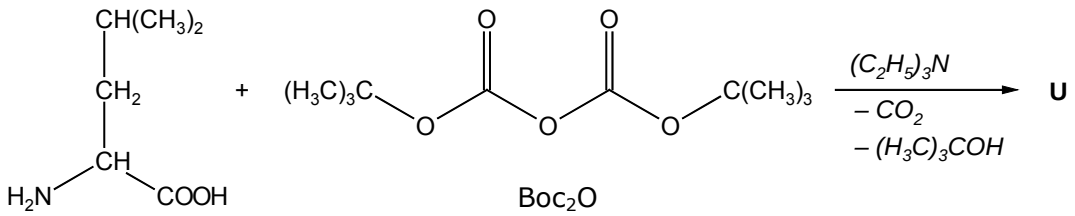
b) H – Arg – Pro – OH

c) H – Pro – Leu – Gly – OH

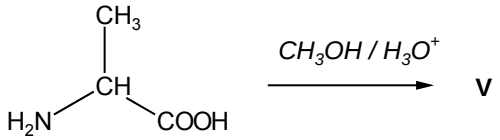
a) Write down the sequence of amino acids of the peptide.

The following scheme (not always stoichiometric) shows the synthesis of H – Leu – Ala – OH with Leucin and Alanin as reactants.

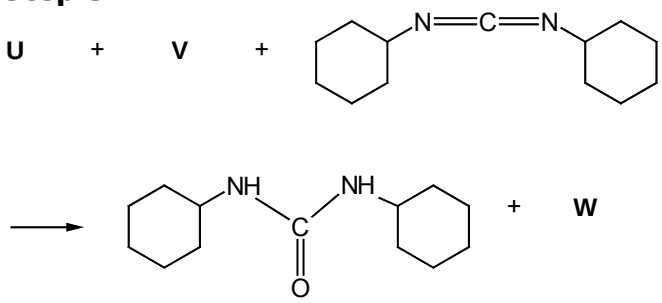
Step 1:



Step 2:

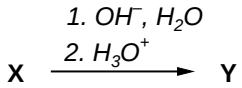


Step 3:



Step 4:

Step 5:



*2. Give the structural formulae of **U** to **Y**.*
Give the reasons why the different steps are carried out.

Fourth Round (practical problems)

Problem 4-11 Synthesis of Cinnamic Acid Methyl Ester

In this experiment the methyl ester is prepared from trans-cinnamic acid (E-3-phenylpropenoic acid) catalyzed by protons.

Equipment:
100 mL round bottomed flask, 10 mL graduated cylinder, 1 mL graduated pipette, reflux condenser, 300 mL beaker, stand with clamps, tubing, heating unit, pressure tubing, vacuum attachment, suction flask with rubber ring, Büchner funnel, filter paper, thin layer chromatography plate, chamber for thin layer chromatography

Substances:		**R phrases**	**S phrases**
cinnamic acid	$C_9H_8O_2$ (s)	36-38	22-24/25-36/37/39-38
methanol	H_3COH (l)	11-23/25	7-16-37/39
ethanol	C_2H_5OH (l)	11	7-16
conc. sulfuric acid	H_2SO_4 (l)	35	26-30-45
eluent toluene/glacial acetic acid (30:5),		11-38-48/20-63-65-67 10-35	(2)-36/37-62 (1/2)-23-26-45
demineralized water, ice			

Safety precautions:
Be cautious when working with concentrated sulfuric acid, wear eye protection.

Procedure:
Add 5.00 g of cinnamic acid to a 100 mL round bottomed flask followed by 10 mL of methanol. Then add 0.7 mL of conc. sulfuric acid using the graduated pipette in the fume cupboard and shake awhile.
Heat the mixture under reflux for half an hour.
Allow the reaction mixture to cool down for a short time. Transfer it to a 300 mL beaker with crushed ice.
Collect the precipitate under suction (Büchner funnel) and wash on the filter with a small amount of cold demineralized water.

Recrystallize the product from ethanol. Transfer it to the provided tared beaker. Run a thin layer chromatogram of cinnamic acid and your product on a silica plate using toluene/glacial acetic acid (30:5) as the eluent. Record the R_f values and hand in the plate and the beaker with the product to the assistant.

Disposal:
Give all organic liquids into the container for organic waste.

a) Draw the structural formula of trans-cinnamic acid.
b) Calculate the maximum theoretical yield of cinnamic acid methyl ester.
c) Calculate the R_f values of the reagent and the product.

Problem 4-12 Preparation and Standardization of a Zinc Sulfate Solution

Equipment:
Funnel (∅ = 10 cm), 250 mL volumetric flask with stopper, 20 mL pipette with pipette control, 300 mL Erlenmeyer flask (wide mouth), 5 mL graduated pipette, 25 mL burette with funnel and clamp, stand, spatula

Substances:		*R phrases*	*S phrases*
zinc sulfate	$ZnSO_4 \cdot 7\ H_2O$ (s)	52/53	61
indicator buffer	pills	22-36-42/43	22-24-37-45
ammonia	$w(NH_3)$ = 25 %,	34-50	26-36/37/39-45-61
EDTA disodium salt	c = 0.1 mol/L	36/38	26-36
demineralized water			

Safety precautions: Wear eye protection.

Procedure:
Transfer the provided zinc sulfate heptahydrate totally into a 250 mL volumetric flask, dissolve it under shaking in 50 - 100 mL of demineralized water, fill up with demineralized water upto 250 mL and shake sufficiently.
Transfer exactly 20 mL of standardized Na_2EDTA solution, $c(Na_2EDTA)$ = 0.1 mol/L, to an Erlenmeyer flask using a pipette, and fill up to 100 mL. Add 1 indicator buffer pill and – after it is dissolved – 2 mL of ammonia ($w(NH_3)$ = 25 %).

Titrate speedily with your prepared zinc sulfate solution. The end-point is given by the colour change from green to red.

Disposal:
The titrated solutions are given into the container for aqueous heavy metal waste.

a) Calculate the mass concentration β (mg/L) of zinc in your solution!
b) Calculate the concentration (mol/L) of zinc sulfate in your solution.

Problem 4-13 Complexometric Determination of Iron and Aluminum

In this experiment the amount of iron and aluminum ions are determined using complexometric methods. At first you have to quantify the mass concentration β_1 of iron by direct titration with standardized Na_2EDTA solution using 5-sulfosalicylic acid as indicator followed by the determination of aluminum in the same sample with the method of back titration of standardized Na_2EDTA solution with standardized zinc sulfate solution using xylenolorange as indicator.

Equipment:
100 mL volumetric flask with stopper, 10 mL pipette, 25 mL pipette, 5 mL graduated pipette, pipette control, 300 mL Erlenmeyer flask (wide mouth), spatula, Pasteur pipettes with rubber caps, indicator paper, 25 mL burette with funnel and clamp, stand with clamps, Bunsen burner, tetrapod with plate

Substances:		**R phrases**	**S phrases**
EDTA disodium salt	c = 0.1 mol/L	36/38	26-36
EDTA disodium salt	c = 0.01 mol/L	36/38	26-36
solution of 5-sulfosalicylic acid			
xylenolorange trituration with sodium chloride w($C_{31}H_{32}N_2O_{13}S$) = 1 %			
sodium acetate			22-24-25
zinc sulfate solution	c = 0.1 mol/L	52/53	61
hydrochloric acid	c = 2 mol/L	34	26-36/37/39-45
demineralized water			

Safety precautions: Wear eye protection.

Procedure:

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

To determinate iron exactly 10 mL of the given solution are transferred to an Erlenmeyer flask and filled up to 150-200 mL with demineralized water.

The pH value of the solution is adjusted to 2–2.5 using diluted hydrochloric acid. After addition of 1 mL of 5-sulfosalicylic acid you titrate with standardized Na_2EDTA solution **(c = 0.01 mol/L)**, end-point is the colour change from violet to slightly yellow. Shortly before the end the addition of Na_2EDTA solution should be done very slowly.

To quantify aluminum exactly 25 mL of standardized Na_2EDTA solution **(c = 0.1 mol/L)** are added to the solution of the iron determination. Heat it to boiling for 5 to 10 minutes.

Allow the solution to cool down to room temperature. Then add 2 to 4 spatula of sodium acetate to adjust the pH value to 5, and 2 spatula-tipfull of the xylenol-orange trituration. Titrate with standardized zinc sulfate solution (c = 0.100 mol/L, end-point is the colour change from yellow to pink/red.

Disposal:

The titrated solutions are given into the container for aqueous heavy metal waste. Leftovers of Na_2EDTA solution can be poured out directly into the sink.

a) *Calculate the mass concentration β_1 (mg/L) of iron in your test solution.*
b) *Calculate the mass concentration β_2 (mg/L) of aluminum 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) $5\ H_2O_2 + 2\ MnO_4^- + 6\ H^+ \longrightarrow 5\ O_2 + 2\ Mn^{2+} + 8\ H_2O$

b) Lotion A: average consumption = 19.10 mL (titration no. 4 is not considered)

$$\text{mass percentage} = \frac{\text{consumption} \cdot 0{,}02\ \text{mol/L} \cdot 5 \cdot M(H_2O_2) \cdot 4 \cdot 100}{2 \cdot m(\text{lotion A})}\ \%$$

$$= \frac{19.10\,\text{mL} \cdot 0.02\,\text{mol/L} \cdot 5\ 34.02\,\text{g/mol} \cdot 4 \cdot 100}{2 \cdot 4 \cdot 1.15\,\text{g}}\ \% = 2.51\ \%$$

Loton B: average consumption = 19.98 mL (titration no. 3 is not considered)

$$\text{mass percentage} = \frac{\text{consumption} \cdot 0.02\ \text{mol/L} \cdot 5 \cdot M(H_2O_2) \cdot 5 \cdot 100}{2 \cdot m(\text{lotionB})}\ \%$$

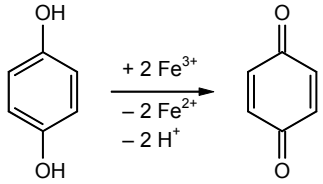
$$= \frac{19{,}98\,\text{mL} \cdot 0{,}02\,\text{mol/L} \cdot 5\ 34{,}02\,\text{g/mol} \cdot 5 \cdot 100}{2 \cdot 3 \cdot 1.15\ \text{g}}\ \% = 4.93\ \%$$

Lotion B should be the blond dyeing lotion because of the higher content of hydrogen peroxide.

c) $2\ Ce^{4+} + H_2O_2 \longrightarrow 2\ Ce^{3+} + O_2 + 2\ H^+$

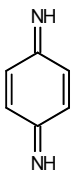
d) In neutral and especially in alkaline solutions sparely soluble cerperoxide hydrates of the composition $Ce(OH)_3(OOH)$ and according to the pH-value also $Ce(OH)_4$ form so that no reduction takes place. In strongly acidic solutions Ce(IV) is reduced quanitatively by H_2O_2.

e) Oxidation of 1.4-dihyroxybenzene (hydroquinone)

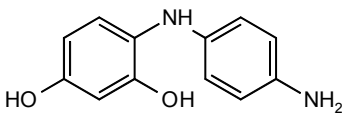


f) Dihydroxybenzenes and diaminobenzenes possess the same number of electrons. they are isoelectronic: Phenylene groups with the substituents –OH and $–NH_2$. which possess 7 electrons each. The oxidation products with $=\ddot{O}$ and $=\bar{N}H$ as substituents with 6 electrons each are isoelectronic. too. In this sense the reactions are comparable.

g) Structure of compound X.

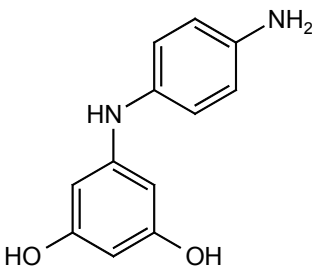


h) Y(1)

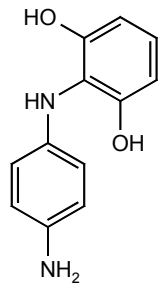


Answers Round 1

Y(2)



Y(3)



Y(1) is formed preferentially. Reason: Substitution of substituted benzene in ortho and para position.

Y(2) Disadvantaged because substitution in meta position has a higher activation energy than that in ortho and para position.

Y(3) Side reaction as there is steric hinderence of the substitution in ortho position.

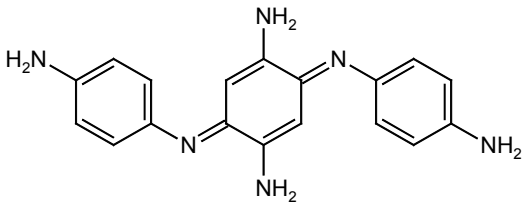
i) Colour: Organic molecules with a "chromophor" (from greek: chroma = colour phoros = carrying) are coloured. In general. the chromophoric groups are formed by large π-electron systems which are built up by unsaturated groups of atoms. e.g. C=C. C=O. C=S. C=N. N=O. If such a group is isolated it does not show any colour because it absorbs in the short-wave band. But if these individual groups built up a large conjugated π system, molecules form which absorb in the visible range. Highly conjugated systems built up of individual chromophores show colour. Therefore organic dyes often contain azo-. azoxy- or chinone-groups and have chinoide and indigoide systems.

j) 1.4-diaminobenzene (1.4-phenylendiamine): R 23/24/25-36-43-50/53. S 28.1-36/37-45-60-61

resorcin: R 22-36/38-50. S 26-61

hydrogen peroxide w(H_2O_2) = 35 %: R 22-37/38-41. S 26-39

k) strukture of Z:



l) The reaction to form Z can be suppressed by adding an excess of the coupling agent (resorcin).

m) Wear waterproof gloves. no contact with the scalp (no defatting of the scalp by washing). avoid long-term resorption through the scalp (e.g. do not exceed the exposure time).

n) The pigment is a mixture of zinc sulfide and barium sulfate (Lithopone).

A Detection of sulfide as black lead sulfide:

$S^{2-} + 2\ H^+ \longrightarrow H_2S$

$Pb(OAc)_2 + H_2S \longrightarrow PbS + 2\ HOAc$

B Precipitation of white zinc sulfide:

$ZnCl_2 + Na_2S \longrightarrow ZnS + 2\ NaCl$

C Formation of a green compound (in German: Rinmans Grün):

$2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2$

$ZnO + 2\ Co(NO_3)_2 \longrightarrow ZnCo_2O_4 + 4\ NO_2 + ½\ O_2$

D

$BaSO_4 + Na_2CO_3 \longrightarrow BaCO_3 + Na_2SO_4$

E Detection of sulfate anions as white barium sulfate:

$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2\ NaCl$

F Precipitation of white barium carbonate:

$BaCl_2 + (NH_4)_2CO_3 \longrightarrow BaCO_3 + 2\ NH_4Cl$

G Detection of barium as white barium sulfate:

$BaCl_2 + CaSO_4 \longrightarrow BaSO_4 + CaCl_2$

H Detection of barium as yellow barium chromate:

$Ba(OAc)_2 + K_2CrO_4 \longrightarrow BaCrO_4 + 2\ KOAc$

o) Ratio at time t_x $\quad n(^{14}C)/n(^{12}C) = 1.176 \cdot 10^{-12}$

ratio at time t_{2002} $\quad n(^{14}C)/n(^{12}C) = 1.1034 \cdot 10^{-12}$

$$\Rightarrow \quad n(^{14}C_{tx}) = \frac{n(^{14}C_{t2002}) \cdot 1.176 \cdot 10^{-12}}{1.1034 \cdot 10^{-12}} = 1.0658 \cdot n(^{14}C_{t2002})$$

using $n(^{14}C_{t_{2002}}) = n(^{14}C_{t_x}) \cdot e^{-\lambda \cdot t}$. $\lambda = \ln 2 / t_{1/2}$ and $t = (2002 - t_x)$ years):

$$\ln \frac{1.0658 \cdot n(^{14}C_{t2002})}{n(^{14}C_{t2002})} = \frac{\ln 2}{5730\ a} \cdot t \quad \Leftrightarrow \quad t = 526.8\ a$$

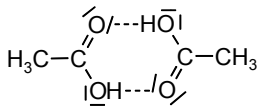
$t_x = 2002 - 526.9 = \underline{\underline{1675.2}}$

The hair originates presumably from the year 1675.

Answers Round 2

Solution to problem 2-1

a) Hydrogen bridge bonds form increasing the solubility in non-polar solvents.



b) $c_{total}(HA) = \frac{n_{total}}{V_{toluol}} = \frac{m_{total}}{M_{HA} \cdot V_{toluol}} = \frac{5.5 \cdot 10^{-5} g}{152.15\,g/mol \cdot 0.5\,L} = 7.23 \cdot 10^{-5}$ mol/L

$2\ HA \rightleftharpoons (HA)_2 \quad K_{dim}$

$\frac{c((HA)_2)}{c(HA)^2} = 16.4\ (mol/L)^{-1} \qquad c((HA)_2) \cdot 1\ mol/L = 16.4 \cdot c(HA)^2 \qquad (1)$

furthermore $c_{taotal}(HA) = c(HA) + 2 \cdot c((HA)_2)$

$7.23 \cdot 10^{-5}\ mol/L = c(HA) + 2 \cdot c((HA)_2) \qquad (2)$

$\Rightarrow$ with x = c(HA)/(mol/L): $7.23 \cdot 10^{-5} = x + 2 \cdot 16.4 \cdot x^2$

$x^2 + (2 \cdot 16.4)^{-1} \cdot x - 7.23 \cdot 10^{-5}/(2 \cdot 16.4) = 0$

$x = 7.21 \cdot 10^{-5} \qquad c(HA) = 7.21 \cdot 10^{-5}\ mol/L \qquad c((HA)_2) = 1 \cdot 10^{-7}\ mol/L$

$\beta = c((HA)_2)/\ c_{toal}(HA) = 10^{-7}/7.23 \cdot 10^{-5} \qquad \mathbf{\beta = 1.38 \cdot 10^{-3}}$

(If you use equation (1) for the calculation of $c((HA)_2)$ you get $c((HA)_2) = 8.53 \cdot 10^{-8}$ mol/L and $\beta = 1.18 \cdot 10^{-3}$.)

Conclusion: The amount of dimerisation is so small that you do not have to take it into account for the following calculations.

c) The following equations (3) and (4) apply to all of the three cases:

$m_{totao}(HA) = 5.5$ mg, $\quad n_{total} = 3.62 \cdot 10^{-5}$ mol (see b)

$\frac{c(HA)_{toluol}}{c(HA)_{water}} = 2 \qquad \frac{n(HA)_{toluol}/0.5\,L}{n(HA)_{water}/0.25\,L} = 2 \quad \Rightarrow \quad n(HA)_{toluol} = 4 \cdot n(HA)_{water} \qquad (3)$

$n_{total} = n(HA)_{toluol} + n(HA)_{water} + n(A^-)_{water} \qquad (4)$

(i) Simplification: The solution is so acidic that practically the acid HA does not un dergo protolysis that is to say $n(A^-)_{water} = 0$ mol/L,
With (3) and (4) $\Rightarrow n_{total} = 5 \cdot n(HA)_{water}$
$\Rightarrow \quad n(HA)_{water} = 0.2 \cdot n_{gesamt} \qquad \Rightarrow$ 20% (w/w) are extracted.

(ii) Simplification: The amount of extracted acid is so small that $c(OH^-) = 1$ mol/L practically does not change, thus $c(H_3O^+) = 10^{-14}$ mol/L.

$n_{total} = 5 \cdot n(HA)_{water} + n(A^-)_{water}$

$K_a = \frac{c(A^-)_{water} \cdot 10^{-14}}{c(HA)_{water}} \Rightarrow c(HA)_{water} = 10^{-11.03} \cdot c(A^-)_{water}$

$\Rightarrow n_{total} = (5 \cdot 10^{-11.03} + 1) \cdot n(A^-)_{twater} \qquad \Rightarrow \quad n(A^-)_{water} = n_{total}$

i.e. all the acid is existent as A^-, **100 %** of the acid are transferred into the aqueous phase.

(iii) Because of the protolysis of the acid in water you find $c(H_3O^+) = c(A^-)_{water}$

$10^{-2.97} = c^2(A^-)_{water} / c(HA)_{water}$ $\quad c(HA)_{water} = 10^{+2.97} \cdot c^2(A^-)_{water}$ (8)

$\frac{c(HA)_{toluol}}{c(HA)_{water}} = 2$ $\quad c(HA)_{toluol} = 2 \cdot c(HA)_{water}$ (9)

$n_{total} = c(HA)_{toluol} \cdot 0.5\ L + [c(HA)_{water} + c(A^-)_{water}] \cdot 0.25\ L$ (10)

$\Rightarrow$ $3.62 \cdot 10^{-5}\ mol/L = 1 \cdot 10^{2.97} \cdot c^2(A^-)_{water} + 0.25 \cdot 10^{2.97} \cdot c^2(A^-)_{water} + 0.25 \cdot c(A^-)_{water}$

$$c^2(A^-)_{water} + \frac{0{,}25}{1{,}25 \cdot 10^{2{,}97}}\ c(A^-)_{water} - \frac{3{,}62 \cdot 10^{-5}}{1{,}25 \cdot 10^{2{,}97}}\ mol/L = 0$$

$(c_1(A^-)_{water} = 9.903 \cdot 10^{-5}\ mol/L)$ $\quad c_2(HA)_{water} = 9.153 \cdot 10^{-6}\ mol/L$

$\Rightarrow$ $\quad c(HA)_{toluol} = 1.83 \cdot 10^{-5}\ mol/L.$

with $c_{total}\ (HA) = 7.23 \cdot 10^{-5}\ mol/L$

$\frac{1{,}83 \cdot 10^{-5}}{7{,}23 \cdot 10^{-5}} \cdot 100\% = 74.7\ \%$ are transferred into the aqueous phase.

d) If at least 76 % of the acid have to be extracted at most 24 % remain dissolved in toluol. After extracting once still (100 – 21) % of the amount of the beginning remain in the organic phase.

After 1. pouring out $\quad n_{1.\ toluol} = n_{total} \cdot 0.79$

after 2. pouring out $\quad n_{2.\ toluol} = n_{1.toluol} \cdot 0.79 = n_{total} \cdot 0.79^2$ ect.

after i. pouring out $\quad n_{i.\ toluol} = n_{total} \cdot 0.79^i$

$n_{i.\ toluol} \leq 0.24 \cdot n_{total} = n_{total} \cdot 0.79^i$

$\Rightarrow$ $\lg 0.24 = i \cdot \lg 0.79$ $\quad i = 6.05$

You have to extract 7 times.

Soltution to problem 2-2

a) $Ca(NO_3)_2\ (aq) + (NH_4)_2C_2O_4\ (aq) \longrightarrow CaC_2O_4 \cdot H_2O + 2\ NH_4NO_3\ (aq)$

A **B** **C**

b) $n(C) : n(H) : n(N) = \frac{16.41}{12.011} : \frac{1.39}{1.008} : \frac{0.11}{14.007} = 1.37 : 1.38 : 0.008$

$n(C) : n(H) : n(N) = 171.3 : 172.5 : 1$ nitrogen was not considered, (it originates from contaminations)

$n(C) : n(H) = 1 : 1$

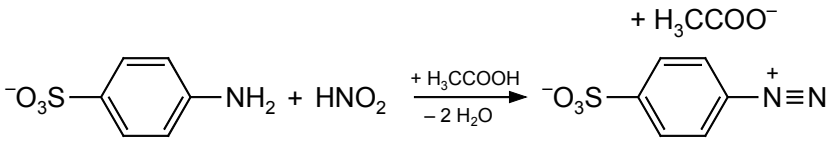
$M(CaC_2O_4 \cdot H_2O) = 146.11\ g/mol \Rightarrow$ theoretically: C: 16.44%. H: 1.38 %. N: ./.

c) i) $Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4$

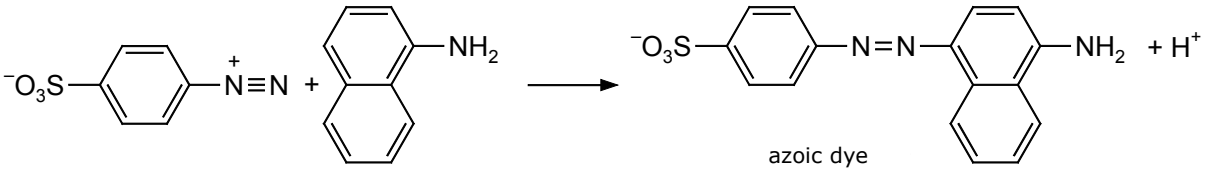
ii) $SO_4^{2-} + Sr^{2+} \rightleftharpoons SrSO_4$

iii) $NO_3^- + Zn + 2\ H^+ \rightleftharpoons NO_2^- + Zn^{2+} + H_2O$

Answers Round 2



Sulfanilic acid (anion) Diazonium salt (zwitterionic compound)



α-naphthaylamine

iv) $NO_3^- + 4\ Zn + 7\ OH^- + 6\ H_2O \rightleftharpoons NH_3 + 4\ [Zn(OH)_4]^{2-}$

v) $NO_3^- + 3\ Fe^{2+} + 4\ H_3O^+ \rightleftharpoons 3\ Fe^{3+} + NO + 6\ H_2O$

$NO + [Fe(H_2O)_6]^{2+} \rightleftharpoons [Fe(NO)(H_2O)_5]^{2+} + H_2O$

vi) $2\ Ag^+ + C_2O_4^{2-} \rightleftharpoons Ag_2C_2O_4$

vii) $2\ MnO_4^- + 5\ C_2O_4^{2-} + 16\ H_3O^+ \rightleftharpoons 2\ Mn^{2+} + 10\ CO_2 + 24\ H_2O$

viii) $CO_2 + Ba(OH)_2 \rightleftharpoons BaCO_3 + H_2O$

ix) $NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$

d) 1. reaction: H_2O. theo.: 12.3%. exp.: 12.3%

$CaC_2O_4 \cdot H_2O \longrightarrow CaC_2O_4 + H_2O$

2. reaction: CO. theo.: 19.2%. exp.: 18.0%

$CaC_2O_4 \longrightarrow CaCO_3 + CO$

3. reaction: CO_2. theo.: 30.1%. exp.: 28.8%

$CaCO_3 \longrightarrow CaO + CO_2$

e) Calcite, aragonite, vaterite

f) Calcite

g) Allotropism

h) Calcite forms

i) In mathematical terms the unit cell is a rectangular prism with a rhombus as base.

Base: $A = a^2 \cdot \sin\gamma \quad \Rightarrow \quad V = a^2 \cdot \sin\gamma \cdot c$

$\Rightarrow \quad A = 21.512\ Å^2.$ **$V = 368.3\ Å^3$ ($0.3683\ nm^3$)**

j) $d = m/V$; $M(CaCO_3) = 100.08$ g/mol. $Z = 6$. $N_A = 6.022 \cdot 10^{23}$

$$d = \frac{M \cdot Z}{N_A \cdot V} = \frac{100.08\,g/mol \cdot 6}{6.022 \cdot 10^{23}\,mol^{-1} \cdot 368.3 \cdot 10^{-24}\,cm^3} = 2.71\ g/cm^3$$ **$d = 2.71\ g/cm^3$**

k) Calcium carbonate forms which disolves in an excess of carbon dioxide because of shift in the equilibrium:

$CaO + H_2O \rightleftharpoons Ca(OH)_2$

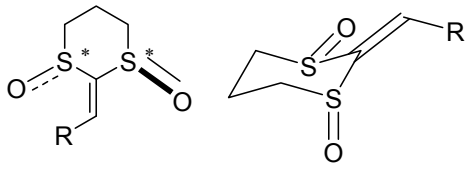
$Ca(OH)_2 + CO_2 \rightleftharpoons CaCO_3 + H_2O$

$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$

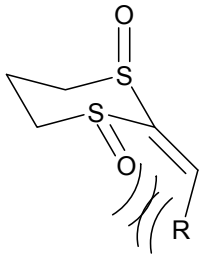
Solution to problem 2-3

a) **1** [1.3]-Dithiane **2** 2-Trimethylsilyl-[1.3]-dithiane

b)



4

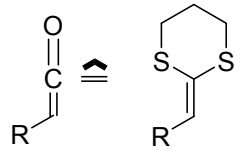


steric hindrance

The conformation with equatorial position of the CHR group is sterically less hindered and should be formed preferentially.

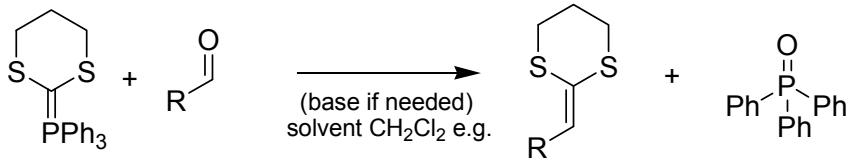
c) You have to use (-)-DET in the Sharpless oxidation in **3** → **4**.

d)



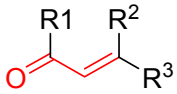
Looking at the left compound which is called a ketene you get compounds of type **3** by a formal dithioacetalation.

e)



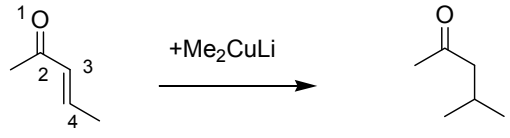
3

f)



It is an α.β-unsaturated carbonyl compound. Reactivity: In β-position an attack of a nucleophile is favoured (1.4-addition).
Der An attack of nuclephiles directly at the carbonyl C-atom is possible, too, and leads to the 1.2-addition product.

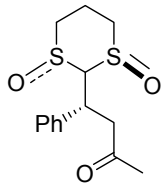
g)



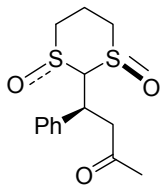
5

You get only 4-methyl-2-oxopentane shown above as a product.
You do not find the1.2-adduct.
Cuprate (Me_2CuLi) used in the reaction leads only to 1.4-addition.

h)

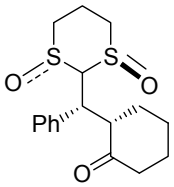


7a

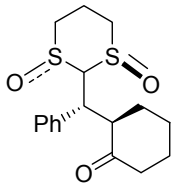


7b

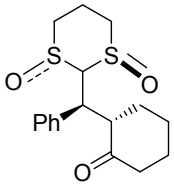
diasteromers



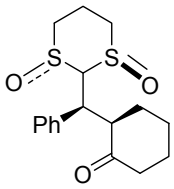
8a



8b



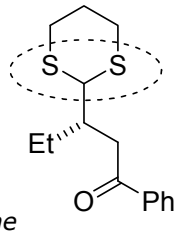
8c



8d

all of them are diastereomeric to each other

i)



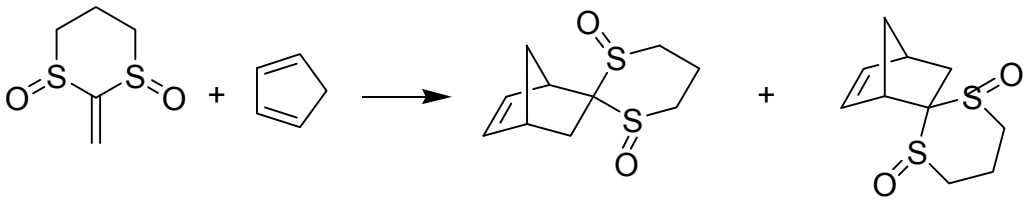
S,S-dithioacetal

ketone

10

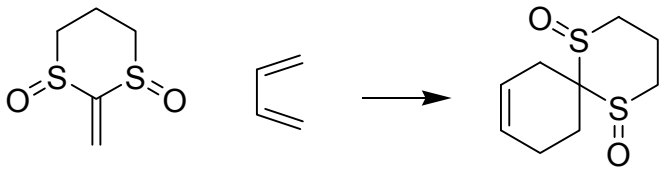
j)

1)



Note: Both products (endo and exo) form. As the stereochemistry of the methylen-bissulfoxide is not given you may assume that you get a racemate, i.e. you get two endo products (enantiomers) and two exo products.

2)



Only one product forms in this case.

Answers Round 3 Test 1

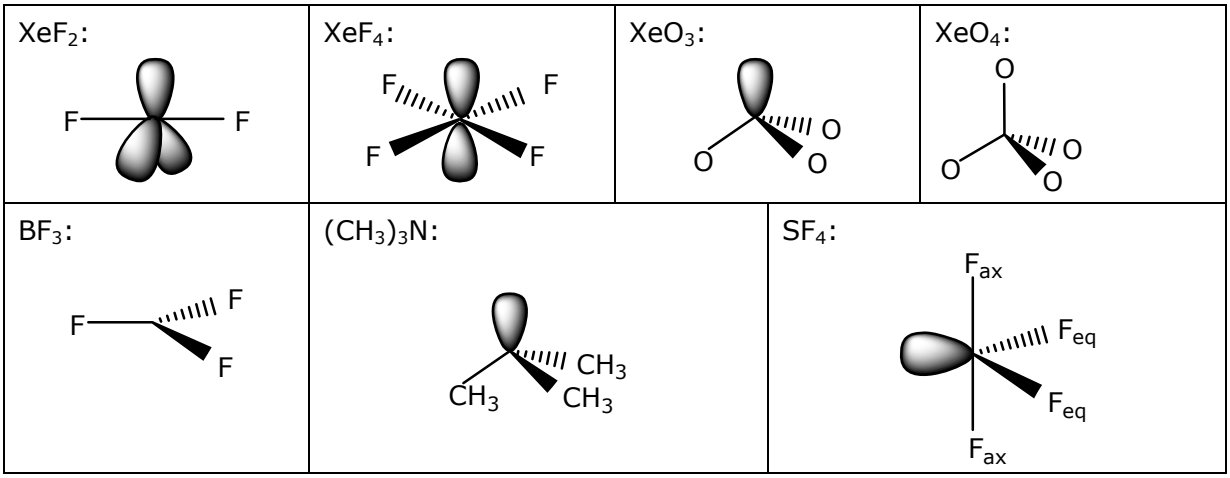
(more detailed than expected from the students)

Solution to problem 3-1

a) C b) C c) A, B, E d) Ae) Bf) B g) E

Solution to problem 3-2

a)	a_1)	XeF_2	linear	no deviation
	a_2)	XeF_4	quadratic planar	no deviation
	a_3)	XeO_3	trigonal pyramidal	distorted *
	a_4)	XeO_4	tetrahedral	no deviation
	a_5)	BF_3	trigonal planar	no deviation
	a_6)	$(CH_3)_3N$	trigonal pyramidal	distorted *
	a_7)	SF_4	(distorted) tetrahedral	distorted **



* The free electron pair occupies more space thus the angles (OXeO) and (CNC), respectively, should be smaller than the angles in a tetrahedron.

** For the same reason: angle ($F_{ax}SF_{ax}$) < 180° (173°) and angle ($F_{eq}SF_{eq}$) < 120° (101°).

b) Both xenon fluorides are formed by the reaction of the elements using appropriate activation (e.g. radiation).

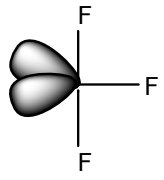
Oxide: $XeF_6 + 3\ H_2O \longrightarrow XeO_3 + 6\ HF$

but also $3\ XeF_4 + 6\ H_2O \longrightarrow Xe + 2\ XeO_3 + 12\ HF$

Helium, neon and argon do not react similar because of higher ionisation energies.

c) This planar geometry is associated with the bond between the nitrogen and the carbonyl carbon having partial double-bond character.

d) The 5 electron pairs arrange themselves to form a trigonal bipyramid to minimize their repulsion.



The assumption is that the repulsion between a bonding and a lone pair is greater than the repulsion between two bonding pairs. This difference in repulsion would mean that the Cl-F bonding pairs could move closer together resulting in a reduction of the F-Cl-F bond angle.

Solution to problem 3-3

Reactions: $2\ NO + O_2 \longrightarrow 2\ NO_2$ (1)

$2\ NO_2 \rightleftharpoons N_2O_4$ (2)

amounts at the beginning: n mol O_2 + 3·n mol NO, Σ = 4·n mol

amounts after reaction (1): 2·n mol NO_2 + n mol NO, Σ = 3·n mol

expected difference in height at the manometer: 10 cm · ¾ = 7.5 cm

but after reaction (2) only 7.1 cm could be detected ⇒

n_{total} = 3·n · 7.1/7.5 = 2.84·n 1 n mol of which is NO

i.e. 2 n mol NO_2 form 1.84 n mol of a mixture of NO_2 and N_2O_4 ⇒

2·(2-1.84)·n = 0.32 n mol NO_2 have reacted, that are $\frac{0.32\,n}{2\,n}$ · 100% = 16 %

Solution to problem 3-4

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

$2\ Cr + 6\ H_3O^+ \longrightarrow 2\ Cr^{3+} + 3\ H_2 + 6\ H_2O$

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

$5\ (COOH)_2 + 2\ MnO_4^- + 6\ H_3O^+ \longrightarrow 10\ CO_2 + 2\ Mn^{2+} + 14\ H_2O$

Cr^{3+} ions do not react under the given conditions.

b) Determination of the concentration of the permanganate solution:
10 cm^3 of oxalic acid contain $5\cdot10^{-4}$ mol $(COOH)_2$. You need n = 2/5·5·10^{-4} mol = $2\cdot10^{-4}$ mol of permanganate to oxidize.
⇒ c(permanganate) = n/V = 0.0205 mol/L.
Determination of iron:
20.08 cm^3 of this permanganate solution contain $4.12\cdot10^{-4}$ mol permanganate which oxidize $20.6\cdot10^{-4}$ mol of Fe^{2+}.
m(Fe) = $20.6\cdot10^{-4}$ mol·55.85 g·mol^{-1} = 0.1150g 0.1150/0.1331 = 0.8640
⇒ 86.4 % of iron and 13.6 % of chromium in the alloy

c) At the cathode hydrogen forms, at the anode oxygen.

d) Charge Q = I·t Q = 1500 A · 10·60·60 s Q = $54\cdot10^6$ C
Because of $CrO_4^{2-} + 8\ H^+ + 6\ e^- \longrightarrow Cr + 4\ H_2O$ and Q = n·z·F the yield of 100% current efficiency is $n(Cr) = \frac{Q}{6\cdot F}$ $n(Cr) = \frac{54\cdot10^6}{6\cdot96485}\text{mol} = 93.28$ mol.
But only 670 g of chromium were achieved, this is 670/52.00 mol = 12.88 mol.

Thus the current efficiency amounts to 100% · 12.88/93.28 = 13.81%.

e) At the cathode the reaction $2\ H_3O^+ + 2\ e^- \longrightarrow 2\ H_2O + H_2$ takes place, too.
In this reaction the electrons not involved in the electrodeposit of chromium are engaged. $n(H_2) = \frac{54\cdot10^6}{2\cdot96485}\cdot\frac{100-13.81}{100}\text{mol}$ $n(H_2) = 241.19$ mol.
with $p\cdot V = n\cdot R\cdot T$ that is $V(H_2) = 5.98\ m^3$ of hydrogen.
At the anode the reaction $6\ H_2O \longrightarrow 4\ H_3O^+ + 4\ e^- + O_2$ runs.
The total charge is used to form oxygen: $n(O_2) = \frac{54\cdot10^6}{4\cdot96487}\text{mol} = 139.92$ mol.
with $p\cdot V = n\cdot R\cdot T$ that is $V(O_2) = 3.47\ m^3$ of oxygen.

Solution to problem 3-5

a) $3\cdot(-0.744\ V) = -0.408\ V + 2\cdot y$ $y = -0.912\ V$
$0.55\ V + 1.34\ V + x - 3\cdot0.744\ V = 6\cdot0.293\ V$ $x = +2.1\ V$

b) $2\ Cr(IV) + 2\ e^- \longrightarrow 2\ Cr(III)$ $E° = 2.1\ V$ $\Delta G_1^0 = -2\cdot F\cdot 2.1\ V$
$1\ Cr(VI) + 2\ e^- \longrightarrow 1\ Cr(IV)$ $E° = ½\cdot(0.55 + 1.34)\ V$
$\Delta G_2^0 = -2\cdot F\cdot ½\cdot(0.55+1.34)\ V$
Disproportionation: $3\ Cr(IV) \longrightarrow 2\ Cr(III) + Cr(VI)$
$\Delta G^0 = \Delta G_1^0 - \Delta G_2^0$ $\Delta G^0 = -2\cdot F\cdot(2.1-1.89/2) < 0$
$\Rightarrow$ Cr(IV) disproportionates.

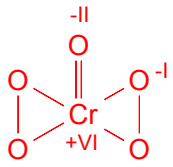
c) $Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightleftarrows 7\ H_2O + 2\ Cr^{3+}$

$$E_1 = 1.33\ V + \frac{R\cdot T}{6\cdot F}\cdot\ln\frac{c(Cr_2O_7^{2-})\cdot(10^{-pH}\text{mol/L})^{14}}{c(Cr^{3+})^2}$$

$$E_2 = 1.33\ V + \frac{R\cdot T}{6\cdot F}\cdot\ln\frac{c(Cr_2O_7^{2-})\cdot(10^{-(pH+1)}\text{mol/L})^{14}}{c(Cr^{3+})^2}$$

$E_2 - E_1 = \frac{8{,}314\cdot298}{6\cdot96485}V\cdot14\cdot\ln10^{-1} = -0.138\ V$ *is the change in potential.*

d) The oxidation numbers do not change; neither oxidation nor reduction takes place.
H_2O_2 is attached as peroxide dianion to the chromium centre.



+VI,-II +I,-I +I +VI,-II/-I +I,-II
$Cr_2O_7^{2-} + 4\ H_2O_2 + 2\ H^+ \longrightarrow 2\ CrO_5 + 5\ H_2O$

Solution to problem 3-6

a) $2\ CrO_4^{2-} + 2\ H^+ \rightleftarrows Cr_2O_7^{2-} + H_2O$

pH = 1: only $Cr_2O_7^{2-}$ but no CrO_4^{2-} is present $\Rightarrow$ $E = \varepsilon(Cr_2O_7^{2-})\cdot c(Cr_2O_7^{2-})\cdot d$
$0.214 = \varepsilon(Cr_2O_7^{2-})\cdot2\cdot10^{-4}$ mol/L·1 cm $\Rightarrow$ $\varepsilon(Cr_2O_7^{2-}) = 1.07\cdot10^3\ L\cdot mol^{-1}\cdot cm^{-1}$

pH = 12: only CrO_4^{2-} but no $Cr_2O_7^{2-}$ is present $\Rightarrow$ $E = \varepsilon(CrO_4^{2-})\cdot c(CrO_4^{2-})\cdot d$
(2 mol of chromate form 1 mol of dichromate!)
$0.736 = \varepsilon(CrO_4^{2-})\cdot 4\cdot 10^{-4}$ mol/L·1 cm $\Rightarrow$ $\varepsilon(CrO_4^{2-}) = 1.84\cdot 10^3$ L·mol^{-1}·cm^{-1}

pH = 5.6: CrO_4^{2-} and $Cr_2O_7^{2-}$ are present. Let be $c(CrO_4^{2-}) = x$ and $c(Cr_2O_7^{2-}) = y$
$0.827 = (1.84\cdot x + 1.07\cdot y)\cdot 10^3$ L·mol^{-1} (i)
$1/2\cdot x + y = 4\cdot 10^{-4}$ mol/L (ii)
$\Rightarrow$ $x = 3.06\cdot 10^{-4}$ mol/L $y = 2.47\cdot 10^{-4}$ mol/L

$K = \frac{c(Cr_2O_7^{2-})}{c(CrO_4^{2-})^2\cdot c(H^+)^2}$ $K = \frac{2.47\cdot 10^{-4}}{(3.06\cdot 10^{-4})^2\cdot (10^{-5.6})^2}$ $K = 4.2\cdot 10^{14}$

b)

the equilibrium	shifts to the left	shifts to the right	does not shift
i)		✓	
ii)	✓		
iii)		✓	
iv)	✓		

Justification:
The results of (i) and (ii) is taken directly from the reaction equation. In (iii) insoluble $BaCrO_4$ forms.
Adding water to a solution of dichromate (in iv) means dilution e.g. to a twofold increase of volume. Thus the concentration is halved. If you look now at the formula of the equilibrium constant and insert there half of the original equilibrium concentrations there you can see that the value of the denominator decreases more than the value of the numerator. To install the equilibrium again the numerator has to become smaller, the denominator thus greater and so the equilibrium shifts to the left.

Solution to problem 3-7

a) O_2-rich $\Rightarrow$ CO_2-poor $\Rightarrow$ less acidic $\Rightarrow$ higher pH value = 7.40
O_2-poor $\Rightarrow$ CO_2-rich $\Rightarrow$ more acidic $\Rightarrow$ lower pH value = 7.37

b) (2) + (3) = (4) $\Rightarrow$ $K_4 = K_2\cdot 10^{-pKs} = 4.68\cdot 10^{-3}\cdot 10^{-3.77}$ $K_4 = 7.95\cdot 10^{-7}$

c) $K_4 = \frac{c(H_3O^+)\cdot c(HCO_3^-)}{c(CO_{2(aq)})\cdot 1\text{mol/L}}$ $c(CO_{2(aq)}) = \frac{10^{-7.40}\cdot 24\cdot 10^{-3}}{7.95\cdot 10^{-7}}$ mol/L

$c(CO_{2(aq)}) = 1.20\cdot 10^{-3}$ mol/L

d) $K_H = \frac{c(CO_{2(aq)})}{p(CO_2)}$ $p(CO_2) = \frac{1.20\cdot 10^{-3}\text{mol/L}}{3.40\cdot 10^{-2}\text{mol/(L·atm)}}$

$p(CO_2) = 3.53\cdot 10^{-2}$ atm = 0.0358 bar (i.e. ≈ 4% of the exhaled air)

e) The exhaled CO_2 ($V(CO_{2,\,exhl.})$ per 1 L of blood corresponds to the concentration difference of carbon dioxide rich (pH = 7.37) to carbon dioxide poor blood.

$V(CO_{2,\,exhl.})/L = \frac{274\,mL\,CO_2}{5{,}4\,L\,Blut} = 50.74$ mL CO_2 per 1 L of blood

with n = p·V/(R·T): $n(CO_{2,\,exhl.})/L = \frac{1013\cdot10^2 Pa\cdot50.74\,10^{-6}m^3}{8.314 JK^{-1}mol^{-1}\cdot310.15\,K}\cdot\frac{1}{L}$

$c(CO_{2,\,exhl.}) = 1.993\cdot10^{-3}$ mol/L $\Rightarrow$

$[c(CO_2(aq)) + c(HCO_3^-)]_{CO_2\,rich} = [c(CO_2(aq)) + c(HCO_3^-)]_{CO_2\,poor} + 1.99\cdot10^{-3}$ mol/L

$[c(CO_2(aq)) + c(HCO_3^-)]_{CO_2\,rich} = (1.20 + 24.0 + 1.99)\cdot10^{-3})$ mol/L

$[c(CO_2(aq)) + c(HCO_3^-)]_{CO_2\,rich} = 27.19\cdot10^{-3}$ mol/L

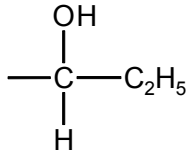
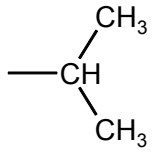
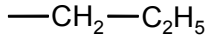
moreover $K_4 = \frac{c(H_3O^+)\cdot c(HCO_3^-)}{c(CO_{2(aq)})\cdot 1mol/L}$.

$$7.95\cdot10^{-7} = \frac{10^{-7.37}\cdot c(HCO_3^-)_{CO_2\,rich}}{27.19\cdot10^{-3}mol/L - c(HCO_3^-)_{CO_2\,rich}}$$

$\Rightarrow$ $c(HCO_3^-)_{CO_2\,rich} = 25.8\cdot10^{-3}$ mol/L $c(CO_2)_{CO_2\,rich} = 1.39\cdot10^{-3}$ mol/L

Solution to problem 3-8

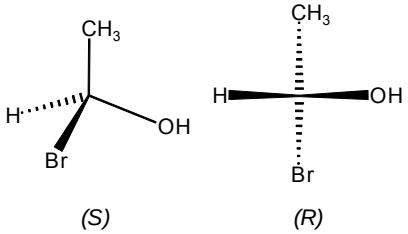
a) Priorities

	atomic number of the first atoms following the stereogenic center	atomic number of the second atomsfollowing the stereogenic center	priority
	6 (C)	8 (O) 6 (C) 1 (H)	1
	6 (C)	6 (C) 6 (C) 1 (H)	2
	6 (C)	6 (C) 1 (H) 1 (H)	3
	1 (H)		4

b) i) identical molecules, S configuration

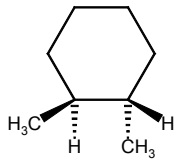
ii) enantiomers:

iii) identical molecules, S configuration



(S) *(R)*

c)



(1S,2S)-1,2-Dimethylcyclohexane

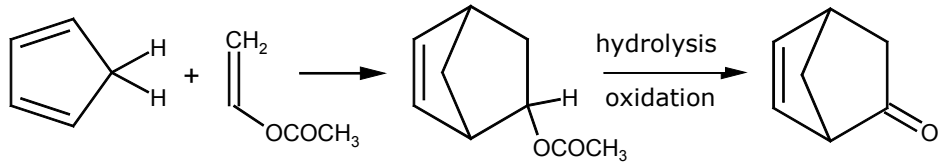
Solution to problem 3-9

a) In the Diels-Alder reaction the diene (e.g. 1,3-butadiene) provides 4 π electrons, while the dienophile (e.g. ethene) contributes two π electrons (4+2). 3 π bonds in the reactants change to several σ bonds in the product. σ-Bonds have lower energy therefore the reaction is exothermic.

b) Functional groups to improve the reactivity:

diene		dienophile	
$-CH_3$	$-OCH_3$	-CHO	–CN

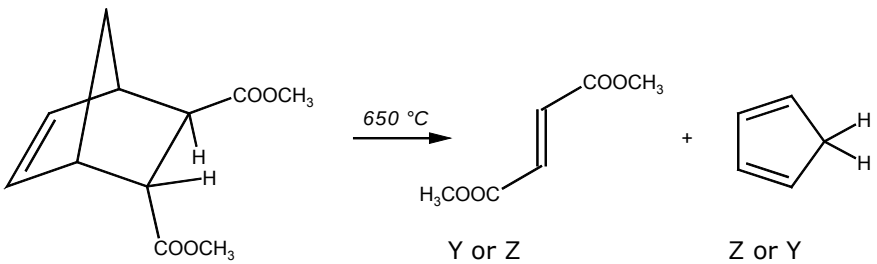
c)



A B X

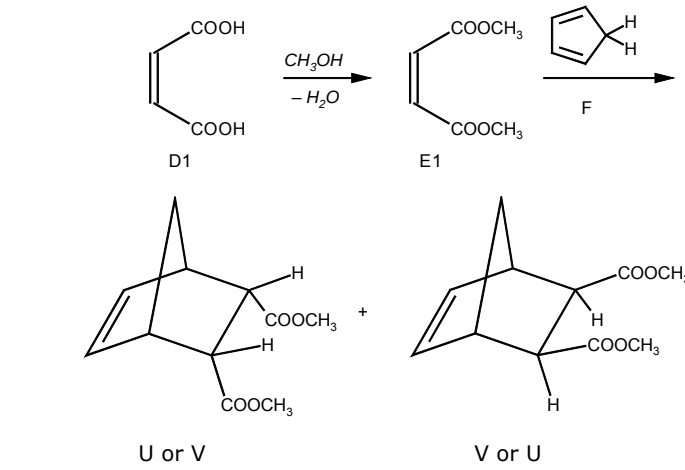
d) Compound A: cyclopentadiene; compound: vinyl acetate, acetic-acid vinyl ester

e)

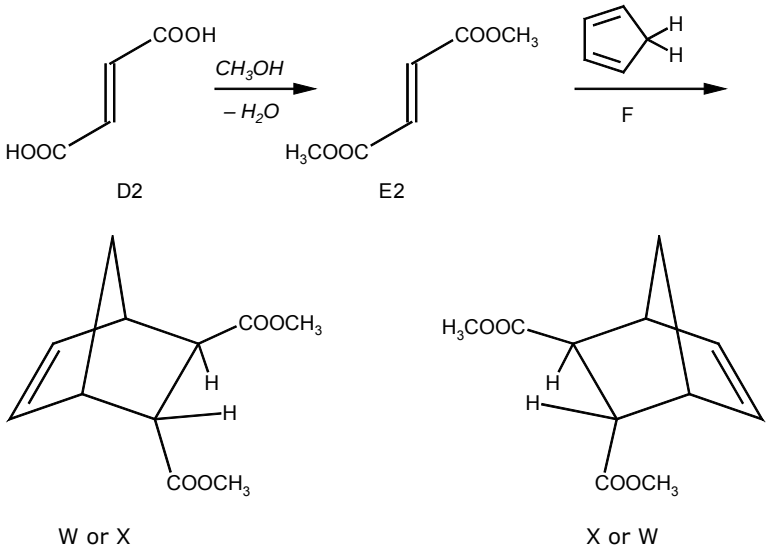


Y or Z Z or Y

f)



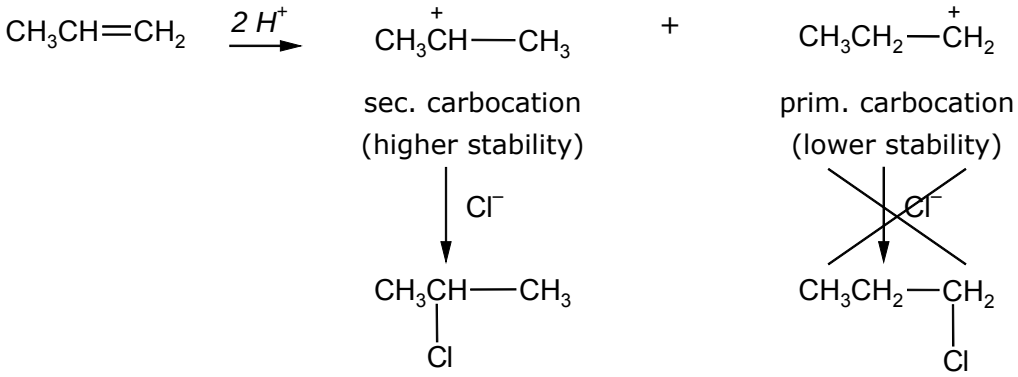
both groups axial both groups equatorial (diastereomers)



enantiomers

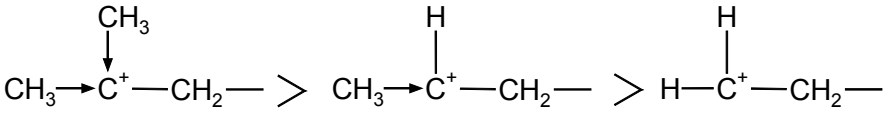
Solution to problem 3-10

a)



Answers Round 3 Test 1

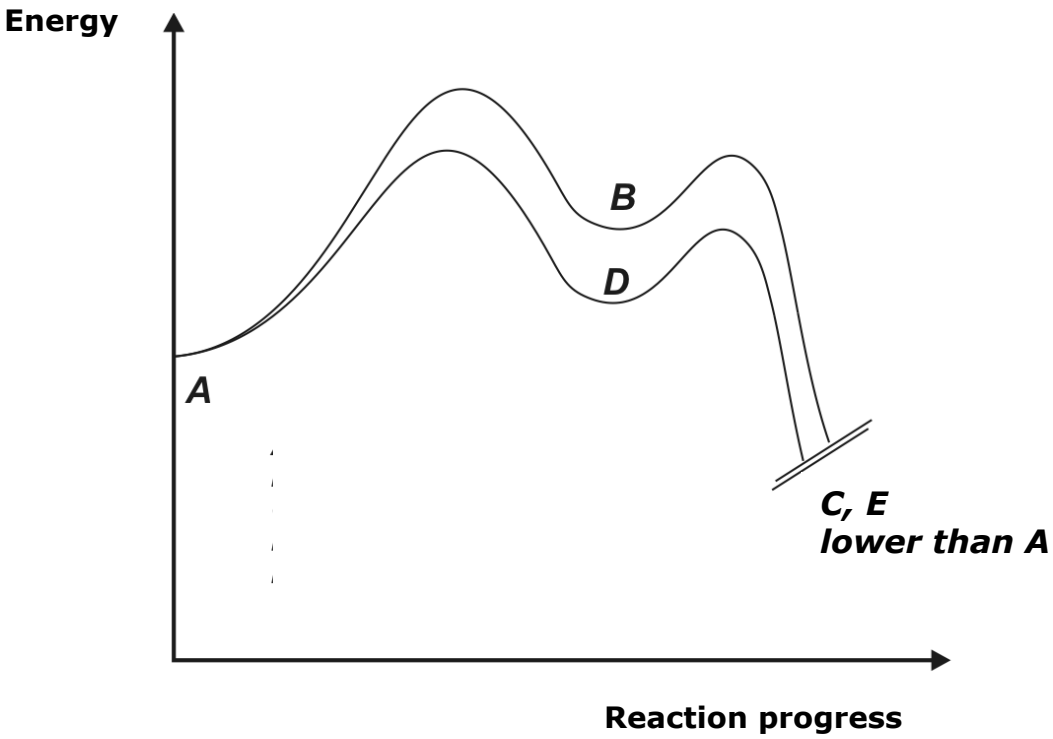
Stability of carbocations due to inductive effects of alkyl groups:



tertiary carbocation > secondary carbocation > primary carbocation

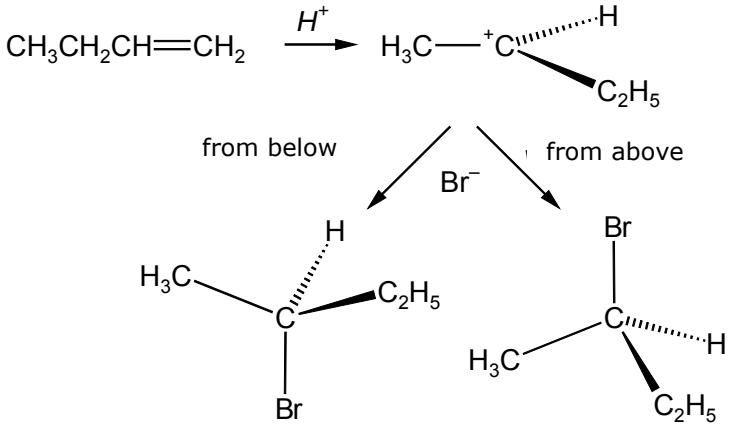
> meaning here: "is more stable as"

b)



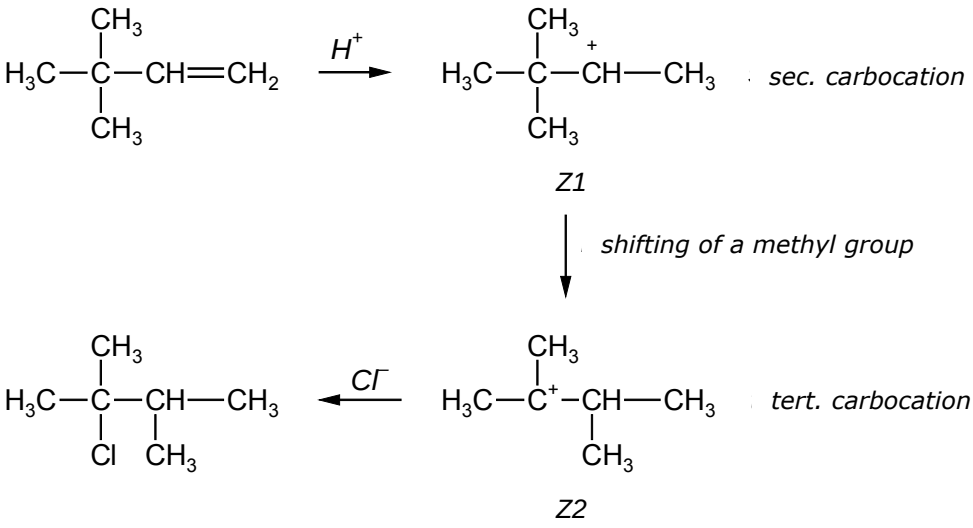
A = Propene
B = primary carbocation
C = 1-chloropropane
D = secondary carbocation
E = 2-chloropropane

c) Mechanism of racemate formation:



racemate: (2S)-2-bromobutane (2R)-2-bromobutane

d) Shnifting of a methyl group



Rule: By shifting a methyl group (or hydrogen) carbocations generate more stable carbocations.

Answers of Round 3 Test 2

Solution to problem 3-11

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

Solution to 3-12

a) $Ag^+ + Br^- \longrightarrow AgBr$

$n(Ag) = (0.1000 - 0.0291)\ L \cdot 0.1\ mol/L = 7.090 \cdot 10^{-3}\ mol$

$m(Ag) = 7.090 \cdot 10^{-3}\ mol \cdot 107.9\ g/mol = 0.765\ g$

$SO_2 + Ba(OH)_2 \longrightarrow BaSO_3\downarrow + H_2O$ with $M(BaSO_3) = 217.37\ g/mol$

$n(S) = 1.156\ g / 217.37\ g/mol = 5.318 \cdot 10^{-3}\ mol$

$m(S) = 5.318 \cdot 10^{-3}\ mol \cdot 32.07\ g/mol = 0.1706\ g$

b) The amount of sulfur ions in argyrodite is higher than needed for the charge equalisation of the silver ions.

Determination of the amounts of silver sulfide (Ag_2S) and the remaining sulfur ions:

$n(S^{2-}_{remainng}) = 5.318 \cdot 10^{-3}\ mol - ½ \cdot 7.090 \cdot 10^{-3}\ mol = 1.773 \cdot 10^{-3}\ mol$

$m(X) = 1g - (0.7650\ g + 0.1706\ g) = 0.0644\ g$

Assuming the oxidation number of X iis +4 the formula XS_2 results for the sulfide.

$n(X) = n(XS_2) = ½ \cdot n(S^{2-}_{remaining})$

$$M(X) = \frac{m(X)}{n(X)} = \frac{m(X)}{½ \cdot n(S^{2-}_{remaining})} = \frac{2 \cdot 0.0644\ g}{1.773 \cdot 10^{-3} mol} = 72.65\ g/mol$$ X = Ge

$n(GeS_2) = n(S^{2-}_{Rest})/2 = 1.773 \cdot 10^{-3}\ mol/2$ $n(GeS_2) = 0.8865 \cdot 10^{-3}\ mol$

$n(Ag_2S) : n(GeS_2) = (7.090/2) : 0.8865 = 4 : 1$

$\Rightarrow$ the empirical formula of argyrodite is Ag_8GeS_6.

c) $GeO_2 + 4HCl \longrightarrow GeCl_4 + 2H_2O$

$GeO_2 + 2NaOH \longrightarrow Na_2GeO_3 + H_2O$

Note: The properties of germanium (Latin *Germania* for Germany) were similar to the element ekasilicon that Mendeleev predicted to exist. The discovery was an important confirmation of the idea of element periodicity.

Solution to problem 3-13

a) Oxidizing agent: Pt^{4+} in $[PtCl_6]^{2-}$

b) Reduction agent: N(III) in NH_4^+

c) $3\ (NH_4)_2[PtCl_6] \longrightarrow 3\ Pt + 2\ N_2 + 2\ NH_4Cl + 16\ HCl$

d) Ammonium hexachloroplatinate(IV) [(IV) is not essential]

e) $NH_3 + H_3O^+ \longrightarrow NH_4^+ + H_2O$

f) $Ni^{2+} + 2OH^- \longrightarrow Ni(OH)_2$

g) $2\ MnO_4^- + 5\ H_2O_2 + 6\ H_3O^+ \longrightarrow 2\ Mn^{2+} + 5\ O_2 + 14\ H_2O$

h) $Cl_2 + 2\ I^- \longrightarrow 2\ Cl^- + I_2$

i) $CH_3COOH + NaHCO_3 \longrightarrow CH_3COO^- + Na^+ + CO_2 + H_2O$

j) $4\ NH_3 + Zn^{2+} \longrightarrow [Zn(NH_3)_4]^{2+}$ also
$6\ NH_3 + Zn^{2+} \longrightarrow [Zn(NH_3)_6]^{2+}$

k) $C_2H_5OH + H_2SO_4 \longrightarrow C_2H_4 + H_3O^+ + HSO_4^-$

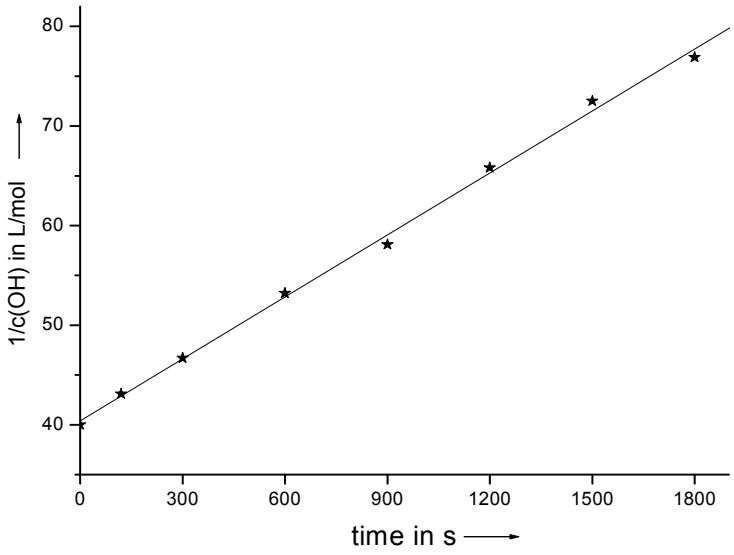
Solution to problem 3-14

a) $n_{titr.} = v_{titr.} \cdot 0.02$ mol/L $\qquad n_{sample}(OH^-) = n(HCl) - n_{titr.} = 5 \cdot 10^{-4}$ mol $- n_{titr.}$

$c_{sample}(OH^-) = n_{sample}(OH^-)/0.01$ L

1	2	3	4	5	6	7
t/s	$\frac{V_{titr.}}{cm^3}$	$\frac{n_{titr.}}{mol}$	$\frac{n_{sample}(OH^-)}{mol}$	$\frac{c_{sample}(OH^-)}{mol/L}$	$\frac{1\,mol/L}{c_{sample}(OH^-)}$	$\ln\frac{c_{sample}(OH^-)}{mol/L}$
0	12.5	$2.50 \cdot 10^{-4}$	$2.50 \cdot 10^{-4}$	0.025	40	- 3.69
120	13.4	$2.68 \cdot 10^{-4}$	$2.32 \cdot 10^{-4}$	0.0232	43.1	- 3.76
300	14.3	$2.86 \cdot 10^{-4}$	$2.14 \cdot 10^{-4}$	0.0214	46.7	- 3.84
600	15.6	$3.12 \cdot 10^{-4}$	$1.88 \cdot 10^{-4}$	0.0188	53.2	- 3.97
900	16.4	$3.28 \cdot 10^{-4}$	$1.72 \cdot 10^{-4}$	0.0172	58.1	- 4.06
1200	17.4	$3.48 \cdot 10^{-4}$	$1.52 \cdot 10^{-4}$	0.0152	65.8	- 4.19
1500	18.1	$3.62 \cdot 10^{-4}$	$1.38 \cdot 10^{-4}$	0.0138	72.5	- 4.28
1800	18.5	$3.70 \cdot 10^{-4}$	$1.30 \cdot 10^{-4}$	0.0130	76.9	– 4.34

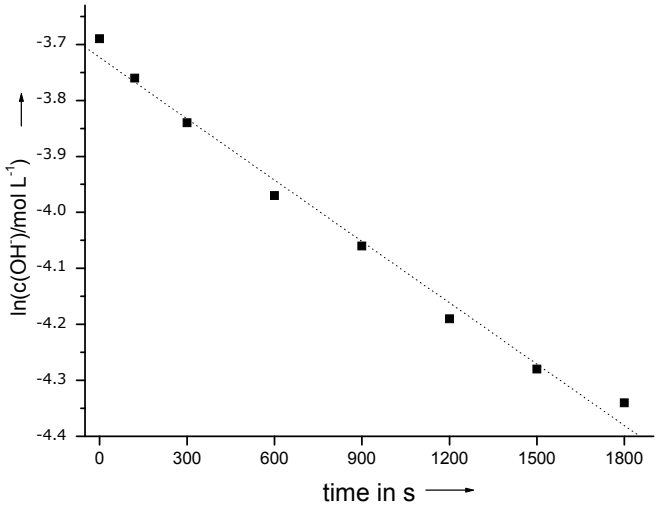
b)



c) k_2 is the slope m of the straight line $\frac{1}{c} = k_2 \cdot t + \frac{1}{c_0}$.

m = 0.021 k_2 = 0.021 $s^{-1}mol^{-1}L$

d) The rate law of a reaction of first order is $c = c_0 \cdot e^{-kt} \Leftrightarrow \ln c = - k \cdot t + \ln c_0$, thus a plot of ln c as a function of t should show a straight line.



A straight line does not occur. This is particularly obvious if you try to draw a line of best fit.

Solution to problem 3-15

a) 1 mol of metal ions is complexed by 1 mol of EDTA.

b) <u>1. titration:</u> All metal ions are complexed

$n_{total} = c_{EDTA} \cdot V_{EDTA}$ n_{total} = 0.04500 mol/L·39.98 mL = $1.7991 \cdot 10^{-3}$ mol

<u>2. titration:</u> Determination of the concentration of Mg^{2+}

$n_{Mg} = c_{Mn} \cdot V_{Mn}$ n_{Mg} = 0.02065 mol/L·10.26 mL = $0.2119 \cdot 10^{-3}$ mol

<u>3. titration:</u> Determination of the concentration of Zn^{2+}

$n_{Zn} = c_{Mn} \cdot V_{Mn}$ n_{Zn} = 0.02065 mol/L·15.47 mL = $0.3195 \cdot 10^{-3}$ mol

$n_{Mn} = n_{total} - n_{Mg} - n_{Zn}$ $n_{Mn} = 1.2677 \cdot 10^{-3}$ mol

$m = n_{metal\ lion} \cdot M_{metal\ ion}$

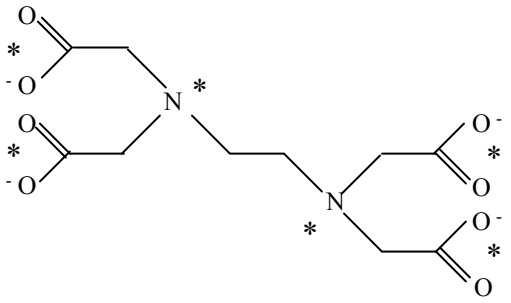
m_{Mn} = 69.65 mg

m_{Mg} = 5.151 mg

m_{Zn} = 20.89 mg

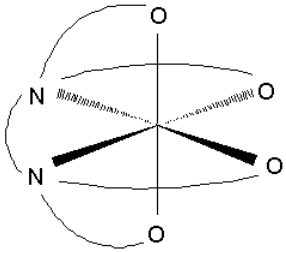
c) $[NH_3(OH)]Cl$ is a reduction agent to avoid the oxidation of Mn^{2+}.

d)



Note (not demanded in the solutions of the students): The anion of ethylenediamine tetraacetic acid ($^{-}OOC\text{-}CH_2)_2$ N-CH_2-CH_2-N (CH_2-$COO^{-})_2$ possesses 6 coordination sites to bind one metal ion.
One of the two equivalent (mesomeric) oxygen atoms of a COO^{-} group is coordination side.

The shape of the complex is shown with the metal ion in the complex middle.



Mg^{2+} and Ca^{2+} form a red complex with the indicator, the *free indicator is blue.*

Thus the solution of Ca^{2+} und Mg^{2+} turns red when the indicator is added.
By titration with an EDTA solution the red coulour disappears,
At the equivalent point the solution turns blue immediately, which is the colour of the free indicator.

Solution to 3-16

a) (i) (K, ΔG) is strongly dependant on temperature
(ii) (ΔH) is closely related to bond strength
(iii) (K) is related to the quantity of reactants and products of a reaction
(iv) (ΔG) is a measure of spontaneity of a reaction
(v) (ΔH) is a measure of heat released or absorbed in a reaction

b) ΔG = - RTlnK ΔG_1 = (-8.314·373.15·ln0.472) J/mol = 2329 J/mol
ΔG_2 = (-8.314·373.15·ln0.128) J/mol = 6378 J/mol
Thus adduct 2 is more stable regarding dissociation.

c) ΔG = ΔH – T·ΔS ΔH_1 = (2329 + 373.15·191.3) J/mol = 73.7 kJ/mol
ΔH_2 = (6378 + 373.15·167.6) J/mol = 68.9 kJ/mol
More heat is needed to dissociate Me_3NBMe_3 Therefore the N-B bond is stronger.

d) ΔG_{RT} = - 2·72.1 kJ/mol = - 144200 J/mol ΔG_R = - R·T·lnK_p

$$\ln K_p = \frac{-144200\ \mathrm{J\cdot mol^{-1}}}{-8.314\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}\cdot 1900\ \mathrm{K}} = 9.129 \qquad K_p = 9214\ (9219)$$

$K_p = \frac{p_o}{p(O_2)}$ $\quad p(O_2) = \frac{1{,}000 \cdot 10^5 Pa}{9214}$ $\quad p(O_2) = 11$ Pa

$p(O_2) = 11$ Pa is the pressure of oxygen in equilibrium. As long as $p(O_2) > 11$ Pa the reaction can proceed spontaneously in the forward direction, so the answer of this problem is "yes if 11 Pa < $p(O_2)$ < 150 Pa".

Solution to problem 3-17

a)

(i) As the number of oxygen atoms increases, H^+ is released more readily because the oxygen atoms additional bonded to Chlorine withdraw electron density from Cl and therefore from ←O←H, too.

(ii) If an H^+ ion has already split off the next H^+ has to be eliminated from a particle with greater negative charge. The greater energy required for this separation results in a lower K_a (by about the factor 10^{-5}).

(iii) In water these three acids are quasi totally protolysed due to the basicity of water (leveling effect of water). The lower attraction between H^+ and a less basic solvent such as CH_3COOH makes it possible to realize differences in the H^+ releasing tendency of the anions, in the different degrees of protolysis.

b)

(i) pH at the beginning: The ph value is determined only by the 1st step of protolysis.

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$$

concentr. at equilibrium: 0,10-x x x

$K_{a1} = \frac{x^2}{0.10 - x} \Rightarrow x^2 + 1.5 \cdot 10^{-4} - 1.5 \cdot 10^{-5} = 0$ $\quad x = 3.8 \cdot 10^{-3}$ $\quad pH = 2.4$

(ii) At the 1st equivalence point (1.EP) is n(KOH)= 0.010 mol, at the 2.EP n(KOH) = 0.020 mol.

At 1.EP you have a solution of KHA, at the 2.EP a solution of K_2A.

1.EP: $pH = ½ \cdot (pK_1 + pK_2)$ $\quad pH = ½ \cdot (3.8 + 6.1)$ $\quad pH = 5.0$

2.EP: $A^{2-} + H_2O \rightleftharpoons HA^- + OH^-$ $\quad K_B = 10^{-14}/K_{a2}$

concent. at equilibrium 0.10-x x x

$1.25 \cdot 10^{-8} = \frac{x^2}{0{,}10 - x} \Rightarrow x^2 + 1.25 \cdot 10^{-8} x - 1.25 \cdot 10^{-9} = 0$ $\quad x = 3.53 \cdot 10^{-5}$

$pOH = 4.5$ $\quad pH = 9.5$

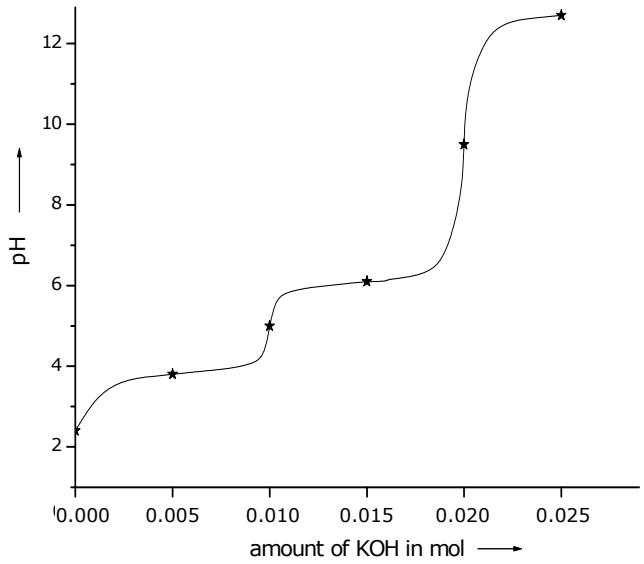
(iii) At half-equivalence points (HEP) there is $c(H_2A) = c(HA^-)$ and $c(HA^-) = c(A^{2-})$, respectively. Following the equation of Henderson-Hasselbalch you find $pH = pK_1$ and $pH = pK_2$, respectively.

1. HEP: $pH = 3.8$ $\quad$ 2. HEP: $pH = 6.1$

(iv) After adding of 0.025 mol of KOH a solution of the salt K_2A (c = 0.01 mol/L) is exis-

tent with an OH^- concentration of 0.005 mol/100 ml = 0.05 mol/L. These OH^- ions determine the pH value.

$c(OH^-)$ = 0.05 mol/L pOH = 1.3 pH = 12.7



Solution to problem 3-18

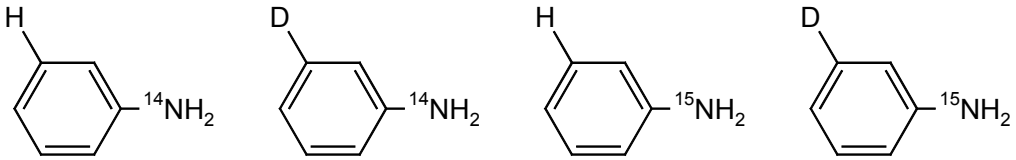
a) m/z = mass to charge ratio, ration between the mass (m) of a molecule or of a fragment to its charge (z).
Further notes to mass spectrometry:
In a mass spectrometer only ions can be detected. The ions are deflected by a magnetic field according not only to their mass but also to their charge. All ions of the same m/z ratio give the same signal. Thus the mass spectrum shows signals in the unit m/z.)

b) Pentane: C_5H_{12}

c) m/z = 72: parent (or molecular) peak of pentane, shows the molar mass
m/z = 57: fragment, molar mass minus mass of a methyl group (72 – 15)
m/z = 43: fragment, molar mass minus mass of a ethyl group (72 – 29)
m/z = 29: fragment, ethyl group (29)

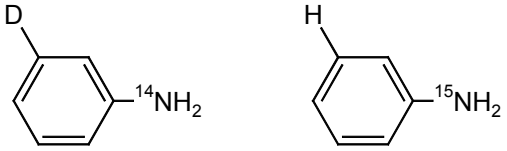
d) m/z = 73: M + 1-peak because of the presence of the isotope of ^{13}C atoms (ca. 1%).

e) Intermolecular mechanism leads to three different molecular peaks:



m/z = 93 *m/z = 94* *m/z = 94* *m/z = 95*

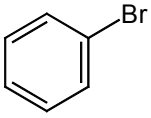
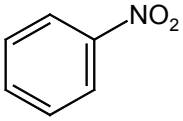
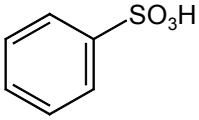
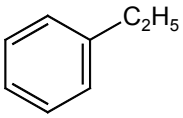
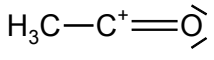
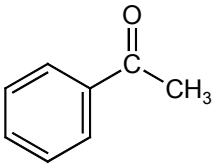
Intramolecular mechanism leads only to the peak of m/z = 94:



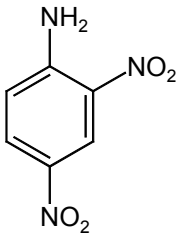
m/z = 94 *m/z = 94*

Solution to problem 3-19

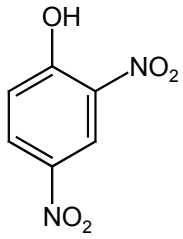
a) Electrophilic substitution

Reaction with	**Electrophile**	**Catalyser**	**Product**
i) Br_2 (halogen)	Br^+	$FeBr_3$ in general Lewis acids	
ii) HNO_3	NO_2^+	H_2SO_4	
iii) H_2SO_4 / SO_3	SO_3, HSO_3^+	-	
iv) C_2H_5Cl (alkyl halide)	$C_2H_5^+$ ($C_2H_5^+$-$ClAlCl_3$)	$AlCl_3$ in general Lewis acids	
v) CH_3COCl (acyl halide)		$AlCl_3$ in general Lewis acids	

b) X and Y



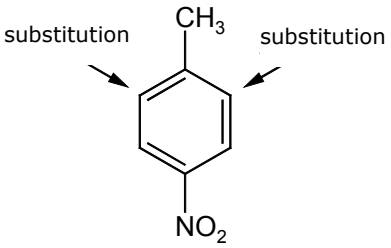
X



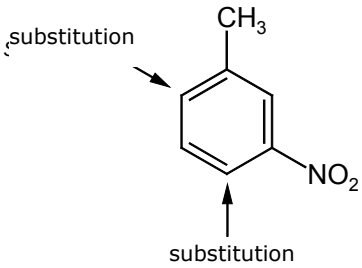
Y

c) Nucleophilic aromatic substitution, favoured by two NO_2 groups which withdraw electrons from the benzene ring. Thus a nucleophilic attack is made possible.

d) Substitutions at the ring



A



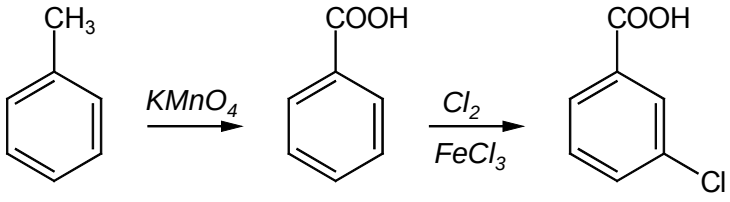
B

Explanations:

to A: $-CH_3$ (leads to o- and p-substitutions)
$-NO_2$ (leads to m- substitutions)
result: both groups strengthen their directing effects.

to B: $-CH_3$ (leads to o- und p- substitutions)
$-NO_2$ (eads to m- substitutions)
result: the directing effect of both groups is contradictory. The directing effect of the methyl group prevails.

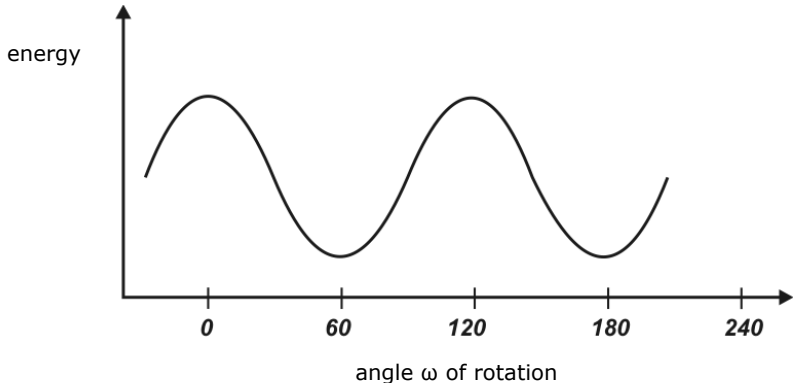
e) Formation of substituted benzoic acid



It is necessary to oxidize the methyl group first to form benzoic acid. In contrast to the methyl group the carboxyl groups directs the halide into the desired meta position.

Solution to problem 3-20

a) Graph of potential energy versus bond rotation



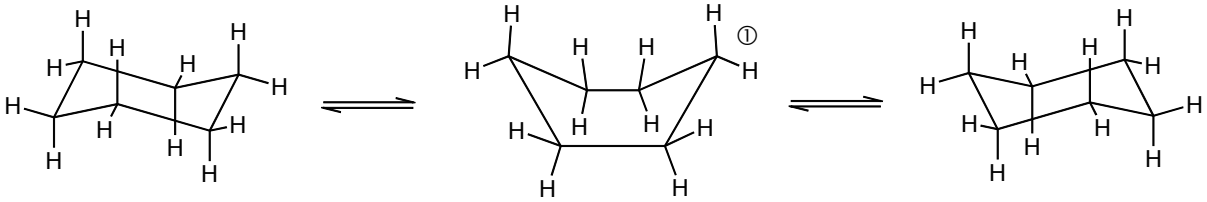
b) Interpretation of the energy diagram

ω = 0: At this angle the six C-N bonds are as close as possible. In this eclipsed con-formation the torsional strain has its maximum

ω = 60°: Turning one methyl group by ω the torsional strain is reduced and reaches at ω = 60° a staggered conformation with a minimal strain of the C-H bonds in the two methyl groups.

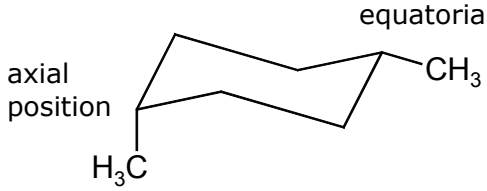
ω = 120°: At a higher angle of ω the strain will increase again to reach a new maximum in an eclipsed conformation at ω = 120°. Continuing the turning of one methyl group until ω = 180° a new minimum is reached.

c) Conformers of cyclohexane



d) The boat conformation has the higher torsional strain (potential energy).
Reason: In both chair-form conformers the six C-C bonds in the ring with their C-H bonds are in gauche position analogous to the staggered conformation in ethane. The molecule has reached an energy minimum.
In contrast to the chair conformations in the boat conformation two C-C bonds with their C-H bonds are arranged in ecliptic position (C2 to C3 and C5 to C6) with high steric interference. The molecule has reached an energy maximum.

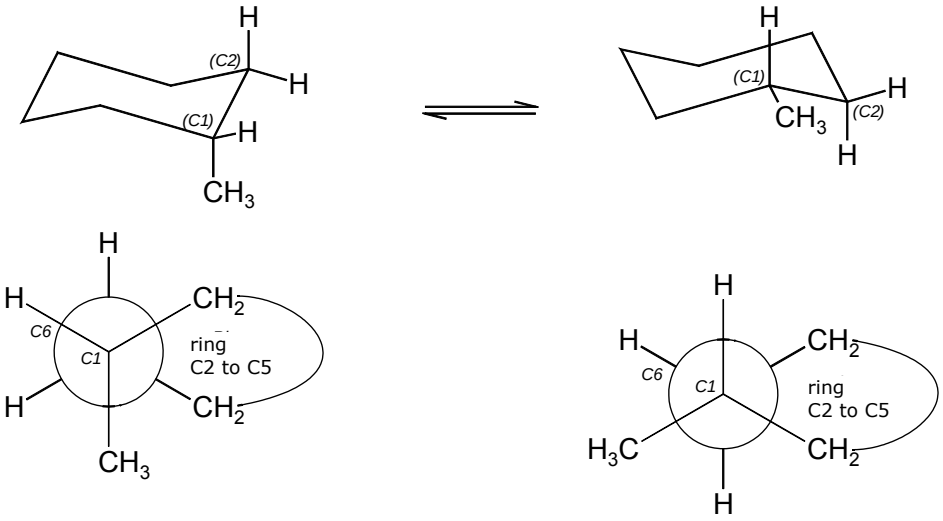
e)



(C–H-bonds are not shown to reach a clear view)

f) The cis-trans symmetry does not change if one chair form converts to the second one, but ligands in a-positions convert to e-positions and vice versa.

g)



axial position
CH_3 group near to C6 (ring)

higher steric interference

equatorial position
CH_3 group in anti position to C6 (ring)

lower steric interferende

There will be an excess of the chair structure with the methyl group in equatorial position.

Answers Round 4 (theoretical)

Solution to problem 4-1

a) α-decay: atomic number -2 Δ(atomic mass) ≈ -4u

β-decay: atomic number+1 Δ(atomic mass) = 0

b) In the mineral there is not only ^{206}lead („uraniumlead") produced by the decay of uranium but also natural ^{206}lead. In order to apply the law of decay you have to determine the amount of uraniumlead first.

Natural ratio $\frac{n(^{206}Pb)}{n(^{204}Pb)} = \frac{23.6}{1.48} = 15.95.$

From 0.1224 mol ^{206}Pb there are

0.1224 mol · $\frac{15{,}95}{75{,}41}$ = 0.0259 mol of natural ^{206}lead

and (0.1224 - 0.0259) mol = 0.0965 mol of uraniumlead

$\Rightarrow \quad \frac{n(^{206}Pb_{uranium})}{n(^{238}U)} = 0.0965.$

So 1 mol of uranium (of today) is accompanied by 0.0965 mol of ^{206}Pb which arose from 0.0965 mol uranium originally $\Rightarrow \quad \frac{n_0(^{238}U)}{n_t(^{238}U)} = \frac{1+0{,}0965}{1} = 1.0965$

$n_t = n_0 \cdot e^{-k \cdot t} \quad \Rightarrow \quad t = k^{-1} \cdot \ln\frac{n_0}{n_t}$ mit k $= \ln 2 / t_{1/2}$

$t = (\ln 1.0965) \cdot 4.511 \cdot 10^9$ a / ln2 $\quad t = 600 \cdot 10^6$ a

Solution to problem 4-2

a) $k_{25} = A \cdot e^{-Ea/R \cdot 298.15\ K}$ (1)

$k_{35} = 4.1 \cdot k_{25} = A \cdot e^{-Ea/R \cdot 308.15\ K}$ (2)

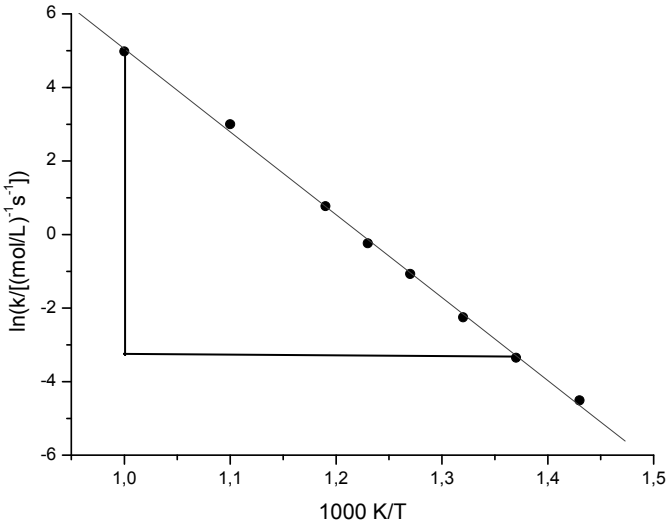
(2) / (1) $\quad 4.1 = e^{-Ea/R \cdot 308.15\ K} / e^{-Ea/R \cdot 298.15\ K}$

$\Rightarrow \quad E_a = R \cdot (\ln 4.1) \cdot \left(\frac{1}{298{,}15\,K} - \frac{1}{308{,}15\,K}\right)^{-1} \quad E_a = 107.8$ kJ/mol

b) $k = A \cdot e^{-Ea/(R \cdot T)} \quad \Rightarrow \quad \ln k = \frac{-E_a}{R} \cdot \frac{1}{T} + \ln A$

If you plot ln k against 1/T you should get a straight line with a slope of m = - R/E_a and an intercept of b = ln A.

$(1/T) \cdot 10^3$ K	1.43	1.37	1.32	1.27	1.23	1.19	1.10	1.00
$\ln \frac{k}{(mol/L)^{-1} \cdot s^{-1}}$	-4.51	-3.35	-2.25	-1.07	-0.24	0.77	3.00	4.98



$m = \frac{-3.35 - 4.98}{(1.37 - 1.00)/1000} = -2.25 \cdot 10^4 \quad \Rightarrow \quad E_a = 187$ kJ/mol

ln A = ln k + 22500/T replacement of the point (1.23/-0.24):

$A = e^{27.4}$ (mol/L)$^{-1}\cdot$s^{-1} = $7.9 \cdot 10^{11}$ (mol/L)$^{-1}\cdot$s^{-1}

c) 1) S 2) P 3) P 4) I 5) T

d) $k_b \cdot [HBr] \approx 0 \quad \Rightarrow \quad \frac{d[HBr]}{dt} = k_a \cdot [H_2] \cdot [Br_2]^{1/2}$

4. $H\cdot + HBr \longrightarrow Br\cdot + H_2$ can be ignored.

e) $(d[H\cdot]/dt =) \quad 0 = k_2\cdot[Br\cdot]\cdot[H_2] - k_3\cdot[Br_2]\cdot[H\cdot]$ (1)

$(d[Br\cdot]/dt =) \quad 0 = 2\cdot k_1\cdot[Br_2] - k_2\cdot[Br\cdot]\cdot[H_2] + k_3\cdot[Br_2]\cdot[H\cdot] - 2\cdot k_5\cdot[Br\cdot]^2$ (2)

(1) + (2) $\quad 0 = 2\cdot k_1\cdot[Br_2] - 2\cdot k_5\cdot[Br\cdot]^2 \quad \Rightarrow \quad [Br\cdot] = (\frac{k_1}{k_5}\cdot[Br_2])^{1/2}$ (3)

$\frac{d[HBr]}{dt} = k_2\cdot[Br\cdot]\cdot[H_2] + k_3\cdot[Br_2]\cdot[H\cdot]$

because of (1): $k_2\cdot[Br\cdot]\cdot[H_2] = k_3\cdot[Br_2]\cdot[H\cdot] \quad \Rightarrow \quad \frac{d[HBr]}{dt} = 2\cdot k_2\cdot[Br\cdot]\cdot[H_2]$

with (3) $\quad \frac{d[HBr]}{dt} = 2\cdot k_2\cdot(\frac{k_1}{k_5}\cdot[Br_2])^{1/2}\cdot[H_2]$

This is the expected rate law with $k_a = 2\cdot k_2\cdot(k_1/k_5)^{1/2}$.

Solution to problem 4-3

a) $N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$

$\Delta_rH^0 = -91.8$ kJ·mol^{-1} $\Delta_rS^0 = -198.1$ J·mol^{-1}·K^{-1}

$\Delta_rG^0 = \Delta_rH^0 - 298.15\ K \cdot \Delta_rS^0$ $\Delta_rG^0 = -32.7$ kJmol^{-1}

$\Delta_r G^0 = - R \cdot T \cdot \ln K_p$ $\quad\quad$ $\ln K_p = - \Delta_r G^0 \, (R \cdot T)^{-1}$

$\ln K_p = 13.19$ $\quad\quad$ $K_p(298.15) = 5.35 \cdot 10^5$

b) $K_p = \dfrac{(p(NH_3)/p_0)^2}{p(N_2)/p_0 \cdot (p(H_2)/p_0)^3}$

The ratio of amounts is equal to the ratio of the partial pressures and the total pressure and $V(N_2) : V(H_2) = 1 : 3$.

$p(NH_3) = 0.18 \cdot 200$ bar $\quad\quad$ $p(N_2) = (1-0.18) \cdot 200/4$ $\quad\quad$ $p(N_2) = 0.205 \cdot 200$ bar

$p(H_2) = 3 \cdot p(N_2)$ $\quad\quad$ $p(H_2) = 0.615 \cdot 200$ bar

$K_p(T) = \dfrac{(0{,}18)^2}{0{,}205 \cdot (0{,}615)^3 \cdot 200^2}$ $\quad\quad$ $K_p(T) = 1.70 \cdot 10^{-5}$

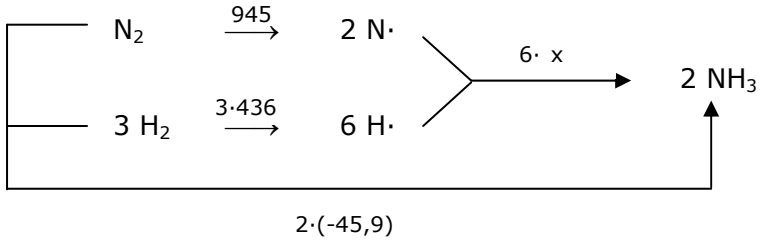
c) Using the van't Hoff isochore you get

$$\ln \frac{K_p(T)}{K_p(298{,}15)} = -\frac{\Delta_r H}{R}\left(\frac{1}{T} - \frac{1}{298{,}15\,K}\right) \quad \Rightarrow \quad T = \left(-\frac{R}{\Delta H} \cdot \ln \frac{K_p(T)}{K_p(298{,}15\,K)} + \frac{1}{298{,}15\,K}\right)^{-1}$$

$$T = \left(-\frac{8{,}314\ JK^{-1}mol^{-1}}{-91800\ J\,mol^{-1}} \cdot \ln \frac{1{,}70 \cdot 10^{-5}}{5{,}36 \cdot 10^5} + \frac{1}{298{,}15\,K}\right)^{-1} \quad\quad T = 859\ K$$

d) The assumptions of the calculation do not match the actual conditions:
ΔH and ΔS are not constant in this interval of temperature – but the van't Hoff isochore is based on this precondition.
Furthermore gases at such a high pressure do not behave ideal which makes the calculation of partial pressures imprecise.

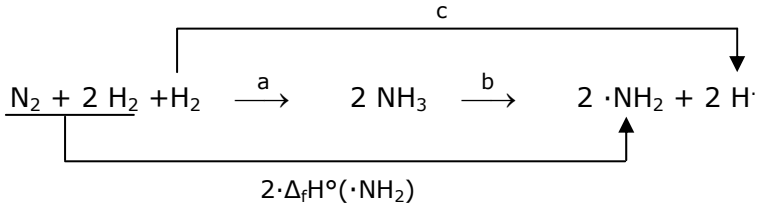
e)



$945 + 3 \cdot 436 + 6 \cdot x = - 2 \cdot 45{,}9$ $\quad\quad$ $x = - 391$

$\Rightarrow \quad \Delta_b H°(\text{N-H bond}) = + 391\ kJ \cdot mol^{-1}$

f)



$2 \cdot \Delta_f H°(\cdot NH_2) + c = a + b$

a = $2\cdot\Delta_f H°(NH_3)$ b = $2\cdot\Delta_b H°$(N-H bond) c = $\Delta_b H°$(H-H)

$\Delta_f H°(\cdot NH_2) = ½ \cdot(- 2\cdot45{,}9 + 2\cdot380 - 436)$ kJ·mol^{-1}

$\Delta_f H°(\cdot NH_2) = 116$ kJ·mol^{-1}

Solution to problem 4-4

a) In the first step H_2SO_4 is totally protolysed. $c(SO_4^{2-})$ is determined by K_{a2}.

	$HSO_4^- + H_2O \rightleftharpoons$	$SO_4^{2-} + H_3O^+$
c(beginning)/c_0	10^{-2}	0 10^{-2}
c(equilibrium)/c_0	$10^{-2} - x$	x $10^{-2} + x$

$K_{a2} = \frac{x\cdot(10^{-2}+x)}{10^{-2}-x} \Rightarrow x^2 + x\cdot(10^{-2} + 10^{-1.92}) - 10^{-1.92}\cdot 10^{-2} = 0$

$x_1 = 4.53\cdot10^{-3}$ ($x_2 = - 0.027$)

$c(SO_4^{2-}) = 4.53\cdot10^{-3}$ mol/L $c(H_3O^+) = 14.53\cdot10^{-3}$ mol/L pH = 1.84

b) $H^+ + e^- \longrightarrow ½ H_2$ and $PbSO_4 + 2\ e^- \longrightarrow Pb + SO_4^{2-}$

c) E(cell) = E(right half cell) – E(left half cell)

$- 0.188\ V = E(PbSO_4 + 2\ e^- \longrightarrow Pb + SO_4^{2-}) - (0\ V + \frac{R\cdot T}{F}\ln\frac{15\cdot10^{-3}}{(1)^{1/2}})$

$E(PbSO_4 + 2\ e^- \longrightarrow Pb + SO_4^{2-}) = - 0.188\ V - 0.108\ V = - 0.296\ V$

$E(PbSO_4 + 2\ e^- \longrightarrow Pb + SO_4^{2-}) = E(Pb^{2+}/Pb)$ with $c(Pb^{2+}) = x$ mol/L.

x is the actual Pb^{2+} concentration in the right half cell.

$E = E°(Pb^{2+}/Pb) + \frac{R\cdot T}{2\cdot F}\cdot\ln(c(Pb^{2+})/c_0)$

$- 0.296\ V = - 0.126\ V + \frac{R\cdot T}{2\cdot F}\cdot\ln x$ $x = 1.79\cdot10^{-6}$

$K_{sp} = c(SO_4^{2-})/c_0 \cdot c(Pb^{2+})/c_0$ $K_{sp} = 5\cdot10^{-3}\cdot1.79\cdot10^{-6}$ $K_{sp} = 0.90\cdot10^{-8}$

d) $\Delta E = \frac{R\cdot T}{F}(\ln\frac{15\cdot10^{-3}}{(½)^{1/2}} - \ln\frac{15\cdot10^{-3}}{(1)^{1/2}}) = -\frac{R\cdot T}{2\cdot F}\ln ½$ $\Delta E = 0.0089$ V

e) (1) $Au^{3+} + 3\ e^- \longrightarrow Au$ $E_1° = + 1.50$ V $\Delta G_1° = -3\cdot F\cdot1.5$ V

(2) $[AuCl_4]^- + 3\ e^- \longrightarrow Au + 4\ Cl^-$ $E_2° = + 1.00$ V $\Delta G_2° = -3\cdot F\cdot1.0$ V

The equilibrium constant K_b of the reaction is asked for

(3) $Au^{3+} + 4\ Cl^- \rightleftarrows [AuCl_4]^-$

(3) = (1) – (2) $\Delta G_3 = -3\cdot F\cdot(1.50\ V - 1.00\ V)$

$\Delta G_3 = - R\cdot T\cdot\ln K_b$ $\ln K_b = 58.39$ $K_b = 2.27\cdot10^{25}$

Solution to problem 4-5

a) 1 Joule = 1 Nm $= 1\ kg{\cdot}m^2{\cdot}s^{-2}$

p = force/area = mass·acceleration/area

$[p] = kg{\cdot}m{\cdot}s^{-2}/m^2 = kg{\cdot}m^{-1}{\cdot}s^{-2}$

$[\sqrt{2\pi \cdot m \cdot k_b \cdot T}\,] = \sqrt{kg \cdot J \cdot K^{-1} \cdot K} = \sqrt{kg \cdot kg \cdot m^2 \cdot s^{-2}} = kg{\cdot}m{\cdot}s^{-1}$

$[Z] = \dfrac{kg \cdot m^{-1} \cdot s^{-2}}{kg{\cdot}m{\cdot}s^{-1}} = m^{-2}{\cdot}s^{-1}$

i.e. $Z_{surface}$ gives the number of collisions per square meter per second.

b) $Z_{total} = \dfrac{1.013{\cdot}10^5\ Pa}{\sqrt{2{\cdot}\pi{\cdot}0.032\,kg/mol \cdot (6.022{\cdot}10^{23}/mol)^{-1} \cdot 1.38{\cdot}10^{-23}\,J{\cdot}K^{-1} \cdot 293.15\,K}} \cdot 75\ m^2 \cdot 5\ s$

$Z_{total} = 1.034{\cdot}10^{30}$ collisions

c) 270 mL/min. = 22.5 mL/5 s

with p·V = n·R·T $n = 8.839{\cdot}10^{-4}$ mol $= 5.323{\cdot}10^{20}$ molecules CO_2

The same number of O_2 molecules is exchanged,

that is $\dfrac{5.323{\cdot}10^{20}}{9{\cdot}10^{31}} \cdot 100\% = 5.9{\cdot}10^{-10}$ %.

Solution to problem 4-6

a) $A_{circle} = \pi{\cdot}r^2$, $r = 2{\cdot}10^{-3}$ m $A_{circle} = 1.257{\cdot}10^{-5}\ m^2$

Number of molecules in this circle $N = 1.257{\cdot}10^{-5}\ m^2 \cdot 10/(10^{-6}\ m)^2 = 1.257{\cdot}10^8$

They are transferred onto the surface by a drop of 10 µL

⇒ concentration = $1.257{\cdot}10^8$ molecules/$(10{\cdot}10^{-6}$ L) $= 1.257{\cdot}10^{13}$ molecules/L

$c = 1.257{\cdot}10^{13}\ L^{-1} / N_A = 2.087{\cdot}10^{-11}$ mol/L

b) $E = h{\cdot}\dfrac{c}{\lambda}$ $E = 6.6261{\cdot}10^{-34}\ J\,s{\cdot}3{\cdot}10^8\ m\ s^{-1}/(543.5{\cdot}10^{-9}\ m) = 3.657{\cdot}10^{-19}$ J

with $3{\cdot}10^{10}$ photons/s you get

$P = 3.657{\cdot}10^{-19}\ J{\cdot}3{\cdot}10^{10}\ s^{-1} = 1.10{\cdot}10^{-8}\ J\ s^{-1}$ P = 11.0 nW

c) On average there are 10 molecules/µm², so that one molecule occupies statistically an area of $(10^{-6}\ m)^2/10 = 10^{-13}\ m^2$.

d) The total illuminated area of $\pi{\cdot}(50{\cdot}10^{-9}\ m)^2 = 7.85{\cdot}10^{-15}\ m^2$ receives $3{\cdot}10^{10}$ photons/s, and the area occupied by one single molecule receives

$3{\cdot}10^{10}\ s^{-1} \cdot 10^{-13}\ m^2/7.85{\cdot}10^{-15}\ m^2 = 3.82{\cdot}10^{11}$ photons/s.

Only $2.3{\cdot}10^5$ photons/s are absorbed so the area which is capturing photons is

$\sigma = 10^{-13}\ m^2 \cdot 2.3{\cdot}10^5\ s^{-1}/3.82{\cdot}10^{11}\ s^{-1} = 6{\cdot}10^{-20}\ m^2 = 6$ Å².

Solution to problem 4-7

a) Formation of sodium hypochlorite: $Cl_2 + 2\ NaOH \rightleftharpoons NaCl + NaOCl$ (**A**) $+ H_2O$

b) $2\ NaOCl \rightleftharpoons 2\ NaCl + O_2$

c) The compound which is asked for is dichlorine monoxide, the anhydride of hypochloric acid. It forms on concentrating to small volumes.
$2\ NaOCl \rightleftharpoons Cl_2O + Na_2O$ (in aqueous solution: formation of NaOH)

d) $3\ NaOCl \rightleftharpoons NaClO_3$ (**B**) $+ 2\ NaCl$

e) $2\ NaClO_3 + Ba(NO_3)_2 \rightleftharpoons 2\ NaNO_3 + Ba(ClO_3)_2$ (**C**)

f) $4\ Ba(ClO_3)_2 \rightleftharpoons 3\ Ba(ClO_4)_2$ (**D**) $+ BaCl_2$

g) $Cl_2 + {}^2/_8\ S_8 \rightleftharpoons S_2Cl_2$ (**E**)
or $4\ Cl_2 + S_8 \rightleftharpoons 4\ S_2Cl_2$ or $Cl_2 + 2\ S \rightleftharpoons S_2Cl_2$

h) S_2Cl_2 (**E**) $+ Cl_2 \rightleftharpoons 2\ SCl_2$ (**F**)

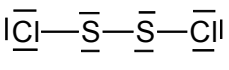
i) $2\ SCl_2 + O_2 \rightleftharpoons 2\ SOCl_2$ (**G**)

$SCl_2 + O_2 \rightleftharpoons SO_2Cl_2$ (**H**)

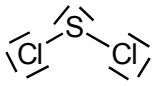
j) $SOCl_2 + H_2O \rightleftharpoons SO_2 + 2\ HCl$

k)

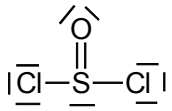
E



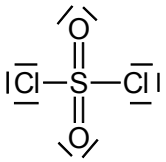
F

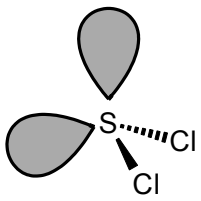


G

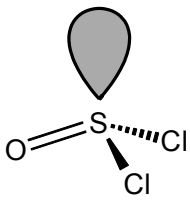


H

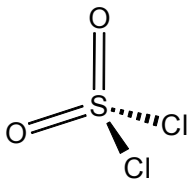




bent



trigonal pyramidal

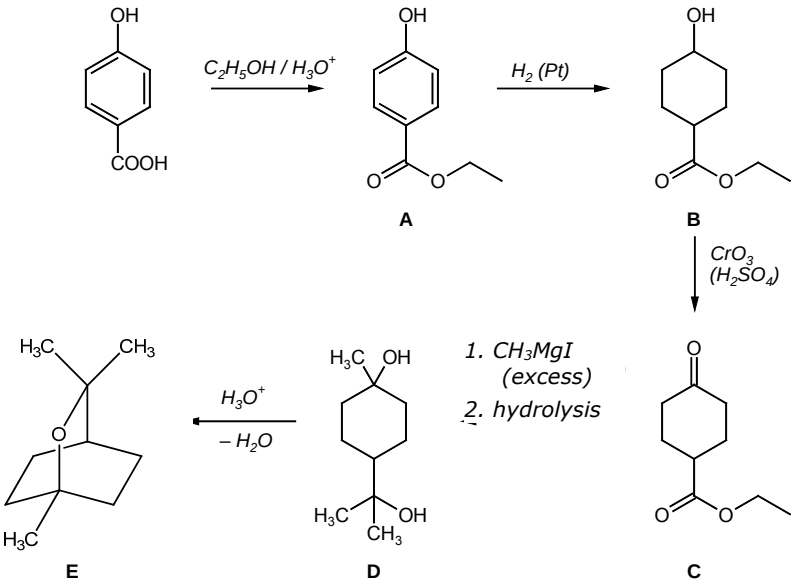


tetrahedral

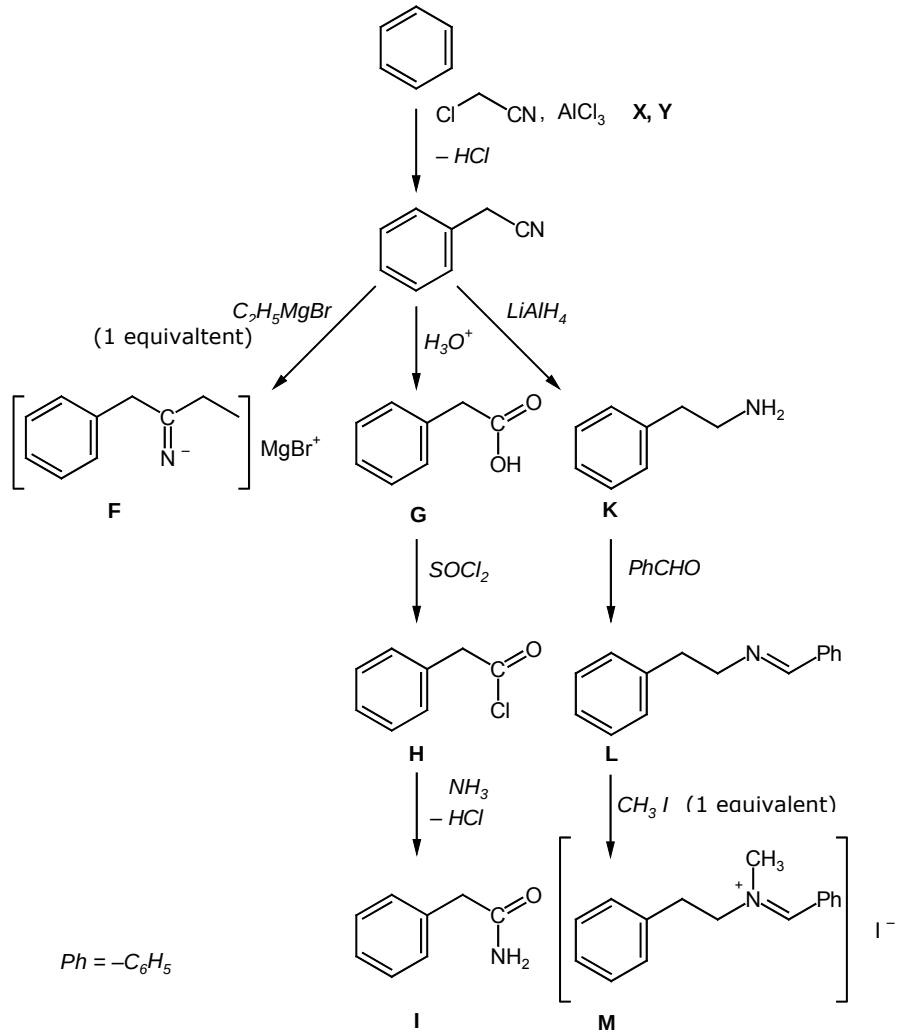
l) **G** can be derived from sulfurous acid (two OH groups replaced by -Cl), **H** from sulfuric acid (two OH groups replaced by –Cl).

Solution to problem 4-8

a)



b)



Solution to problem 4-9

a) Number of signals

	I)	II)	III)	IV)	V)	VI)	VII)
^{13}C-NMR	2	1	1	4	3	3	3
^{1}H-NMR	1	1	1*	2	2	2	3**

* At low temperatures you may distinguish between equatorial and axial protons when the chair conformation flips more slowly than the duration of the NMR measuring.

** (cis-trans position of H!)

b) Assignment of the signals

δ_1 und δ_2 (doublet): both doublets belong to the 4 protons of the ring. Due to the symmetry of the compound the protons in position 2 and 6 are magnetically equivalent and interact with their neighbours. Together they give one signal (doublet). The same applies to the protons in positions 3 and 5.

δ_3 (singlet): due to protons in OCH_3, no interaction with neighbouring protons.

δ_4 (quartett): due to the CH_2 group adjacent the carbonyl group; interaction with the CH_3 group.

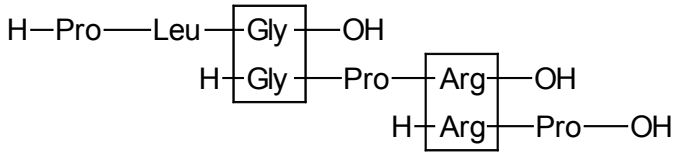
δ_5 (triplett): due to the CH_3 group; interaction with the CH_2 group.

c) Structural formula: $Cl–CH_2–CH_2–O–CH_2–CH_2–Cl$

The compound contains two different kinds of protons. They interact with two equivalent nuclei to form a triplet.

Solution to problem 4-10

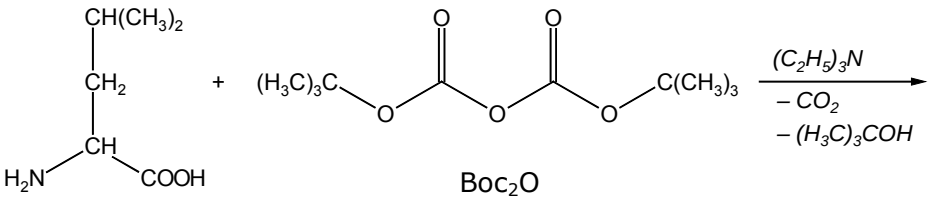
a)

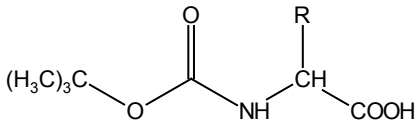


Sequence of the peptide H – Pro – Leu – Gly – Pro – Arg – Pro – OH

b) **Step 1:** Introducing a protecting group for the NH_2 group of Leu:

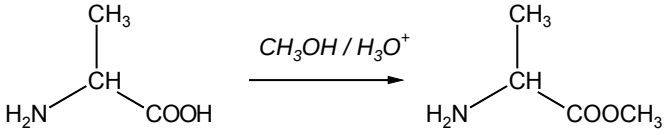
(R = $–CH_2–CH(CH_3)_2$)





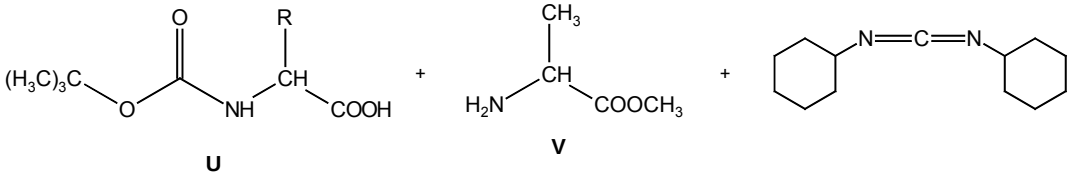
U

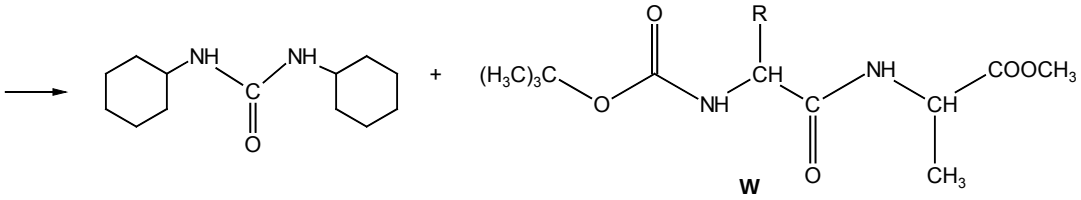
Step 2: Introducing a protecting group for the acid group of Ala.



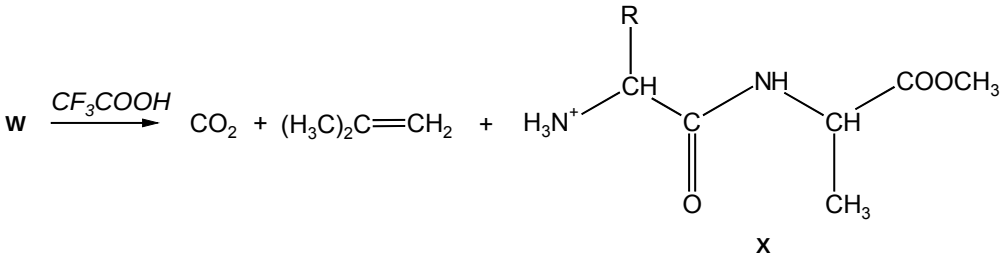
V

Step 3: Coupling of the (protected) amino acids.

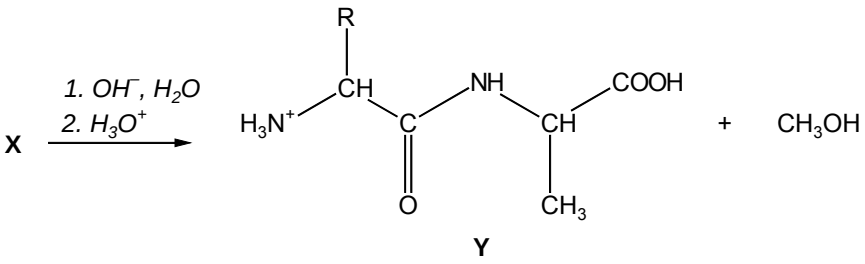




Step 4: Elimination of the protecting group of Leu

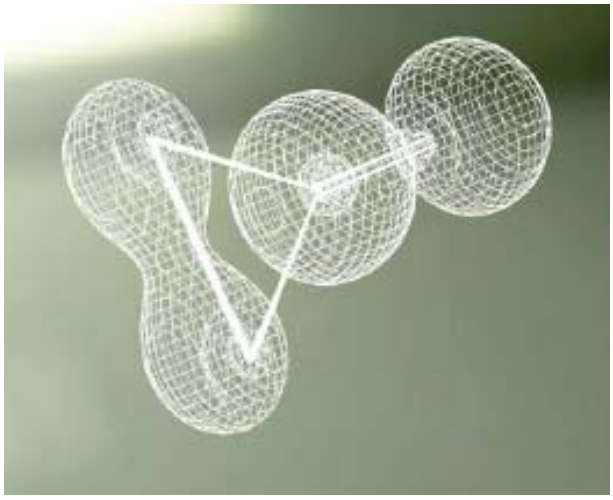


Step 5: Elimination of the protecting group of Ala leads to **Y** = H-Leu-Ala-OH



Y

Part 3



41st International Chemistry Olympiad

Theoretical and Practical Problems

23. + 21. July 2008

Theoretical Test

Physical constants

Name	Symbol	Value
Avogadro constant	N_A	6.0221×10^{23} mol^{-1}
Boltzmann constant	k_B	1.3807×10^{-23} J K^{-1}
Gas constant	R	8.3145 J K^{-1} mol^{-1}
Faraday constant	F	96485 C mol^{-1}
Speed of light	c	2.9979×10^{8} m s^{-1}
Planck constant	h	6.6261×10^{-34} J s
Standard pressure	$p°$	10^5 Pa
Atmospheric pressure	p_{atm}	1.01325×10^5 Pa
Zero of the Celsius scale		273.15 K
Standard acceleration of free fall	g	9.807 m s^{-2}
Bohr magneton	$\square_B$	9.274015×10^{-24} J T^{-1}

Usefull formulae

Volume of a cube $V = l^3$

Volume of sphere $V = (4/3)\ \pi\ r^3$

Potential energy in a field of gravity $E = mgh$

Equation of ideal gases $pV = nRT$

Arrhenius equation $k = A \exp(-E_a / RT)$

Magnetic moment $\mu_{eff} = \sqrt{n(n+2)}$ BM

A periodic table with relative atomic masses was available

Problem 1

Many different methods have been used to determine the Avogadro constant. Three different methods are given below.

Method A – from X-ray diffraction data (modern)

The unit cell is the smallest repeating unit in a crystal structure. The unit cell of a gold crystal is found by X-ray diffraction to have the face-centred cubic unit structure (i.e. where the centre of an atom is located at each corner of a cube and in the middle of each face). The side of the unit cell is found to be 0.408 nm.

a) Sketch the unit cell and calculate how many Au atoms the cell contains.

b) The density of Au is 1.93×10^4 kg m^{-3}. Calculate the volume and mass of the cubic unit cell.

c) Hence calculate the mass of a gold atom and the Avogadro constant, given that the relative atomic mass of Au is 196.97.

Method B – from radioactive decay (Rutherford, 1911)

The radioactive decay series of ^{226}Ra is as follows:

$$^{226}\text{Ra} \xrightarrow{t} {}^{222}\text{Rn} \xrightarrow{3.825\ \text{d}} {}^{218}\text{Po} \xrightarrow{3.10\ \text{m}} {}^{214}\text{Pb} \xrightarrow{26.8\ \text{m}} {}^{214}\text{Bi} \xrightarrow{19.9\ \text{m}}$$

$$^{214}\text{Po} \xrightarrow{164.3\ \mu\text{s}} {}^{210}\text{Pb} \xrightarrow{22.3\ \text{y}} {}^{210}\text{Bi} \xrightarrow{5.013\ \text{d}} {}^{210}\text{Po} \xrightarrow{138.4\ \text{d}} {}^{206}\text{Pb}$$

The times indicated are half-lives, the units are y = years, d = days, m = minutes. The first decay, marked *t* above, has a much longer half-life than the others.

d) In the table on the answer sheet, identify which transformations are α-decays and which are β-decays.

e) A sample containing 192 mg of ^{226}Ra was purified and allowed to stand for 40 days. Identify the first isotope in the series (excluding Ra) that has not reached a steady state.

f) The total rate of α-decay from the sample was then determined by scintillation to be 27.7 GBq (where 1 Bq = 1 count s^{-1}). The sample was then sealed for 163 days. Calculate the number of α particles produced.

g) At the end of the 163 days the sample was found to contain 10.4 mm^3 of He, measured at 101325 Pa and 273 K. Calculate the Avogadro constant from these data.

h) Given that the relative isotopic mass of ^{226}Ra measured by mass spectrometry is 226.25, use the textbook value of the Avogadro constant (6.022×10^{23} mol^{-1}) to calculate the number of ^{226}Ra atoms in the original sample, n_{Ra}, the decay rate constant, □, and the half-life, t, of ^{226}Ra (in years). You need only consider the decays up to but not including the isotope identified in (**e**).

Method C – dispersion of particles (Perrin, 1909)

One of the first accurate determinations of the Avogadro constant was carried out by studying the vertical distribution under gravity of colloidal particles suspended in water. In one such experiment, particles with radius 2.12×10^{-7} m and density 1.206×10^3 kg m^{-3} were suspended in a tube of water at 15 °C. After allowing sufficient time to equilibrate, the mean numbers of particles per unit volume observed at four heights from the bottom of the tube were:

height / 10^{-6} m	5	35	65	95
mean number per unit volume	4.00	1.88	0.90	0.48

i) Assuming the particles to be spherical, calculate: the mass, m, of a particle; the mass of the water it displaces, m_{H2O}; and the effective mass, m^*, of the particle in water accounting for buoyancy (i.e. taking account of the upthrust due to the displaced volume of water). Take the density of water to be 999 kg m^{-3}.

At equilibrium, the number of particles per unit volume at different heights may be modelled according to a Boltzmann distribution:

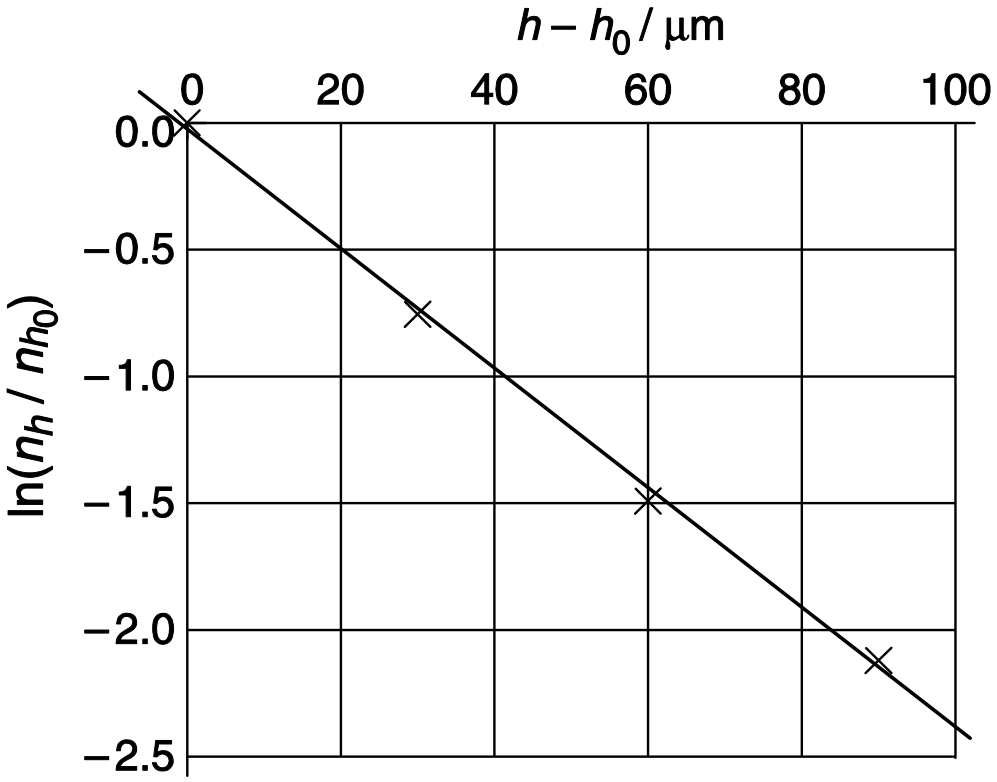
$$\frac{n_h}{n_{h_0}} = \exp\left[-\frac{E_h - E_{h_0}}{RT}\right]$$

where n_h is the number of particles per unit volume at height h,

n_{h0} is the number of particles per unit volume at the reference height h_0,

E_h is the gravitational potential energy per **mole** of particles at height h relative to the particles at the bottom of the tube,
R is the gas constant, 8.3145 J K^{-1} mol^{-1}.

A graph of $\ln(n_h / n_{h0})$ against $(h - h_0)$, based on the data in the table above, is shown below. The reference height is taken to be 5 □m from the bottom of the tube.



j) Derive an expression for the gradient (slope) of the graph.

k) Determine the Avogadro constant from these data.

Problem 2

If two atoms collide in interstellar space the energy of the resulting molecule is so great that it rapidly dissociates. Hydrogen atoms only react to give stable H_2 molecules on the surface of dust particles. The dust particles absorb most of the excess energy and the newly formed H_2 rapidly desorbs. This question examines two kinetic models for H_2 formation on the surface of a dust particle.

In both models, the rate constant for adsorption of H atoms onto the surface of dust particles is $k_a = 1.4\times10^{-5}$ cm^3 s^{-1}. The typical number density of H atoms (number of H atoms per unit volume) in interstellar space is [H] = 10 cm^{-3}.
[Note: in the following, you may treat numbers of surface-adsorbed atoms and number densities of gas-phase atoms in the same way as you would normally use concentrations in the rate equations. As a result, the units of the rate constants may be unfamiliar to you. Reaction rates have units of numbers of atoms or molecules per unit time.]

a) Calculate the rate at which H atoms adsorb onto a dust particle. You may assume that this rate is constant throughout.

Desorption of H atoms is first order with respect to the number of adsorbed atoms. The rate constant for the desorption step is $k_d = 1.9\times10^{-3}$ s^{-1}.

b) Assuming that only adsorption and desorption take place, calculate the steady-state number, N, of H atoms on the surface of a dust particle.

The H atoms are mobile on the surface. When they meet they react to form H_2, which then desorbs. The two kinetic models under consideration differ in the way the reaction is modelled, but share the same rate constants k_a, k_d, and k_r, for adsorption, desorption, and bimolecular reaction, as given below.
$k_a = 1.4\times10^{-5}$ cm^3 s^{-1} $\quad$ $k_d = 1.9\times10^{-3}$ s^{-1} $\quad$ $k_r = 5.1\times10^{4}$ s^{-1}

Model A

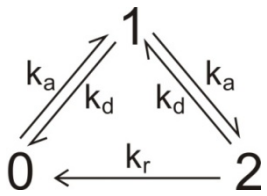
Reaction to form H_2 is assumed to be second order. On a dust particle the rate of removal of H atoms by reaction is $k_r N^2$.

c) Write down an equation for the rate of change of N, including adsorption, desorption and reaction. Assuming steady state conditions, determine the value of N.

d) Calculate the rate of production of H_2 per dust particle in this model.

Model B

Model B attempts to analyse the probability that the dust particles carry 0, 1 or 2 H atoms. The three states are linked by the following reaction scheme. The assumption is made that no more than 2 atoms may be adsorbed simultaneously.



x_0, x_1 and x_2 are the fractions of dust particles existing in state 0, 1 or 2, respectively. These fractions may be treated in the same way as concentrations in the following kinetic analysis. For a system in state m with fraction x_m, the rates of the three possible processes are

Adsorption ($m \rightarrow m + 1$): rate = $k_a[H]x_m$

Desorption ($m \rightarrow m - 1$): rate = $k_d m x_m$

Reaction ($m \rightarrow m - 2$): rate = ½ $k_r m(m - 1)x_m$

e) Write down equations for the rates of change, dx_m / dt, of the fractions x_0, x_1 and x_2.

f) Assuming steady-state conditions, use the above rate equations to find expressions for the ratios x_2/x_1 and x_1/x_0, and evaluate these ratios.

g) Evaluate the steady state fractions x_0, x_1 and x_2

[If you were unable to determine the ratios in (f), use $x_2/x_1 = a$ and $x_1/x_0 = b$ and give the result algebraically].

h) Evaluate the rate of production of H_2 per dust particle in this model

i) It is currently not possible to measure the rate of this reaction experimentally ., but the most recent computer simulations of the rate give a value of 9.4×10^{-6} s^{-1}. Which of the following statements on the answer sheet apply to each model under these conditions? Mark any box you consider to be appropriate.

Problem 3

The unfolding reaction for many small proteins can be represented by the equilibrium:

Folded $\rightleftharpoons$ Unfolded

You may assume that the protein folding reaction takes place in a single step.
The position of this equilibrium changes with temperature; the melting temperature T_m is defined as the temperature at which half of the molecules are unfolded and half are folded.

The intensity of the fluorescence signal at a wavelength of 356 nm of a 1.0 μM sample of the protein Chymotrypsin Inhibitor 2 (CI2) was measured as a function of temperature over the range 58 to 66 °C:

Temp /°C	58	60	62	64	66
Fluorescence intensity (arbitrary units)	27	30	34	37	40

A 1.0 μM sample in which all of the protein molecules are folded gives a fluorescence signal of 21 units at 356 nm. A 1.0 μM sample in which all of the protein molecules are unfolded gives a fluorescence signal of 43 units.

a) Assuming that the fluorescence intensity from each species is directly proportional to its concentration, calculate the fraction, *x*, of unfolded molecules present at each temperature.

b) Give an expression for the equilibrium constant, *K*, in terms of *x*, and hence calculate the value of *K* at each temperature.

c) Estimate the value of T_m for this protein (to the nearest 1°C).

Assuming that the values of $\Delta H°$ and $\Delta S°$ for the protein unfolding reaction are constant with temperature then:

$$\ln K = -\frac{\Delta H^\circ}{RT} + C \qquad \text{where C is a constant.}$$

d) Plot a suitable graph and hence determine the values of $\Delta H°$ and $\Delta S°$ for the protein unfolding reaction.

e) Calculate the equilibrium constant for the unfolding reaction at 25 °C.

The first order rate constant for the CI2 protein folding reaction can be determined by following the fluorescence intensity when a sample of unfolded protein is allowed to refold (typically the pH of the solution is changed). The concentration of protein when a 1.0 μM sample of unfolded CI2 was allowed to refold was measured at a temperature of 25 °C:

time / ms	0	10	20	30	40
concentration / μM	1	0.64	0.36	0.23	0.14

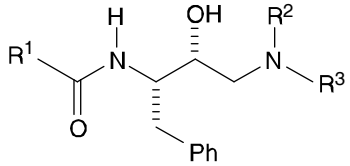
f) Plot a suitable graph and hence determine the value of the rate constant for the protein folding reaction, k_f, at 25 °C.

g) Determine the value of the rate constant for the protein *unfolding* reaction, k_u, at 25 °C.

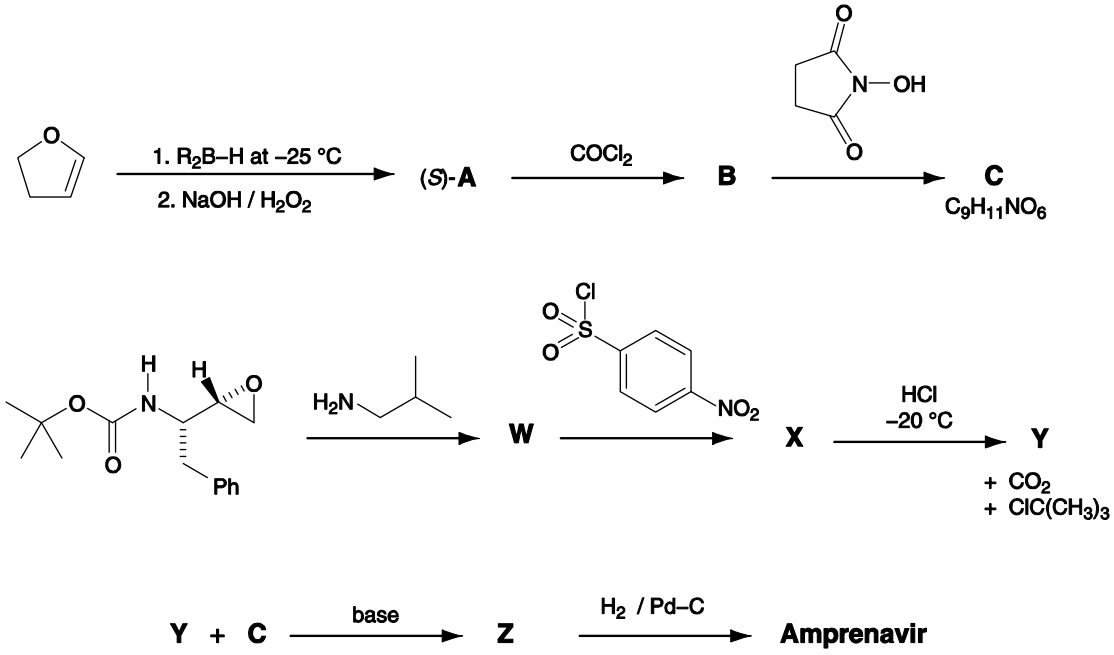
h) At 20 °C the rate constant for the protein folding reaction is 33 s^{-1}. Calculate the activation energy for the protein folding reaction.

Problem 4

One class of anti-HIV drugs, known as *protease inhibitors*, works by blocking the active site of one of the enzymes used in assembly of the viruses within the host cell. Two successful drugs, *saquinavir* and *amprenavir*, contain the structural unit shown below which mimics the transition state within the enzyme. In the structure, R^1, R^2 and R^3 may represent any atom or group other than hydrogen.



Amprenavir may be synthesised as shown in the convergent scheme below.

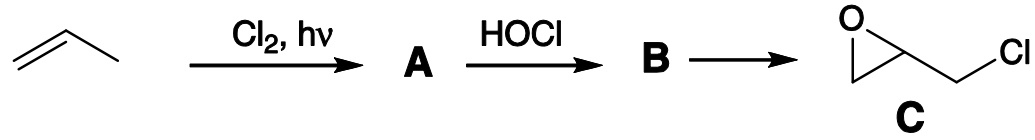


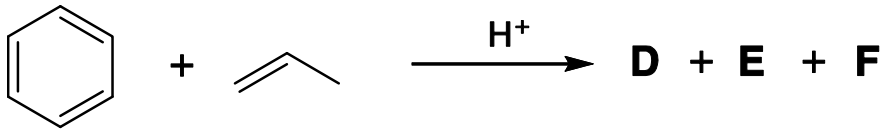
The reagent R_2B–H used in the first step is chiral. Product **A** is formed as the (*S*)-enantiomer.

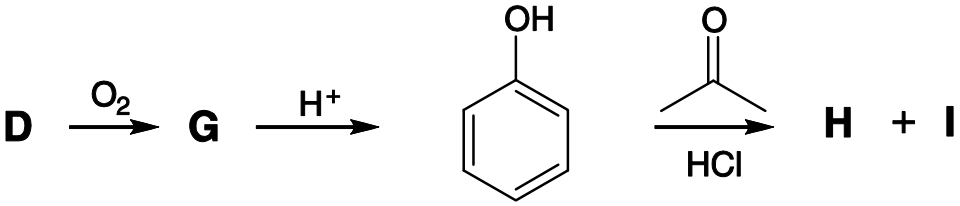
3 of the signals in the ^{1}H NMR spectrum of Amprenavir disappear on shaking with D_2O: δ 4.2 (2H), δ 4.9 (1H) and δ 5.1 (1H).
Suggest structures for **a)** the intermediates **A**, **B**, **C**, **W**, **X**, **Y** and **Z**, and **b)** for *Amprenavir*. Your answers should clearly show the stereochemistry at each centre.

Problem 5 Epoxy resins

The synthesis of epoxy resins is a multi-billion dollar industry worldwide. Epoxy resins are high performance adhesives synthesised from the reaction of a bis-epoxide with a diamine. The bis-epoxide is made from **H** and epichlorohydrin, **C**. **C** and **H** can be synthesised according to the schemes below.







The synthesis of epichlorohydrin **C** begins with the reaction of propene with chlorine in the presence of light.

a) Draw the structures of **A** and **B**:

b) Give the formula of a suitable reagent for the conversion of **B** into epichlorohydrin **C**:

The synthesis of **H** commences with the reaction of benzene with propene in the presence of an acid catalyst which gives **D** as the major product and **E** and **F** as minor products.

c) Draw the structures of **D**, **E**, and **F** from the following data:

D: Elemental compos.: C 89.94%, H 10.06%; 6 signals in the ^{13}C NMR spectrum

E: Elemental compos.: C 88.82%, H 11.18%; 4 signals in the ^{13}C NMR spectrum

F: Elemental compos.: C 88.82%, H 11.18%; 5 signals in the ^{13}C NMR spectrum

Bubbling oxygen through a hot solution of **D** gives **G** which on exposure to acid gives phenol (hydroxybenzene) and acetone (propanone).

G turns starch iodide paper from white to dark blue. **G** has 6 signals in the ^{13}C NMR spectrum and the following signals in the ^{1}H NMR spectrum: δ 7.78 (1H, s), 7.45-7.22 (5H, m), 1.56 (6H, s); addition of D_2O results in the disappearance of the signal at δ = 7.78.

d) Draw the structure of **G**.

Exposure of phenol and acetone to hydrochloric acid gives compound **H**. The ^{13}C NMR spectrum for **H** is shown in Fig. 1. The ^{1}H NMR spectrum is shown in Fig. 2 together with a four-fold expansion of the region 6.5 – 7.1 ppm. The ^{1}H NMR spectrum after the addition of a drop of D_2O, is shown in Fig. 3. Peaks due to the solvent are marked with an asterisk (*).

Fig. 1

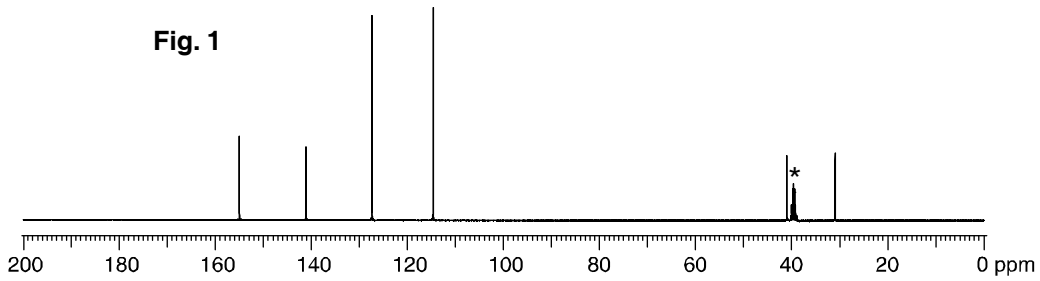


Fig. 2

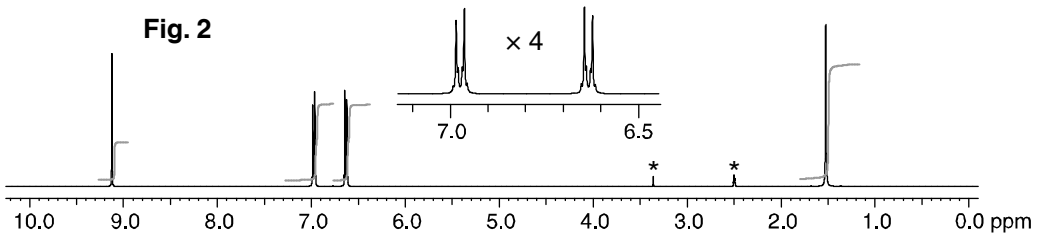
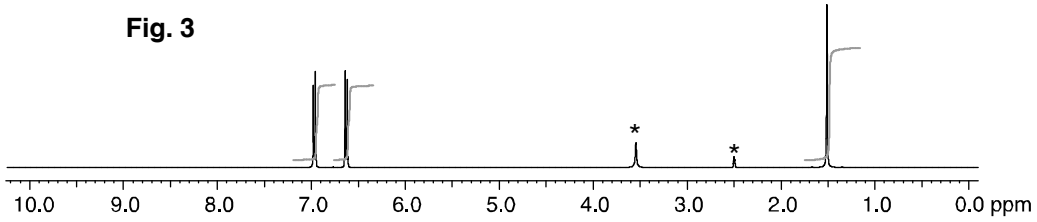


Fig. 3



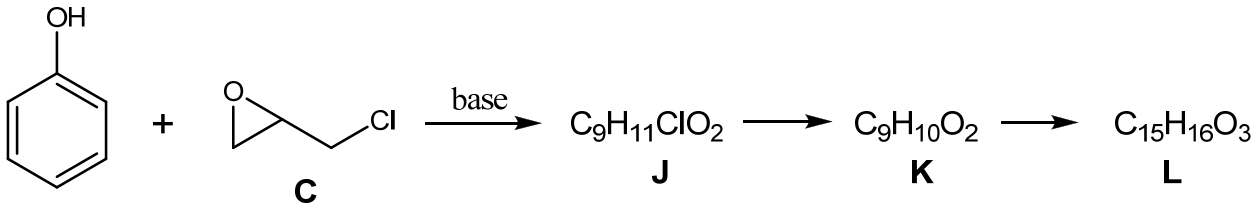
e) Draw the structure of **H**.

f) Draw one resonance structure of phenol which explains the regioselective formation of **H**.

A second compound, **I**, is also formed in the reaction of phenol with acetone. The ^{13}C NMR spectrum of **I** has 12 signals. The ^{1}H NMR spectrum has the following signals: δ 7.50-6.51 (8H, m), 5.19 (1H, s), 4.45 (1H, s), 1.67 (6H, s); addition of D_2O results in the disappearance of the signals at δ = 5.19 and 4.45

g) Draw a structure for **I**.

Excess phenol reacts with epichlorohydrin **C** in the presence of base to give compound **L** which has 6 signals in its ^{13}C NMR spectrum. If the reaction is stopped before completion compounds **J** and **K** can also be isolated. Compound **L** is formed from compound **K** and compound **K** is formed from compound **J**.



C

h) Draw the structures of **J**, **K** and **L**.

Treatment of **H** with a large excess of epichlorohydrin **C** and base gives a monomeric bis-epoxide **M**. **M** contains no chlorine atoms or OH groups.

i) Draw the structure of **M**.

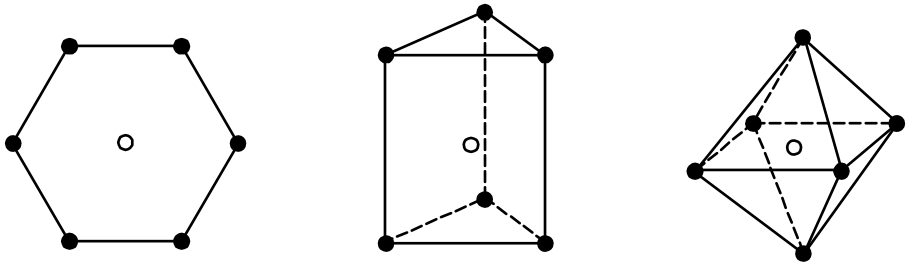
Treatment of **H** with a small excess of epichlorohydrin and base gives **N**. **N** has the form: **endgroup1-[repeat unit]$_n$-endgroup2** where *n* is approximately 10 – 15. **N** does not contain chlorine atoms and contains one OH group per repeat unit.

j) Draw the structure of **N** in the form indicated above (**endgroup1-[repeat unit]$_n$-endgroup2**).

k) Draw the repeat unit of the polymeric epoxy resin **O** formed from the reaction of the bis-epoxide **M** with ethane-1,2-diamine.

Problem 6 Transition metal complexes

Alfred Werner used the technique of 'isomer counting' to deduce the structure of metal complexes with coordination number six. Three of the shapes he considered are shown below.



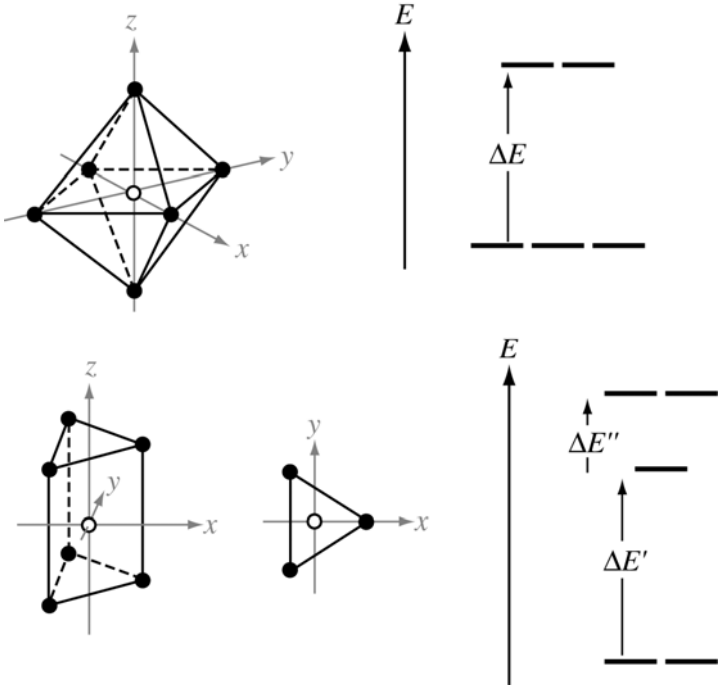
X **Y** **Z**

In each structure, the empty circle shows the location of the central metal atom and the filled circles show the location of the ligands. Structure **X** is hexagonal planar, structure **Y** is trigonal prismatic and structure **Z** is octahedral.
For each of the three shapes, there is just one structure when all of the ligands are the same, i.e. when the complex has the general formula MA_6 where A is the ligand. However, when achiral ligands A are substituted by one or more achiral ligands, it may be possible for each structure to form geometrical isomers. It might also be possible for one or more of the geometrical isomers to be optically active and exist as pairs of enantiomers.

a) Fill in the table below to indicate how many geometrical isomers may be formed for each structure **X**, **Y**, and **Z** as the monodentate ligands A are substituted by monodentate ligands B or by symmetrical bidentate ligands, denoted C—C. Bidentate ligand C—C can only link between two atoms on adjacent positions, i.e. those positions connected by a line in the structures **X**, **Y**, and **Z**.
In each case write the number of geometrical isomers in the space provided. If one of the isomers exists as a pair of enantiomers, include an asterisk, *, in the box. If two exist as two pairs of enantiomers, include two asterisks and so on. For example, if you think there are five geometrical isomers of a particular structure, three of which exist as pairs of enantiomers, write 5***.

	Number of predicted geometrical isomers		
	Hexagonal planar **X**	Trigonal Prismatic **Y**	Octahedral **Z**
MA_6	1	1	1
MA_5B			
MA_4B_2			
MA_3B_3			
$MA_4(C\text{-}C)$			
$MA_2(C\text{-}C)_2$			
$M(C\text{-}C)_3$			

There are no known complexes that adopt the hexagonal planar geometry **X**, but structures are known for both the trigonal prismatic geometry **Y** and the octahedral geometry **Z**. In these complexes, the orbitals derived from the metal d orbitals have different energies depending on the geometry of the complex. The splitting patterns for the trigonal prismatic geometry and for the octahedral geometry are shown below.



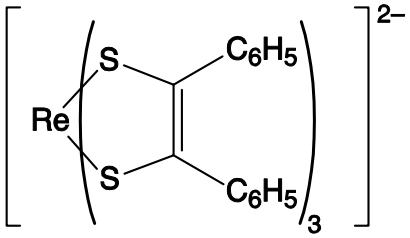
The separations in energy, ΔE, $\Delta E'$ and $\Delta E''$ depend on the particular complex.

b) For each of the splitting patterns shown below label which d orbitals are which.

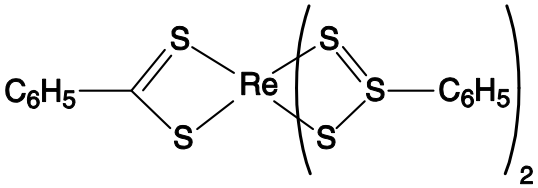
The two complexes $[Mn(H_2O)_6]^{2+}$ and $[Mn(CN)_6]^{2-}$ are both octahedral. One has a magnetic moment of 5.9 BM, the other has a magnetic moment of 3.8 BM but you must decide which is which.

c) On the diagram below, draw the electronic arrangements for each of the complexes.

The magnetic moments of complexes **A** and **B** shown below have been measured and found to be 1.9 and 2.7 BM but you must decide which is which.



A



B

d) Draw the orbital splitting diagrams for the two complexes, including the arrangements of the electrons.

Octahedral complexes are far more common than trigonal prismatic. Werner isolated five compounds **C** – **G** containing Co(III), Cl, and NH_3 only, each of which contained one octahedral complex. (There is actually a sixth compound but Werner could not isolate it). Werner's five compounds had the molar conductivities shown below. The conductivities are extrapolated to infinite dilution and are expressed in arbitrary units. Compound **G** does not react with aqueous $AgNO_3$; compounds **C**, **D**, and **E** react with different stoichiometric ratios of aqueous $AgNO_3$; **E** and **F** react with the same stoichiometric ratio of aqueous $AgNO_3$.

	C	**D**	**E**	**F**	**G**
molar conductivity	510	372	249	249	~0

e) As far as you are able, <u>suggest</u> a structure for each of the compounds **C** – **G**.

Werner was also the first person to separate the enantiomers of an octahedral compound ,**H**, which contained no carbon atoms. The compound, **H**, is composed of only cobalt, ammonia, chloride and an oxygen species which could be either H_2O, or $HO^{\square}$ or $O^{2\square}$. The compound contains octahedrally coordinated cobalt ions. All of the chloride is easily removed from the compound by titration

with aqueous silver nitrate. A 0.2872 g sample of **H** (containing no water of crystallization) required 22.8 cm^3 of 0.100 M silver nitrate to exchange all of the chloride.

f) Calculate the percentage, by mass, of chloride in **H**.

H is stable to acids, but is hydrolysed in alkali. A 0.7934 g sample of **H** (containing no water of crystallization) was heated with excess aqueous sodium hydroxide. Cobalt(III) oxide was formed and ammonia gas given off. The ammonia produced was distilled off and absorbed into 50.0 cm^3 of 0.500 M aqueous HCl. The residual HCl required 24.8 cm^3 of 0.500 M aqueous KOH to be neutralized.
The remaining suspension of cobalt(III) oxide was allowed to cool, approximately 1g of potassium iodide was added, and then the mixture was acidified with aqueous HCl. The liberated iodine was then titrated with 0.200 M aqueous sodium thiosulfate and required 21.0 cm^3 for complete reaction.

g) Calculate the percentage, by mass, of ammonia in **H**.

h) Give the equation for the reaction of cobalt(III) oxide with potassium iodide in aqueous acid.

i) Calculate the percentage, by mass, of cobalt in **H**.

j) Calculate the identity of the oxygen species contained in **H**. Show your working.

k) Give the empirical formula of **H**.

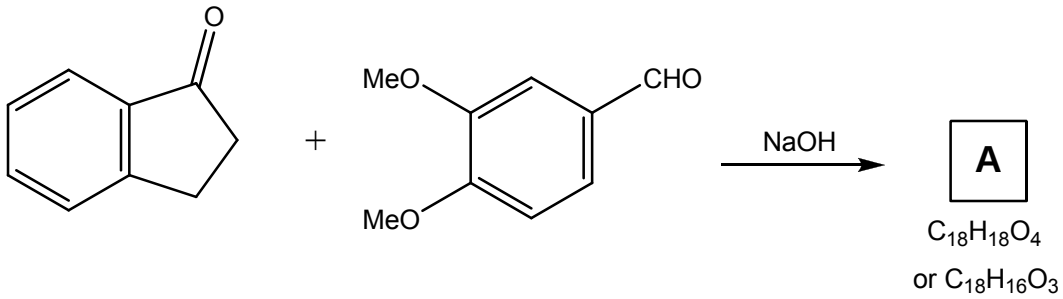
l) Suggest a structure for the chiral compound **H**.

Practical Test

Given was a list of general information, apparatus per student, chemicals on each desk, risks and safety phrases and a Periodic table with relative atomic masses

Task 1 – An Environmentally Friendly Aldol Condensation

In attempts to become more environmentally friendly, increasing attention is being paid to minimising the large amounts of solvents used in chemical reactions. In the following experiment, an aldol condensation reaction is carried out in the absence of solvent.



1. Add 3,4-dimethoxybenzaldehyde (DMBA 0.50 g, 3.0 mmol) and 1-indanone (0.40 g, 3.0 mmol) to a 25 cm^3 beaker. Use a metal spatula to scrape and crush the two solids together until they become a clear oil.

2. Add NaOH (0.1 g, 2.5 mmol) to the reaction mixture, crush any lumps formed and continue scraping and crushing until the mixture becomes solid.

3. Allow the mixture to stand for 20 minutes. Then add 4 cm^3 HCl (3 M aqueous) and scrape around the beaker so as to dislodge all product from the walls. Use a flat-ended glass rod to crush any lumps present.

a) Measure and <u>record</u> the pH of the solution.

4. Isolate the crude product using vacuum filtration through a Hirsch funnel. Rinse out the beaker with 2 cm^3 HCl (3 M aqueous) and pour over the crude product in Hirsch funnel to wash, continuing to pull air through the solid for 10 minutes to facilitate drying.

b) <u>Report</u> the mass of the crude product (which may still be a little wet), using the vial labeled 'CPA' as a container.

5. Take a TLC to assess whether the reaction is complete, using Et_2O:heptane (1:1) as the eluant. Solutions of both starting materials in ethyl ethanoate are provided. The crude product is soluble in ethyl ethanoate. [Note: three TLC plates are provided. You may use them all, but you must only submit *one* in your labelled Ziploc bag. This should be the plate that you draw in your answer booklet.]

c) Using UV light to visualize, draw around the spots on the plate in pencil to show where they are, copy your plate onto the answer sheet, and place your plate in the Ziploc bag labeled with your student code. Determine and record the relevant R_F values.

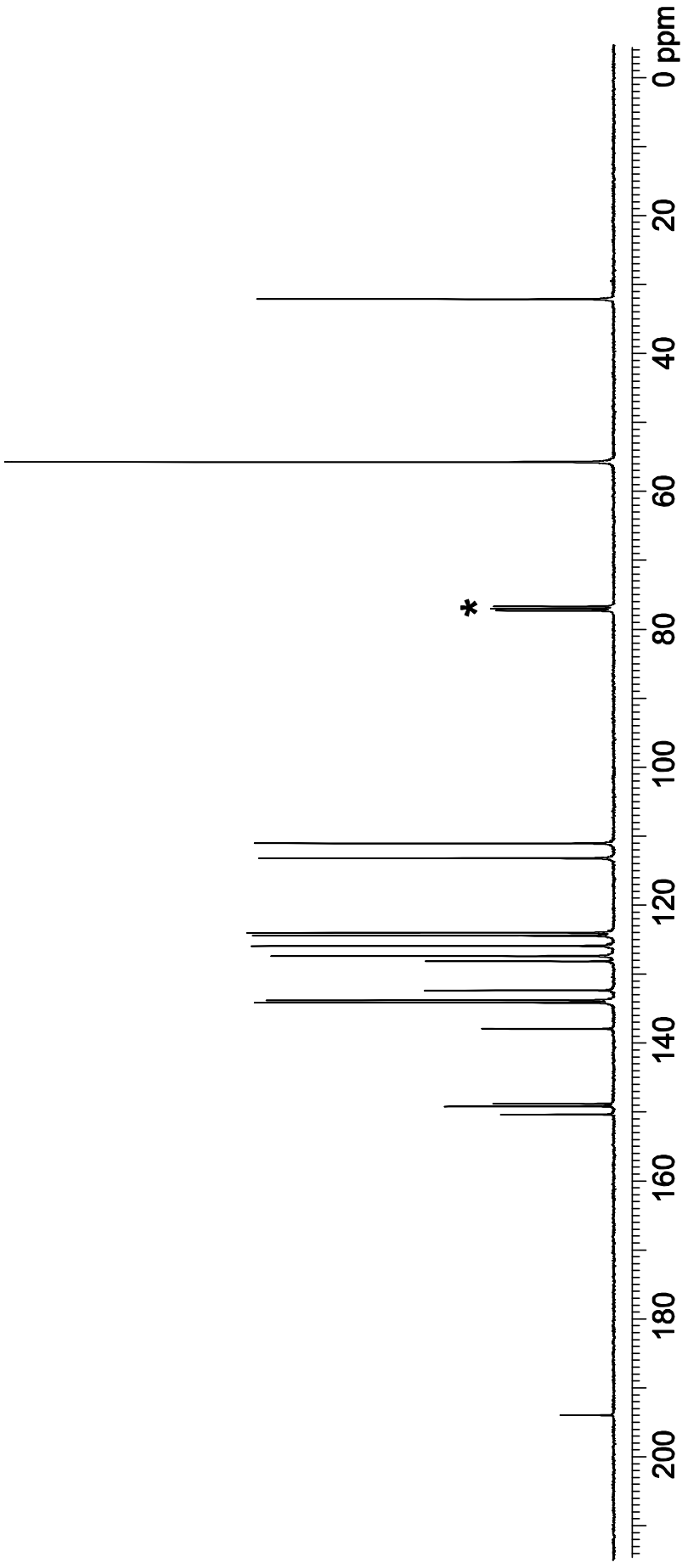
6. Using a 100 cm^3 conical flask with a stir bar in the bottom, recrystallise the product from 9:1 EtOH:H_2O (N.B. A hot filtration, using the glass funnel provided, is required as part of this process to remove small amounts of insoluble impurities). Any lumps may be crushed using the flat-ended glass rod. Allow the conical flask containing the filtered solution to cool to room temperature and then cool in an ice bath (use the polystyrene tray to make the ice bath in) for one hour before filtration through a Buchner funnel to collect your product. Suck air through for 10 minutes to dry the product. Place your product in the vial marked with your code and labeled 'RPA'.

d) Report the mass of the purified product.

e) Determine the potential structures for Product A, using the information on the answer sheet.

f) The ^{13}C NMR spectrum for A is shown on the next page. Peaks due to the solvent, $CDCl_3$, are marked with an asterisk. With the aid of the spectrum, decide which is the correct formula for A. Mark your answer on the answer sheet.

g) Calculate the percentage yield of the purified product, based on the formula you gave for its structure.


0 ppm
20
40
60
80
100
120
140
160
180
200
*

Task 2 – Analysis of a Copper(II) Complex

You are provided with a sample of an inorganic copper(II) complex, the anion of which is made from copper, chlorine, and oxygen. The counter ion is the tetramethyl ammonium cation. There is no water of crystallisation. You are required to determine proportions of copper ions and chloride ions by titration and hence determine the composition of the complex.

Titration to determine the proportion of copper ions

1. You are provided with three accurately pre-weighed samples of copper complex, each of approximately 0.1 g. These are labeled "Sample 1", "Sample 2", "Sample 3", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

2. Add pH 10 ammonia buffer solution until the precipitate which forms initially just redissolves (about 10 drops).

3. Add 10 drops of the murexide indicator.

4. Titrate with the 0.0200 mol dm^{-3} EDTA solution until the solution turns violet and the colour persists for at least 15 seconds. Record the volume of solution used in the titration.

5. Repeat if necessary with samples 2 and 3.

Note: you will be marked only on a single value you report in the answer booklet. This may either be an average value, or a single value you feel most confident in.

a) Calculate the volume of EDTA solution needed to react completely with 0.100 g of complex.

b) Give an equation for the titration reaction.

c) Calculate the percentage by mass of copper in the sample.

You will need to wash out your burette before you start the titration for the determination of chloride ions. Any remaining EDTA solution may be disposed of into the waste containers labelled 'EDTA'.

Titration to determine the proportion of chloride ions present

1. You are provided with three accurately pre-weighed samples of copper complex each of approximately 0.2 g. These are labeled "Sample 4", "Sample 5", "Sample 6", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

2. Add 5 drops of ethanoic acid, followed by 10 drops of dichlorofluorescein indicator and 5 cm^3 dextrin (2% suspension in water). N.B. Shake the bottle well before adding the dextrin suspension.

3. Titrate with the 0.1000 mol dm^{-3} silver nitrate solution, swirling constantly until the white suspension turns pink and the colour does not disappear after swirling.

4. Repeat if necessary.

Note: you will be marked only on a single value you report in the answer booklet. This may either be an average value, or the value you feel most confident in.

d) Calculate the volume of silver nitrate solution needed to react completely with 0.200 g of complex.

e) Give an equation for the titration reaction.

f) Calculate the percentage by mass of chloride ions in the sample.

The percentage of carbon, hydrogen and nitrogen in the complex was determined by combustion analysis and found to be as follows:

Carbon: 20.87 %	Hydrogen: 5.17 %	Nitrogen: 5.96 %

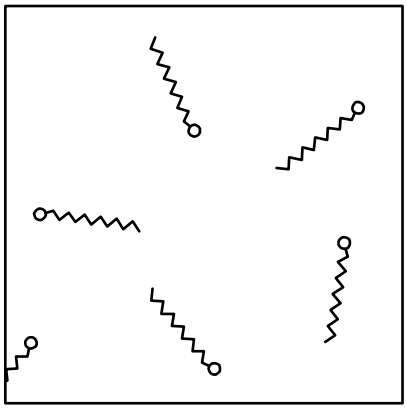
g) Mark in the answer booklet, which element in the complex has the greatest percentage error in the determination of its proportion.

h) Determine the formula of the copper complex. Show your working.

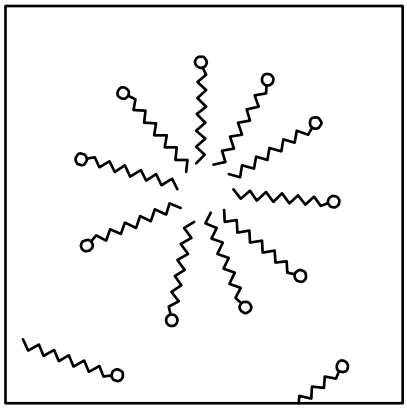
Task 3 – The Critical Micelle Concentration of a Surfactant

Surfactants are used extensively in many everyday cleaning products, such as shampoos or detergents for washing clothes. One such surfactant is SDS, sodium *n*-dodecyl sulfate, $CH_3(CH_2)_{11}OSO_3Na$ (Relative Molecular Mass: 288.37).

Very dilute aqueous solutions consist of solvated individual molecules of SDS. However, if the concentration is gradually increased beyond a specific concentration, the concentration of monomeric SDS does not change, but instead the surfactant begins to form clusters known as *micelles*. It is these micelles that assist in the removal of grease and dirt. The concentration at which the micelles form is called the *critical micelle concentration*. This process is shown schematically in the figure below.



low SDS concentration
free monomer only



high SDS concentration
micelles and some free monomer

In this experiment, you will determine the critical micelle concentration of SDS by measuring the conductivity of different concentrations of SDS.

1. You are provided with approximately 4.3 g SDS, accurately pre-weighed in a vial, a 250 cm^3 volumetric flask, a 50 cm^3 burette, 50 cm^3 bulb pipette, a conductivity meter, conductivity solution (used only for calibration), and a tall plastic vessel.

2. You need to measure the conductivity (σ, in $\mu S\ cm^{-1}$) of various concentrations of aqueous SDS (c, up to 30 $mmol\ dm^{-3}$). [Note: you may assume all volumes are additive.]

a) Give the concentration of your stock SDS solution.

b) Use the table given in the answer booklet to record your results and plot a suitable graph to determine the critical micelle concentration (CMC) on the paper provided.

c) State the concentration at which micelles begin to form (the critical micelle concentration).

Notes

1) Solutions of SDS readily form bubbles if shaken.

2) The conductivity meter needs at least 50 cm^3 of solution to be inside the plastic vessel in order to work correctly.

3) To calibrate the meter:

- Switch the meter on by pressing the ON/OFF button once.
- Press and hold the ON/OFF button again, this time for about 3 seconds, until you see the letters 'CAL' on the screen, indicating that the calibration mode has been entered. Let go of the ON/OFF button and '1413' will start blinking on the display. To calibrate, carry out the next step immediately, before the meter has reverted back to reading '0' on the screen (meaning you have exited the calibration mode)
- Immerse the probe in the pouch containing the 'HI 70031' calibration solution, without exceeding the maximum immersion level.
- Stir gently and wait for about 20 seconds to confirm the reading.
- Once the display stops blinking, the meter is calibrated and ready for use.
- Rinse the meter with distilled water and dry before making measurements.

4) To record the reading:

- Switch the meter on by pressing the ON/OFF button
- Immerse the probe in the sample without exceeding the maximum immersion level and being above the minimum immersion level.
- Stir gently and wait for the reading to stabilize. The meter automatically compensates for temperature variations.
- The conductivity value of the sample will be shown on the LCD.

The Answers to the Theoretical Problems of the IChO

Solution to problem 1

a) face-centred cubic unit cell: see textbooks
number of gold atoms = $8 \cdot \frac{1}{8}$ (from each corner) + $6 \cdot \frac{1}{2}$ (from each face) = 4

b) $V_{Zelle} = a^3$ $V_{cell} = (0.408\ nm)^3 = 6.79 \cdot 10^{-29}\ m^3$
$m_{cell} = V_{Zelle} \cdot$ Dichte $m_{cell} = 6.79 \cdot 10^{-29}\ m^3 \cdot 1.93 \cdot 10^4\ kgm^{-3} = 1.31 \cdot 10^{-24}$ kg

c) $m_{gold\ atom} = m_{Zelle}/4$ $m_{gold\ atom} = 3.28 \cdot 10^{-25}$ kg
$N_A = 196.97\ gmol^{-1}/3.28 \cdot 10^{-22}$ g $N_A = 6.01 \cdot 10^{23}\ mol^{-1}$

d)

	α-decay	β-decay		α-decay	β-decay
$^{226}Ra \longrightarrow {}^{222}Rn$	✓		$^{214}Po \longrightarrow {}^{210}Pb$	✓	
$^{222}Rn \longrightarrow {}^{218}Po$	✓		$^{210}Pb \longrightarrow {}^{210}Bi$		✓
$^{218}Po \longrightarrow {}^{214}Pb$	✓		$^{210}Bi \longrightarrow {}^{210}Po$		✓
$^{214}Pb \longrightarrow {}^{214}Bi$		✓	$^{210}Po \longrightarrow {}^{206}Pb$	✓	
$^{214}Bi \longrightarrow {}^{214}Po$		✓			

e) ^{210}Pb

f) $27.7 \cdot 10^9\ s^{-1} \cdot 163 \cdot 24 \cdot 60 \cdot 60$ s $= 3.90 \cdot 10^{17}$ α particles

g) $n = p \cdot V/(R \cdot T)$ $n_{He} = 4.64 \cdot 10^{-7}$ mol
$N_A = 3.90 \cdot 10^{17}/4.64 \cdot 10^{-7}$ mol $N_A = 8.4 \cdot 10^{23}\ mol^{-1}$

h) $n_{Ra} = 0.192\ g \cdot 6.022 \cdot 10^{23}\ mol^{-1}/226.25\ gmol^{-1}$ $n_{Ra} = 5.11 \cdot 10^{20}$ atoms
$\lambda = 27.7 \cdot 10^9\ s^{-1}/(4 \cdot 5.11 \cdot 10^{20}) = 1.36 \cdot 10^{-11}\ s^{-1}$ (only ¼ of the decays are from ^{226}Ra)
$t_{½} = \ln 2\ /\lambda$ $t_{½} = 5.12 \cdot 10^{10}$ s $t_{½} = 1620$ years

i) $V_{particle} = (4/3) \cdot \pi \cdot (2.12 \cdot 10^{-7})^3$ $V_{particle} = 3.99 \cdot 10^{-20}\ m^3$
$m_{particle} = V_{Teilchen} \cdot 1.206 \cdot 10^3\ kgm^{-3}$ $m_{particle} = 4.81 \cdot 10^{-17}$ kg
$m_{H2O} = 3.99 \cdot 10^{-17}$ kg
$m^* = m_{particle} - m_{H2O}$ $m^* = 8.26 \cdot 10^{-18}$ kg

j) $\frac{n_h}{n_{h_o}} = \exp(-\frac{E_h - E_{h_0}}{R \cdot T})$ $E_h = m^* \cdot N_A \cdot g \cdot h$
$\ln (n_h/n_{ho}) = - m^* \cdot N_A \cdot g/(R \cdot T) \cdot (h - h_0)$
gradient = $- m^* \cdot N_A \cdot g/(R \cdot T)$

k) read from the graph: slope = $- 0.0235\ \mu m^{-1}$
or calculation of the 3 points and forming the linear fit

$(h - h_0)/\mu m$	30	60	90
$\ln(n_h - n_{ho})$	- 0.7550	-1.4917	-2.1203

slope of the linear fit = - 0.02275 μm^{-1}

$$-0.02275\cdot(10^{-6}\,m)^{-1} = -\frac{N_A \cdot 8.26\cdot10^{-18}\,kg\cdot 9.81\,ms^{-2}}{8.3145\,JK^{-1}mol^{-1}\cdot 288.18\,K} \qquad N_A = 6.70\cdot10^{23}\ mol^{-1}$$

Solution to problem 2

a) rate = $k_a\cdot[H]$ $\qquad r = 1.4\cdot10^{-4}\ s^{-1}$

b) $1.4\cdot10^{-4}\ s^{-1} = N\cdot 1.9\cdot10^{-3}\ s^{-1}$ $\qquad N = 7.4\cdot10^{-2}$

c) $dN/dt = 0 = k_a\cdot[H] - k_d\cdot N - k_r\cdot N^2$

$$N = \frac{-k_d+\sqrt{k_d^2+4\cdot k_r\cdot k_a\cdot[H]}}{2\cdot k_r} \qquad N = 5.2\cdot10^{-5}$$

d) $\tfrac{1}{2}\cdot k_r\cdot N^2 = 7.0\cdot10^{-5}\ s^{-1}$

e) $dx_0/dt = -k_a\cdot[H]\cdot x_0 + k_d\cdot x_1 + k_r\cdot x_2$ (1)

$dx_1/dt = k_a\cdot[H]\cdot x_0 - (k_a\cdot[H] + k_d)\cdot x_1 + 2\cdot k_d\cdot x_2$ (2)

$dx_2/dt = k_a\cdot[H]\cdot x_1 - (2\cdot k_d + k_r)\cdot x_2$ (3)

f) (3) $\quad k_a\cdot[H]\cdot x_1 = (2\cdot k_d + k_r)\cdot x_2$

$$x_2/x_1 = \frac{k_a\cdot[H]}{2\cdot k_d + k_r} \approx \frac{k_a\cdot[H]}{2\cdot k_r} = 2.70\cdot10^{-9}$$

(1) $\quad k_a\cdot[H]\cdot x_0 = k_d\cdot x_1 + k_r\cdot x_2 \quad$ mit $\; x_2 = x_1\cdot\frac{k_a\cdot[H]}{2\cdot k_d + k_r}$

$$k_a\cdot[H]\cdot x_0 = x_1\cdot\left(k_d + k_r\cdot\frac{k_a\cdot[H]}{2\cdot k_d + k_r}\right)$$

$$= x_1\cdot\left(\frac{k_d\cdot(2\cdot k_d + k_r) + k_r k_a\cdot[H]}{2\cdot k_d + k_r}\right.$$

$$x_1/x_0 = \frac{k_a\cdot[H]\cdot(2\cdot k_d + k_r)}{k_d\cdot(2\cdot k_d + k_r) + k_r\cdot k_a\cdot[H]} = 6.86\cdot10^{-2}$$

g) $x_2 = 2.70\cdot10^{-9}\cdot x_1$ $\qquad x_1 = 6.86\cdot10^{-2}\cdot x_0$ $\qquad x_2 + x_1 + x_0 = 1$

$x_0 = 0.94$ $\qquad x_1 = 0.06$ $\qquad x_2 = 1.7\cdot10^{-10}$

h) $k_r\cdot x_2 = 9.0\cdot10^{-5}\ s^{-1}$

i)

Statement	Model A	Model B	Neither model
The rate determining step is adsorption of H atoms.	✓	(✓)	
The rate-determining step is desorption of H_2 molecules.			✓
The rate determining step is the bimolecular reaction of H atoms on the surface.			✓

The rate determining step is adsorption of the second H atom.		✓	
The implicit assumption that reaction can take place regardless of the number of atoms adsorbed leads to substantial error (at least a factor of two).	✓		
Limiting the number of atoms adsorbed on the particle to 2 leads to substantial error (at least a factor of two).			✓

Solution to problem 3

a) e.g. $(1 - x) \cdot 21 + x \cdot 43 = 27$ $\quad x = 0.27$

Temp /°C	58	60	62	64	66
x	0.27	0.41	0.59	0.73	0.86

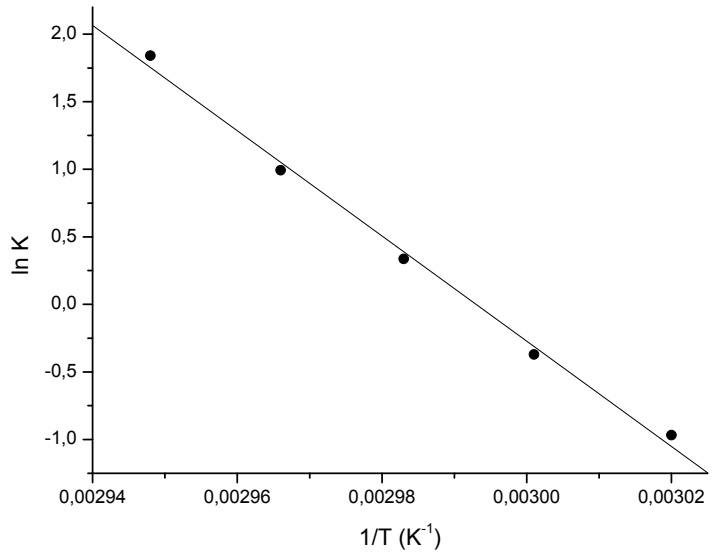
b) $K = \frac{x}{1-x}$

Temp /°C	58	60	62	64	66
K	0.38	0.69	1.4	2.7	6.3

c) $T_m \approx 61°C$

d)

$1/T\ K^{-1}$	$3.020 \cdot 10^{-2}$	$3.001 \cdot 10^{-2}$	$2.983 \cdot 10^{-2}$	$2.966 \cdot 10^{-2}$	$2.948 \cdot 10^{-2}$
ln K	- 0.9675	- 0.3711	0.3364	0.9933	1.841



m = - 39000 K

- 39000 K = - ΔH/R

$\Delta H° = 324\ kJmol^{-1}$

$\Delta G° = - RT \cdot lnK$ and

$\Delta G° = \Delta H° - T \cdot \Delta S°$

lead for e.g. 58°C to

$\Delta G° = 2664$ J and

$\Delta S° = 971\ J\ K^{-1}mol^{-1}$

mean value:

$\Delta S° = 970\ JK^{-1}mol^{-1}$

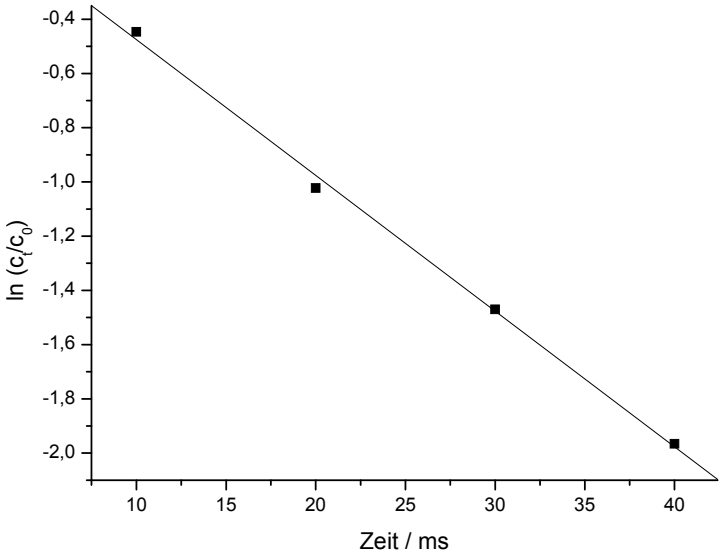
$\Delta G = 324000\ Jmol^{-1} - 298.15\ K \cdot 970\ JK^{-1}mol^{-1}$ $\quad \Delta G = 34795\ Jmol^{-1}$

ln K = - ΔG/(RT) lnK = - 14.04 $K = 8.0 \cdot 10^{-7}$

(different rounding leads to slightly different values)

f) $c_t = c_0 \cdot e^{- k_f \cdot t}$ $\ln(c_t/c_0) = - k_f \cdot t$

Zeit / ms	10	20	30	40
$\ln(c_t / c_0)$	- 0.4463	-1.022	- 1.470	-1.966



slope = - k_f

slope = - 0.05 $(ms)^{-1}$

$k_f = 50\ s^{-1}$

g) Folded $\underset{k_f}{\overset{k_u}{\rightleftharpoons}}$ Unfolded mit $K = \frac{c(\text{Unfolded})}{c(\text{Folded})} = 8.0 \cdot 10^{-7}$ (from e))

in equilibrium: $k_u \cdot c(\text{Folded}) = k_f \cdot c(\text{Unfolded}) \Rightarrow k_u = k_f \cdot K$ $k_u = 4.0 \cdot 10^{-5}$

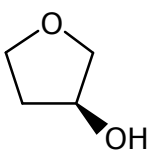
h) T = 298.15 K: ln 50 = - $E_A/(R \cdot 298)$

T = 293.15 K ln 33 = - $E_A/(R \cdot 293)$

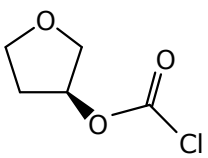
$E_A = - \ln\frac{50}{33} \cdot R \cdot (298^{-1} - 293^{-1})^{-1}$ $E_A = 60.3\ kJmol^{-1}$

Solution to problem 4

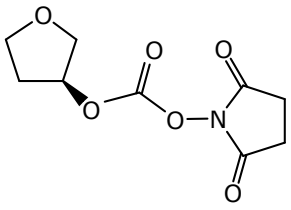
A



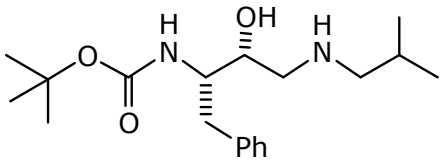
B



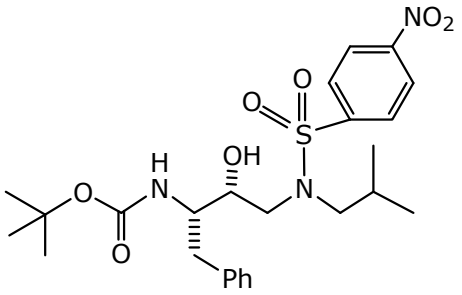
C



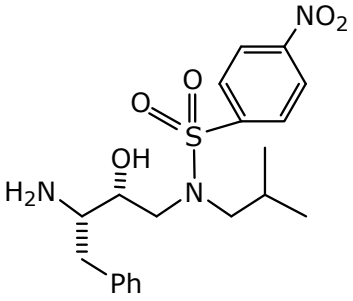
W



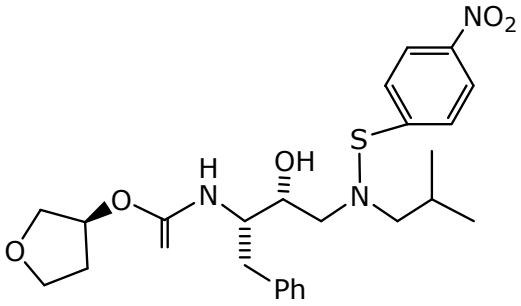
X



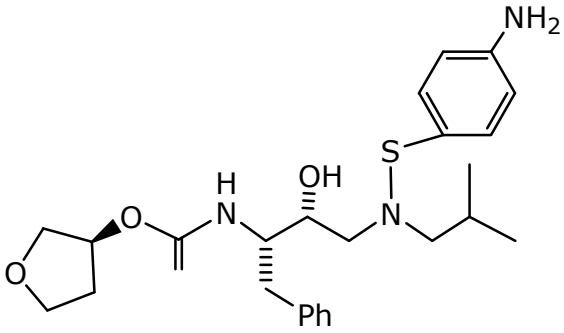
Y



Z



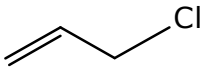
Amprenavir



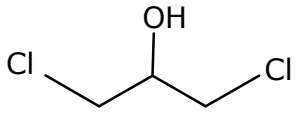
Solution to problem 5

a)

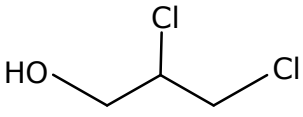
A



B



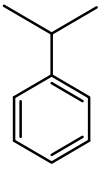
or



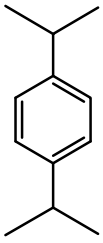
b) NaOH

c)

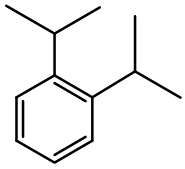
D



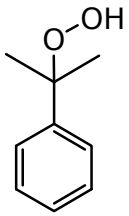
E



F

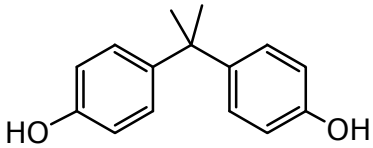


d)



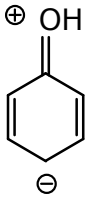
G

e)



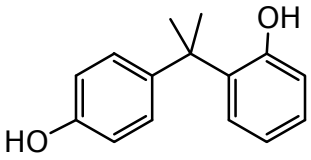
H

f)



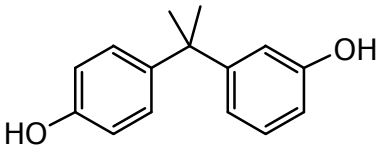
H

g)



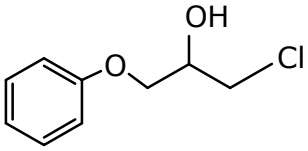
I

also fits the data

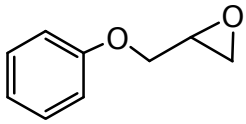


h)

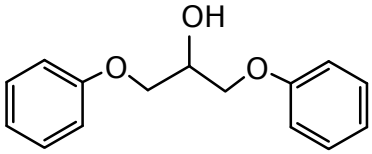
J



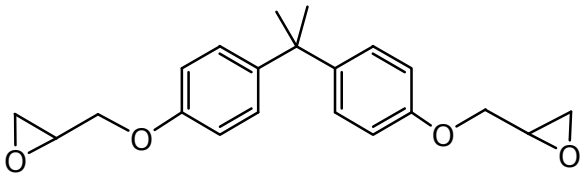
K



L

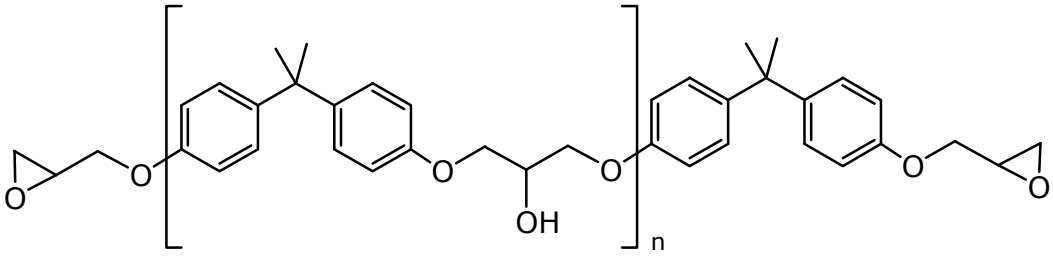


i)



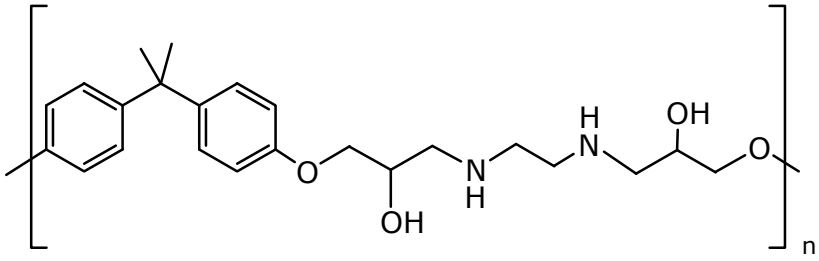
M

j)



N

k)

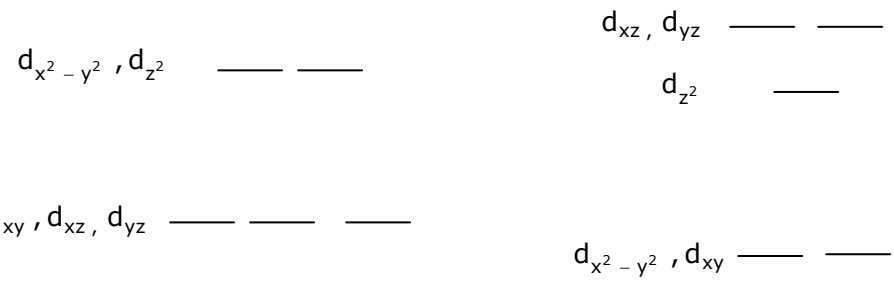


Solution to problem 6

a)

	Number of predicted geometrical isomers		
	Hexagonal planar **X**	Trigonal Prismatic **Y**	Octahedral **Z**
MA_6	1	1	1
MA_5B	1	1	1
MA_4B_2	3	3*	2
MA_3B_3	3	3*	2
$MA_4(C\text{-}C)$	1	2	1
$MA_2(C\text{-}C)_2$	2	4*	2*
$M(C\text{-}C)_3$	1	2	1*

b)

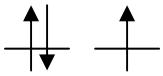


c)

$[Mn(H_2O)_6]^{2+}$ $[Mn(CN)_6]^{2-}$

d)

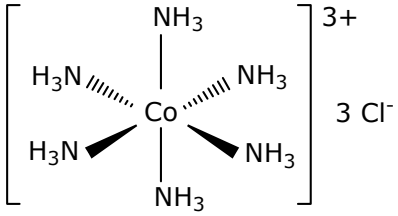
A



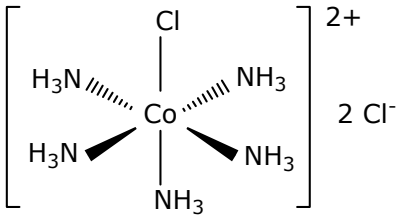
B

e)

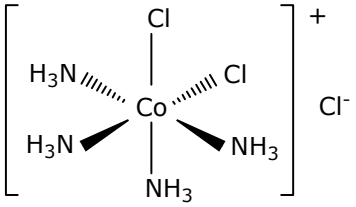
C



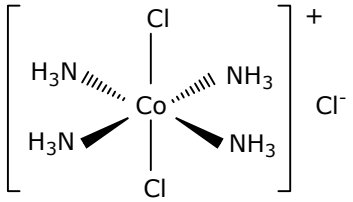
D



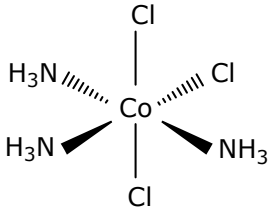
E

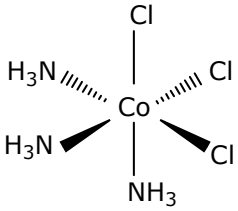


F



G





or

f) $n(Ag^+) = n(Cl^-) = 2.28 \cdot 10^{-3}$ mol $\quad m(Cl^-) = 8.0826 \cdot 10^{-2}$ g

$\Rightarrow \quad 100\% \cdot 8.0826 \cdot 10^{-2}$ g/0.2872 g = 28.1 % (w/w)

g) $n(KOH) = 0.0124$

$n(HCl \text{ to neutalize } NH_3) = 0.025 \text{ mol} - 0.0124 \text{ mol} = 0.0126 \text{ mol}$

$m(NH_3) = 0.2146$ g $\quad \Rightarrow \quad 100\% \cdot 0.2146$ g/0.7934 g = 27.1 %

h) $Co_2O_3 + 2\ KI + 6\ HCl \longrightarrow 2\ Co^{2+} + I_2 + 3\ H_2O + 6\ Cl^- + 2\ K^+$

i) $n(S_2O_3^{2-}) = 4.20 \cdot 10^{-3}$ mol $\quad \Rightarrow n(I_2) = 2.10 \cdot 10^{-3}$ mol

1 mol I_2 is equivalent to 2 mol Co$\Rightarrow$ m(Co) = $4.20\cdot10^{-3}$ · 58.93 g = 0.2475 g

$\Rightarrow$ 100% · 0.2475 g/0.7934 g = 31.2 %

j) 13.6 % until now not defined as O^{2-}. OH^- or H_2O

n(Co):n(NH_3) n(Cl^-):n(X) = 31.19/58.93 : 28.14/35.45 : 27.05/17.03 : 13.6/M(X)

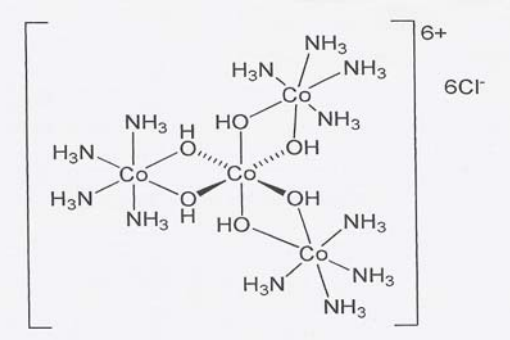
= 0.529 : 1.588 : 0.7939 : 13.6/M(X)

= 2 : 6 : 3 : 51.4/M(X)

charge balance: 2·(+3) + 6·(0) + 3·(-1) = - 3. thus X = OH^-

M(OH^-) = 17.01 $gmol^{-1}$. 51.4/17 ≈ 3 $\Rightarrow$ the missing species is OH^-

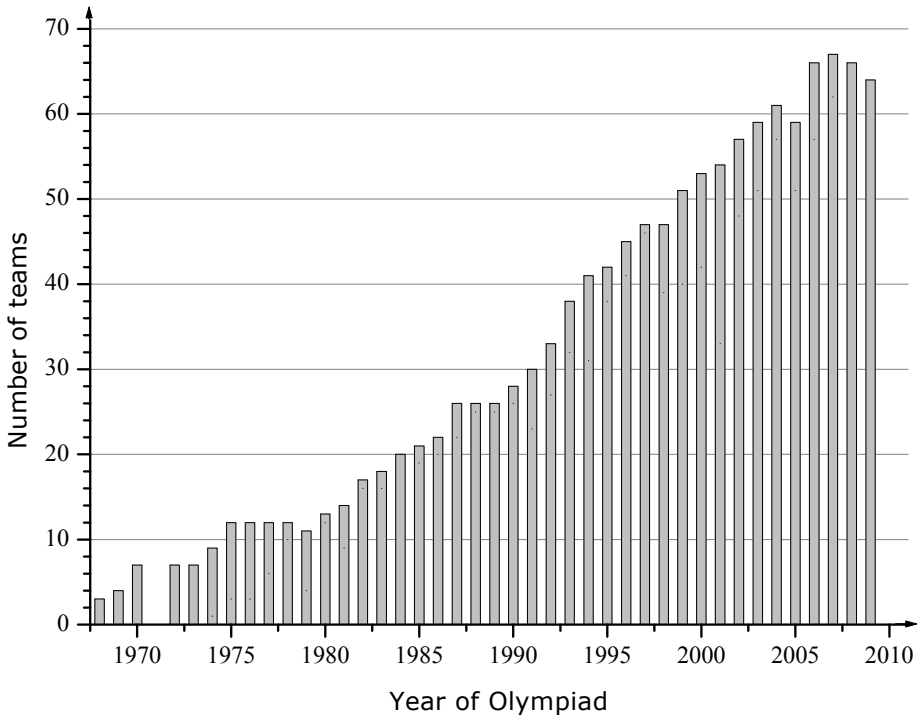
k) $Co_2N_6H_{21}O_3Cl_3$



About the history of the International ChemistryOlympiads

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



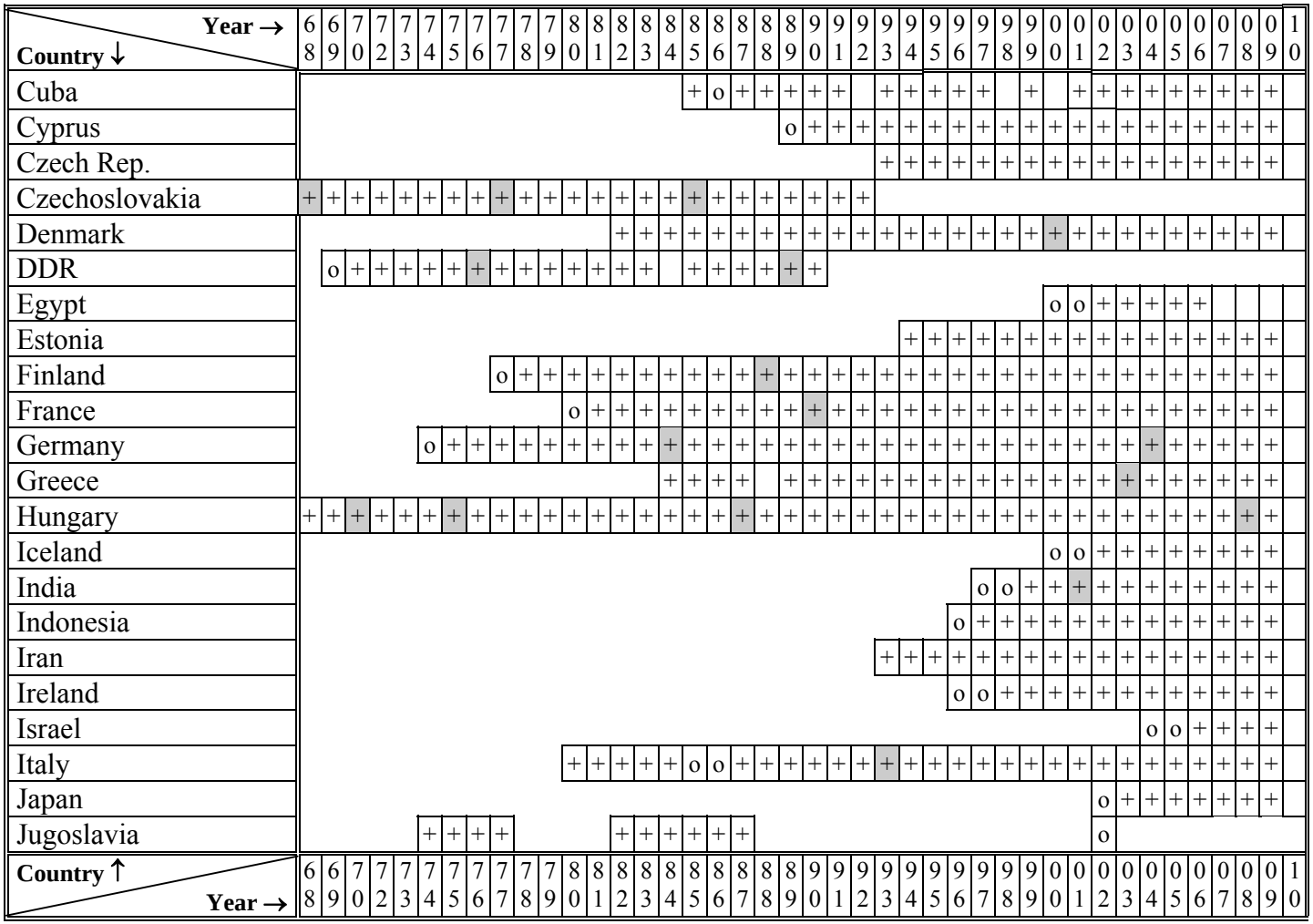
The participating countries are shown in the following table.

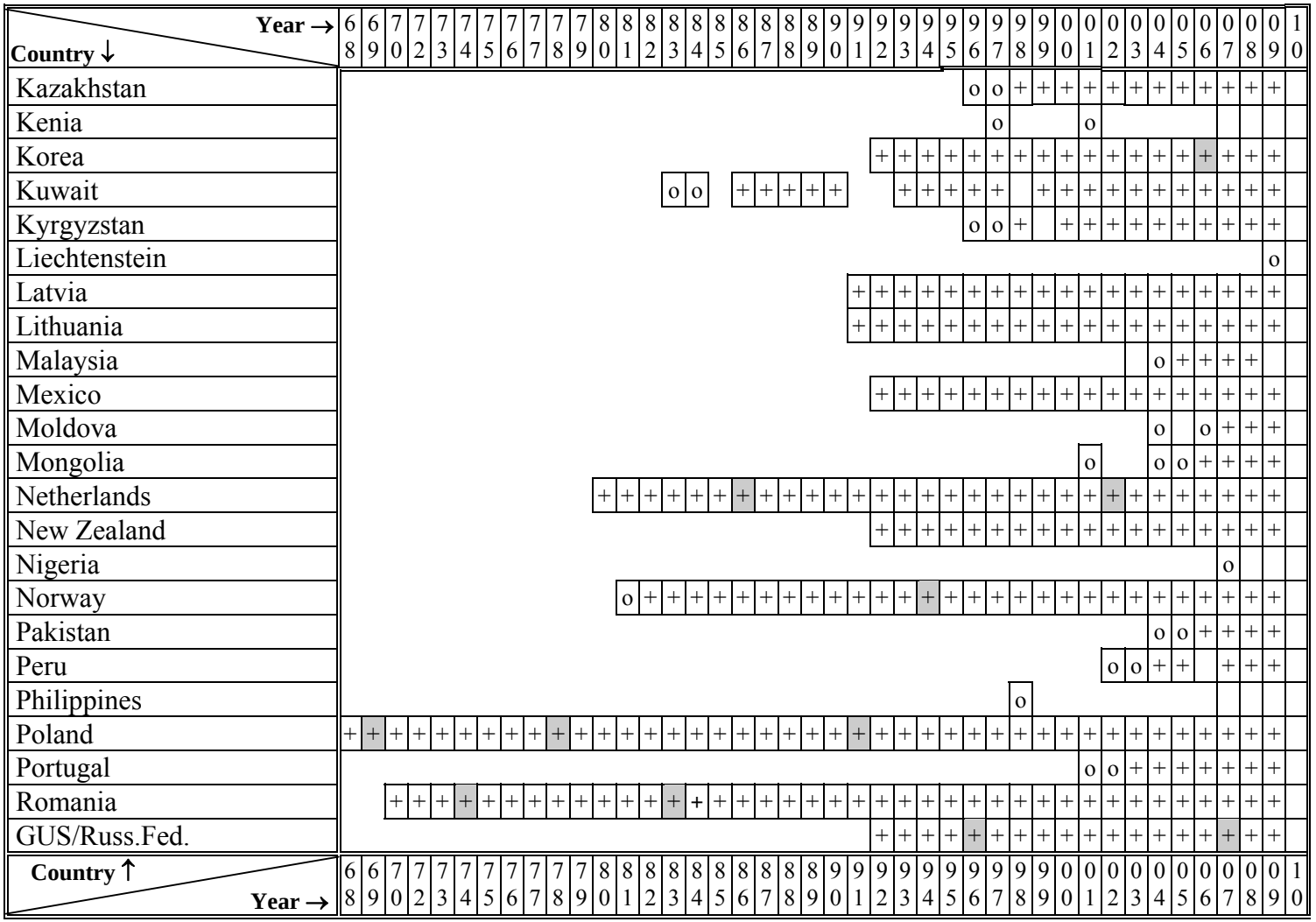
Participating Delegations

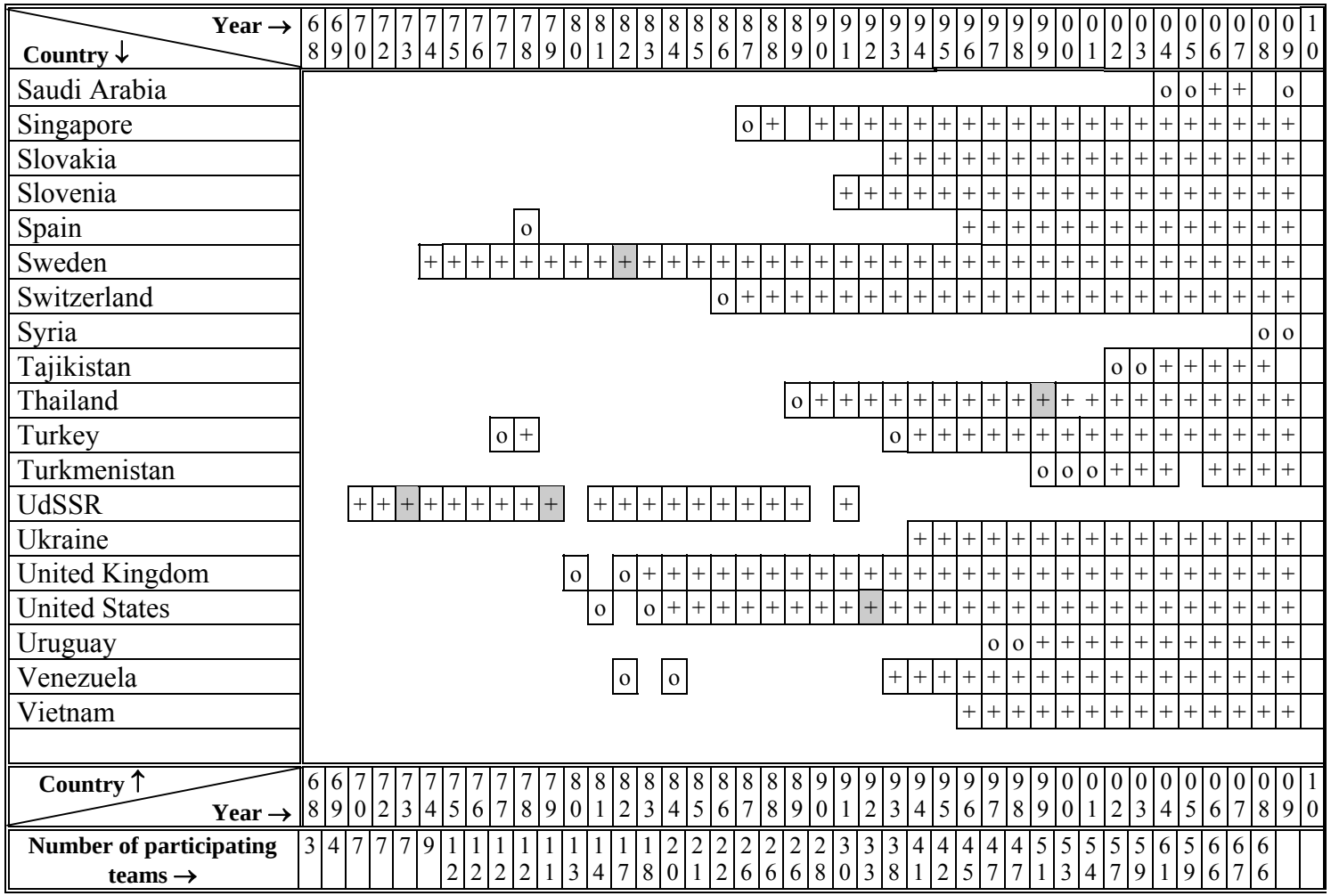
in alphabetical order

+ = host. + = participant. o = observer

Country ↓ \ Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10
Argentina																											+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Armenia																																				o	o	+	+	+	+		
Australien																			o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Austria							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Azerbaijan																													o	o		+	+	+	+	+	+	+	+	+	+	
Belarus																											+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Brasil																													o	o	+	+	+	+	+	+	+	+	+	+	+	
Bulgaria		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Canada																	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
China																			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+	+	+	+	
Chinese Taipei																								+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Costa Rica																																									o	o	
Croatia																														o	o	+	+	+	+	+	+	+	+	+	+	
↑ Country / Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10


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
Cuba
Cyprus
Czech Rep.
Czechoslovakia
Denmark
DDR
Egypt
Estonia
Finland
France
Germany
Greece
Hungary
Iceland
India
Indonesia
Iran
Ireland
Israel
Italy
Japan
Jugoslavia
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
Kazakhstan
Kenia
Korea
Kuwait
Kyrgyzstan
Liechtenstein
Latvia
Lithuania
Malaysia
Mexico
Moldova
Mongolia
Netherlands
New Zealand
Nigeria
Norway
Pakistan
Peru
Philippines
Poland
Portugal
Romania
GUS/Russ.Fed.
Country ↑
Year →


Year →
Country ↓
68 69 70 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 00 01 02 03 04 05 06 07 08 09 10
Saudi Arabia
Singapore
Slovakia
Slovenia
Spain
Sweden
Switzerland
Syria
Tajikistan
Thailand
Turkey
Turkmenistan
UdSSR
Ukraine
United Kingdom
United States
Uruguay
Venezuela
Vietnam
Country ↑
Year →
Number of participating teams →
3 4 7 7 7 9 12 12 12 12 11 13 14 17 18 20 21 22 26 26 26 28 30 33 38 41 42 45 47 47 51 53 54 57 59 61 59 66 67 66

Inofficial ranking since 1974

(set up by adding the points of the teams. up to position 50)

	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988
IChO held in	**RO**	**H**	**DDR**	**CS**	**PL**	**SU**	**A**	**BG**	**S**	**RO**	**D**	**CS**	**NL**	**H**	**FIN**
1	SU	SU	DDR	CS	SU	PL	PL	H	CS	RO	D	SU	NL	SU	RC
.	RO	H	SU	SU	PL	SU	D	CS	D	SU	CS	CS	PL	RC	D
.	CS	PL	H	H	D	RO	DDR	PL	PL	D	SU	D	D	RO	USA
.	H	BG	PL	PL	DDR	CS	H	BG	NL	CS	H	A	SU	CS	PL
5	PL	RO	A	S	CS	A	A	A	A	H	A	NL	A	D	GB
.	DDR	DDR	RO	A	H	S	RO	D	SU	A	GB	H	USA	F	DDR
.	BG	S	BG	D	A	H	BG	DDR	H	F	PL	DDR	H	GB	N
.	YU	CS	CS	DDR	RO	D	CS	RO	BG	DDR	USA	PL	BG	PL	RO
.	S	A	S	RO	S	BG	S	SU	DDR	PL	RO	USA	F	H	H
10	D*	D	D	BG	BG	FIN	FIN	NL	S	NL	DK	F	RO	DDR	SU
.		YU	YU	YU	TR	DDR	NL	FIN	F	BG	S	GB	CS	NL	I
.		B	B	B	FIN		I	S	FIN	GB	NL	RO	GB	USA	NL
.							B	F	N	N	FIN	BG	S	BG	BG
.								I	RO	DK	F	N	DDR	A	CS
15			* hors concours						DK	FIN	BG	S	CDN	S	AUS
.									YU	S	N	FIN	N	FIN	SGP
.									I	I	I	YU	DK	N	F
.										YU	GR	B	B	DK	A
.											YU	GR	FIN	I	FIN
20											B	DK	GR	GR	CDN
.												C	KWT	C	DK
.													YU	B	C
.														YU	S
.														CDN	B
25														CH	CH
.														KWT	KWT

(List of abbreviations see page 131)

	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 131)

	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**		
1	RC	RC	RC	RC	ROK	RC	RC	RC	TPE			
.	ROK	T	IR	ROK	VN	TPE	RUS	RUS	RC			
.	USA	TPE	ROK	RUS	IR	ROK	TPE	UA	ROK			
.	RUS	ROK	T	UA	RUS	RUS	PL	ROK	RUS			
5	IR	A	BY	D	AZ	VN	ROK	T	SGP			
.	TR	UA	RUS	PL	TPE	T	D	BY	J			
.	IND	USA	IND	TPE	T	J	T	VN	USA			
.	AUS	PL	SGP	H	RA	Pl	IND	TPE	H			
.	TPE	IND	D	TR	D	IND	H	H	IR			
10	T	D	TPE	VN	IND	D	SK	SGP	GB			
.	SGP	IR	UA	IND	A	SK	LT	KZ	RO			
.	PL	H	PL	IR	CZ	DK	USA	A	T			
.	RO	RUS	CDN	RO	UA	SGP	VN	PL	D			
.	F	CDN	CZ	LT	PL	BR	GB	IR	IND			
15	SK	TR	RO	CZ	AUS	CDN	BY	IND	PL			
.	H	AUS	KZ	USA	TR	AZ	EST	RO	AUS			
.	VN	GB	VN	SGP	H	UA	UA	AUS	A			
.	CZ	SGP	EST	CDN	SK	USA	RI	D	BY			
.	RA	E	GB	AZ	USA	H	IR	SK	VN			
20	BY	SK	AUS	AUS	GB	CZ	RO	TR	F			
.	C	BY	H	KZ	RO	AUS	AUS	LT	RI			
.	D	VN	SK	GB	BY	IRL	A	EST	TR			
.	GB	FIN	USA	J	SGP	F	KZ	I	LT			
.	UA	F	YV	A	J	IR	SGP	GB	UA			
25	A	LT	IND	BY	RI	A	NZ	CDN	EST			
.	MEX	CZ	F	SK	LV	TR	CZ	NZ	CZ			
.	DK	KZ	A	T	BG	RI	F	BR	SK			
.	CDN	LV	I	RA	HR	GB	TR	USA	CDN			
.	EST	NL	TR	EST	MEX	RO	J	LV	I			
30	RI	RO	AZ	F	KZ	NL	ARM	RI	RA			
.	HR	RA	MEX	NZ	LT	HR	SLO	F	NZ			
.	I	EST	LT	SLO	F	LT	RA	CZ	TM			
.	N	HR	NL	HR	EST	KZ	BR	J	MEX			
.	BG	BG	FIN	LV	CDN	SLO	CDN	DK	KZ			
35	CY	NZ	HR	NL	I	EST	I	RA	IL			
.	KZ	I	J	I	DK	RA	MAL	MEX	BR			
.	B	DK	DK	CH	SLO	BR	IL	SLO	HR			
.	LT	SLO	RA	FIN	FIN	TJ	IRL	IL	AZ			
.	NZ	N	GR	RI	NL	LV	NL	AZ	DK			
40	CH	YV	LT	S	IRL	MAL	CH	HR	S			
.	E	MEX	E	BG	GR	S	S	TM	LV			
.	FIN	BR	TM	KS	NZ	IRL	LV	BG	IRL			
.	SLO	S	BR	E	KS	IL	DK	MGL	FIN			
.	NL	RI	BG	GR	S	FIN	MD	IRL	N			
45	LV	TM	CH	BR	B	IS	E	MAL	E			
.	BR	B	NZ	TM	BR	I	BG	E	NL			
.	S	IRL	IS	CY	CH	CY	TM	S	MGL			
.	YV	CH	IRL	YVA	P	N	HR	NL	PE			
.	IRL	C	CY	IRL	IS	TM	PK	CH	PK			
50	GR	CY	KS	IS	N	CH	N	ROU	SLO			

(List of abbreviations see page 131)

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